Dissertation

Surfactant-Assisted Zerovalent Iron Dechlorination Of Polychlorinated Biphenyl In Contaminated Sediment

Submitted by

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Publications and international meetings resulting from this thesis

Articles:

1) **Wu Y.X.**, Wu Z.H., Huang X.F., Simonnot M.O., Zhang T., Qiu R.L.* (2015). Synergistical enhancement by Ni^{2+} and Tween-80 of nanoscale zerovalent iron dechlorination of 2,2',5,5'-tetrachlorinated biphenyl in aqueous solution. Environmental Science and Pollution Research, 22(1): 555-564.

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Communications:

1) **Wu Y.X.**, Wu Z.H., Huang X.F., Simonnot M.O., Zhang T., Qiu R.L.*. Synergistical enhancement by Ni^{2+} and Tween-80 of nanoscale zerovalent iron dechlorination of 2,2',5,5'-tetrachlorinated biphenyl in aqueous solution. Contaminated Site Management in Europe (CSME SARCLE), Brussels, Belgium, 20-22 October 2014.
2) **Wu Y.X.**, Lin Q.Q., Wu Y., Huang X.F., QIU R.L.*. Current status of soil contamination in e-waste recycling sites in south China. 20th World Congress of Soil Science, Jeju, Korea, June, 2014.

Résumé

La contamination des sols et des sédiments par des polluants organiques hydrophobes, comme les polychlorobiphényls (PCB) pose un problème sanitaire et environnemental majeur, puisque ces composés sont très toxiques et très difficiles à éliminer. L'objectif de cette thèse est d'apporter des connaissances dans le domaine du traitement de sols et sédiments contaminés par des PCB, en étudiant particulièrement la réduction chimique par le fer zérovalent (Fe^0).

Cette thèse part du diagnostic de la contamination des sites de recyclage des électroniques a été mené en Chine du Sud, à Guiyu et Qingyuan, en vue de comprendre les distributions de contaminants dans les sols. Les résultats montrent que la contamination par les PCB n'est pas aussi grave que prévu sur les deux sites, probablement à cause de l'attention portée sur la question et à l'effort entrepris pour arrêter la pollution, surtout à Guiyu. Toutefois, la co-contamination par des PCB et métaux représente une menace potentielle pour les populations locales et les écosystèmes, et augmente la difficulté de la remédiation.

En vue d'appliquer la déchloration réductive à la décontamination de sols de sites de recyclage de déchets électroniques, nous avons étudié les effets d'un tensioactif non ionique, de la MOS, et d'ions métalliques sur la réduction par le Fe^0 du 2, 2', 5, 5' tétra chloro-biphényle (PCB 52), en utilisant une solution modèle. La déchloration du PCB-52 par le Fe^0 en solution aqueuse a été favorisée de manière synergique par la présence d'ions Ni^{2+} et de Tween-80. L'effet de l'acide humique était négligeable, dans les conditions du système étudié. La voie de dégradation du PCB-52 présentait une régiospécificité et une spécificité pour les congénères qui minimise la production de PCB coplanaires toxiques pour l'environnement.

Par la suite, un plan d'expérience orthogonal a été réalisé pour étudier les effets des concentrations en Ni^{2+}, H^+, acide humique et de deux tensioactifs (Tween 80 et Envirosurf (Environium)). Les résultats montrent que l'importance relative des facteurs étudiés se classe dans l'ordre : tensioactifs> acide humique> pH>Ni^{2+}. Le type de surfactant et sa concentration sont les facteurs les plus importants pour le système étudié, car ils jouent sur le transfert de matière du PCB-52 vers la surface des particules de Fe^0. L'ajout de SDBS (sodium dodécyl benzène sulfonate) anionique améliore la réduction lors des traitements avec une forte concentration de tensioactif non ionique. En effet, il atténue les effets négatifs des concentrations élevées de tensioactif non ionique et d'acide humique en modifiant la sorption. La formation de $FeCO_3$ observée a été attribuée à l'oxydation de l'acide humique, ce qui indique l'implication de l'acide humique dans la réaction redox comme agent réducteur.

La quantité de Ni n’a pas eu d’influence ici, ce qui suggère que pour l'application pratique du Fe^0 pour la dégradation des contaminants organiques hydrophobes en solution aqueuse, le transfert de masse est plus limitant que le transfert d’électrons.

En s’appuyant sur les résultats précédents, on propose d’étudier la déchloration d’un sédiment contaminé par les PCB au moyen de Fe^0 et en présence de tensioactifs. Deux approches sont proposées: la désorption par un tensioactif suivie d'un traitement de la solution par le Fe^0; traitement par le Fe^0 d’un sédiment contaminé en présence de tensioactif. Les comparaisons entre les résultats des deux approches révèlent qu'un mélange de Fe^0 et de sédiments contaminés dans une solution de tensioactif est plus efficace et réalisable qu’une désorption de PCB par tensioactif suivie d’un traitement de l’eau.

Mot-clé : sites de recyclage de déchets électroniques, polychlorobiphényls (PCB), fer zérovalent, tensioactif, transfert de matière, réduction chimique

Abstract

Contaminations of soils and sediments by hydrophobic organic pollutants such as polychlorinated biphenyls (PCBs) are among the common environmental concerns, since they are difficult to be eliminated and their potential toxicological impacts are significant. Thus the aim of this thesis is to find a remediation process to soils/sediments contaminated by PCBs by using zerovalent iron (ZVI).

To begin the studies on remediation, a survey on e-waste contamination in south China was conducted to understand the distributions of contaminants in soils. Results show that the contamination was not as severe as previously, whereas the co-existence of PCBs and heavy metals in these areas is a potential threat to local people and ecosystems, and increases the difficulty of remediation.

Afterwards, the feasibility of ZVI degradation on the reduction of PCBs in aqueous solutions was investigated. Results confirmed the stepwise dechlorination of PCBs by ZVI and the major pathway with regiospecifity. The synergistical enhancement on dechlorination rate by Tween-80 and Ni^{2+} was identified during the degradation course, while the influence by humic acid or Cu^{2+} was found negligible.

The factors influencing the reduction of PCBs by ZVI in aqueous solution, in addition with the possible mechanisms were investigated to optimize the conditions for applications. The relative importance of the studied factors was in the order of surfactants > humic acid > pH > Ni^{2+}. Surfactants on the iron surface were found to decrease interfacial tension, while aqueous micelles were found to sequestrate PCB-52 and humic acid. Surfactants, especially the anionic surfactant, were able to alleviate the adverse effect of humic acid by reducing its adsorption. The participation of humic acid as a reductant was suggested by the fact that the mineral $FeCO_3$ was detected on the iron surface.

The lab-scale application of remediation to the contaminated sediment began with the trial on surfactant enhanced desorption of PCBs. Two commercially available surfactants were selected for the desorption experiment. Results recommended the sequential washing by 1% of Tween-80 or Envirosurf as the cleanup protocol for the PCBs contaminated sediment (washing efficiency could be as high as 47.45% and 65.24%, respectively). However, none of the surfactants was effective in the removal of present Ni. A subsequent post-treatment of the washing solution by ZVI was conducted and demonstrated to be ineffective as suggested by the aqueous experiments. Aggregates of iron particles and discrete coverage by soil organic matters could be observed during the treatment.

Finally, the remediation of PCB-contaminated sediment was investigated by mixing ZVI and sediment in aqueous solution, with low contents of surfactants to enhance the mass transfer and prevent iron passivation. Mixture without surfactant was able to degrade PCBs by facilitating the mobility of target compounds yet the further degradation was restricted by the latter passivation of iron particles. As low content as 0.04% of Tween-80 and Envirosurf were able to further reduce PCB mixtures to low CBs or biphenyl that are less toxic or hydrophobic. Hence the mixture of ZVI and sediment in surfactant solution is suggested to be a promising approach to remediate PCBs contaminated sediment.

Keywords: e-waste sites, polychlorinated biphenyls (PCBs), zerovalent iron (ZVI), surfactant, mass transfer, chemical reduction

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General Introduction

0.1 Background

E-waste contamination and the elimination of poly Chlorinated biphenyls (PCBs) are among the most concerning global environmental issues.

In Asia, especially China, a huge amount of e-waste are generated and imported each year, awaiting for recycling and discard. Due to the improper disposal, innumerous amount of multiple pollutants has been released to the surrounding environments. High contents of heavy metals and toxic organic pollutants were detected in air, water, sediment and soil in e-waste contaminated sites, threatening the local ecosystem and residents, as revealed by surveys on native plants and animals, together with epidemiological investigations on local inhabitants [1]. Although it is urgent and necessary for the decontamination in e-waste sites, several obstacles restrict the progress:

1) the co-existence of contaminants with different properties. Despite the valuable and reusable materials, there are more than 1000 species of chemical compounds in e-waste [2]. Most of them are toxic to organisms. Heavy metals and organic pollutants have been detected simultaneously in the ambient environments. Most frequent pollutants are Pb, Zn, Cu, Cd, Ni and other toxic metals released from wires, chips, semiconductor devices, batteries and cathode ray tubes *et al.*; in addition with organic pollutants such as poly aromatic hydrocarbons (PAHs), poly brominated diphenyl ethers (PBDEs), PCBs and dioxin from printed circuit boards, phone cases, computer cases and other plastic components [3].

2) the complexity of contamination. The abovementioned contaminants released from a large amount of e-wastes enter into the surrounding environments. In vicinity of different workshops involved in different disposal, the distribution and contents of multiple contaminants were different. The toxicity and availability of released contaminants depend on the properties of water, soils and air. In this case, a simple clean up approach is not sufficient to meet every cleanup attempt.

3) high contents of pollutants. Several primitive methods of disposal led to severe environmental problems in e-waste sites. For instance, along with the effluent of acid washing workshops, a large amount of undesired metals such as Cu was discharged into local waters and lands without any pretreatment [4]. Cadmium in surrounding farmlands could be as high as 4.01 mg/kg, which was higher than that in former itai-itai disease area in Japan [5]. PCBs

and PBDEs in the soils of these areas were detected as 297.2-5789.5 ng/g (dw) and 180.8-9478 ng/g (dw), respectively, which were much higher than uncontaminated areas [6-8]. The severe contamination has been revealed and described in detail by several researchers.

Among the varieties of toxic pollutants in e-waste sites, PCBs are of great concern due to its toxicity and accumulation in ecosystem. Not only in e-waste sites, the PCBs issue also receives widespread attention all over the world as a result of previously extensive, enormous production and utilization of these synthesized compounds [9]. Industrial areas in France, for example, along the lower Rhône River, was reported to be severely contaminated by PCBs [10]. Similar survey was conducted in other European countries and America, indicating the global contamination of PCBs.

The high stability, low aqueous solubility and high organic affinity of PCBs determine that the major sinks for these congeners are soil and sediment. Soils/sediments from brown sites or other sites affected by industrial activities are often found contaminated by PCBs. For instance, surveys conducted in e-waste contaminated sites reported high levels of PCBs in surrounding soils.

Several trials at lab and pilot scale have been conducted to remove PCBs from soils and sediments. These trials include phytoremediation and microbial degradation enhanced by surface active materials or ameliorants [11-14], cyclodextrin enhanced electrokinetic remediation [15], chemical-enhanced soil washing/flushing with proper washing agents (surfactants, chelators, organic acids and their mixtures *etc.*) [16]. Each of the trials requires different applicable conditions and operations.

In recent decades, a mild and cost-effective method to reduce chlorinated organic pollutants and toxic metals has been developed by introducing zerovalent iron (ZVI) to contaminated soils, sediments and solutions [17]. ZVI was initially applied in the form of permeable reactive barriers to the decontamination in underground water. Nowadays, by *in situ* injection or *ex situ* compiling methods, ZVI has been used to remediate soils and sediments. Previous studies demonstrated the excellent performance of ZVI on the reduction of metals (Cr, As, *et al.*) and halohydrocarbons (chlorinated methane, PCBs, PBDEs, *et al.*) [18]. Thus it is promising to apply ZVI to the remediation of PCBs contaminated soils/sediments such as those in e-waste sites. The co-existed metal ions in PCBs contaminated soils/sediments including Ni or Cu could be immobilized by the reduction of iron, meanwhile serve as catalysts on the surface of iron, accelerating the degradation of PCBs.

Besides ZVI reduction process, soil washing is another promising technique to remediate PCBs contaminated soils/sediments. It is one of the most frequent used process in remediation with the advantage of rapidness and flexibility. Whereas a problem for this process is the post-treatment of washing solution [19]. Based on the knowledge of ZVI degradation, it is likely that ZVI reduction could be employed to remove PCBs in washing solution to achieve the goal of solution reuse and recycle.

In order to apply ZVI to contaminated soils/sediments or to the washing solutions, it is important to understand the mechanisms and constraints during the reduction process. The removal efficiency of target pollutants by ZVI is limited by the practical conditions. The mass transfer and electron transfer process are crucial to the reaction rate, both of which are influenced by pH value, contents of soil/natural organic matters (SOM/NOM), surface active materials, redox potential and the coexisting metal ions. The complexity of solutions and soils/sediments increase the difficulty of ZVI application to the abovementioned situations.

To achieve the removal of PCBs from soils/sediments, this thesis attempts to apply ZVI reduction as a cleanup process for sediments contaminated by PCBs with the assistance of surfactant.

0.2 Scope and objectives

The ultimate aim of this thesis is to determine a cost-effective cleanup method to remediate soils contaminated with PCBs by ZVI reduction with the assistance of surfactants,. Before the application, it is of necessity to understand the roles of both surfactants and ZVI. Afterward, the cleanup process could be established by adjusting the condition of each reaction unit.

The specific objectives of this thesis are as follows:

1) To investigate the soil contamination in typical e-waste sites at Guiyu and Qingyuan, China, with special focus on PCBs and heavy metals. Parameters of the subsequent experiments are set according to the contents of these contaminants.

2) To evaluate the potential of ZVI on the removal of PCBs and metals in aqueous solution and to identify the reaction mechanisms and pathway during the course.

3) To investigate factors affecting dechlorination of PCBs by ZVI particles and corresponding mechanisms. The crucial limited factor is to be recognized and adjusted for the achievement of integrated cleanup process.

4) To evaluate the feasibility of selected commercial surfactants to remove PCBs in contaminated sediment, together with the present heavy metals. The optimal operating conditions including contact time and applied contents are to be determinated.

5) To combine both surfactant desorption and ZVI reduction as the approach to decontamination. The lab-scale trial is performed in two approaches: a, PCBs desorption from samples by surfactants with ZVI reduction as solution post-treatment; b, mixture of ZVI and contaminated samples in surfactant solution.

0.3 Structure of the thesis

The present thesis is organized as follows:

Part 1: the issue, the challenges, the state-of-the art

Chapter 1 Literature review

Chapter 2 Survey on the contamination in e-waste sites

Part 2: ZVI reduction process and mechanism

Chapter 3 The reduction pathway with/without surfactants, humic acid and metals

Chapter 4 Factors and processes influencing ZVI reduction

Part 3: the lab-scale treatment processes

Chapter 5 Surfactant-assisted PCBs reduction by ZVI in contaminated sediment

Part 4: general discussion & conclusion/perspectives: from the reality to the mechanisms then to the application

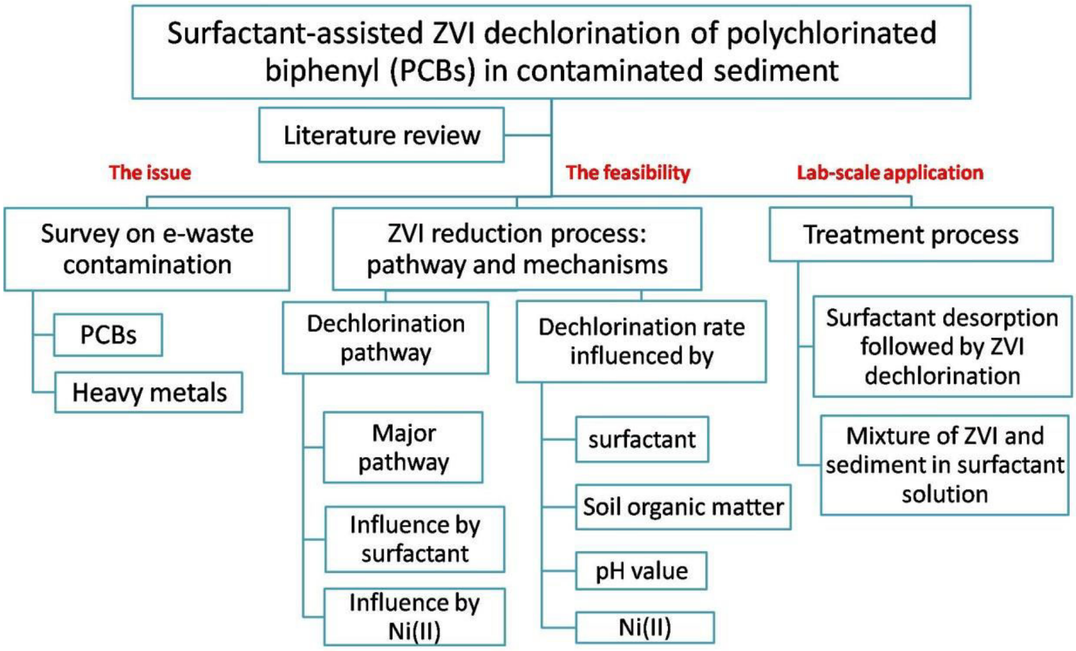


Figure 0.1 Structure of the thesis.

Chapter 1.

Literature Review

1.1 Contamination in soils and sediments by improper disposal of e-waste

According to Basel Action Network (BAN) and Silicon Valley Toxics Coalition (SVTR), electronic and electric waste (e-waste) is defined as various abandoned electronic devices which are soaring numerically and are originated from large-size household appliances, including refrigerators, air-conditioners, cell-phones, personal sound equipment and computer components [3]. The generation of e-waste is becoming a large problem as obsolete electronic products prevail due to rapid development of technology and economy. For instance, the generation of e-waste in European Union was estimated to be 7.0 million tons in 2010, while that of USA increased from 1.90 million tons by the year 2000 to 3.41 million tons by the year 2011; a prediction from United Nations announced 500% increase of e-waste from old computers in India by the year 2020; 700% and 1800% increase of e-waste from obsolete mobile phones in China and India compared to the level in 2007, respectively [20, 21].

Figure 1.1 E-waste in China: (a) piling-up of e-waste residues after disposal in Guiyu, China; (b) printer rollers being dismantled in Guiyu.

Since many species of valuable metals and specific compounds such as ferrous alloys, aluminum, copper and precious metals are contained in e-waste, the recovery and recycle of e-waste are necessary and profitable [21]. To manage the recycling activities, many developed countries enacted wide-ranging laws during the 1970s and 1980s, enhancing the local cost of recycling and subsequently began the transboundary shipment of e-waste to developing regions such as China, India, Pakistan, southeast Asia, Nigeria, Ghana, *etc.* [22]. Although laws and regulations have been enacted to forbid the export and import of e-waste, huge amounts of e-waste are still being smuggled to the abovementioned areas and being improperly disposed [3, 23]. Contaminations in these areas due to primitive disposal have been extensively reported and evoked social concerns [1].

1.1.1 Hazard and harm

Despite the valuable and reusable materials, there are more than 1000 species of chemical compounds in e-waste, including heavy metals and organic pollutants. Most of them are toxic to organisms [2]. Typical types of hazardous contaminants are listed in table 1.1 and 1.2. The lists include highly toxic metals such as Pb, Zn, Cu, Cd and Ni, some of which are carcinogenic;

together with several species of organic pollutants, most of which are identified as persistent organic pollutants (POPs). In addition, more hazardous contaminants could be generated during the disposal processes. For instance, polycyclic aromatic hydrocarbons (PAHs) generated during the combustion of waste [24]. Dioxin-like substances, i.e. polychlorinated dibenzo-p-dioxins/ dibenzofurans (PCDD/Fs) and polybrominated dibenzo-p-dioxins/ dibenzofurans (PBDD/Fs), derive from the combustion of compounds containing chlorine and bromine, respectively. To make it worse, copper, a widespread metal in e-waste, often acts as a catalyst for the formation of dioxins [4]. These contaminants could leak to the environment during primitive disposal processes and lead to detrimental effects.

The primitive e-waste processing (illustrated as figure 1.2) usually begins with manual dismantling by backyard or informal recyclers. In this step, equipments or parts containing valuable and reusable materials are separated and collected for further treatment. During this process, dust particles with metals and POPs were released into the atmosphere, then either deposit in vicinity or transported for a long distance [2].

Subsequently, acid stripping (of printed circuit boards *e.g.*) and refining (of cables *e.g.*) are conducted to recover metals, both of which were inefficient in backyard workshops and cause leaching of metals to soils, waters and atmosphere [25]. After collection and recovery, unsalvageable components are abandoned and piled up on crop fields and residential areas. To solve the problem, open-air combustion was conducted without any pretreatment, which does not only speed up the diffusion of contaminants but can also generate secondary pollutants such as PAHs and dioxin substrates.

The threat of e-waste contamination to the local people and ecology has been recognized and intensively studied. High levels of metals were detected in children's blood and crops [26, 27], and flame retardants were detected in human hair in e-waste contaminated sites [28], indicating the severe harm resulted by the disposal activities. Elevated levels of contaminants in aquatic species and birds have been reported in e-waste sites, together with the bioaccumulation of some POPs [29-32].

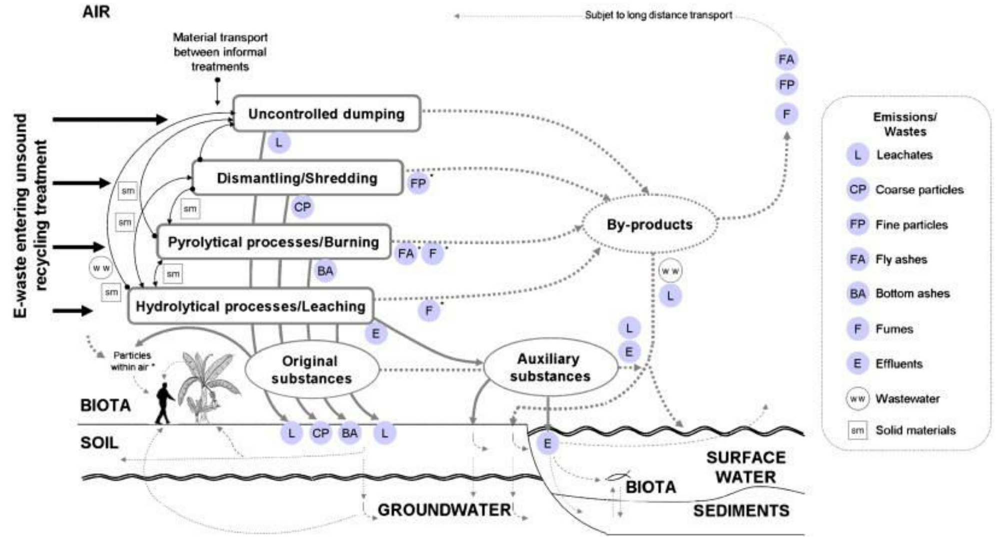


Figure 1.2 E-waste processing flow and the emission of wastes in China and India [2].

Table 1.1 Heavy metals contained in e-waste and their toxicity

Metals	location in electric parts	Toxicity	Reference
Lead (Pb)	Batteries, cables, glass panels and gasket in cathode ray tube (CRT) monitors, solders in circuit boards, *etc.*	Damage to the central and peripheral nervous systems, blood systems, kidney, reproductive system, endocrine system and children's brain development.	[3]
Cadmium (Cd)	Batteries, circuit boards, resistors of surface mounted devices, infrared detectors, semiconductors, old CRT monitors, plastics, *etc.*	Acute poisoning: pulmonary edema, hemorrhage, fulminate hepatitis, testicular injury, and lethality; chronic effects: nephrotoxicity, osteotoxicity, and immunotoxicity; carcinogenicity.	[33, 34]
Mercury (Hg)	Batteries, switches and flat screen monitors, circuit boards, lightings, *etc.*	The chief target organ of mercury is the brain, while peripheral nerve function, renal function, immune function, endocrine and muscle function could be damaged; genotoxicity.	[3, 35]
Chromium (Cr)	Corrosion protection layer for steel plates, steel housings, *etc.*	Carcinogenicity; sensitization; genotoxicity; immunotoxicity.	[3, 36]
Copper (Cu)	Batteries, Wires and cables, motherboards, monitor yokes, "finger clips", printers, *etc.*	Acute poisoning: damage to gastrointestinal tract, liver and kidney; chronic effects: damage to liver, kidney, brain, *etc.*	[37, 38]
Nickel (Ni)	Batteries, steel housings, CRT, circuit boards, *etc.*	Embryotoxicity; teratogenicity; sensitization; carcinogenicity.	[3, 39]
Zinc (Zn)	Batteries, CRT, circuit boards, *etc.*	Acute poisoning causes gastrointestinal and central nervous system symptoms; chronic exposure leads to copper deficiency and cell death.	[3, 40]
Tin (Sn)	CRT, circuit boards, *etc.*	Skin and eye irritation; damage to biliary tract; cytotoxicity, hepatotoxicity and neurotoxicity.	[3, 41]
Arsenic (As)	Doping agents in transistors, circuit boards.	Acute poisoning could lead to death. Chronic exposure causes damage to skin, liver, nerves, kidney, endocrine, cardiovascular and hematological system; carcinogenicity; genotoxicity; cytotoxicity.	[3, 42]

Table 1.2 Organic contaminants contained in or originated from e-waste and their toxicity

Organic contaminants	Chemical formula	Usage in electric parts/origin	Toxicity	Reference
Polycyclic aromatic hydrocarbons (PAHs)	–	Primarily originated from the combustion process.	Carcinogenicity; teratogenicity; mutagenicity.	[43]
Polychlorinated biphenyls (PCBs)	$C_{12}H_{10-x}Cl_x$ (x=1-10)	Insulating oil, heat carrier, lubricant; plasticizer and flame retardant in plastics.	Carcinogenicity; toxic to dermal, reproductive, immune, nervous, endocrine and development systems	[9，44-46]
Polybrominated diphenyl ethers (PBDEs)	$C_{12}H_{10-x}Br_xO$ (x=1-10)	Brominated flame retardant (BFR)	Disruption of thyroid hormone homeostasis and oxidative phosphorylation, altered estradiol synthesis, and neurotoxic effects	[47]
Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs)	$C_{12}H_{8-x}Cl_xO_2$/ $C_{12}H_{8-x}Cl_xO$ (x=1-8)	Originated from the combustion process.	Carcinogenicity; damage to immune, reproductive, development and endocrine systems.	[48]
Polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs)	$C_{12}H_{8-x}Br_xO_2$/ $C_{12}H_{8-x}Br_xO$ (x=1-8)	Unintentional formation and release throughout the life cycle of BFRs.	Similar to PCDD/Fs.	[49]
Polyvinyl chloride (PVC)	$[C_2H_3Cl]_n$	Plastics	Potential source of PCDD/Fs.	[3]
Hexabromocyclododecanes (HBCDs)	$C_{12}H_{18}Br_6$	BFR	Histopathological effects on liver and endocrine	[50]
Dechlorane plus (DP)	$C_{18}H_{12}Cl_{12}$	Flame retardant	Low acute toxicity; histopathological effects on liver.	[51，52]
Polybrominated biphenyl (PBBs)	$C_{12}H_{10-x}Br_x$ (x=1-10)	BFR	Carcinogenicity; low acute toxicity; histopathological effects on liver, thymus and endocrine.	[50]
Tetrabromobisphenol A (TBBPA)	$C_{15}H_{12}Br_4O_2$	BFR	Low acute toxicity; limited informations on other toxicity effects.	[50]

Table 1.3 Contents of heavy metals in soils, sediments and dusts due to e-waste recycling activities (unit: mg/kg dw)

Region	Concerned samples	Statistics	Cr	Ni	Cu	Zn	Cd	Hg	Pb	Reference
Guiyu, CHINA	sediments from Lianjiang River (n=15)	M±SD^{a}		181±156	1070±1210	324±143	4.09±3.92		230±169	[53]
		Range		26.0-543	125-4540	121-628	n.d.^{b}-10.3		79.5-590	
	sediments from Nanyang River (n=10)	M±SD		25.2±10.5	65.1±101	107±54.9	n.d.		47.3±13.8	
		Range		12.4-39.8	17.0-346	51.3-249	n.d.-0.57		28.6-76.9	
	Sediment (< 20 cm) near acid leaching site (15 cores)	Mean	10.2	216	3370	1190	5.66		2170	[54]
	soil near the printer roller dumping area (n=6)	Mean	74.9	87.4	712	n.d.	3.1		190	[34]
	soil from a plastic burn site (n=5)	Mean	28.6	155	496	258	1.7		104	
	soils from e-waste dumpsite (n=20)	Mean	153.6	114.2	787.7		1.96		1431	[55]
	dust from printed circuit board recycling workshop (n=16)	GM^{c}		1500	8360	4420			110000±61200	[34]
		Range		76.1-7967			9.34-66.8		22900-206000	
	dust from backyard recycling workshop (n=29)	Mean	61	69	2740	1120	1.9		892	[56]
	Surface soil from abandoned acid processing site	Mean	2600	480	4800	330	1.21	0.21	150	[57]
	Residues from combustion site	Mean	320	1100	12700	3500	10.02	0.19	480	
	surface soils near backyard recycling workshop	Mean	26.3	12.6	36	75.3	0.2	0.1	57.7	
Taizhou, CHINA	Paddy soils (< 20 cm) in an e-waste recycling area (n=6)	GM	61.21	34.65	98.81		1.19	0.33	55.81	[58]
		Range	54.41-74.12	25.83-46.19	56.07-236.89		0.55-7.86	0.24-0.76	51.96-64.56	
	Background		57.96	226.434	20.85		0.14	0.14	29.76	
	Soil (< 15 cm) from abandoned e-waste recycling plant (n=16)	M±SD	771.5±44.9		2364.2±288.6	5995.6±497.1	42.3±8.4	4.1±0.8	6082.9±1972.6	[59]
		Range	696.1-821.2		2059.2-2826.3	5353.6-6741.3	34.4-57.2	3.1-4.9	4032.42-8547.9	
	Soil (< 15 cm) near abandoned e-waste recycling plant (n=32)	M±SD	69.5±10.3		57.6±153.7	275.5±99.2	2.2±1.5	0.8±0.4	167.4±136.7	
		Range	57.0-89.1		48.4-240.8	179.4-543.9	0.8-6.8	0.1-1.4	55.7-531.5	

Region	Concerned samples	Statistics	Cr	Ni	Cu	Zn	Cd	Hg	Pb	Reference
	Paddy soils in an e-waste recycling area									
	A (n=3) no recycling operation	M±SD	9.78±7.97		41.39±18.81	74.88±19.29	0.09±0.20		28.13±19.29	[60]
	B (n=3) no recycling operation	M±SD	10.40±8.71		46.93±17.89	94.64±20.89	0.17±0.02		49.63±20.55	
	C (n=4) chipped circuit boards piled	M±SD	10.64±8.32		39.94.15.42	114.46±33.58	0.09±0.01		49.63±25.64	
	D (n=4) another chipped circuit boards piled	M±SD	21.66±6.02		46.63±1.20	138.0±7.51	0.11±0.13		65.16±2.40	
	E (n=5) un-dismantle computers piled	M±SD	33.49±28.74		51.19±10.64	145.45±29.35	0.33±0.08		67.04±19.90	
	F (n=5) recycling operations	M±SD	20.95±2.63		97.90±50.34	281.38±127.99	0.62±0.92		44.29±16.33	
	G (n=5) legal metal recycling center	M±SD	26.75±6.09		256.38±99.70	209.85±32.89	6.37±5.91		46.84±12.18	
	Control (n=3)	M±SD	6.33±1.03		32.08±2.11	111.99±37.77	0.15±0.01		33.45±1.33	
	Surface sediments in Nanguan river on									[61]
	Control site	mean	55.8		51.2	112	1.37	0.158	55.8	
	near backyard workshop		81.1-387		305-14000	278-1740	1.93-13.9	0.419-3.82	113-869	
	near two industrial park site	Range	176-497		1260-4180	594-1300	3.23-4.69	0.884-1.21	174-300	
	soils (< 30 cm) from large scale e-waste recycling plants in Wenling (n=14)	mean	16.4-269.1		77.9-296.3	177.7-660.8	1.7-3.3	0.2-1.0	81.3 - 501.9	[7]
	soils (< 30 cm) from large scale gold recovery in Wenling (n=5)	Range	88.6-91.3		272.3-576.7	143.8-263.0	0.6-9.6	0.4-3.2	102.8-184.4	
	Soils (< 30 cm) from household recycling workshops in Wenling (n=18)	Range	40.5-125.9		222.5-1641.3	221.2-518.7	2.8-12.5	1.7-654.1	200.1-2374.1	
	Reference site (n=1)	mean	56.5		32.3	157.8	0.04	n.d.	33	
	Agricultural soil (< 30 cm)									[62]
		mean	76.7		176.2	121.3	2.02		223.8	

Region	Concerned samples	Statistics	Cr	Ni	Cu	Zn	Cd	Hg	Pb	Reference
	near recycling workshops (n=5)	Range	31.5-164.2		39.9-465.9	116.6-270.3	0.59-4.06		107.4-395.9	
	near open burning and recycling sites (n=7)	mean	59.2		88.5	155.5	2.04		80.9	
		Range	20.0-127.2		29.3-220.1	93.1-184.5	1.28-2.94		42.9-119.8	
	with less or no open burning and e-waste recycling activities (n=8)	mean	53.7		59.2	140.9	1.39		77.0	
		Range	20.5-92.0		31.1-90.7	55.2-195.6	0.20-1.88		52.7-139.3	
	Background value (Zhejiang province)		54.5		17.6	70.6	0.07		23.7	
Qingyuan, CHINA	soils (<15 cm) from an combustion site (n=11)	M±SD	68.9±53	60.1±59	11140±9000	3690±2680	17.1±12.5		4500±3370	[26]
		Range	23.6-122	12.2-132	1500-21400	682-8970	3.05-46.8		629-7720	
	Paddy soil (< 15 cm) near combustion site (n=11)	M±SD	17.3±8.1	34.5±26.6	155±94	166±76.7	1.0±0.4		61.8±24	
		Range	10.5-24.1	10.8-66	40.1-260	62.1-252	0.04-1.43		48.1-97.0	
	soils (< 15 cm) from vegetable garden near combustion site (n=16)	M±SD	12.3±5.1	80.83±2.9	324±172	122±55.7	0.9±0.8		95.6±19.5	
		Range	9.66-19	70.04-10.3	210-450	92.4-142	0.26-1.17		73.3-134.0	
	Deserted soil (< 15 cm) near combustion site (n=8)	M±SD	6.41±4.04	10±8.4	72.4±52.8	62.6±25.7	0.25±0.19		52.2±24.0	
		Range	3.84-11.1	40.58-19.7	49.9-95.4	44.5-72.3	0.08-0.39		47.2-60.2	
	soils (<15 cm) from pond area near combustion site (n=10)	M±SD	38.9±38.4	32.2±20.7	3550±5480	1160±1580	5.45±7.43		1880±3340	
		Range	14.4-105	18.9-44.9	142-12,900	123-3800	0.57-18.3		37.9-7760	
	Background value (Guangdong province)		50.5	14.4	17	47.3	0.06		36	
	Chinese national maximum allowable concentration		250	40	50	200	0.3	0.3	250	[63]

[a] M±SD: mean ± standard deviation;

[b] n.d.: not detected;

[c] GM: geometric mean.

1.1.2 Soil and sediment contamination by improper disposal of e-waste

China has been the country most involved in e-wastes disposal all over the world through generating its own wastes (up to 17 million tons in 2006) and receiving e-wastes from U.S.A, Europe and other Asian countries [3, 64]. A remarkable amount of research has reported the severe pollution in China as a result of inappropriate e-wastes treatment [4, 65]. The main e-waste dumping sites include Guiyu (Guangdong Province, South China), Foshan (Guangdong Province), Longtang Town and Shijiao Town, Qingyuan (Guangdong Province) and Taizhou (Zhejiang Province, Southeast China), as illustrated in figure 1.3. Although disposal of e-wastes has been gradually regularized in factory scale, the contamination caused by crude and improper operations remains to be controlled.

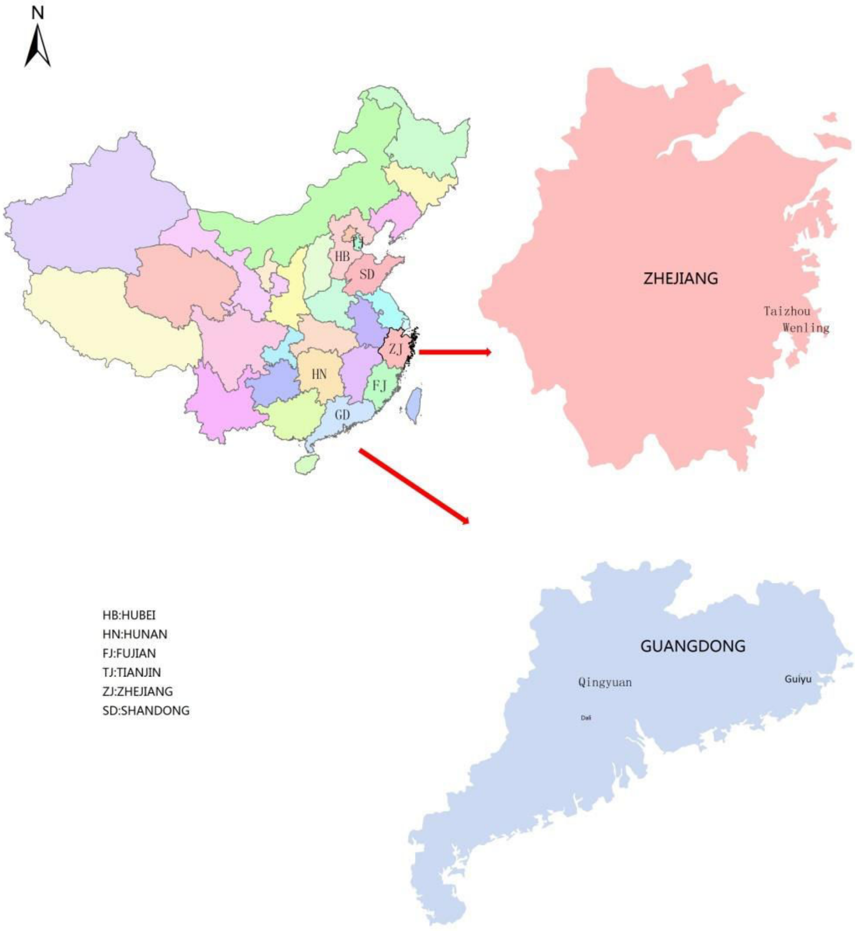


Figure 1.3 Areas involved in e-waste recycling activities in east and south China.

As an important sink for pollutants, soils and sediments under water bodies accumulate contaminants from e-wastes, leading to the loss of ecological functions and negative impacts on food chain stability. Soil and sediment pollution caused by e-wastes is influenced by many factors: (1) land use patterns and characteristics of soils and rivers differ in various regions. Contamination can occur in lands with different properties, such as farm lands, urban green lands, public construction sites and residential areas; (2) the pollution patterns were determined by the processing methods, durations and components of e-wastes; (3) regional climate and surface conditions strongly affect the migration and distribution of contaminants; (4) the extent of pollution was also influenced by regional policies and management.

Surveys on the contaminants have been conducted in the major sites in south and east China [1]. Results show that soil and sediment pollution is severe and complex.

1.1.2.1 Contaminations by metals

Contaminations of metals in e-waste sites are summarized as table 1.3. As presented, high contents of heavy metals, mainly Cu, Zn, Pb, Ni, Cr and Cd, were detected in soils, sediments and also dust. Elevated levels of contamination were identified in comparison to the Chinese national maximum allowable concentrations. Based on available data (table 1.3), Cu is usually of highest concentration among all heavy metals, and Zn is of the second highest [4, 5]. Open burning or combustion process is the most polluted approach among all, while acid washing and dismantling could lead to the release of metal-containing leachate and dust, respectively.

Despite the abovementioned commons, comparison among different regions and various processing approaches suggested diverse contamination patterns. The regions of e-waste sites seemed to be a less significant influential factor on the contaminating patterns compared to varied processing approaches. The levels of contamination are more related to the processes. For instance, the contents of Cu and Zn were comparable in both combustion sites of Qingyuan and Guiyu [26, 57], while survey conducted in Taizhou indicated that soil contamination pattern is related to the scale of workshops and that small-scale simple workshops caused more severe pollution with higher percentage of Pb and Hg compared to large-scale factories [62].

Soils and sediments in the vicinity of e-waste recycling sites were inevitably contaminated due to these activities. Paddy soils receiving the dust and leachate from combustion sites were recognized to be contaminated mainly by Cd [26, 60]. And 24 of the 29 soil samples from the vicinity of dismantling sites were found to contain Cd at a very high content, which even surpasses the Cd concentration (4.01 mg/kg) detected in Japan Itai-Itai disease area. Contaminations by Zn and Cd around workshops were demonstrated more severe than that in open burning soils [66].

Besides soils, sediment is another important sink of pollutants, and may act as a carrier and source of heavy metals in estuary systems [54, 67], as waters across the e-waste sites were often the acceptors for industrial waste, which is thus severely contaminated by heavy metals. A study showed that two mainstreams in Guiyu catchment are contaminated by Cd (n.d. - 10.3 mg/kg), Cu (17.0 - 4540 mg/kg), Ni (12.4 - 543 mg/kg), Pb (28.6 - 590 mg/kg) and Zn (51.3 - 324 mg/kg). Non-residual metals are of higher proportion than that in control area, which imposes a risk on local environment and downstream ecology [53].

To summarize, different processing approaches determine the components and the quantity of the released metals from e-wastes, and as a result processing approaches determine the contamination patterns. Owing to the characteristics of geochemistry, soils and e-waste components different from region to region, contamination patterns of heavy metals vary across different sites. Thus it is important to understand the contamination pattern in a specific area and the goal of treatment before taking any remediation action. Decontamination strategy should be designed accordingly and one approach of an area should not be imposed directly to another one.

1.1.2.2 Contaminations by POPs

Similar to the situations of metal contaminations, the contaminations by organic pollutants (most of which are POPs as presented in table 1.2) varied diversely among regions and processing approaches. Surveys and reviews on the issue have been extensively and intensively conducted for the last decades [4].

One family of the typical contaminants is PAHs, which is primarily originated from the combustion process. The contaminations varied largely among surveys and are highly dependent on the sampling sites and methods. Commonly, elevated levels of PAHs (usually in the sum of the 16 PAHs in priority suggested by USEPA) in soils were detected at and near combustion sites, with the contents from 899.9 to 40000 μg/kg (dw) [68, 69]. In addition, soils near dismantling workshops and recycling facilities [6, 7, 61] were also contaminated by high contents of PAHs from 190.8 to 9156 μg/kg (dw). Based on the Dutch list: the optimal cumulative concentration of 10 PAHs, most of the soil samples near e-waste sites did not exceed the optimal values except for several sites near combustion or recycling facilities [4].

Besides PAHs, brominated flame retardants (BFRs) are also typical contaminants in these sites as many materials of electric and electronic products are flame retarded and most of the BFRs are not chemically bound to the materials [70]. Dismantling, shredding, combustion and other disposal treatments are able to accelerate the release of BFRs to the environment. The concerned species of BFRs are listed in table 1.2.

Among all the BFRs, PBDEs are one of the most concerned species as penta-BDEs and octa-BDEs have been officially listed as persistent organic pollutants (POPs) [28]. The total concentrations of PBDEs from e-waste sites were high in soils and dusts. The two soil samples most burdened by PBDEs (sum of 37 congeners) were reported in Guiyu that 25478.84 μg/kg (dw) in the surface soil near an abandoned dump/burying site for unsalvageable materials [71] and 36215 μg/kg (dw) near an opening burning site [72]. Contamination by PBDEs in Qingyuan was similar to that in Guiyu but less severe with 1140 - 1169 μg/kg (dw) of $\sum_{21}$PBDEs, which is 10 - 30 times of the amount in other regions [34]. The indoor and outdoor dust samples from Qingyuan e-waste sites were all found to be PBDEs contaminated. The total PBDE (17 congeners) concentrations for indoor dusts ranged from 230 - 157500 μg/kg (mean = 9400 μg/kg) , and 212 - 25880 μg/kg (mean value = 3311 μg/kg) for outdoor samples, respectively [73]. The high contents of PBDEs in both soils and dusts cast a threat to the health of local people and ecological system [8].

Another typical species of contaminant is PCBs due to their widespread application as insulators and plasticizers in the last century [46]. In soils and sediments around e-waste sites, concentrations and components of PCBs are related to the involved e-waste recycling processes and characteristic of soils and sediments. According to the research on soils of e-waste recycling sites in Taizhou area, the contents of PCBs were 24.8-364.3 μg/kg (dw) in the surface soils near large-scale recycling factories, 297.2-5789.5 μg/kg (dw) near small-scale recycling workshops [6, 7], 16.1-684 μg/kg (dw) in the sediments around industrial zones and as high as 3000 μg/kg (dw) in the sediments in rivers passing through backyard recycling workshops [61]. A report on Guiyu area (Guangdong, China) indicated that the contents of PCBs were up to 1443 μg/kg (dw) in the surface soils around dismantling sites, 73.8-1443 μg/kg (dw) in open burning sites [74] and 743 μg/kg (dw) in river sediments nearby [34]. No reports on PCB pollution have been conducted so far in Qingyuan. Generally, most of the surveys indicated that PCB pollution in soils and sediments is significantly severe in these areas, especially around open burning sites [6, 75].

The available surveys significantly indicate the complex and severe contaminations in all the e-waste sites in China, which is a problem urgent to be solved. Global perspectives on this issue also suggest the similar situation in other developing countries such as Ghana in Africa, where trace metals, PCBs and PAHs were detected in the environment around local e-waste sites [76, 77]. Studies in both China and other regions involved in e-waste recycling indicated that improper disposal of e-waste can lead to complex multi-contamination in sediments.

In summary, contamination caused by improper e-waste disposal is complicated, combining both heavy metals (Ni, Pb, Zn, Cu, Cd, Cr, *etc.*) and POPs (PCBs, BFRs, PCDD/Fs, PBDD/Fs, *etc.*). The complex pollution usually occurs in soils and sediments with weak pollutant migration. Thus to control e-waste pollution, more understandings should be conducted to study the toxicity of complex pollution and corresponding remediation strategies.

1.2 PCBs in soils and sediments

As mentioned above, the burden of multiple contaminants is common in the environment around e-waste sites and is a threat to the health of local residents and ecosystem. Among those contaminants, PCBs are one of the most concerned species, due to their well-recognized properties of high toxicity, bioaccumulation, biomagnification, recalcitrance and persistence [46, 78]. Although extents of human exposure to PCBs and contents in environment and food webs have declined consistently in a global scale over the last three decades [79], severe PCB pollution still occurs primarily in e-waste sites and vicinity, due to the widespread application of PCBs from electronic or electrical products and their release to environment [74, 80]. As a consequence, local residents and ecological systems in vicinity of the e-waste sites are under the threat by PCBs pollution. In addition, occasional accidental leakages of PCBs all over the world attribute to the pollution and risk to human beings and ecosystem. Therefore, contamination by PCBs is still a global environmental issue to be solved. Thus PCBs are considered as the model pollutants derived from the e-waste contamination issue.

The problem caused by PCBs was initially recognized by several public nuisance events such as Yusho Disease in Japan (1960s) and Taiwan (1970s). Since then, PCBs have been gradually forbidden in production. Although small amount of PCBs still existed in hermetic electrical systems (*e.g.* capacitors and transformers), those products were gradually replaced by updated substitutions [9, 80]. Even with all of these controls, public concerns on PCBs did not decline for the reason that they had been broadly used and were one of the most durable and stable artificial compounds [81]. In 1997, PCBs were listed as one of the twelve POPs that have most detrimental effects on human health and natural environment in *Stockholm Convention on Persistent Organic Pollutants* [82]. Since then, studies on the properties, toxicity, environmental behavior, contamination profiles and remediation trials of PCBs were conducted to gain understandings on the contaminants.

1.2.1 Chemical and physical properties of PCBs

The toxicity and behavior of PCBs in the environment are highly related to their properties. From 1920s to 1970s, PCB congeners (structure presented as figure 1.4) were often synthesized at industrial scale directly through chlorinated reaction on the molecule of biphenyl under high temperature and with metal catalysts. Theoretically, there are 209 congeners with various numbers of chlorine atoms on different substitution positions. Pure PCB compounds are in crystalline state at normal temperature and pressure while a mixture of PCBs is an oily liquid at the same condition. The mobility of a PCB compound decreases with higher number of chlorine atoms in the molecule, with its physical state shifting from mobile viscous liquid to solid resin. PCBs are stable with low aqueous solubility (-logSw=5.26-10.49) and relatively high octanol-water partition coefficient (logKow=4.66-8.02) [83]. The persistence of PCBs increases along with higher number of substituted chlorine atoms. PCBs are recognized as POPs, considering the durability, lipotropy, toxicity, the ability of long-distance migration and low bio-degradation rate [84].

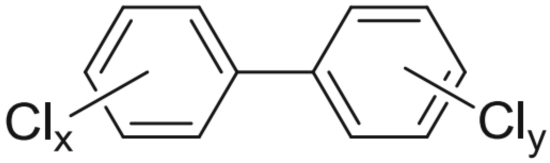


Figure 1.4 Structure of PCBs (x+y ≤ 10).

With stable physical and chemical properties, PCBs are strongly resistant to acids and alkalis. Besides, they are heat-resistant materials and favorable insulators, which do not corrode metals. Based on these features, PCBs were once widely used as insulating oil, heat carrier, lubricant, combustion improver, *etc.* They were also added in rubber, resin and paints to enhance the stability and anti-oxidation in products [9].

1.2.2 Toxicity and bioaccumulation of PCBs

Dated back from 1930s, public attention has been paid to the negative effects of PCBs on occupational population (because of chloracne, for instance). Thus in 1940s, the USA established a criterion for a recommended standard to control occupational exposure to PCBs [79]. Despite that, the health risk of PCBs received little concerns until the eruption of Yusho

Disease in Japan (1960s) and Taiwan (1970s). In both of the public health incidents, rice bran oil was polluted by heat carriers containing PCBs and was unfortunately mistakenly consumed. Victims suffered from the toxicity of PCBs, especially the newborns, with the experience of chloracne, excess skin pigmentation (hyperpigmentation), low birth weights and so on [85, 86].

In addition to the clinical manifestations mentioned above, a number of toxicological experiments on animals indicated that PCBs are not only carcinogenic [44, 45], but also toxic to integumentary, reproductive, immune, nervous and endocrine systems as well as development system. The toxic impacts also involve dysfunction of liver, thyroid and several types of enzyme [46]. The chemical properties of PCB homologues implicate different toxicity: an experiment on Sprague-Dawley rats manifested that nonpersistent PCBs cause slight and reversible damage in liver [87]; while persistent PCBs could lead to large area of hepatocellular lesions and even hepatocellular carcinomas [88, 89]. Nevertheless, all of the PCB homologues were identified by US Environmental Protection Agency (USEPA) as potential carcinogens.

Through food chains, lipotropic compounds such as PCBs are able to be accumulated in aquatic organisms [90]. PCBs are prone to accumulate in hydrophobic micro-environment, for example, sediment organic matters because of their high octanol-water partition coefficients. In aquatic systems, PCBs are uptaken by benthic organisms through consumption or surface contact (figure 1.5). Subsequently, PCBs are accumulated in fish via predation on benthic organisms. During the metabolism in fish, some PCB congeners are degraded while the majority accumulates in adipose tissues [9]. As a result of biomagnification, PCBs are consumed and accumulated in human beings, followed by related toxic effects.

A survey on several aquatic species including Chinese mysterysnail, prawn, fish, and water snake from a reservoir surrounded by several e-waste recycling sites in South China indicates that log BAF (bioaccumulation factor) ranges from 1.2 to 8.4 for PCBs, which is in consistence with the status of accumulation in other ecosystems [29].

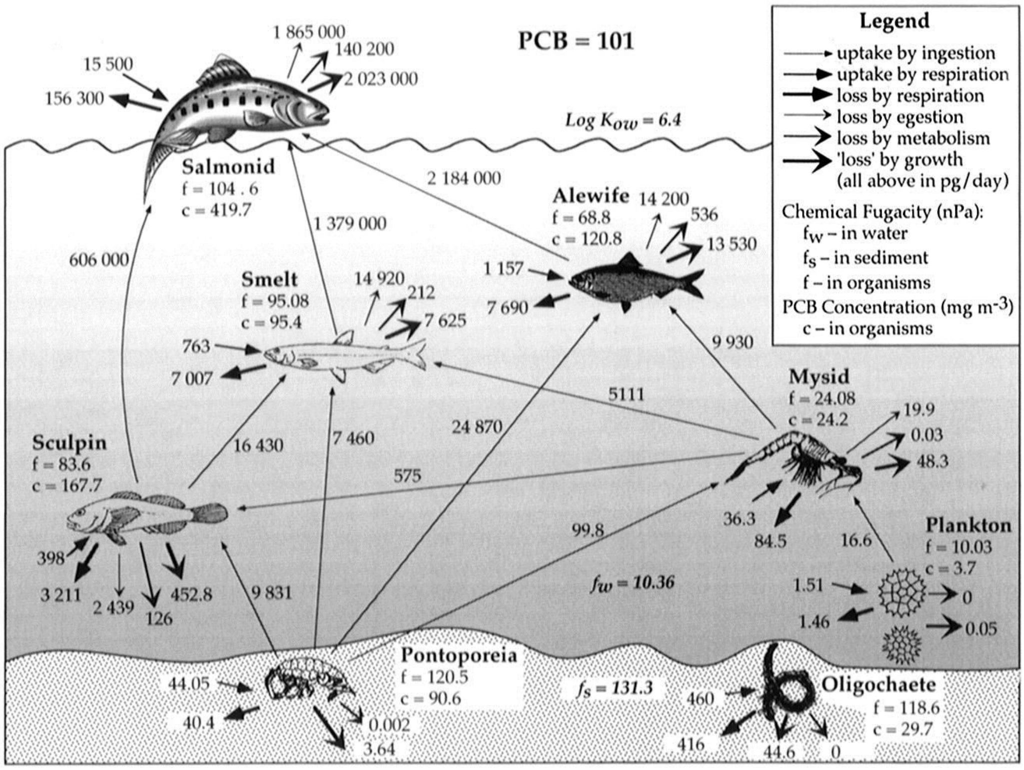


Figure 1.5 Schematic diagram of concentrations, fugacities, and fluxes (μg/day) in Lake Ontario organisms of PCB-101 [91].

1.2.3 Environmental behavior of PCBs in soils and sediments

The retention of PCBs on soils and sediments by sorption and/or partitioning on organic matters of soils and sediments is a result of their hydrophobicity and lipophilicity. Thus PCBs are more persistent in soils with higher content of organic carbons [92, 93]. It is estimated that in the British environment, 93.1% of PCBs burden is associated with soils and 2.1% with marine sediments [94]. Thus it is essential to study the environmental behavior of PCBs for further remediation strategies.

PCBs in soils are mainly from atmospheric particle deposition and landfill leachate, with a low decontamination rate and a half-life of approximately 10-20 yr [95]. In natural soils, the removal of PCBs is limited via microbiological degradation. Other processes as volatilization, leaching, plant uptake and soil erosion, have negligible influences on the content of PCBs in soils [96].

PCBs enter into water bodies through atmospheric deposition or accepting industrial and municipal wastewater. Although a small amount of PCBs is soluble in water, the majority attaches on suspended particles and deposits to sediments at different speeds depending on particle features [97, 98]. PCBs accumulated in sediments can be degraded by anaerobic microorganisms yet at a low degradation rate. The half-life of PCBs varies greatly depending on the properties of different sediments and PCB congeners. Half-life of tetra-CBs and penta-CBs in Hudson River sediments in USA was estimated as approximately 10 yr [99]; half-life of PCB-105, PCB-126, PCB-156 and PCB-169 in the Rhine River sediments was 9 yr; half-life of PCB-31 in New Bedford Harbor sediments was as long as 465 yr while half-life of PCB-105 was only 4.4 yr, that of other congeners ranges from several years to several decades [100].

1.2.4 Contamination by PCBs in soils and sediments

The large varieties of PCB congeners cause difficulties when making comparisons among different studies. To solve the problem, seven commonly used PCB congeners (PCB-28, -52, -101, -118, -138, -153 and -180) with different extent of chlorinated substitution are used as representatives to assess the contamination by PCBs [101, 102]. The contaminations by PCBs at global scale are illustrated as table 1.4 with the exemption of the contamination in e-waste sites of mainland China.

According to a report on National Priorities List (NPL) sites conducted by USEPA, approximately one third of the polluted areas of superfund were contaminated by PCBs to various extents [103], the most well-known example among which is Hudson River in New York State. The river had been contaminated by industrial activities in vicinity from 1950s to 1970s with up to 1000 mg/kg of PCBs at some sampling sites in 1980s [104]. Many industrial countries in Europe, from as south as the Mediterranean Sea to as north as the Baltic Sea [102] and across a large variety of latitude, from Slovenia to Scotland, have been contaminated by

PCBs to various degrees [105]. In China, it is known that e-waste sites are the main PCB contaminated sites, of which contamination levels have been well-studied and discussed in section 1.1.2.2.

Based on the introduction and discussion above, it is of necessity and importance to gain more understandings on the contamination and adverse effects of PCBs. Remediation technologies to remove the contaminations also need to be developed.

Table 1.4 Examples of studies on the PCB contaminations at global scale.

Continent	area	sample	PCB congeners (IUPAC Number)	statistics	sampling year	Contents (µg/kg dw)	reference
Europe	lower Rhône River, France	Sediment (52.5 cm)	28, 52, 101, 118, 138, 153, and 180	mean	1991	282	[10]
	Seine River basin, France	Sediment (3-10 cm)	28, 52, 101, 118, 138, 153, and 180	Ranges	2000	0.09 -150	[106]
	Katowice, Poland	Topsoils (<5 cm)	technical Kanechlor PCB formulations	M±SD[a]	1994	380±300	[107]
		Sediment (< 10 cm)		mean	1994	1300	
	Torino, Italy	Topsoils (<10cm)	1, 5, 18, 31, 44, 52, 66, 87, 101, 110, 138, 141, 151, 153, 170, 180, 183, 187, 206	Ranges	2009	1.8-172	[105]
	Glasgow, England					4.5-78	
	Aveiro, Portugal					0.62-73	
	Ljubljana, Slovenia					2.8-48	
	Uppsala, Sweden					2.3-73	
	Waters of Berlin, Germany	Sediment (< 10 cm)	28, 52, 77, 101, 105, 114, 118, 123, 126, 138, 153, 156, 157, 167, 169, 170, 180	Ranges	1996	7.5-370	[108]
	Southern Baltic	Sediment (< 10 cm)	28, 52, 101, 118, 138, 153, and 180	Ranges	1996-1999	∼1–149	[102]
America	Coast of USA	Sediment	-		1984–1990	～10-1000	[109]
	Hudson River, USA	Sediment	-		1980s	< 1000	[104]
	Lakes of Mexico city, Mexico	Sediment	totally 76 congeners	Ranges	2000-2004	63.7-621	[110]
	North America	grassland soil	28, 52, 101, 118, 138, 153, and 180	Ranges	2000	6.9–3042	[111]

Continent	area	sample	PCB congeners (IUPAC Number)	statistics	sampling year	Contents (µg/kg dw)	reference
Asia	E-waste dismantling workshop of Hongkong, China	Topsoils (<5 cm)	37 PCB congeners including PCB-28, 52, 101, 118, 138, 153, and 180	Ranges	2011	7.13–14542	[112]
	Urban areas, Mongolia	Topsoils (<5 cm)	37 PCB congeners including PCB-28, 52, 101, 118, 138, 153, and 180	Ranges	2010–2011	0.53-114	[113]
	Shiwa industrial complex, South Korea	Topsoils (<5 cm)	-	Ranges	2007	2.43-274	[114]

[a] M±SD: mean ± standard deviation.

1.3 Remediation trials on e-waste contaminated soils and complex co-contaminated soils

Remediation on e-waste sites is challenging due to the complex co-contamination of heavy metals and organic pollutants. Nowadays several remediation techniques are available although with several drawbacks. Efforts have been made to invent remediation techniques to remove both organic and inorganic pollutants in soils and sediments. These techniques include phytoremediation, electrokinetic remediation, soil washing, *etc.*

1.3.1 Phytoremediation

Phytoremediation is the use of plants and their associated microorganisms for environmental cleanup [115]. It is a cost effective method to remove a variety of organic and inorganic pollutants [116]. According to the remediation goals and the properties of contaminants, phytoremediation is available via several processes or strategies: (1) phytostabilization, the use of plants to stabilize pollutants in soil, plant uptake of the pollutants is not desired [117]; (2) phytoextraction, the use of plants to extract and accumulate pollutants in the tissues followed by the harvest for further processing, plant uptake is desired and promoted [118]; (3) phytodegradation, the use of plants or associated microorganisms to convert pollutants into nontoxic materials [119]; (4) phytovolatilization, the release of pollutants by plants in volatile form; (5) phytostimulation or rhizodegradation, degradation of pollutants in the rhizosphere due to microbial activity, a process usually stimulated by plants.

With the advantages of cost effectiveness and being environment-friendly, phytoremediation has gained popularity with the public and agencies. Efforts have been made to develop this technique in a variety of remediation projects [116]. Despite the advantages, there are still limitations and challenges for the technique. One of the limitations is the bioavailability of target pollutants, which is defined as the fraction of the total amount of a contaminant in the soil that is available or can become available for uptake by organisms in a given time span [120].

POPs such as PCBs and PBDEs in soils could be removed *via* phytoextraction or mineralized *via* phytodegradation or phytostimulation. Nevertheless, the low bioavailability of hydrophobic organic compounds (HOCs) due to hydrophobicity and affinity to SOMs constraints the application. A solution is to enhance the mobility of HOCs by adding surface active materials such as surfactants and cyclodextrin. For instance, plant uptake efficiency of Cd and PCBs could be enhanced by tea saponin, a plant-derived surfactant [11]. The removal of PCBs was accelerated by adding cyclodextrin *via* the promotion of the microbe activities in the rhizosphere [11, 121]. The results of these studies provide a reference for the practical utilization of phytoremediation on e-waste contaminated sites, whereas field demonstration and full-scale application are needed to understand the feasibility.

Another limitation or challenge to phytoremediation is that in severely contaminated sites (such as open-burning sites), plants are often exposed to high concentrations of heavy metals and organic pollutants, leading to the declined function of decontamination and even the risk to survival. Several species of plants (for instance cucumbers and pumpkins) were identified to be effective in PCBs removal by stimulating the soil microbial community development [122-124], which seems to be promising in phytoremediation. Whereas other studies figured out the toxicity of metals to these species [125, 126], declining the plausibility. In addition, the soil properties may vary dramatically with the e-waste process, such as combustion and acid leaching. Water holding capacity of soils and the contents of nutrients (P, N, *etc*.) are affected correspondingly and may adversely affect the growth of plants. The relievement of environment stress on plants by adding soil amendments may be available for the application of phytoremedation. For example, vermiculite and activated carbons loaded with nanoscale zerovalent iron can stimulate Impatiens Balsamina to remediate e-waste contaminated soils [14].

1.3.2 Physico-chemical remediation

Apart from phytoremediation, physico-chemical remediation approaches such as electrokinetic remediation and soil washing techniques are also well established. These approaches are usually more expensive than phytoremediation, however in some cases, they could provide more rapid and complete decontamination results if with appropriate engineering design.

Electrokinetic remediation is the use of electric currents to extract radionuclides, metals, certain organic compounds, or mixed inorganic species and organic wastes from soils and slurries [127]. It is efficient in fine-particle medium. Pollutants can be removed through electromigration, electroosmotic flow and electrophoresis. Heavy metals are usually removed via electromigration and organic pollutants *via* electroosmotic flow [128]. With well-controlled conditions, it is able to remove HOCs and heavy metals simultaneously [129, 130]. Although electrokinetic remediation was demonstrated efficient in laboratory scale, this technique is not applied to contaminated land remediation in practice. Its efficiency on complex co-contamination remains to be studied.

On the contrast to electrokinetic remediation, soil washing has been employed to practical remediation for decades, as it is one of the few permanent and rapid treatment processes to remove contaminants from soils. Soil washing is the use of water with or without additives to solubilize contaminants from soils. Unlike electrokinetic remediation, soil washing is more feasible for the application in sandy soils. The application could be flexible, depending on the soil properties and types of contaminants [131]. Accordingly, the remediation could be conducted *in situ* or *ex situ*. The *in situ* process conducted is also named “soil flushing”, which does not require the transfer of soils. While ex situ process is usually performed in batch system without concerning the soil heterogeneity [132]. Schematic diagram of *ex situ* soil washing procedures is illustrated as figure 1.6.

The additives used in soil washing are usually chemical extractants such as acid, chelating agents, surfactants, *etc*. In order to enhance the extracting efficiency of washing process, it is crucial to select a proper additive or a combination of them abased on the contaminations.

Inorganic and organic acids are able to effectively remove metals from soils by dissolution, complexation and ion exchanges, while they could acidify soil matrix and decrease soil productivity [133]. An alternative is the chelating agents due to the formation of strong metal–ligand complexes and less adverse influence compared to acids [134].

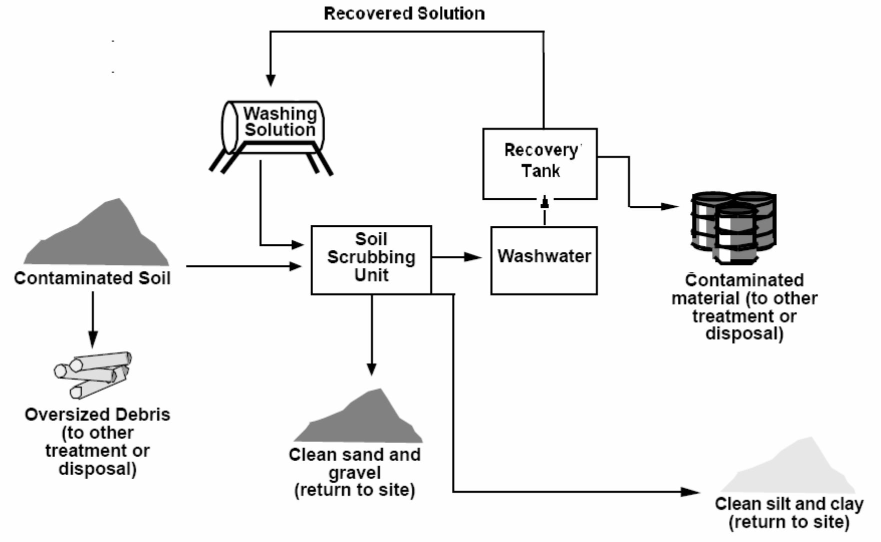


Figure 1.6 Schematic diagram of *ex situ* soil washing procedures.

While in terms of the extraction of HOCs, neither type of the above mentioned extractants is effective as they could hardly complex with HOCs. For hydrophobic compounds that are affinitive to soil matrix, surfactants are able to enhance their desorption by decreasing interfacial tensions and by enhancing the mobilization/solubilization of HOCs [135]. A surfactant is a substrate with amphiphilic molecules having both a hydrophilic (polar group) head and a hydrophobic (nonpolar group) tail [136]. Adsorption of surfactants decreases the surface tension between interfaces, increases the mobility of components and changes their partition. This effect is called mobilization. Once their concentrations reach to the critical micellar concentration (CMC), surfactants in liquid start to cluster into globular or more complex micellar structure, which enhances the solubility of hydrophobic compounds. This is called solubilization. This two mechanisms attribute to the application of surfactants to soil remediation.

Besides HOCs, heavy metals could also be partially removed by surfactants, especially by anionic surfactants. The removal mechanisms are ascribed to counter ion exchange, complexation between metals and anionic head, matrix dissolution, *etc.* [137]. Surfactants can be used to wash soils contaminated by multiple chemicals, since they are able to remove organic pollutants efficiently and partially remove heavy metals [138].

1.3.3 Removal of multiple contaminants by soil washing

Several studies of the trials on simultaneous removal of metals and organic pollutants are summarized in table 1.5. So far not a single extractant has been found to remove heavy metals and HOCs from soils with multiple contaminants except for a case of plant-derived biosurfactant [139]. Mixture of extractants with different functions or sequential washing is more feasible to clean up coexisting contaminants. Among a number of combinations, surfactants and chelating agents are the most effective. Surfactants extract HOCs by decreasing interfacial tension and increasing micellar solubilization. Besides, surfactants enhance the solubility of heavy metals through electrostatic attraction and ion exchange. Chelating agents derive heavy metals from soil surface by forming stable water-soluble complex with the metal ions.

A defect of all these trials is that they merely focus on a certain categories of heavy metals and HOCs, which might not be appropriate to the e-waste sites with multiple pollutants. The complicated interactions among pollutants, among extractants, and among both of them should be considered. Comprehensive understanding of these interactions is also needed so that soil washing can be widely adapted to remediation.

Table 1.1.5 Trials on simultaneous removal of metals and HOCs at laboratory scale.

Concerned pollutant		Concerned soil	Washing operations	Removal efficiency		Reference
HOCs	Metals			HOCs	Metals	
PAHs	Pb	contaminated soils	Flotation by 0.5% (w/w) cocamydopropyl hydroxysultaine (CAS)	46 ± 2%	21 ± 5%	[142]
Phenanthrene	Pb, Zn	contaminated silty soil	A sequential washing by EDTA followed by Tween-80	> 90%	100%	[143]
			A sequential washing by Tween-80 followed by citric acid	> 75%	100%	
Phenanthrene	Ni	spiked kaolin	A sequential washing by 5% Tween 80 followed by 1 M citric acid	85%	~50%	[16]
			A sequential washing by 1 M citric acid followed by 5% Igepal CA-720	90%	~50%	
Phenanthrene	Cd	spiked soil	washing by saponin, a plant-derived biosurfactant	76.20%	87.70%	[139]
Marine diesel fuel (MDF)	Pb	contaminated sandy soil	EDTA-washing followed by SDS-washing	38-46%	85-95%	[144]
			SDS-washing followed by EDTA-washing	40-48%	82-85%	
			Washing by SDS-EDTA mixture	40-45%	82-90%	

It is worth noting that soil washing is a transfer of contaminants from soils to aqueous solution without the decrease in the total amount. Washing solutions could be reused after the removal of contaminants, while the contaminants should be recovered or removed. The recovery of heavy metals could be performed through reduction by zerovalent Mg and Pd [140], or precipitation as sulphides [141], *etc.* The HOCs in washing solution could be biologically or chemically degraded. Techniques of chemical oxidation or reduction have been developed to solve the problem [132]. Post-treatments of the washing solutions should be designed based on the characteristics of contaminants and washing agents. It is typically a tough target for washing solutions containing both metals and HOCs. One of the feasible procedures to simultaneously degrade HOCs and recover metals is to use zerovalent metals (*e.g.* Fe, Mg) as reducing agents.

1.4 Zerovalent iron (ZVI) mediated reduction

In the last two decades, ZVI has been used for the decontamination of ground waters and soils. The process of reactions together with influencing factors, mechanisms and applications have been intensively studied. As a strong reductant, ZVI is ready to be oxidized. The oxidation of ZVI in anaerobic condition could be described as below:

$$Fe^0 + 2H^+ \longleftrightarrow Fe^{2+} + H_2$$ *Equation 1.1*

$$Fe^0 + 2H_2O \longleftrightarrow Fe^{2+} + H_2 + 2OH^-$$ *Equation 1.2*

The reactivity of ZVI allows its application to the reduction of a variety species of contaminants, including metals, POPs and chlorohydrocarbons [145]. The reduction rate varies according to the surface properties of iron (such as the specific surface area, the number of catalytic sites and oxidative status) and the transfer efficiency of target compounds onto the iron surface as ZVI-mediated reduction is surface reaction.

1.4.1 Factors influencing ZVI degradation

1.4.1.1 Particle size

The correlations between the reaction rate and particle size of ZVI have been well recognized. Nano-scale ZVIs (nZVI) with mean particle diameter lower than 100 nm have larger specific surface area and higher surface energy and thus are more efficient than larger ZVI particles [146-148]. Li *et al*. (2004) compared the removal of acid orange 7 by different ZVI particles and in this case they found that nano-ZVI is 5 times more accelerated compared to micro-ZVI and 115 times compared to millimetre-scale ZVI [149].

Although reduction by nZVI is efficient, the application of nZVI is restricted to several physico-chemical factors: (1) nZVI particles are unstable and prone to agglomeration because of the small diameter, large specific surface area, high surface tension and magnetic induction. Any measures to prevent agglomeration can cause the raise of costs; (2) iron particles are strongly reductive. The rapid redox reaction with oxygen and even self-combustion, reduces the reaction efficiency; (3) nZVI itself has potential toxicity on organisms and its risk assessment is necessary; (4) the production and storage of nZVI require specific conditions and strict regulations with additional costs [18, 150, 151].

1.4.1.2 Bimetallic particles

Reduction rate by ZVI is normally limited, especially for halogenated aromatic hydrocarbons with complex structure, such as chlorophenol, PCBs and PBDEs. Reaction rate of some halogenated hydrocarbons is even close to zero [152-154]. Researchers manage to solve this problem by adding transitional metals like Pd, Ni or Pt as catalyst [145]. ZVI together with metal catalysts are called bimetallic particles, in which Fe^0 serves as the negative electrode in redox reaction while transition metal element serves as an electron carrier [151].

Bimetallic particles effectively catalyze dehalogenation by ZVI. For example, in a laboratory trial, the half-life of PCB-21 is approximately 1 yr if dehalogenated by nZVI. With the addition of Pd, the dehalogenation efficiency is 500 times more rapid. Transition metal particles not only catalyze the reaction but also prevent the oxidation on Fe surface [17].

Ni-Fe bimetallic particles can be used as an example to demonstrate the mechanism (figure 1.7). ZVI reacts with water in alkalescent condition and generates reductive hydrogen gas. Ni inserts in C-X bond of halogenated aromatic hydrogens, reducing the energy required to break the bond. Hydrogen molecule attacks the unstable C…Ni…X and C-X is broken down. Ni is released and continues to insert into another C-X bond. In general, Ni serves as the catalyst and Fe the reductant.

Theoretically speaking, catalysts are not consumed during the reaction. Since the metal catalysts attach to the iron surface, the contact probability with target pollutants is essential to the reaction. Fang *et al.* (2011) revealed the positive correlation between amount of attached Ni and dehalogenation rate of BDE-209. They illustrated that with more Ni attached on ZVI, more hydrogen gas is available on the surface and speeds up the reaction [155]. Gunawardana *et al.* (2012) also found that dehalogenation rate of pentachlorophenol increases along with higher Ni loaded [156].

Despite the effective reduction promoted by the catalysts, there are several limitations for the introduction of noble or heavy metals to ZVI including the elevated cost for the remediation and the potential toxicity of the catalysts. Understandings on the reactions and risks of the bimetal materials should be obtained before large scale applications.

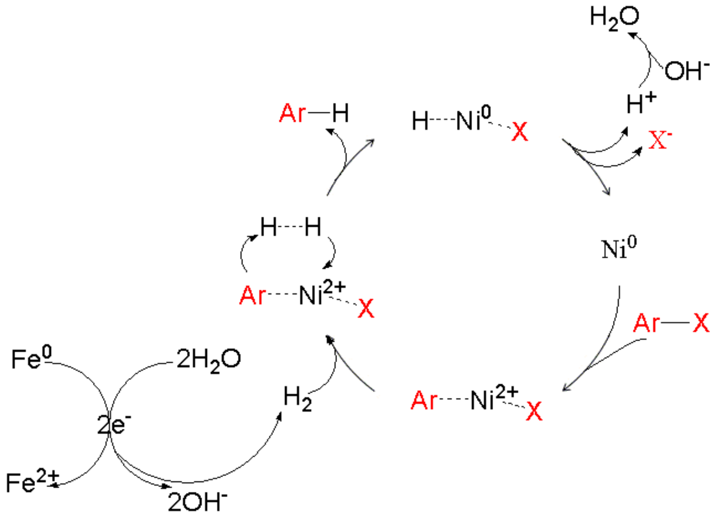


Figure 1.7 Schematic of dehalogenation on the surface of Ni-Fe bimetal.

1.4.1.3 Surfactants

It is mentioned above that the reduction rate of target compounds by ZVI is dependent not only on the iron properties but also the mass transfer of the compounds. Thus the reductions of HOCs such as PCBs and PBDEs are constrained by their lipophicility. This situation could be improved by employing surface active agents (i.e. surfactants) [157].In ZVI reduction system, natural or anthropogenic surfactants bear affinities to both HOCs and ZVI. Different mechanisms of surfactants including solubilisation, mobilization and its competitive adsorption sites as well as its stimulation on adsorption can affect the reaction rate of HOC dehalogenation [158]. The mechanism and efficacy of a surfactant varies according to the type and the applied concentration.

Previous studies indicated that cationic surfactants such as dodecyl trimethyl ammonium chloride (DDTMA), hexadecyl trimethyl ammonium bromide (HDTMA), and octyltrimethylammonium chloride (OTMA) are able to enhance the dechlorination rate of perchloroethylene (PCE) by ZVI [159-162]. On the contrary, anionic surfactants such as sodium dodecyl benzene sulfonate (SDBS) and Sodium Dodecyl Sulfonate (SDS) suppress the reduction reaction. A possible mechanism is that anionic surfactants are attracted to the surface of ZVI and constrain mass transfer [159, 162, 163]. Effects of nonionic surfactants are not sufficiently studied and their performance depends on specific types [164].

It was demonstrated that the performance of surfactants is affected by the utilized concentrations. Loraine (1996) found that when its concentration is lower than CMC, nonionic surfactant TX-100 facilitated the dehalogenation of PCE while the surfactant inhibited dehalogenation with TX-100 concentration higher than CMC. Concentration of SDS also influences the reaction rate of HOCs. Dehalogenation of HOCs remains unchanged with concentration of SDS below CMC while the reaction is suppressed with SDS concentration above CMC [165]. Generally speaking, surfactants with concentrations below CMC increase the adsorption of target pollutants on ZVI surface through solubilization, stimulating the dehalogenation. With concentration of surfactants above CMC, pollutants are mainly distributed in the hydrophobic kernel of surfactant micelle, which slow down the process of dehalogenation [164-166].

1.4.1.4 Humic acid

Natural or soil organic matter (NOM/SOM) is an important organic component in waters and soils, most of which are decomposed from animal and plant residues (70%-80%). In natural environment, humin-like humic acid influence electron transfer and mass transfer, affecting the dehalogenation of HOCs by ZVI [167].

(1) Effects of humic acids on mass transfer

Humic acids were demonstrated to inhibit the dechlorination of chlorinated organic compounds including 2,4-dichlorophenol [167], carbon tetrachloride [168], PCE [158, 169, 170] and p-nitrchlorobenzene [171]. It is deduced that the suppression is caused by the competition between humic acids and target pollutants for the limited adsorption sites on ZVI surface. The adsorption of humic acids on ZVI reduces the transfer rate of pollutants onto ion surface [172]. Doong *et al.* (2005) observed the attachment of humic acids on ZVI particles through scanning electron microscope [169]. Adsorption isotherms of TCE and humic acids on iron surface manifested their adsorption competition [158]. Tan *et al.* (2004) assume that adsorption of humic acids is attributed to the benzene carboxylic and phenolic hydroxyl groups in HA, which occupy the surfactant reactive sites of ZVI [173].

Meanwhile, surfactive humic acids and NOM/SOM increase the distribution coefficient of target pollutants through physical and chemical adsorption. It has been found that soluble fulvic acids and dissolved organic matters (DOM) exert mobilization effect on HOCs including PCBs, DDT, polystream and chlorinated organic pesticides. With a given DOM sample, the solute partition coefficient increases with an increase of the solute’s octanol-water partition coefficient [174]. Although adsorbed HOCs can be removed through the deposition with NOM/SOM or the sorption on ZVI, the distance between associative HOCs and ZVI surface is longer compared to dissociative HOCs. Less attachment on ZVI hinders the dehalogenation process [162].

Besides, previous research also indicates that as Fe ions are released from ZVI corrosion, humic acids are facilitated to form complexation with Fe ions. As a result, the colloids and aggregates of humic acids suppress the dehalogenation reaction [175].

(2) Effects of humic acids on electron transfer

While most of the researches proved that humic acids constrain dehalogenaion of HOCs, some of them demonstrated that humic acids may speed up the reaction rate by increasing electron transfer rate. Doong *et al.* (2005) found that humic acids reduce the rate of PCE dehalogenation by Pd/Fe particles. While after 24 h of equilibrium between humic acid and palladized irons prior to the addition of PCE, the efficiency of PCE dechlorination increases with increasing humic acid concentrations [169]. Feng at al. (2008) found that at relatively low concentration (<0.1 g/L), the humid acids significantly accelerate the dechlorination rate of chloroform by nZVI [176].

A couple of previous studies have shown that during the dehalogenation of chlorinated organics by microbial anaerobic respiration and by ZVI, quinones of NOM/ SOM molecules including humic acids serve as electron shuttle and accelerate the electron transfer in the reaction (Figure 1.8).

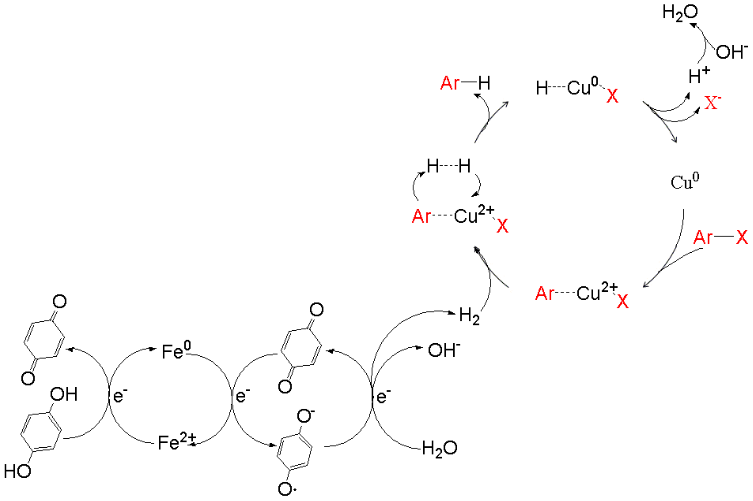


Figure 1.8 Possible mechanism of quinones as electron shuttle.

1.4.1.5 pH

ZVI reduction reaction involves electron and proton transfer, thus the reaction is sensitive to the ambient pH. Normally dehalogenation rate is negatively correlated to pH [148, 177, 178]. As ZVI is oxidized, protons in H_2O are transferred, making the system tend to be alkaline. As a consequence, ferric oxides and hydroxides generated and deposit on the surface of ZVI, passivating the ZVI particles [148]. Thus pH buffers and pH auto-control system are utilized to maintain a relative low pH (4.9-5.1) and reactivity of ZVI in lab-scale trials [177, 179].

To sum up, it is necessary to understand and control all the factors that can affect the reaction so that dehalogenation by ZVI would be efficient in application.

1.4.2 Mechanisms of halogenated hydrocarbon degradation by zerovalent iron

Zerovalent iron (ZVI) is a frequently used material in permeable reactive barriers (PRBs) during the in situ remediation of contaminated groundwater. ZVI reacts with chlorinated hydrocarbon through beta-elimination reduction via stepwise hydrogenolysis (replacement of halogen by hydrogen) [180-182]. In the hydrogenation reduction, iron and hydrogen are regarded as electron donors while chlorinated pollutant serves as an electron receiver. This reduction is heterogeneous, reacting between between ZVI (solid) and liquid. The final products are mainly hydrocarbons with low-halogenated intermediates.

Research on ZVI degradation has been arisen to seek solutions to contaminations by PBDEs and PCBs. A study indicates that sequential debromination goes through different pathways in ZVI and bimetallic system. The reaction pathways with bimetallic system favor removal of para-halogens first then ortho-halogens on PBDEs and PCBs. While in ZVI system, ortho-halogens are preferentially removed followed by para-halogen removal [152]. Zhuang *et al.* (2011) inferred that the steric hindrance of ether bond and benzene ring hinders the catalyst (Pd) to insert in C-Br bond at ortho-position, slowing down the catalyzing reaction. While in bimetallic system, removal of para-halogens is favored [183]. Nano-scale ZVI also features in sequential dechlorination of PCBs. Chlorines in the para and meta position are predominantly removed over chlorines in the ortho position [18, 154]. Normally ring-opening reactions are not involved for the dehalogenation of halogenated biphenyls or diphenyl ethers, and the final products remain biphenyls or diphenyl ethers, respectively. Even though halogen removal reactions partially decrease the toxicity and hydrophobicity of pollutants, it is impossible to decompose and mineralize dehalogenated hydrocarbons by microbes in natural environment in a short term. Therefore, the application of ZVI degradation techniques is still restricted.

Along with the chemical reduction mechanisms, ZVI could also promote the degradation of target compounds by microorganisms under anaerobic conditions. The combined use of ZVI and anaerobic microbes for the treatment of various pollutants, including perchlorate, azos, PCBs and nitrates, has been demonstrated effective [184-186]. Two possible mechanisms are suggested to explain the role of ZVI herein: (1) ZVI has a significant selective effect on anaerobic microorganisms and influences their succession [187]; (2) H_2 generated during the aqueous ZVI reaction may be a preferred electron donor for many bacteria, thus promoting the growth and activity of microorganisms [185].

The chemical and biological processes of reduction mediated by ZVI are often simultaneous and difficult to distinguish, especially during field applications. Insights into the mechanisms are still needed for comprehensive understandings.

1.4.3 Application of ZVI degradation in remediation

The application of ZVI is flexible since it could be used *in situ* or *ex situ*, on waters or soils (as illustrated by figure 1.9) [188]. ZVI was initially used as an active material in permeable reactive barriers (PRBs) for underground water treatment. According to a report from USEPA, ZVI has been applied to *in situ* remediation of contaminated ground water for more than two decades [189]. A survey in 2002 conducted in US revealed that the effective remediation material in 55% of PRB is ZVI [190].

Ground water treatment systems use ZVI fillings in PRB to degrade the chlorinated hydrocarbons in Denver area, Colorado, as well as to intercept pollutions of chromium VI and chlorinated hydrocarbons in Elizabeth City [191]. In long-term application, PRB surface not only undergoes geochemical changes, but also experiences an increased microbial activities which biologically mediate the dehalogenation [192]. The Monkstown ZVI-PRB in Northern Ireland, the oldest commercially installed ZVI-PRB in Europe, has been used to remove TCE for nearly 20 years. According to the data from 2001 to 2006, TCE was still being reduced effectively, and mineral precipitation and great variety of microbial communities were detected [193].

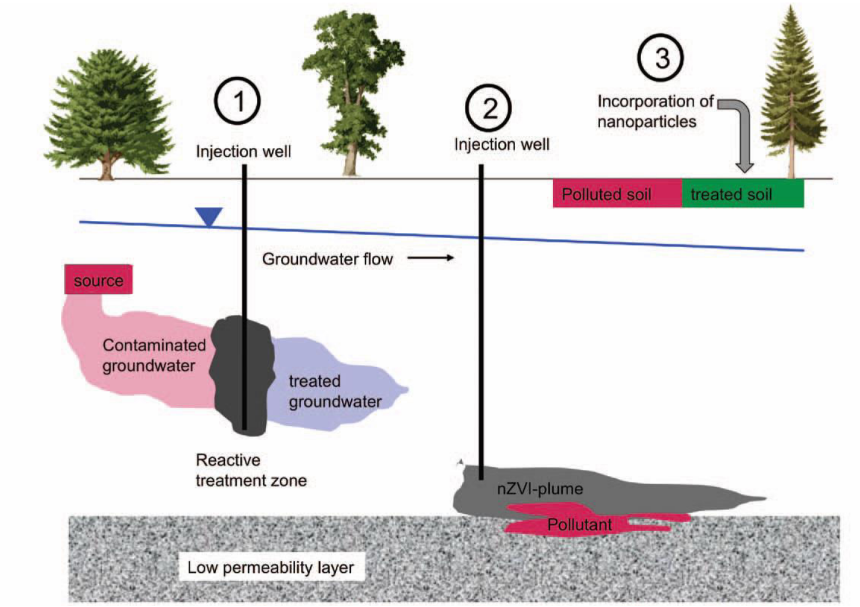


Figure 1.9 Schematic of in situ remediation of ground water and soils by ZVI: (1) formation of PRB (2) nZVI plume; (3) soil mixed with ZVI [188].

PRB is durable and effective for hundreds of years under ideal conditions. In reality, the longevity of PRB is limited by design defects, imperfect hydraulic characterization, losses of reactivity and permeability, *etc.* [194]. In order to enhance the long-term performance of ZVI in PRB, studies have been conducted to improve the PRB design in terms of engineering. More importantly, researchers started to improve the efficiency of ZVI particles with further understandings of the reaction mechanisms. An air force station in Florida presents the result that nanoscale bimetallic particles were able to substantially remove TCE but the general efficiency was relatively lower compared to emulsified ZVI due to the rapid passivation [195, 196].

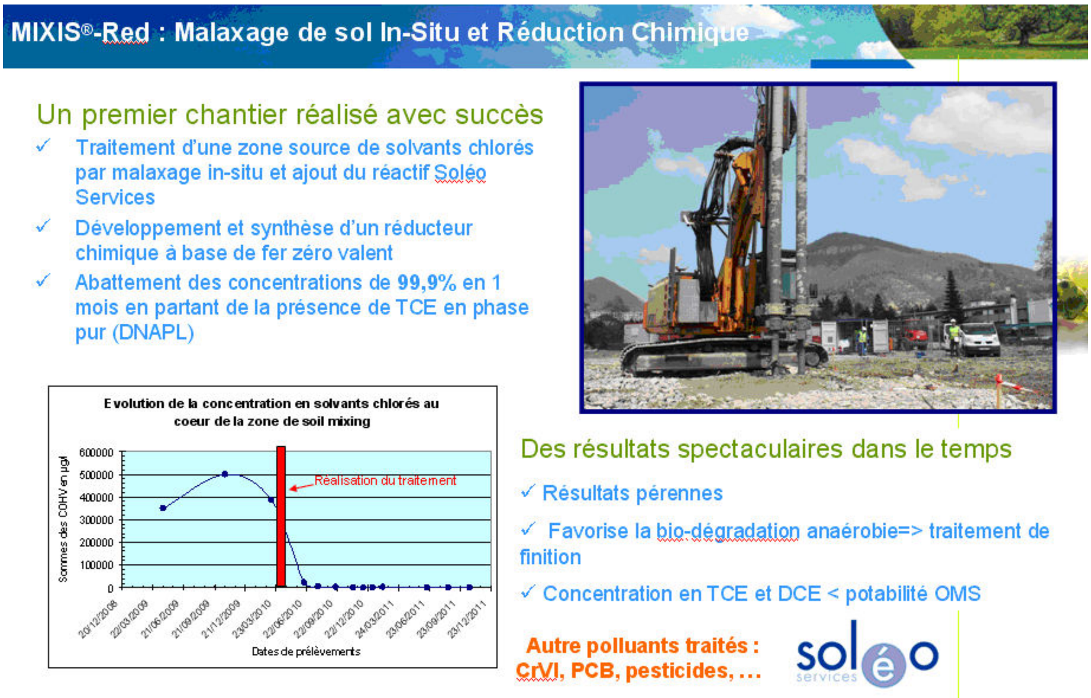
In addition to underground water treatment, ZVI has been applied progressively to remove halogenated organics in soils for the past few years, although much fewer than the application to water. The application to soils is limited probably because the reaction rate is lower in solids (soils and sediments) than in liquid. Besides, longevity of ZVI decreases substantially due to passivation. For example, 90 % of atrazine in solution could be removed within 1 h by mZVI and nZVI while only 75% in soils was removed in 7 d [197]. This is because large amount of NOM/ SOM in soils and sediments decreases the activity of ZVI by absorbing on its surface. Research team in Auburn University injected carboxymethyl cellulose (CMC) stabilized ZVI nanoparticles for in situ soil remediation, with ZVI power exhausted after 14 d. Instead, biological dechlorination of PCE and chloroethylenes was active [198].

On the other hand, the low availability of target compounds, HOCs or metals, in soils also limit the application. Hydrophobic and lipophilic chemicals tend to combine with SOM and a portion of metals tend to be constrained by mineral lattices, leading to a low transfer efficiency to the iron surface [199].

When applying ZVI on field or in projects, we may choose from *in situ* and *ex situ* remediation based on soil characteristics and field conditions. For *in situ* remediation, injection and ZVI-clay soil mixing are commonly used. *In situ* mixing serves more effectively in soils despite of soil heterogeneity. By this method, the degradation of chlorohydrocarbons in soils could achieved as high as 97% [200, 201].

A process of soil decontamination by using ZVI named MIXIS® has been developed by Soléo Services, France, following the principles of *in situ* remediation (figure 1.9 (3)). This approach is conducted by injecting and mixing chemicals with contaminated soils in a reaction core, assisted by adaptive equipments. The chemicals can be oxidants or reductants, in aqueous solution or suspensions, depending on the decontamination protocols. Successful field applications of this approach to remove chlorohydrocarbons by ZVI demonstrated the long-term availability of ZVI with proper design. In a case, TCE could be 99% removed within weeks and anaerobic degradation by microbes were enhanced at the end of the treatment (figure 1.10).

In terms of *ex situ* processes, study from University of Nebraska demonstrated destruction of over 60% of chlorinated pesticides in soil within 90 d through *ex situ* treatment. Addition of aluminum sulphate accelerates the remediation and reaches 90% removal rate [202].



MIXIS®-Red : Malaxage de sol In-Situ et Réduction Chimique

Un premier chantier réalisé avec succès

- ✓ Traitement d'une zone source de solvants chlorés par malaxage in-situ et ajout du réactif Soléo Services
- ✓ Développement et synthèse d'un réducteur chimique à base de fer zéro valent
- ✓ Abattement des concentrations de **99,9%** en 1 mois en partant de la présence de TCE en phase pur (DNAPL)

Des résultats spectaculaires dans le temps

- ✓ Résultats pérennes
- ✓ Favorise la bio-dégradation anaérobie=> traitement de finition
- ✓ Concentration en TCE et DCE < potabilité OMS

Autre polluants traités : CrVI, PCB, pesticides, …

Figure 1.10 A case of MIXIS® to remediate TCE-contaminated soil by ZVI (http://www.soleo-services.fr/mixis/).

1.5 Conclusions

This literature review tried to provide an overview on the background of the subsequent studies, beginning from the contamination in e-waste sites and global PCBs contamination problems and a current state of the remediation progress **(the issue)**; Followed by an introduction to the mechanisms and constraints of ZVI-mediated dehalogenation **(the feasibility)**; Finally to the utilization of this approach in practice to be referred for the PCBs problem **(the application)**, as presented by figure 1.11.

1. **The issue.** The contaminations in sites involved in e-waste recycling activities in south China were complicated, with both heavy metals (Ni, Pb, Zn, Cu, Cd, Cr, *etc.*) and organic contaminants (PCBs, BFRs, PCDD/F, PBDD/F, *etc.*) at various contents in the surroundings. One of the severe problems is PCBs contamination in soils and sediments. Although the global exposure scale of PCBs to human beings and food chains has been declined over decades, the contaminations in many industrial brown sites all over the world are to be cleaned up due to the high toxicity of PCBs. The common coexistence of multiple contaminants makes it even more difficult to remove the pollution and recover the ecological function of soils/sediments.

Efforts have been made to solve the problem. Clean-up process such as phytoremediation, electrokinetic remediation and enhanced soil washing have been studied to achieve the goal of remediation, among which soil washing is a promising physical-chemical approach with the advantage of high efficiency. However the post-treatment for soil washing solution remains a problem.

2. **The feasibility.** The properties and mechanisms of ZVI-mediated reduction were reviewed straight after the overview on contamination issue, together with the influencing factors that constraint the reaction rate. To degrade the PCBs in washing solutions under mild condition,

zerovalent iron seems to be an ideal material for the outstanding reduction performance. However, the coexistence of washing agent, soil organic matters *etc*. in the solution is likely to influence the reaction by ZVI. It is of necessity and interest to understand the influence by the components in the washing solution on the reductive degradation of PCBs by ZVI.

The understanding on the influencing factors facilitates the optimization of conditions during the application of ZVI to the washing solutions.

3. **The application.** ZVI was initially applied as a reactive material in PRB system to enhance the remediation of underground water, which is still one of the most commonly used materials for PRB. The current applications of ZVI in aqua or in soils/sediments offer a demonstration of practical usage and the possible constraints herein. To apply ZVI on the post-treatment of soil washing solutions or directly on the remediation of soils/sediments, several parameters have to be adjusted according to the understanding on the feasibility of this technology.

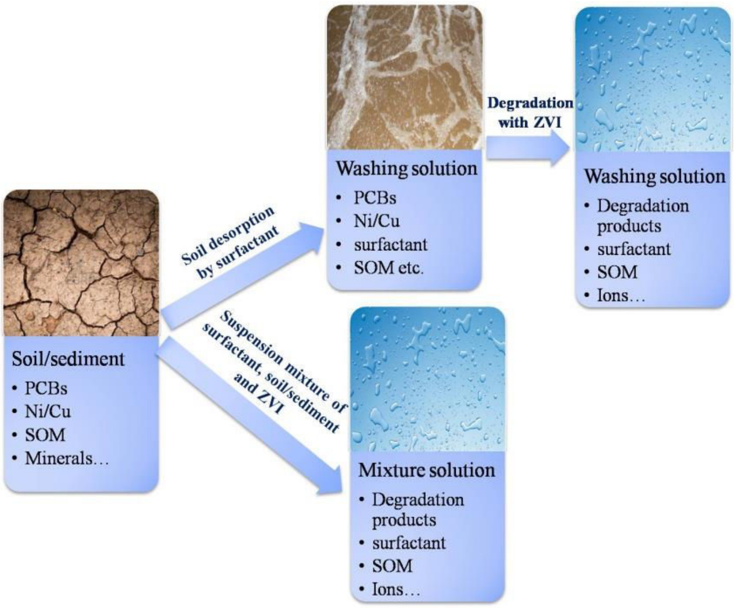


Figure 1.11 Schematic diagram of the lab-scale application of ZVI to PCB-contaminated soil.

Chapter 2.

Soil contamination by polychlorinated biphenyls in e-waste recycling sites in south China

Part of the data and conclusions of this chapter were presented in 20th World Congress of Soil Science as

Yingxin Wu, Qingqi Lin, Yan Wu, Xiongfei Huang, Rongliang QIU*. Current status of soil contamination in e-waste recycling sites in south China. 20th World Congress of Soil Science, Jeju, Korea, June, 2014 (http://www.20wcss.org)

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2.1 Introduction

It is reported that the exposure of PCBs to human and food web has been declining for the last 30 years at a global scale [79], whereas contamination by PCBs is still a problem in some hot spots, such as e-waste recycling sites in south China [34, 61, 68]. Special focus lies on the soil/sediment contaminations by PCBs, because soil and sediment are important sinks and sources for hydrophobic contaminants and also influence their behavior and fate in the environment.

Although several surveys investigated the PCBs contamination of soils and sediments in e-waste sites, little data was obtained about the situation in Qingyuan. Besides, since reports revealed the contamination by e-waste recycling activities, changes occur in Qingyuan, Guiyu and Taizhou. For example, many small-scale backyard workshops were shut down and large-scale plants that are able to handle pollutions were established to be involved in recycling. However, the pollution left by these workshops still need some proper strategies for their remediation, therefore a better understanding of the current situation should be obtained.

In addition to PCBs, other contaminants such as heavy metals were also ubiquitous in soils and sediments of e-waste sites [54, 62, 203]. The coexistence of contaminants may influence the remediation process of PCBs. For instance, PCBs are able to be partially or completely degraded by some microorganisms, while the coexisting heavy metals at the site is likely to depress their growth and activities. Thus it is necessary to understand the levels of co-existing contaminants.

The objectives of this chapter are: (1) to compare the PCBs contents and profile in soils and sediments from Qingyuan, Guiyu and other sites; (2) to evaluate the co-existing species and contents of heavy metals; (3) to provide understandings on the optimization of parameters to the successive studies.

2.2 Experimental

2.2.1 Studied areas and sample collection

A total of 6 areas were investigated in two typical e-waste recycling regions (Qingyuan and Guiyu, China) between October and December, 2011. Three samples were from Qingyuan, including 1 sediment and 2 soil samples; others were from Guiyu, all of which were soils. The locations of study areas are provided in Figure 2.1 and the geographical coordinates of all sampling sites were confirmed by a global positioning system. To understand the contamination around workshops involved in different disposal approaches, sampling was conducted in the vicinity of workshops occupied in dismantling, acid washing and open burning, respectively, as described by Table 2.1. Each surface soil sample (0-20 cm) was composed of four subsamples and was collected using a stainless steel shovel from an area within a radius of 2 m. After removing weeds and stones, all samples were frozen dried and screened through a 100 mesh sieve. The samples were stored at -20 °C until analysis.

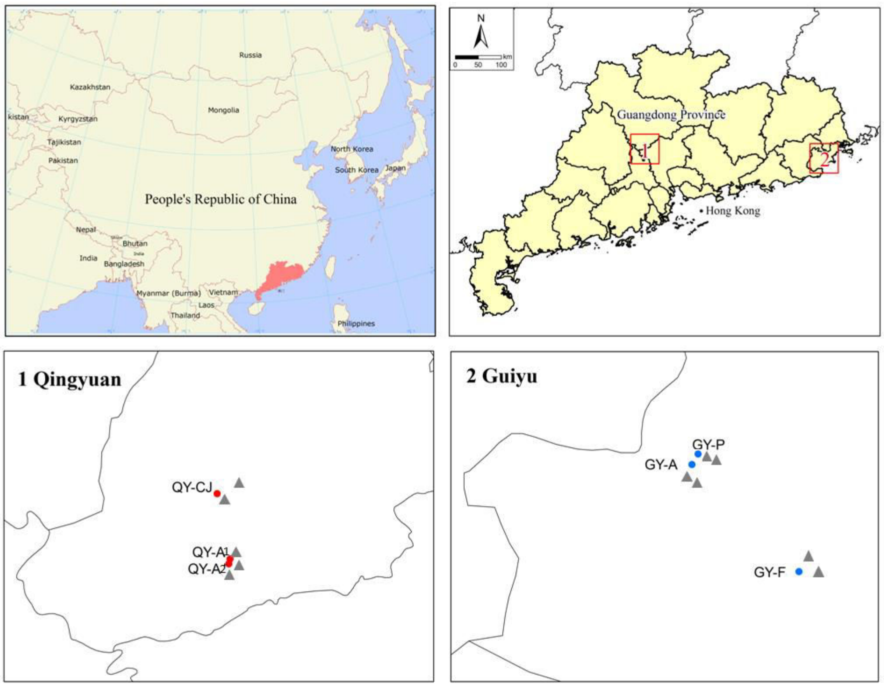

Figure 2.1 Distribution outline of sampling sites and workshops: 1 Qingyuan; 2 Guiyu. Triangles: recycling backyard workshops. Points: Sampling sites.

Table 2.1 Description of sampling sites.

Name	Possible pollution source	Location	Description
QY-A1	Acid washing	Qingyuan	Sediment from a dried up pond that received the leachate of acid washing.
QY-A2	Acid washing	Qingyuan	Soil from a site that may be a recently abandoned acid drain.
QY-D	Dismantling	Qingyuan	Soil from an abandoned backyard workshop with residues of undismantled materials
GY-P	Printer dismantling	Guiyu	Soil from a printer roller dump site
GY-F	Open burning	Guiyu	Paddy soil near combustion site
GY-A	Acid washing	Guiyu	Soil near an acid bath for metal recovery

Figure 2.2 E-waste recycling activities in vicinity to the sampling sites

2.2.2 Characterization of soil samples

The pH values of soil samples in KCl solution were measured following ISO 10390:2005(E), Soil Quality-Determination of pH, MOD.

To measure the content of soil organic carbon (SOC), 0.100-0.500 g soils (60 mesh) were immersed in 5 mL 4.8 mol/L potassium dichromate and 5 mL 98% sulfuric acid, and then heated to 180 °C for 5 min. Afterward, the remained potassium dichromate was titrated by 0.2 mol/L ferrous sulfate with 1,10-Phenanthroline monohydrate as indicator. The content of SOC was calculated by the content of reduced potassium dichromate.

2.2.3 Analysis of heavy metals

Heavy metals in the samples were detected for their total concentrations and the available concentrations, following different extraction methods. Triplicate was conducted for each sample.

The total heavy metals were extracted by an acid digestion method. 2.00 g of a sample (20 mesh) was immersed in 20 mL *aqua regia* and then heated at 150 °C by an electric heating plate for 5-10 min until the complete disappearance of oxynitride; after that, 10 mL 70% perchloric acid were added to the vial and continued to be heated until the complete disappearance of white smoke and the appearance of gray and white residue in the vial. After cooling, the vial was washed by deionized water for three time and the liquid was diluted to 50 mL by a volumetric flask.

To estimate the potential risk of metals and the readiness to be extracted during remediation, the availability of Ni, Pb, Zn, Cu, Cd, Cr was evaluated by the extraction using buffered diethylene triamine pentacetic acid (DTPA) solution. The buffered DTPA solution contained 0.1 mol/L triethanolamine， 0.01 mol/L $CaCl_2$, and 0.005 mol/L DTPA, with a pH value of 7.30.

The concentrations of Ni, Pb, Zn, Cu, Cd, Cr in samples were determined by an inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 5300DV, Perkin-Elmer, USA) and a Graphite Furnace Atomic Absorption Spectrometry (GFAAS, Z-5000, Hitachi, Japan).

2.2.4 Analysis of PCBs and QA/QC

To extract PCBs from samples, activated Cu was added to remove sulfur and then Soxhlet extraction was conducted for 48 h with 200 mL acetone/hexane mixture (1:1, v/v). The extracts were concentrated by rotary evaporation and exchanged to hexane and then fractionated on a multilayer silica/alumina column. 30 mL dichloromethane:hexane (1:1, v/v) were added and the eluate was concentrated to 200 µL under a gentle stream of nitrogen gas. Afterward, the samples were analyzed by a gas chromatograph (Thermo-Ultra Trace GC-DSQ) equipped with mass.

For the GC-MS measurement of PCBs, a 30 m × 0.32 mm × 0.25 µm DB-5 column (J&W Scientific Inc.) was used with different analyzing protocol. The oven temperature was held at 100 °C for 2 min, increased to 180 °C with gradient of 15 °C /min, then to 240 °C with gradient of 3 °C, post run to 285 °C with gradient of 10 °C and held for 10 min. The flow rate of carrier gas (nitrogen 99.999%) was 1.2 mL/min. The temperatures of injector and ion source were 280 and 220 °C, respectively.

During the extraction and cleanup procedure of PCBs, PCB-30, -65, -204 were added as surrogates and PCB-24, 82, -198 as internal standards. A laboratory blank sample, a standard-spiked blank sample, a standard-spiked matrix sample, and a duplicate sample were processed with each batch of 12 samples. Surrogate standards were added to all the samples to monitor matrix effect. PCBs recoveries from the spiked blank sample ranged from 65.5 to 82.6%. Recoveries of spiked matrices were 62.5-132.1%.

2.3 Results and discussion

2.3.1 Properties of sampled soils

As shown in Table 2.2, the properties of the sediment and soils in Qingyuan and Guiyu were quite different from each other. The pH values are ranged from 2.24 (QY-A2) to 7.77 (QY-D) in Qingyuan, while those were 3.53 (GY-A) to 5.20 (GY-F) in Guiyu. Soil samples in Qingyuan were generally more acid and barren, as revealed by the lower soil organic contents. The soil pH seems to be influenced by recycling activities. Acid washing sites generally had a lower soil pH values (2.51 in QY-A1, 2.24 in QY-A2 and 3.53 in GY-A) compared to others.

Table 2.2 Properties and the contents of PCBs in samples of e-waste sites from Guiyu and Qingyuan, China.

Samples		QY-A1	QY-A2	QY-D	GY-P	GY-F	GY-A
SOC (g/kg dw)		0.20	0.59	1.10	2.19	3.41	2.13
pH		2.51	2.24	7.77	4.93	5.20	3.53
PCBs (μg/kg dw)	PCB-28	0.263	0.554	19.515	0.230	0.532	0.125
	PCB-52	0.517	0.655	9.223	0.000	0.566	0.223
	PCB-101	0.179	0.335	1.031	0.330	3.670	0.279
	PCB-118	0.338	0.885	2.332	0.000	0.308	0.192
	PCB-153	0.336	0.766	2.083	0.147	1.145	0.163
	PCB-138	0.397	0.991	2.343	0.224	0.849	0.203
	PCB-180	0.000	1.650	0.524	0.000	1.562	2.058
	Sum	2.029	5.837	37.051	0.932	8.632	3.243

2.3.2 PCB contaminations

Table 2.2 illustrates the contents of PCBs in the 6 samples. Comparison among the data shows that dismantling activities caused more severe contamination than the other recycling activities. Although the paddy soil (GY-F) was in vicinity of an open burning site, it was less contaminated than QY-D, probably because of the adsorption of PCB-containing dust by plant shoots in the field. Yet it was still significantly more contaminated than the other samples. Comparable contents of PCBs were detected in all of the three acid washing sites while QY-A1 was slightly less polluted than QY-A2, although they are at the same site. Printer roller dump site was the least polluted one among all the concerned sites.

Due to the lack of soil standard for PCBs in China, it is difficult to identify if the contaminations in these sites were severe or not. Thus herein we refer to the *Dutch Target and Intervention Values (the new Dutch list, 2000)*, as many studies did [4]. This standard defined the term intervention values to indicate when the functional properties of the soil for humans, plant and animal life, is seriously impaired or threatened. They are representative of the level of contamination above which there is a serious case of soil contamination. The soil/sediment remediation intervention value for PCBs (sum of PCB-28, 52, 101, 118, 138, 153, 180) is 1000 μg/kg (dw) [204]. Thus, despite the contamination levels varied among samples, none of the concerned samples were considered severely contaminated.

Besides the varied contents of different samples, the profiles of PCB congeners also illustrate a variation. The dominant congeners in QY-D is PCB-28 and PCB-52, which is similar to the situation in Taizhou and Guiyu previously, suggesting that the commercial PCBs mixture Aroclor 1242 might be the major origin of PCB contaminations during the recycling of electric power capacitors or transformers [62]. In terms of other samples, the contents of congeners were quite similar to each other, suggesting multiple sources of the PCB contaminants.

It is also of concern to assess if the contamination of PCBs in these areas were improved or worse. A study conducted at Guiyu in the year 2006 shows a content of 31.0 μg/kg (Σ_7PCBs, dw) in soils from printer roller dump site [34], which is 32 times higher than that in this study, indicating a likely improvement in this site. Comparison to similar studies on paddy soils near combustion sites at Guiyu and Taizhou areas also indicates a possible improvement in rice fields [62, 74]. Dismantling sites in Guiyu and Taizhou were commonly more contaminated, with a range of 52.0-2061.0 μg/kg (Σ_7PCBs, dw) [62, 68]. All of the available detected data were higher than QY-D. In fact there are only a few surveys that could be compared with, and none of them concerned about Qingyuan or acid washing sites. Hence the comparison with previous studies could only provide a reference to the present study, conclusions could not be drawn on the changes of contamination herein.

2.3.3 Metal contaminations

Previous studies revealed the co-existence of multiple contaminants in e-waste sites, which is the same in this study. Table 2.3 illustrates the contents of heavy metals in the concerned samples.

Heavy metals, rather than PCBs, were the major concern in acid washing sites, as the metal recovery process deals with dismantled parts, which involves little with the emitting process of organic pollutants. The low pH value of samples indicates the influence of acid washing on surrounding soils. High available contents of metals (figure2.3) in these sites caused by the low pH which pose a threat to the local plants and animals, even humans [205].

Table 2.3 Total metal contents of soil samples from Guiyu and Qingyuan (unit: mg/kg dw).

Heavy metals	Qingyuan QY-A1	QY-A2	QY-D	Guiyu GY-P	GY-A	GY-F
Ni	80.88±7.3*	49.79±1.12	59.49±9.18	21.88±1.05	106.13±0.47	35.13±2.44
Pb	210.25±5	73.96±1.68	297.92±26.34	48.92±3.17	60.46±2.58	67.54±0.79
Zn	482.41±19.22	491.65±16.27	221.6±15.68	109.25±8.49	120.33±20.27	136.33±8.51
Cu	578.83±29.82	503.58±7.56	384.57±38.03	36.46±5.76	103.63±1.77	74.96±3.42
Cd	62.22±1.74	32.20±1.40	1.68±0.21	0.23±0.02	0.22±0	0.26±0.01
Cr	5.03±0.53	18.32±1.09	194.04±26.27	43.81±0.3	41.18±21.06	48.68±1.84

* the metal contents are presented as average value ± standard error.

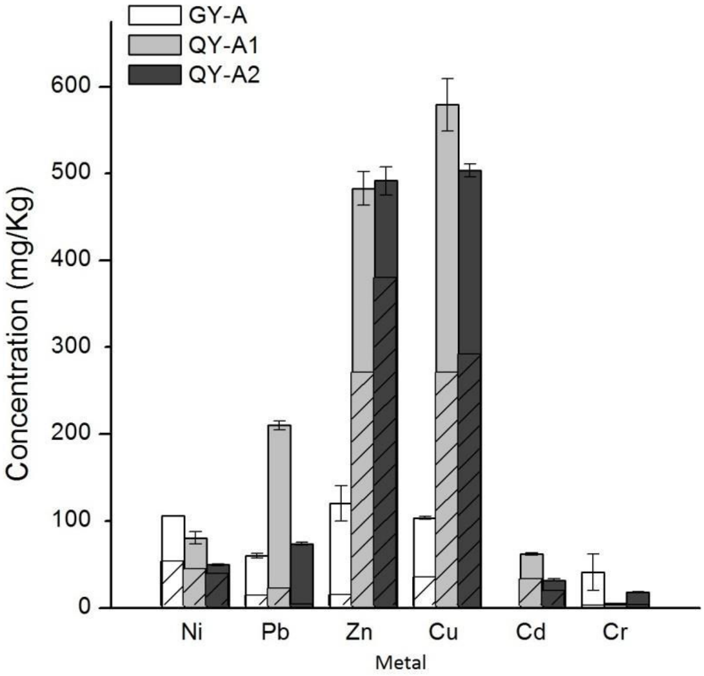

Figure 2.3 Contents of metals in samples from acid washing sites (diagonal portion as the available portion).

A comparison between the two regions shows that sites in Qingyuan dispose a more severe metal contamination than those in Guiyu. Referred to the environmental quantity standard for soils in China [206], the contents of Cd in samples from Qingyuan and Cu in samples from acid washing sites exceeded the level 3 limitation (1.0 and 400 mg/kg dw, respectively) for agricultural soils, those of Zn and Ni from acid washing sites exceeded the level 2 limitation, while those of Pb and Cr was safe to agriculture. These results illustrated the severe threat of metals to the agriculture in Qingyuan area. In Guiyu acid washing site, only the content of Ni exceeded the level 2 limitation, which is less threatening compared to Qingyuan sites.

Comparison to previous surveys on Guiyu area also shows less contamination in our study [207, 208], probably because of the recent shutdown of many workshops in Guiyu due to the uprising attention paid to this area. Moreover, the discharge of acid effluents with metals in Qingyuan is peculiarly primitive that no pipes but tunnels were employed. Where there is the discharge of acid, there is the diffusion of metals to surrounding soils. While in Guiyu site, a rough acid bath was constructed near water, and effluent was discharged with PVC pipes. The difference in disposal led to different extent of pollution on soils. The contaminations by heavy metals are not as significant in other sites as in acid washing sites.

2.4 Conclusions

The contaminations by PCBs in e-waste recycling sites at Qingyuan and Guiyu were not as severe as it used to be, probably because of the raising attention on the issue and the effort undertaken to stop the pollution, especially at Guiyu. Nevertheless, the status of contamination is related to the disposal activities and the soil properties, more details are needed to evaluate if there is an improvement for the situation. Still, the co-existence of multiple contaminants such as PCBs and heavy metals in these areas is a potential threat to local people and ecosystems, and increases the difficulty of remediation.

Chapter 3.

The effect of Tween-80, humic acid and metal ions on the dechlorination of PCBs by ZVI

Part of the data and conclusions of this chapter were published as

Yingxin Wu, Zihao Wu, Xiongfei Huang, Marie-Odile Simonnot, Tao Zhang, Rongliang Qiu*. Synergistical enhancement by Ni2+ and Tween-80 of nanoscale zerovalent iron dechlorination of 2,2',5,5'-tetrachlorinated biphenyl in aqueous solution, Environmental Science and Pollution Research (2015) 22(1): 555-564. (DOI: 10.1007/s11356-014-3278-9)

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And were presented in the conference of Contaminated Site Management in Europe (CSME SARCLE) as

Wu Y., Wu Z., Huang X., Simonnot M.O., Zhang T., Qiu R. Synergistical enhancement by Ni^{2+} and Tween-80 of nanoscale zerovalent iron dechlorination of 2,2’,5,5’-tetrachlorinated biphenyl in aqueous solution, Contaminated Site Management in Europe (CSME SARCLE), Brussels (Belgium), 20-22 October 2014. (oral presentation)

3.1 Introduction

Due to their high stability, low aqueous solubility and high affinity to organic matter, one of the major terrestrial sinks for Polychlorinated biphenyls (PCBs) are soils and sediments [94]. Soils from brown sites affected by industrial activities are often contaminated by PCBs. In particularly, surveys on e-waste contaminated sites have reported high levels of PCBs in surrounding soils [4].

One of the effective methods for removing hydrophobic organic contaminants (HOCs) from soils is surfactant-enhanced soil washing [209, 210]. It has been demonstrated that surfactants transfer HOCs from soil to the aqueous phase by enhancing solubility of HOCs and decreasing the interface tension between aqueous phase and solid phase [135, 211]. However, pollutants in the washing solution are not degraded and remain hazardous, and an effective and environmental-friendly post-treatment for soil washing solutions remains to be developed [19, 212].

Besides PCBs, heavy metals are also ubiquitous in soils affected by industry, and can also be removed by surfactants to some extent [213, 214]. It is not uncommon to find the coexistence of heavy metals and HOCs in soils from contaminated sites. USEPA has reported that as high as 67.7% of National Priority List sites (NPL) were contaminated by both heavy metals and volatile or semi-volatile organic compounds [215]. The difficulty of post-treatment for this kind of washing solution is heightened by the coexistence of HOCs and heavy metals, which are distinguished in properties.

In the last few decades, efficient dechlorination of chlorinated organic pollutants by zerovalent iron (ZVI) with or without catalytic metals in the aqueous phase or soil matrix has been demonstrated [216-218]. With the advantages of low-cost, easy acquisition and high degradation efficiency [155], the ZVI technique can potentially be used for post-treatment of soil washing solutions after surfactant-enhanced washing. However, the degradation efficiency of PCBs by ZVI in such a complicated solution remains unclear. The dehalogenation reaction of HOCs on ZVI is a surface-mediated reaction and thus is likely to be influenced by other solvents or adsorbates present in the system [164].

Recent research has demonstrated the adverse effects of anionic surfactants on ZVI reduction process, while cationic surfactants can enhance the reduction rate [164]. The influence of commonly used nonionic surfactants is dependent on the concentrations in solution [165, 213]. Research on the effect of high concentrations of nonionic surfactants on the reduction rate of PCBs by ZVI is desirable. In addition, the effect of catalytic metals (*e.g.*, Cu, Ni) on the ZVI reduction system needs to be explored [170, 179].

Moreover, a fair amount of soil organic matter (SOM) is brought into the washing solution by surfactants and may cast an influence on the ZVI reduction process, by serving as an electron shuttle or occupying the active sites on the surface of iron particles [169, 219].

With the goal of optimizing the ZVI reduction technique for post-treatment of soil washing solutions, we investigated the effects of nonionic surfactant, SOM and/or metal ions on nanoscale ZVI reduction of 2,2',5,5'-tetrachlorinated biphenyl (PCB-52), using a simulated soil washing solution. Tween-80 (polyoxyethylene(20) sorbitan monooleate, polysorbate 80), a widely studied and employed nonionic surfactant [220-222] was used as a representative of washing agents. Humic acid was applied as the representative of SOM. Also, the degradation pathway of PCB-52 was elucidated in order to better understand the ZVI reaction process.

3.2 Experimental

3.2.1 Chemicals

Standard solutions of PCBs were purchased from AccuStandard Inc. (New haven, USA). 2,2',5,5'- tetrachlorobiphenyl (PCB-52, 97.5%), 2,3,3',4',5'- pentachlorobiphenyl (PCB-82, 98%) and 2,3,5,6- tetrachlorobiphenyl (PCB-65, 98%) were purchased from Labor Dr. Ehrenstorfer Schäfers (Augsburg, Germany) and dissolved in acetone (99.7%) to make stock solutions. Nanoscale zerovalent iron particles (nZVI, Φ< 50 nm, > 99%) were purchased from Aladdin (Shanghai, China) and were stored and used in an anaerobic workstation (Don Whitley Scientific) where the content of oxygen was less than 3 ppm, without any pre-treatment. $CuSO_45H2O$ and $NiSO_46H_2O$ were purchased from Damao Chemical Agent Company (Tianjin, China). Tween-80 (critical micelle concentration [CMC] = 15.8 mg/L at normal temperature and pressure) was purchased from Fuyu fine Chemicals (Tianjin, China). Humic acid (CAS: 1415-93-6, >90%) was purchased from Adamas Reagent Co., Ltd. (Shanghai, China). Before use, ultrapure water was sterilized at 121 °C for 30 min and deoxygenated by purging with pure nitrogen gas for 20 min.

3.2.2 Dechlorination experiments

All the dechlorination experiments were performed in 15-mL glass vials sealed with Teflon screw caps. A 0.05 g of nZVI was added to a thoroughly mixed 5-mL solution containing specified amounts of PCB-52 and Tween-80/humic acid and 5% molar loading of Cu^{2+}/Ni^{2+} on Fe in an anaerobic workstation. Vials were tightly sealed, placed in the dark at 30±2 °C and shaken at 180 rpm. At each certain time interval, two of the vials were sacrificed to extract PCB-52 and its degradation products. Vials without nZVI were also set as blank control. To avoid the chelating effect, NaN_3 was not used for bacteriostasis. Cosolvent effect from acetone was ignorable as only 10 μL of the PCB-52 stock solution was added to each vial.

To confirm the biphenyl loss phenomena, a control experiment with Ni ions, Tween-80 and biphenyl was also conducted with the same method as mentioned above, except that biphenyl was added instead of PCB-52.

3.2.3 PCBs extraction and detection

PCBs are extremely hydrophobic, and pre-experiments showed that only approximately 30% of PCB-52 can be extracted from the aqueous phase without surfactant, while more than 60% can be extracted from the solid phase (data not shown). To extract the PCBs from both phases, 5 mL of hexane were added to each vial and mixed thoroughly before collection, which was performed three times for each vial. Fiberglass was used to separate the mixture of aqueous solution/solid and hexane for treatments with surfactants. To eliminate interference, 5.0 g neutral silica gel and 5.0 g anhydrous sodium sulfate was employed for purification and dehydration. The extractant was concentrated to 1 mL before measurement.

PCB-52 was measured by a gas chromatography (Thermo-Ultra Trace GC-DSQ) equipped with mass spectroscopy in SIM-scan mode. Chromatographic separation was accomplished with a 30 m × 0.25 mm × 0.25 μm DB-5ms column (J&W Scientific Inc., China) using splitless injection mode. The oven temperature was held at 100 °C for 2 min, increased to 180 °C with gradient of 15 °C/min, then to 240 °C with gradient of 3 °C/min, post run to 285 °C with gradient of 10 °C/min and held for 10 min. The flow rate of carrier gas (helium 99.999%) was 1.2 mL/min. The temperatures of injector and ion source were 280 and 220 °C, respectively. To assure extraction efficiency, a certain amount of PCB-65 was added to each vial as a surrogate before extraction. Instrument calibration for measurement of PCB-52 was performed using a series of standard solutions and PCB-82 as an internal standard.

3.2.4 Data analysis

The extent of degradation was evaluated by the relative concentration (RC) of PCB-52 at each predetermined time

$$RC_t = \frac{C_t}{C_0} \qquad \text{Equation 3.1}$$

where C_t is the mass of PCB-52 at time t and C_0 is the initial mass of PCB-52.

The relative abundance (RA) of each chlorinated biphenyl and biphenyl in each vial at each predetermined time was calculated as the ratio of the mass of the measured congener to the total mass of all congeners in the system

$$RA_{i,t}(\%) = \frac{M_{i,t}}{\sum M_t} \times 100 \qquad \textit{Equation} \quad \textit{3.2}$$

where $M_{i,t}$ is the mass of congener i in solution at time t, ΣM_t is the total mass of all congeners including mono-tetra chlorinated biphenyls and biphenyl at time t.

To calculate the relative mass balance in the degradation system, the areas of all detectable PCB congeners and biphenyl were summed, and were compared to the areas of the treatment in 8 h (which are considered 100%).

3.3 Results and discussion

3.3.1 Kinetics

3.3.1.1 Degradation of PCB-52 by nZVI

The kinetics of PCB-52 dechlorination by nZVI are shown in figure 3.1(a). Compared to the control treatment, nZVI alone did not significantly enhance PCB-52 degradation at reaction time, which is in accordance with preliminary studies [154]. In both cases, a degradation rate of *ca* 50% was attained after 120 h. Although nanoscale ZVI has a greater specific surface area than microscale particles, thus providing more reaction sites for degradation, agglomeration is possible within a few minutes in aqueous solution without an effective stabilizer such as polyvinylpyrrolidone [155, 198], resulting in a reduction in the quantity of effective reaction sites and lower degradation efficiency. During the experiment, large particles were observed in the vials, and separation of the solid and liquid phases occurred upon cessation of shaking, which demonstrates the agglomeration of nanoscale particles.

The loss of PCB-52 was also observed in the control reactor over the entire time course (figure 3.1(a)), although the recovery of PCB-65 was relatively constant (79.8% - 101.5%), assuring the reliability of the extraction method. Volatilization of PCBs has been reported to be negligible by the estimation of Henry's constant [223]. Part of the mass loss observed may have been due to irreversible sorption of PCBs onto the glassware and the Teflon-lined septa, especially from aqueous solution [154]. In addition, the effect of microbial degradation was not excluded during the batch experiment, although which was not supposed to be a dominant process. Nevertheless, in succeeding experiments, significant differences among treatments were observed that exceeded the potential error due to the nondestructive mass loss of PCBs.

It is worth noting that studies on the dechlorination of PCBs by nZVI in aqueous solution are limited. Most of the studies concerning ZVI reduction focus on chlorinated hydrocarbons with simple structures or on polybrominated diphenyl ethers (PBDEs), probably because of the complex molecular structure of PCBs and the larger bond dissociation energy of the C-Cl bond (81 kcal/mol) compared to that of the C-Br bond (67 kcal/mol) [183, 224]. Zhuang (2011) reported that the half-life of PCB-21 treated by nZVI alone was 1 yr, even with excess nZVI [183], while Wang and Zhang (1997) found only partial dechlorination of Aroclor 1254 (<25%) in 17 h by nZVI alone [225]. These studies indicate the necessity of catalysis during nZVI-mediated dechlorination.

3.3.1.2 Effect of Ni^{2+} and Cu^{2+} on PCB-52 degradation

To accelerate the degradation process, Ni or Cu can be applied as catalysts [155]. Figure 3.1(a) shows the effects of Cu^{2+} and Ni^{2+} on the kinetics of PCB-52 degradation by nZVI. Ni^{2+} significantly enhanced the degradation rate, while Cu^{2+} had a less significant catalytic effect. Nickel has been reported to be effective in accelerating iron degradation reactions, compared to copper or without catalyst [17, 170, 226-228].

In many studies, Ni^{2+} or Cu^{2+} solution was mixed with iron particles to form a bimetal system (Cu(0)/Fe(0), Ni(0)/Fe(0), *etc.*) that was used in subsequent degradation reactions [17, 227, 229]. With this bimetal system, Cu or Ni can be distributed evenly on the surface of iron particles, providing a greater number of effective catalytic sites. In this study, however, the displacement of metal ions by iron and the reduction of PCBs by bimetal or iron occurred simultaneously and may have influenced each other. Moreover, the rapid and uncontrolled metal displacement reaction may have resulted in heterogeneous distribution of catalyst on the surface of the iron particles. Despite the above factors, the acceleration of PCB-52 degradation by Ni^{2+} was considerable.

Cu was a less effective catalyst than Ni in this study as previous reported [170, 230, 231], which may have been influenced by the degree of Cu loading. Both Ni and Cu could protect the iron surface from oxidation, although their catalytic mechanisms differ. Ni on the surface of particles has high catalytic capability for dehydrogenation reactions, which accelerates dehalogenation *via* hydrogen reduction, while Cu accelerates the reaction primarily *via* promoting electron transfer [170, 232]. The loading amount of Cu massively exceeded the average mass of Cu required for forming a monolayer on the surface of the iron particles, indicating the possible existence of Cu overlayer on over 80% of the iron surface [233]. Although the Cu layers are probably the predominant site of dehalogenation by accelerating electron transfer, the thickness of the Cu layer may influence the mass transfer process of PCBs and possibly inhibit the reaction if not optimal. Optimization of the Cu:Fe ratio may enhance nZVI dehalogenation of washing solutions.

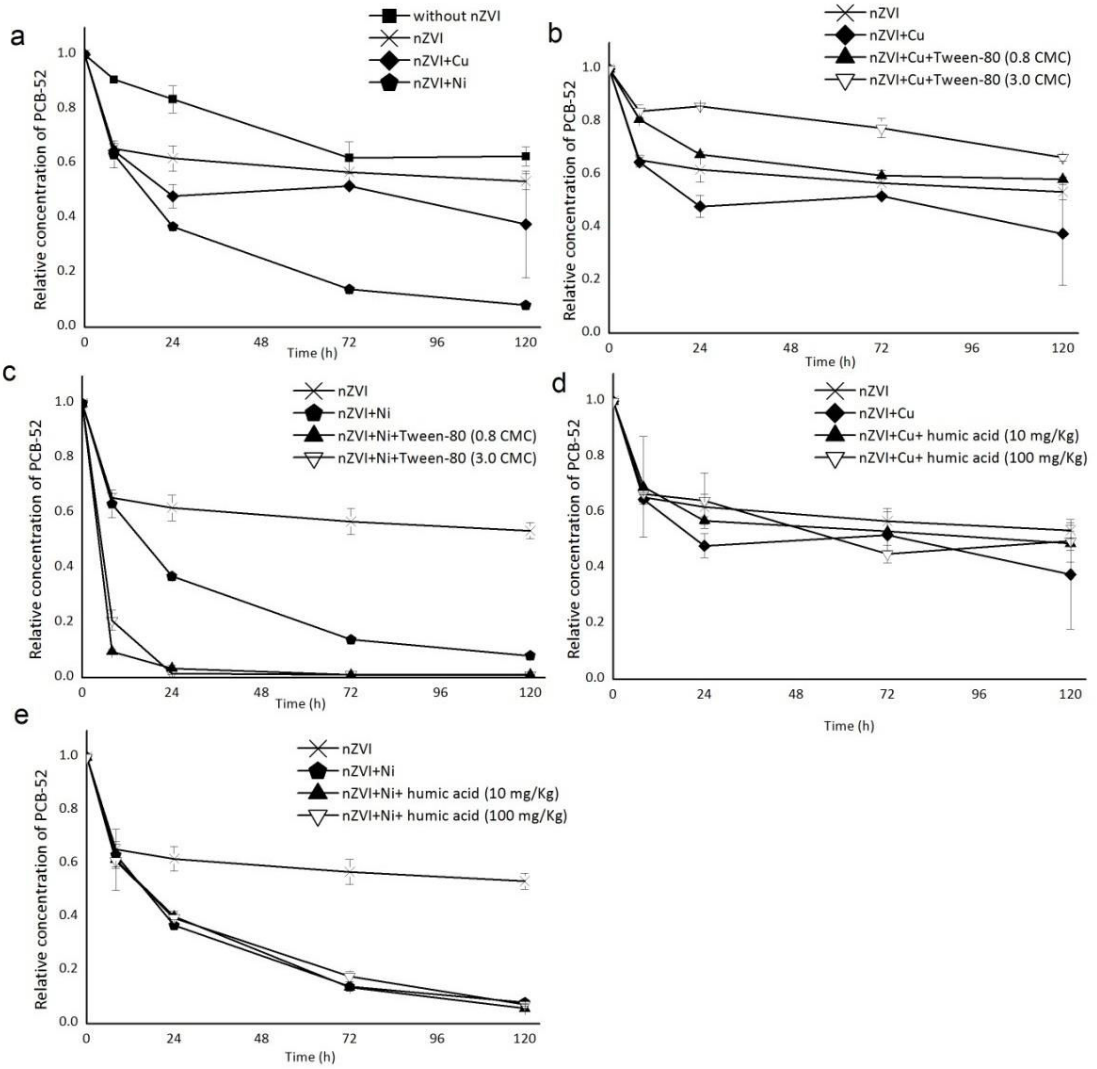

Figure 3.1 Kinetics of degradation of PCB-52 in the aqueous phase: (a) without nZVI particles, with nZVI particles alone and with Cu^{2+} or Ni^{2+} ions; (b) nZVI with Cu^{2+} and Tween-80; (c) nZVI with Ni^{2+} and Tween-80; (d) nZVI with Cu^{2+} and humic acid; (e) nZVI with Ni^{2+} and humic acid.

3.3.1.3 Effects of Tween-80 on PCB-52 degradation

ZVI dehalogenation is a heterogeneous reaction involving adsorption on the particle surface and the subsequent surface reaction. Besides electron transfer, the reaction rate of nZVI dehalogenation is also limited by mass transfer, particularly for PCBs or PBDEs that are highly hydrophobic. In this study, an aqueous solution with ignorable amount of cosolvent was used, which further confined the partitioning of PCBs between the aqueous and solid phases. To improve the partitioning, surfactants have been used in nZVI dehalogenation [162, 230].

The effects of the nonionic surfactant Tween-80 in concentrations of 0.8 CMC and 3.0 CMC on nZVI dechlorination of PCB-52 with and without Cu or Ni catalyst are shown in figure 3.1 (b) and (c). Both concentrations of Tween-80 enhanced PCB-52 degradation in the nZVI+Ni treatment, but inhibited the reaction in the nZVI+Cu treatment, and, at most time points, slightly depressed the reaction in the treatment without metal loading (data not shown). The effect of Tween-80 and Ni^{2+} when used together was synergistic, as their combined effect was greater than the sum of their individual effects.

Shin *et al.* (2008) reported an inhibitory effect of the nonionic surfactants Brij 30-97 on the degradation of trichloroethylene by applying ZVI without modification [234], which is akin to the case of this study. However, inconsistent findings have been reported in several studies concerning bimetals such as Cu(0)/Fe(0), Ni(0)/Fe(0) and Pd(0)/Fe(0) because of differing contaminants, surfactants, iron particles or experimental conditions [164, 179, 230, 235]. Generally, nonionic surfactants at a concentration below the CMC can enhance degradation while they can inhibit the process at concentrations above the CMC, which is not in consistent with our results.

It is recognized that nonionic surfactants can influence the dehalogenation process by altering the partitioning of HOCs via enhancing solubilization, sorption and competitive sorption [158, 164]. The enhancement of solubilization by nonionic surfactants is typically important in the aqueous system used in this study, considering the lack of cosolvent and the hydrophobicity of PCBs. The presence of surfactant greatly enhanced the solubilization of PCB-52, thus enhancing the efficiency of mass transfer.

It has been reported that during dechlorination, a passive layer of iron oxides was gradually formed on the surface of ZVI [236]. In this study, the presence of Ni and nonionic surfactant also prevent the surface oxidation of iron [155, 237], which benefited the dechlorination process compared to the treatment without Tween-80 or nickel.

Further study is needed to explain the contrasting effects of Tween-80 on nZVI degradation with different metal ions.

3.3.1.4 Effects of humic acid on PCB-52 degradation

There are arguments about the influence of humic acid on ZVI-mediated degradation as adverse results have been reported by several researchers. A consensus is that humic acid serves as an electron shuttle to facilitate the reduction process at low concentration and occupies active reaction sites on ZVI surface to inhibit mass transfer process at exceeded content [169, 170].

However in this study, humic acid cast an insignificant influence on ZVI degradation process of PCB-52 in the presence of Ni or Cu ions, regardless of the applied concentrations. This result may be attributed to the equilibrium of positive and negative effects induced by humic acid.

3.3.2 Dechlorination pathway

The 209 PCB congeners have different toxicities. There is a concern that the degradation products may be more toxic than the parent congener, with a consequent increase in environmental risk. Therefore, knowledge of the reaction pathway is crucial. PCB-52 that we used as the parent congener has a simple structure, which facilitates the understanding of its degradation pathway. As we found that treatment with Ni ions resulted in the most rapid degradation, herein we discuss only dechlorination of PCB-52 by nZVI+Ni within 7 d (168 h) of treatment.

3.3.2.1 Pathway of PCB-52 dechlorination by nZVI in the presence of Ni^{2+}

Degradation of PCB-52 by nZVI+Ni2+ during a 7-day batch experiment proceeded primarily by step-by-step dechlorination, as illustrated in figure 3.2(a), which shows the relative abundance of mono-tetra chlorinated biphenyls (CBs) and biphenyl. Degradation was evident after 8 h, with 17.4% of the PCB-52 degraded into lower chlorinated products. By 168 h, more than 95% of the PCB-52 was degraded into mono-tri chlorinated biphenyls (CBs) and biphenyl. Congener-specificity was recognizable during the dechlorination process (table 3.1). In the major degradation pathway, the meta-chlorine was preferentially eliminated compared to the ortho-chlorine (figure 3.4), which agrees with a previous report [154]. Figure 3.2(b) and table 3.1 show that there was accumulation of PCB-18, PCB-9, PCB-4 and PCB-1 up to the 72 h time point; subsequently, the relative abundance of PCB-18 and PCB-9 declined, while that of PCB-4 and PCB-1 continued to increase for another 48 h before slightly decreasing. Biphenyl was the dominant congener after 72 h and dechlorination was predominant over the generation for the tri-CBs, while the rates of dechlorination and generation were roughly equal for the mono-di CBs. Complete dechlorination of PCB-52 would have required measures to accelerate the reaction or longer reaction time.

The congener specificity described above favors the formation of congeners containing ortho-chlorine, which are not coplanar. Since coplanar PCB congeners have higher toxicity in the environment [154], the use of nZVI+Ni^{2+} as a post-treatment for contaminated soil washing solutions would minimize the environmental risk.

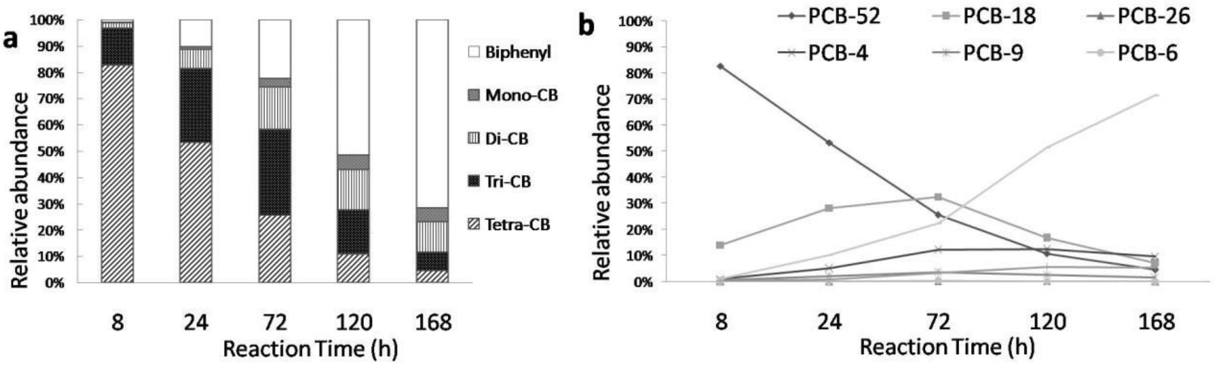

Figure 3.2 Dechlorination of PCB-52 by nZVI in the presence of nickel ions; reaction time = 168 h: (a) relative abundance of PCBs and biphenyl during dechlorination process; (b) relative abundance of detectable congeners during dechlorination process.

Table 3.1 Relative abundance (%) of PCB congeners during dechlorination process by nZVI with Ni^{2+} present and with Ni^{2+} and Tween-80 (3.0 CMC) present.

congener	nZVI+Ni^{2+}					nZVI+Ni^{2+}+Tween-80(3CMC)				
	8 h	24 h	72 h	120 h	168 h	8 h	24 h	72 h	120 h	168 h
PCB-52 (tetra-)	82.64	53.29	25.58	10.79	4.62	27.80	2.96	1.60	0.74	2.30
PCB-18 (tri-)	14.13	28.18	32.57	16.73	7.08	14.73	1.66	0.38	ND*	ND
PCB-26 (tri-)	0.05	0.05	0.13	0.15	0.04	1.09	2.94	11.03	5.47	6.25
PCB-4 (di-)	1.10	5.10	12.13	12.39	9.70	11.29	1.95	3.13	0.64	ND
PCB-9 (di-)	0.62	2.02	3.59	2.75	1.52	3.66	1.07	2.89	8.67	3.30
PCB-6 (di-)	0.12	0.16	0.27	0.15	0.16	0.28	0.16	ND	ND	ND
PCB-11 (di-)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PCB-1 (mono-)	0.29	0.97	3.42	5.56	5.31	6.82	1.36	0.99	ND	0.64
PCB-2 (mono-)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Biphenyl	1.06	10.22	22.31	51.47	71.57	34.34	87.90	79.98	84.49	87.51

*ND=Not Detected

3.3.2.2 Pathway of PCB-52 dechlorination by nZVI in the presence of Ni^{2+} and Tween-80

To understand the effect of Tween-80 on the dechlorination pathway, reaction products from the degradation experiment carried out in the presence of Ni^{2+} and Tween-80 (at a concentration of 3.0 CMC) were also determined. Little difference was found in the degradation pathway with and without Tween-80. However, addition of Tween-80 did result in accumulation of some recalcitrant congeners such as PCB-26 and PCB-9 (table 3.1). Tween-80 may have enhanced the degradation rate of the vulnerable congeners more than that of the recalcitrant congeners. The observed pattern of congener accumulation confirms the major pathway of dechlorination by nZVI illustrated in figure 3.4.

During the Tween-80 degradation experiment, mass loss of biphenyl was observed, which became more pronounced with time, and did not occur in the absence of Tween-80 (figure 3.3(a)). This mass loss did not result from extraction loss, as confirmed by the recovery of PCB-65 during extraction and also by a control experiment with/without Tween-80 (figure 3.3(b)). It is possible that degradation product(s) other than chlorinated biphenyls or biphenyl are generated during this process, or that some congener(s) were volatilized, primarily after the stepwise dechlorination process. Further investigation is needed to understand this phenomenon.

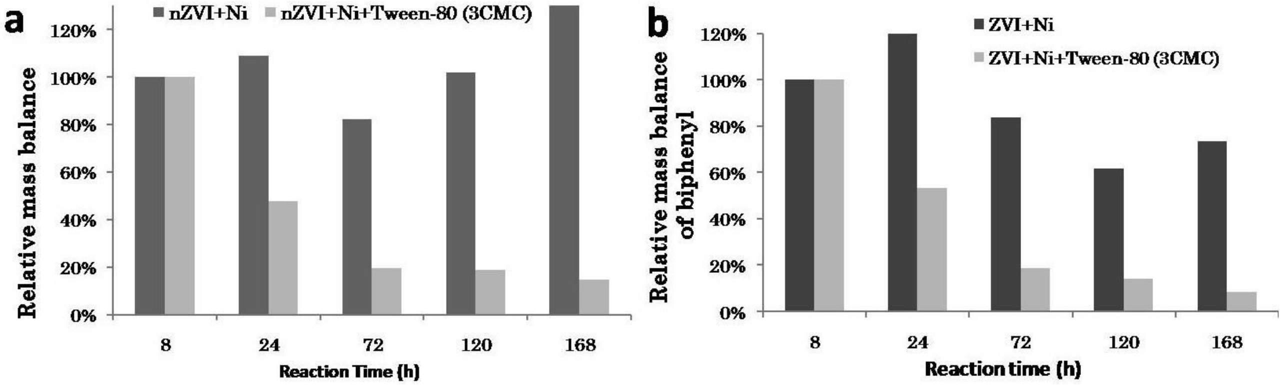

Figure 3.3 (a) Relative mass balance during dechlorination of PCB-52 by nZVI: With Ni^{2+} present (Black bars); with Ni^{2+} and Tween-80 (3.0 CMC) present (Gray bars); (b) Biphenyl loss during dechlorination by nZVI with the presence of Ni^{2+}: Without Tween-80 (Black bars); with 3.0 CMC of Tween-80 (Gray bar).

3.3.3.3 Regiospecificity

In a study of congener-specific dechlorination of PCBs, it was reported that with regard to chlorine position, the priority of dechlorination was para- > meta- > ortho- [154]. This pattern of congener specificity was confirmed by our observation that PCB-18 was accumulated in greater abundance than was PCB-26.

Nevertheless, we also observed a greater abundance of PCB-9 than PCB-6 in the absence or presence of Tween-80 (table 3.1), although both of them possess a meta- and an ortho-chlorine. Both PCB-9 and PCB-6 are derived from elimination of an ortho-chlorine from PCB-18 and elimination of a meta-chlorine from PCB-26, and both are degraded primarily to PCB-1. Evidently there is a preference to derive PCB-9, which has two chlorines on the same benzene ring, rather than PCB-6 with two chlorines on different benzene rings. This is an example of regiospecificity, and can be explained by the different Gibbs free energies of formation in aqueous solution. The standard-state Gibbs free energy of formation in aqueous solution of PCB-6 (-232.7 kJ/mol) is slightly higher than that of PCB-9 (-235.4 kJ/mol), which results in the tendency to form the more stable PCB-9 rather than PCB-6 in aqueous solution [238, 239].

PCB-11 and PCB-2 were not detected at any time during the reaction because of the congener specificity and regiospecificity effects mentioned above. However, generation of PCB-11 and PCB-2 was not excluded, as these two congeners should be subject to rapid degradation owing to their possession of meta-chlorine.

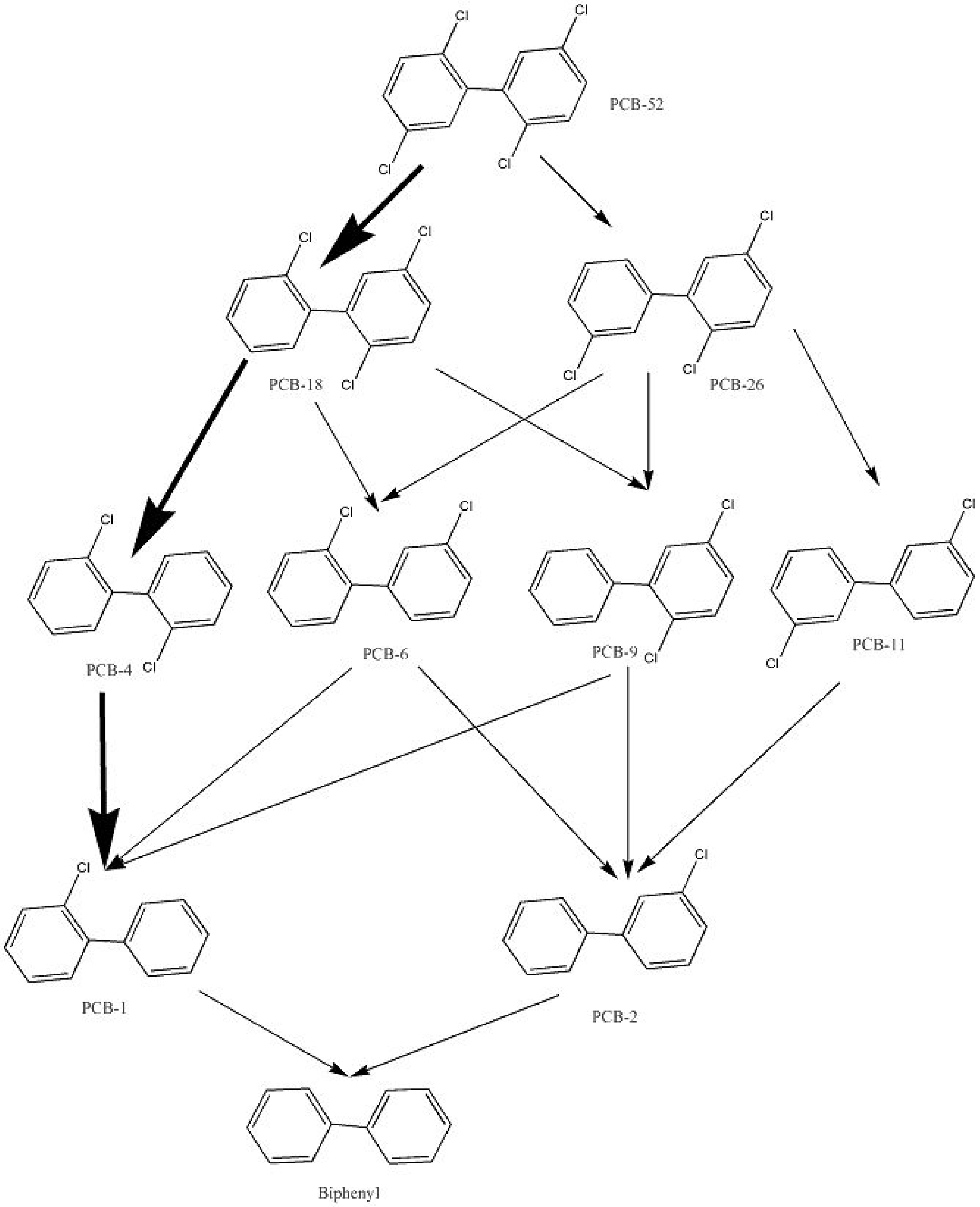

Figure 3.4 Pathways for dechlorination of PCB-52 by nZVI in the presence of Ni^{2+}; bold arrows indicate the major pathway.

3.4 Conclusions

Dechlorination of PCB-52 by nZVI in an aqueous environment was synergistically enhanced by the presence of Ni^{2+} ions and the nonionic surfactant Tween-80. The effect of humic acid on degradation was negligible, in the conditions of the study. The PCB-52 degradation pathway exhibited regiospecificity and congener specificity that minimized the generation of environmentally toxic coplanar PCB congeners. The use of nZVI dehalogenation enhanced by Ni^{2+} and Tween-80 for the post-treatment of PCB-contaminated soil washing solutions is promising. Further studies lie in the mechanisms of the synergetic enhancement by Tween-80 and Ni^{2+}, and also the optimization of the ZVI degradation technique as the post-treatment for PCB-contaminated soil washing solutions. The influence of Tween-80 and also other surfactants at different concentrations is also of necessity.

Chapter 4.

Factors and processes influencing dechlorination of PCBs by ZVI in aqueous solution

4.1 Introduction

In recent years, researchers have investigated the ability of zerovalent iron (ZVI) particles in nano- or micro-scales to facilitate reduction of chlorinated organic compounds [154, 240-242], nitroaromatic compounds [243, 244], dyes [245, 246] and other contaminants [247]. To apply this technique on an industrial scale, it is necessary to investigate the factors limiting the ZVI-mediated reactions. Especially for hydrophobic and recalcitrant contaminants such as polychlorinated biphenyls (PCBs), comprehensive understanding of the influencing mechanisms could lead to an improvement of remediation practices. Based on the available literature, pH, surfactants, natural/soil organic matters (NOM/SOM) and catalytic metals are among the most important factors affecting ZVI-mediated reduction in an aqueous system. The detailed influences by these factors were previously described in section 1.4.1.

Combinations of the factors have also been investigated. For instance, Zhang *et al.* (2011) studied the combined effects of surfactants and SOM on the reduction of trichloroethylene by Fe-Pd bimetals [163], while Doong and Lai showed that the complex of humic acid with Ni(II) was an efficient electron transfer mediator for the reduction of tetrachloroethylene [170]. We have previously demonstrated synergistic enhancement by Ni(II) and Tween-80 of nanoscale ZVI stepwise dechlorination of PCB-52 in aqueous solution [248]. The effects and mechanisms of single factors may differ when they are combined, a situation that better approximates the reality of industrial scale remediation.

This study aimed at investigating the factors influencing the reduction of 2,2′,5,5′-tetrachlorinated biphenyl (PCB-52) by zero-valent iron in aqueous solution as well as the mechanisms by which those factors exert their effects. Specific objectives were focused on mass transfer of PCB-52 and oxidation of iron particles during the process.

4.2 Experimental

4.2.1 Chemicals

Standard solutions of PCBs were purchased from AccuStandard Inc. (New Haven, USA). 2,2′,5,5′-tetrachlorobiphenyl (PCB-52, 97.5%), 2,3,3′,4′,5′-pentachlorobiphenyl (PCB-82, 98%) and 2,3,5,6-tetrachlorobiphenyl (PCB-65, 98%) were purchased from Labor Dr. Ehrenstorfer Schäfers (Augsburg, Germany) and dissolved in hexane to make stock solutions. $NiSO_4 6H_2O$ was purchased from Damao Chemical Agent Company (Tianjin, China). Humic acid (CAS: 1415-93-6, >90%) was purchased from Adamas Reagent Co., Ltd (Shanghai, China). Tween-80 (polyoxyethylene (20) sorbitanmonooleate, polysorbate 80) was purchased from Fuyu Fine

Chemicals (Tianjin, China). The commercial surfactant Envirosurf (Environium, France) was used to provide a mixture of nonionic (polyethoxylated fatty alcohols) and anionic (sodium dodecyl benzene sulfonate [SDBS]) surfactants. Microscale zerovalent iron (ZVI) powder was purchased from BASF (Germany) and was stored and used without any pre-treatment in an anaerobic workstation (Don Whitley Scientific) where the content of oxygen was less than 3ppm. Properties of the selected surfactants are listed in table 4.1.

Table 4.1 Properties of the studied surfactants

Name	Composition	Type	CMC
Tween-80	polyoxyethylene (20) sorbitanmonooleate	Nonionic	15.8 mg/L
Envirosurf	Polyethoxylated fatty alcohols Sodium dodecyl benzene sulfonate	Nonionic Anionic	17.8 mg/L *

* Detected by KRÜSS Processor Tensiometer (data from ENVIRONIUM SARL, France).

4.2.2 Orthogonal experiments

Two series of orthogonal experiments were designed based on the orthogonal test table L9 (3^4) to explore the combined effect of the studied factors, namely pH value, surfactant concentration and properties, concentration of SOM (using humic acid as a surrogate), and loading of catalytic metal (using Ni as a representative). The factors and their levels are listed in Table 4.2. Ultrapure water was used in all procedures. The highest concentration of Tween-80 was based on results of our previous experiment on washing of PCB-contaminated soil, and concentrations of Envirosurf were chosen in order to compare the effect of an anionic surfactant with that of Tween-80. All of the dechlorination experiments were performed in 15-mL brown glass vials sealed with Teflon screw caps. A 0.05-g quantity of ZVI was added to 5 mL of a thoroughly mixed solution containing specified amounts of PCB-52 (with acetone as a cosolvent) and other chemicals according to Table 4.2. Solution pH was adjusted with 1.0 mol/L H_2SO_4 and NaOH. Vials were tightly sealed, placed in the dark at 25 ± 2 °C, and shaken at 180 rpm for 120 h. A blank control was used containing only ZVI and PCB-52 and with an initial pH of 6.1. The cosolvent effect from acetone was regarded as negligible, as only 10 µL of the PCB-52 stock solution was added to each vial.

Table 4.2 Factors and levels in the orthogonal experiments.

Factor	Level 1	Level 2	Level 3
Initial pH	3.0	5.0	7.0
Surfactants (Tween-80/Envirosurf)	1 CMC/10 CMC	25 CMC/56 CMC	500 CMC/560 CMC
Humic acid	10 mg/L	50 mg/L	100 mg/L
Ni^{2+} loading	0.02627g/L (0.5%)	0.10508g/L (2.0%)	0.2627g/L (5.0%)

4.2.3 Extraction and detection of PCB-52

Details of the extraction and detection protocols were described in section 3.2.3.

4.2.4 Surfactant detection

Quantification of Tween-80 and SDBS in aqueous solution was conducted with a UV-vis spectrophotometer (UV-1800, Shimadzu, Japan) by colorimetric measurement methods with cobalt thiocyanate and methylene blue as developers and at wavelengths of 620 and 652 nm, respectively, after liquid-liquid extraction by chloroform [249].

4.2.5 Characterizations of ZVI

Images of the morphology of iron particles together with their elemental composition before and after treatment were obtained by a scanning electron microscope coupled with an energy dispersive X-ray spectrometer (SEM-EDX, S-520/INCA 300, Hitachi, Japan). An X-ray diffractometer (XRD, D/Max-IIIA, Rigaku, Japan) was used to determine the species of iron oxides on the ZVI surface with a Cu Kα radiation, and continuous scans from 10° to 80° 2θ were collected at a scan rate of 2° 2θ/min at 50 kVp and 50 mV.

4.3 Results and discussion

In last chapter, we demonstrated ZVI-mediated stepwise reductive dechlorination of PCB-52, as evidenced by analysis of byproducts and mass balance. Thus degradation of PCB-52 in this study was considered to occur via stepwise reductive dechlorination. The conditions and results of the orthogonal experiments are shown in table 4.3. The observed variation in the dechlorination rate among treatments resulted from interactions between the studied factors. A test of between-subjects effects (table 4.5) showed that the most important influencing factor was surfactant, followed by humic acid, pH, and Ni^{2+} content in that order. This result suggests the importance of mass transfer of PCB-52 in the aqueous system, as surfactants and humic acid have been reported to affect the transfer of target contaminants during ZVI-mediated reduction [151]. In both series of tests, treatments 1, 2, 5, and 8 performed better in comparison to the other treatments. The latter three treatments contained a moderate concentration of surfactants, which further confirms the key role of surfactants in the process.

To better understand the mechanisms of dechlorination, several characterizations of the ZVI particles were conducted by SEM-EDX (figure 4.1, 4.2 and 4.3) and XRD (figure 4.4). In the SEM images, a rough surface on the iron particles was observed for several treatments, indicating corrosion of iron and generation of iron minerals. The iron minerals identified by XRD were ferric hydroxide ($Fe(OH)_3$), iron hydroxide oxide (FeOOH) and siderite ($Fe(CO_3)$). Table 4.4 displays the EDX data for all treatments. A negative correlation between Fe abundance on the ZVI surface and degradation rate was found, as well as a positive correlation between O abundance and degradation rate (table 4.6). This result illustrates the association between iron oxidation and degradation. The corrosion/oxidation process appears to be coupled to the dechlorination process, as suggested by Matheson and Tratnyek [148].

The following sections discuss the impacts on the course of dechlorination brought about by the studied factors, considered from the perspective of mass transfer and iron oxidation.

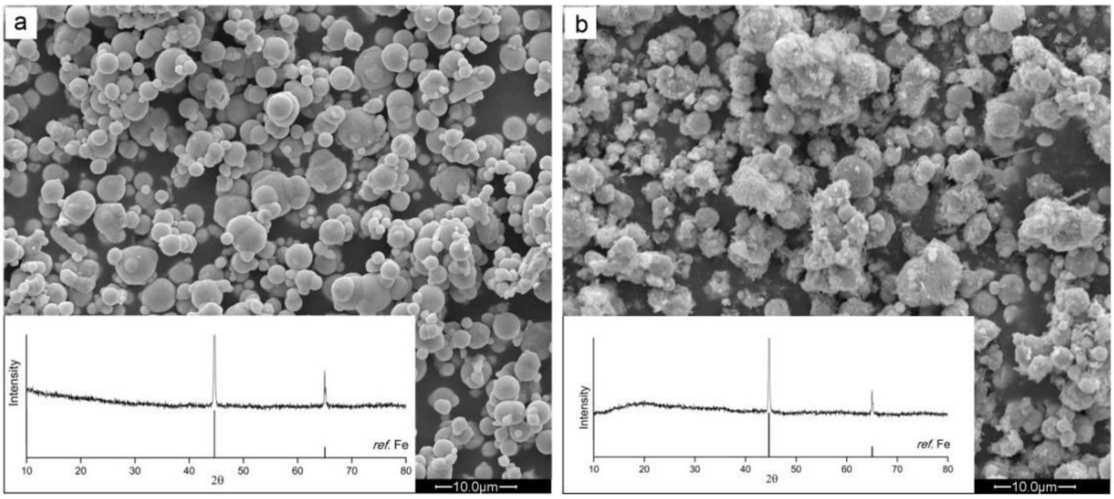

Figure 4.1 SEM images and XRD analysis of ZVI before (a) and after the control treatment (b).

Table 4.3 PCB-52 reduction in orthogonal experiments with Tween-80 (tw) and Envirosurf (e).

Treatment	Initial pH	Surfactant （CMC）	Humic acid (mg/L)	Loading of Ni^{2+} (%)	Reduction rate (%)
control	6.1	0	0	0	47.7
tw1	3.0	1	10	0.50	78.4
tw2	3.0	25	50	2.00	80.2
tw3	3.0	500	100	5.00	15.5
tw4	5.0	1	50	5.00	18.7
tw5	5.0	25	100	0.50	28.4
tw6	5.0	500	10	2.00	15.5
tw7	7.0	1	100	2.00	13.9
tw8	7.0	25	10	5.00	77.9
tw9	7.0	500	50	0.50	17.0
e1	3.0	10	10	0.50	81.6
e2	3.0	56	50	2.00	78.5
e3	3.0	560	100	5.00	20.5
e4	5.0	10	50	5.00	17.1
e5	5.0	56	100	0.50	49.4
e6	5.0	560	10	2.00	21.2
e7	7.0	10	100	2.00	12.8
e8	7.0	56	10	5.00	79.2
e9	7.0	560	50	0.50	12.6

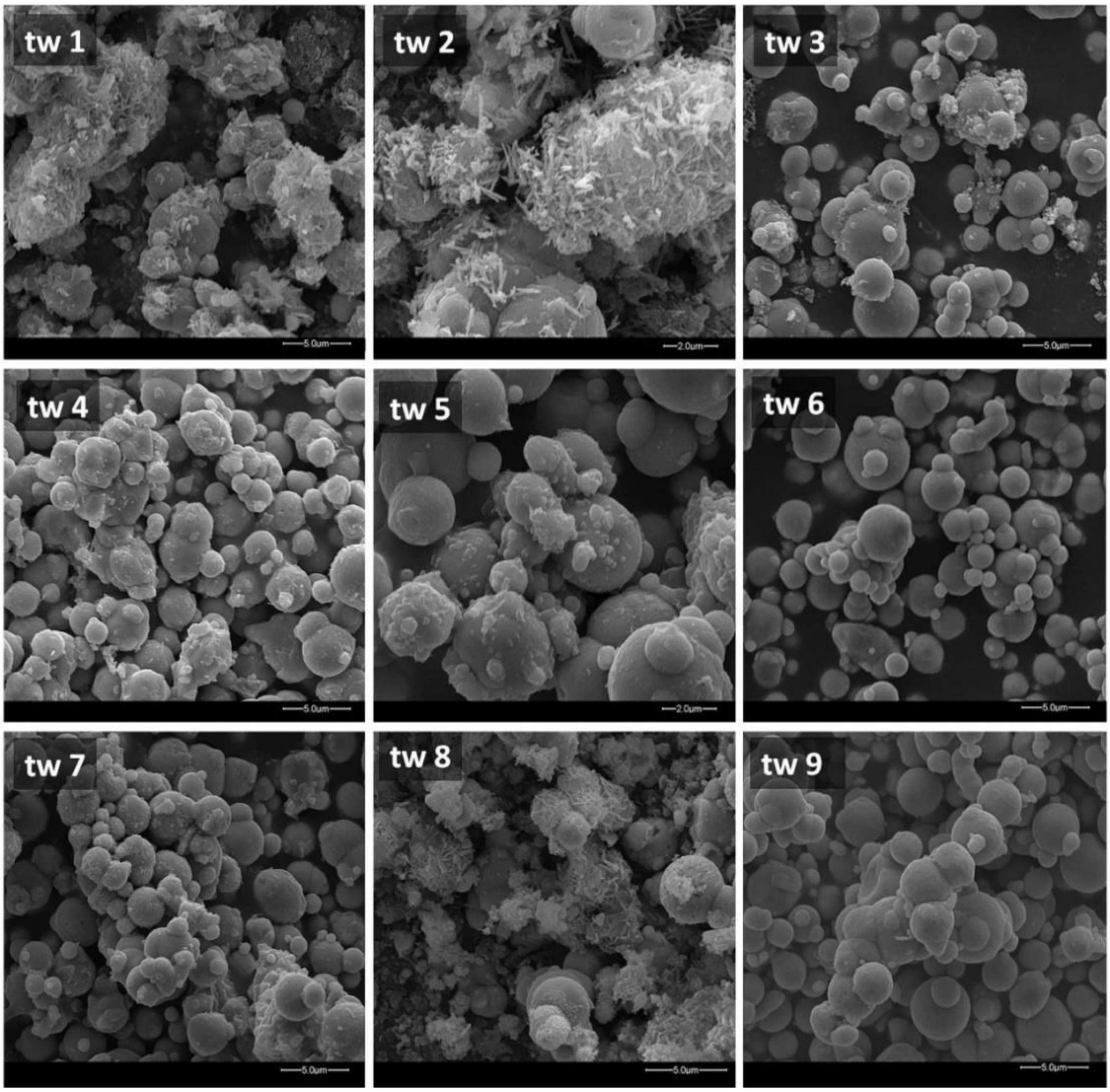

Figure 4.2 SEM images of ZVI after orthogonal experiments with the nonionic surfactant Tween-80. Images are labeled with the treatment abbreviations (tw 1-9).

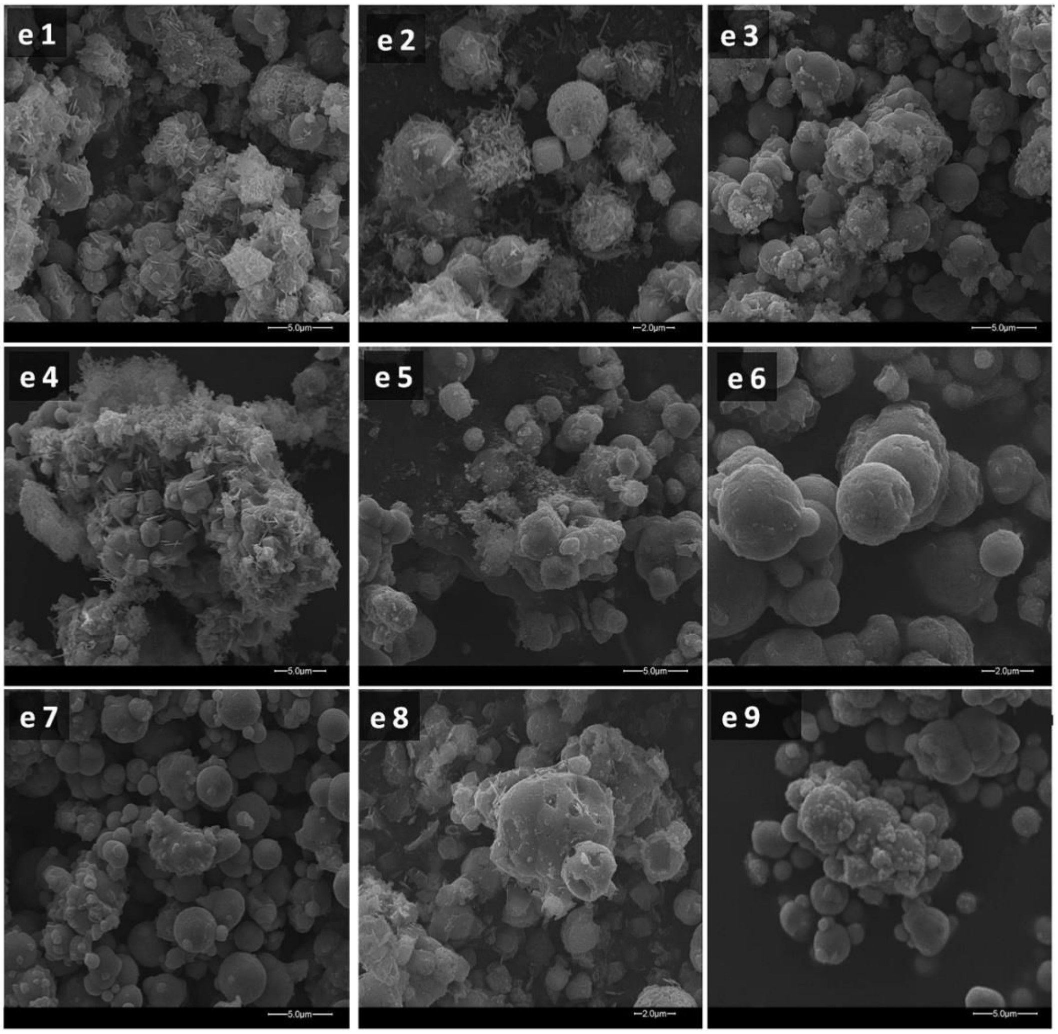

Figure 4.3 SEM images of ZVI after orthogonal experiments with Envirosurf. Images are labeled with the treatment abbreviations (e 1-9).

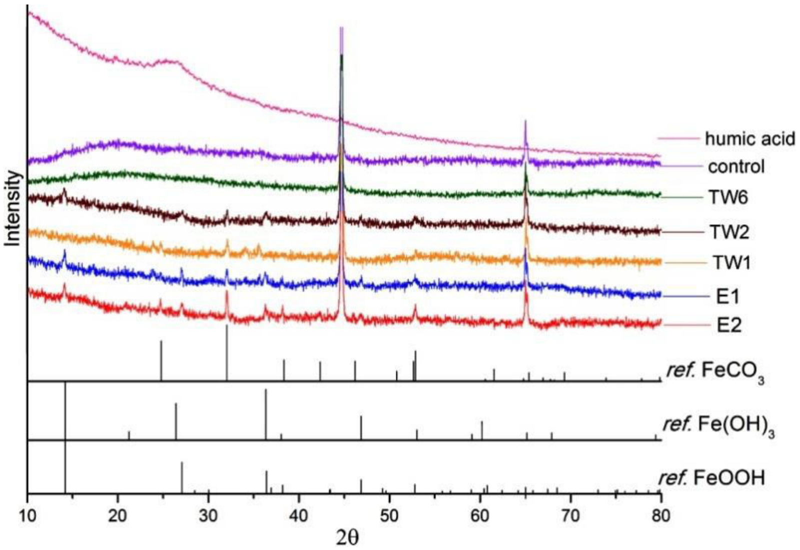

Figure 4.4 XRD spectra of ZVI after experiments with selected treatments, compared with reference spectra of humic acid and the iron minerals $FeCO_3$, $Fe(OH)_3$, and FeOOH.

Table 4.4 Adsorption of surfactants and abundance of elements on the iron surface for treatments with Tween-80 (tw) and Envirosurf (e).

Treatment	Percentage of surfactant adsorbed (%)		Mass % of elements on ZVI surface*			
	nonionic	anionic	C	O	Fe	Ni
ZVI	-	-	11.71	0.75	87.53	0.00
control	-	-	10.97	21.04	67.84	0.00
tw1	100	-	9.06	28.30	62.64	0.00
tw2	99.97	-	13.48	28.74	57.08	0.70
tw3	5.00	-	12.62	22.00	65.13	0.26
tw4	100	-	7.27	3.42	89.31	0.00
tw5	99.92	-	11.01	13.60	75.39	0.00
tw6	5.00	-	6.98	3.54	89.37	0.11
tw7	100	-	5.48	4.96	89.42	0.14
tw8	99.97	-	11.24	17.97	69.24	1.55
tw9	5.00	-	8.33	1.79	89.80	0.09
e1	100	86.53	16.30	14.95	68.27	0.69
e2	99.97	91.26	27.95	22.95	48.38	0.64
e3	46.94	91.94	24.01	11.59	62.98	1.43
e4	100	83.53	25.26	16.11	57.56	1.07
e5	99.96	82.07	27.21	13.77	58.83	0.20
e6	67.60	72.42	12.54	3.62	83.49	0.36
e7	100	78.61	15.36	3.46	81.07	0.13
e8	99.97	94.20	23.02	18.52	57.08	1.40
e9	33.56	57.83	10.65	2.84	86.52	0.00

* Elemental distribution on the ZVI surface was detected by SEM-EDX. Details are presented in supporting information.

4.3.1 Mass transfer

4.3.1.1 Surfactants

Two commercially available surfactants, Tween-80 and Envirosurf, were investigated in order to determine their effects on ZVI-mediated degradation of PCBs. Nonionic surfactants, which exhibit a high degree of surface-tension reduction and relatively constant properties in the presence of salt [250], are commonly used in ZVI remediation. The nonionic surfactant Tween-80 was shown to enhance degradation efficiency synergistically with Ni^{2+} in our previous study [248]. The other surfactant used, Envirosurf, contained a mixture of anionic (i.e., SDBS) and nonionic surfactants. Anionic surfactants have been reported to have an adverse or insignificant effect on the reduction process [164] but also to enhance the solubility of HOCs

[135]; however, the effect of mixtures of nonionic and anionic surfactants was not discussed.

Surfactant type and concentration were the most important factors affecting reduction in the studied system. In two series of orthogonal tests, the abundance of C was significantly impacted by surfactants (Table 4.7), which implies that the surfactants were adsorbed in preference to humic acid. The amphiphilic property of surfactants facilitates their sorption on the surface of iron and decreases the interfacial tension between the solid and liquid phases, thus enhancing the adsorption of PCB-52 onto the iron surface. However, the micelles of surfactants in the aqueous phase can also inhibit PCB-52 adsorption by sequestering it in hydrophobic pseudophases [165]. The positive or negative impact of a nonionic surfactant is contingent on the interaction of both effects. Table 4.3 shows that the best performance was obtained with surfactant concentrations of 25-50 CMC, which is not in accordance with several previous studies that reported that surfactants at concentrations above the CMC inhibited reduction [164, 230, 251].

Adsorption of Tween-80 (Table 4.4) was saturated at high concentration regardless of the levels of other factors. In treatments with 500 CMC of Tween-80, only 5% of the surfactant was adsorbed, which means that approximately 475 CMC of Tween-80 remained in solution, forming micelles with a large quantity of pseudophases wrapping the target compound and inhibiting the transfer process. Adsorption saturation of Tween-80 on the surface of ZVI was calculated to be 500 CMC/g, a value that was attained in treatments with 25 CMC Tween-80 (treatments tw 2, 5, and 8), all of which performed well. For these treatments with 25 CMC Tween-80, interfacial tension was as low as it was in treatments with 500 CMC Tween-80, while at the same time there was not enough Tween-80 in aqueous solution to form micelles. For the treatments with 1 CMC Tween-80, the adsorption of Tween-80 was far from saturation and interfacial tension was supposed to be higher in comparison to the other treatments, leading to less efficient mass transfer of PCB-52. Comparisons of adsorption and performance among treatments with different concentrations of Tween-80 demonstrated that the inhibition of degradation induced by a high concentration of nonionic surfactant should be attributed to the formation of aqueous micelles rather than to multi-layer coverage of the ZVI surface by surfactant. Adsorption saturation on the surface of ZVI is dependent on the properties of both surfactants and iron particles.

Addition of anionic SDBS improved reduction performance in treatments with a high concentration of nonionic surfactant. Compared to the 500 CMC Tween-80 treatments, treatments with 560 CMC Envirosurf slightly improved the degradation rate of PCB-52 (table 4.3) and drastically enhanced the adsorption of nonionic surfactant (table 4.4). Enhanced adsorption of the nonionic surfactant resulted in fewer aqueous molecules available to form micellar pseudophases and therefore less mobilization of PCB-52 to the solution. It is worth noting that the adsorption of SDBS was not saturated regardless of its concentration in the series of tests. A probable explanation is that anionic SDBS is adsorbed primarily on sites with positive charges, the quantity of which is limited by the surface properties of the iron particles, including microdomain pH. From another perspective, adsorption of SDBS neutralized the surface charges of iron particles, leading to higher adsorption of nonionic surfactant.

Consistent with previous reports [234, 252], addition of anionic SDBS alone did not enhance reduction by ZVI, while it significantly depressed dechlorination (figure 4.5). This result further demonstrates that SDBS influenced the reaction primarily by its impact on the adsorption of nonionic surfactant.

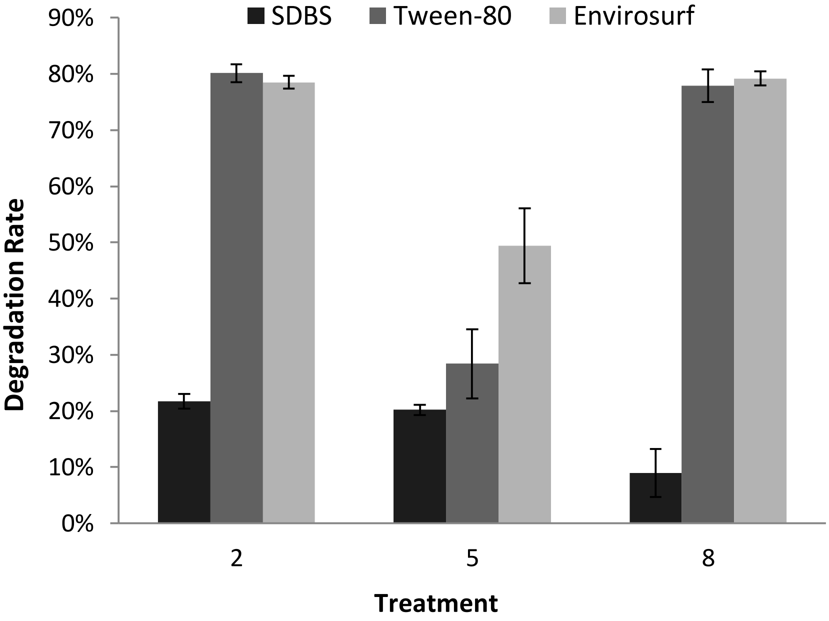

Figure 4.5 Removal of PCB-52 during treatment 2, 5 and 8 with different species of surfactants

4.3.1.2 Humic acid

Although treatment tw 5 contained 25 CMC of Tween-80, it was less efficient than treatments tw 2 and tw 8. The same tendency was also observed in the corresponding treatments with Envirosurf. These phenomena can be attributed to the high loading of humic acid in tw 5 and e 5. As the second most influential factor, the concentration of humic acid was negatively correlated with the degradation rate of PCB-52 (table 4.6). Extensive studies have demonstrated that humic acid or other SOM can enhance degradation by serving as an electron shuttle at low concentration, while it can also depress degradation by occupying reactive sites at high concentration [163, 169, 170].

Unfortunately, we were unable to quantify the precise extent of humic acid adsorption in this study by traditional methods such as UV spectroscopy or total organic carbon, due to weak

UV adsorption by humic acid and its low carbon content in comparison to the surfactants. The test of between-subjects effects (table 4.7) showed that initial humic acid concentration had an insignificant effect on the abundance of C on the ZVI surface, probably because high adsorption of surfactants disguised the variation induced by adsorption of humic acid. However, adsorption of humic acid was detected visually as the disappearance of the dark color of humic acid in the course of the reaction.

Compared to PCB-52, humic acid was preferentially adsorbed on the finite available reactive sites on the surface of ZVI, and consequently it lowered the dechlorination rate. In addition, as an amphiphile, humic acid in the liquid phase is able to form micelle-like structures, further enhancing the solubility of target compounds [174, 253] and restricting their adsorption on the ZVI surface.

4.3.1.3 Interactions of surfactants and humic acid

Surfactants and humic acid are not independent factors in the ZVI degradation system; their interactions also influence the reaction course. Surfactants, especially anionic surfactants, have been reported to dramatically enhance the solubilization of SOM and humic acid [135, 214, 254]. Consistent with those findings, our SEM images of the ZVI surface revealed that there was less adhered humic acid in treatments with Envirosurf than with Tween-80 (figure 4.2 and 4.3). Treatments with the same concentration of humic acid but differing concentrations of surfactant showed a similar influence of surfactant on humic acid adsorption. Reduced adsorption of humic acid on the ZVI surface led to increased efficiency of PCB-52 mass transfer and increased dechlorination. In the liquid phase, the solubilization of humic acid by surfactant also restricted the negative effect of humic acid on PCB-52 mobility, again leading to higher reduction efficiency. From this aspect, a higher concentration of surfactant results in less interference from humic acid. However, excessively high concentrations of surfactant (the primary influencing factor) can also limit reduction as mentioned above. Hence, optimization of these two factors is crucial to the reduction of hydrophobic PCB-52 during ZVI-mediated remediation.

4.3.1.4 pH

The initial pH value had a significant impact on the dechlorination rate, primarily by influencing the process of oxidation on the ZVI surface. In addition, pH can influence the dechlorination rate by its effect on adsorption of ions in solution, *i.e.*, humic acid and SDBS. Humic acid and many other SOM/NOM species usually exist in aqueous solution as ions, the adsorption behavior of which is pH sensitive. SEM images (figure 4.2 and 4.3) shows less adsorbed humic acid in low pH treatments as the negative charges of humic acid was neutralized by H^+. Nevertheless, the impact on humic acid adsorption induced by pH changes was not significant compared to that brought about by surfactants.

For nonionic surfactants such as Tween-80, adsorption behavior is not liable to be influenced by pH. However, the adsorption of anionic surfactants such as SDBS on iron surfaces is higher at lower pH values (table 4.4). Changes in SDBS adsorption also influenced the adsorption behavior of Tween-80 and humic acid, as described above.

4.3.2 Iron oxidation

The other crucial process in ZVI-mediated reduction is iron oxidation/corrosion, *i.e.*, electron transfer. It is technically difficult to quantify electron transfer in ZVI reduction systems, although the phenomenon has been long recognized. Nevertheless, observable effects resulting from the surface oxidation of iron particles can provide clues for understanding how the studied factors influence electron transfer. As an effective reductant, Fe^0 is the main electron donor to PCB-52 and other oxidants such as water and metal ions. To accelerate reduction of the target contaminant, it is important to enhance electron transfer efficiency by such means as forming bimetals and preventing invalid oxidation by interfering oxidants.

4.3.2.1 pH

Previous studies have shown that ZVI-mediated degradation is pH sensitive and that lower pH results in higher degradation [148, 177, 178, 255], which is inconsistent with the results of the present study that degradation at pH 7.0 was comparable to that at pH 5.0. A possible explanation for this discrepancy is that in our study the initial pH value had less of an effect on the dechlorination rate than did surfactants and humic acid (table 4.5). Nevertheless, pH was a significant factor influencing the course of dechlorination, due to its impact on the process of oxidation/corrosion on the surface of iron particles.

In studies of the impact of pH during ZVI-mediated reduction, it has been reported that lower pH increases aqueous corrosion of iron and that higher pH leads to the precipitation of iron hydroxides [148, 178]. Direct evidence is provided in the present study that the mass percentage of oxygen on the surface of the iron particles, which reflects the degree of oxidation, was more affected by pH than by the other factors (table 4.7). The amount of observed iron corrosion was greater at pH 3.0 and 5.0 than at pH 7.0 (figure 4.2 and 4.3). Thus, the pH value (*i.e.*, H^+ activity) influenced the dechlorination course primarily by influencing the surface properties of iron particles. In addition, the neutralization effect of H^+ on the iron surface was illustrated by the greater degree of aggregation of iron particles seen in the low pH treatment compared to the neutral pH treatment.

4.3.2.2 Surfactants

The concentration and type of surfactant did not significantly influence the abundance of oxygen on the iron surface (table 4.7). However, the probability that surfactants affected the process of iron oxidation was suggested by the observations that iron particles treated with a high concentration of surfactant appeared to be less rough or aggregated and had less oxygen in the surface layer than did those in other treatments. The inhibition of oxidation by surfactants is nondirectional, in that it reduces oxidation by both target contaminants and interfering oxidants. Thus, several surface active materials have been applied as modifiers with ZVI to prevent aggregation and oxidation [160, 256].

As the differences described in the previous paragraph were most obvious between treatments with high and moderate surfactant concentration, it could be deduced that the strong dispersion effect and inhibition of oxidation were induced both by adsorption of surfactant on iron surfaces and by formation of micelles in the liquid phase. There are two possible pathways for surfactant micelles to affect oxidation: one is sequestration of oxidants by pseudophases; the other is that micelles are electrostatically attracted to adsorbed surfactant molecules and form multilayers, preventing the mass transfer of oxidants onto ZVI. As described in the previous section, the former pathway was preferred in this study. Possible oxidants in this system include Ni^{2+}, water, PCB-52, humic acid and the surfactants themselves. The reduction of Ni^{2+} and water by Fe^0 is not supposed to be hindered by surfactants, while PCB-52 and humic acid are probably wrapped by micellar pesudophases. As for the surfactants themselves, the relatively lower degree of iron oxidation in treatments with high surfactant levels as well as the XRD image of tw 6 (figure 4.4) eliminate the possibility of oxidation by the surfactant. Thus surfactants affected surface oxidation primarily through their influence on mass transfer of oxidants.

4.3.2.3 Humic acid

There is disagreement on the redox role of humic acid/SOM in ZVI-mediated reduction systems because of the diversity of OM species and of their properties. A recognized opinion is that humic substrates may serve as electron shuttles, accelerating degradation.

The formation of iron minerals such as ferric hydroxide and iron hydroxide oxide during ZVI-mediated reduction has been demonstrated by XRD analysis, while siderite has been shown to be generated on permeable reactive barriers with carbonate in the liquid phase [257, 258]. Although carbonate was not artificially added to our studied system, carbonate appeared to be generated through oxidation of humic acid (rather than of surfactant or of carbon existing in the particles), with the evidence being that siderite was absent in treatment tw 6 (high surfactant, low humic acid) and the control. This result suggests that humic acid not only influences the mass transfer process, but also participates in the oxidation/corrosion process as a reductant.

However, it is not inevitable that humic acid accelerates the efficiency of electron transfer. Comparisons among treatments tw 2, 5, and 8 illustrate the adverse impact of humic acid on PCB-52 degradation and iron oxidation. In treatments with high concentrations of humic acid, adsorption of humic acid on the iron surface hindered iron oxidation rather than accelerating it, which can be attributed to the inhibition of mass transfer by the adsorbed humic acid. As described above, surfactants are able to alleviate the adverse effect of humic acid by decreasing its adsorption. Hence, optimization of the concentrations of humic acid and surfactants are important to the process of ZVI-mediated degradation, from the aspects of both mass transfer and iron oxidation/corrosion.

4.3.2.4 Ni loading

Nickel was chosen to represent catalytic metals in this study, as it has been well studied and is less expensive than noble metals such as Pd and Pt. Moreover, Ni^{2+} is more common in polluted water than are other metal catalysts. It has been postulated that Ni on the surface of iron can serve as a collector of hydrogen, enhancing the corrosion of iron and accelerating the reduction process. Thus, a higher Ni loading content should result in a higher reaction rate [259, 260]. However, according to the test of between-subjects effects (table 4.5), the loading content of Ni was an insignificant factor in our study, a result that is inconsistent with results of previous studies. Moreover, the abundance of Ni on the iron surface had no significant relation to the dechlorination rate (table 4.6), indicating that our results cannot be attributed to incomplete reduction of Ni on the surface of iron particles during the reaction. A possible explanation for the observed discrepancy may be that the acceleration of electron transfer due to catalysis was not as important in this reduction system as the effects of surfactants and humic acid on mass transfer efficiency. In fact, a comparison among cases of field application of ZVI to chlorinated solvent contaminated aquifers concluded that the use of catalysts resulted in statistically insignificant improvement [261].

Based on the finding of last chapter that Ni did not alter the dechlorination pathway of PCB-52, it is probably cost effective to exclude catalytic metal ions from reduction systems for remediating PCBs in aqueous solution. The coexistence of Ni^{2+} may have little impact on ZVI-mediated degradation of PCBs in aqueous solution, while the metal ion can be removed by iron particles through a redox reaction.

4.4 Conclusions

ZVI-mediated reductive dechlorination of hydrophobic PCB-52 in an aqueous solution was influenced primarily by the mass transfer process of PCB-52, and then the electron transfer process. The influences of concerned factors, single or combined, were explained at the perspectives of both processes.

The mass transfer of PCB-52 onto iron surface was significantly enhanced by surfactants adsorbed on the iron surface due to the decreased interfacial tension but hindered by micelle sequestration. The inhibition was alleviated by the introduction of an anionic surfactant (i.e., SDBS), which enhanced adsorption of the nonionic surfactant and reduced the amount of aqueous micelles. Excessive humic acid hindered mass transfer of PCB-52 by covering active sites on ZVI and binding with PCB-52 in the aqueous phase. Surfactants, especially the anionic surfactant, were able to alleviate the adverse effect of humic acid by reducing its adsorption. The pH value of the system influenced the adsorption behavior of humic acid and the anionic surfactant, and consequently influenced the mass transfer process.

The most important factors affecting surface oxidation of ZVI were pH and surfactant. The participation of humic acid as a reductant was indicated by the fact that the mineral $FeCO_3$ was detected on the iron surface. The influence of surfactants on surface oxidation was related to their influence on mass transfer of oxidants. The acceleration of electron transfer by Ni^{2+} was not as important in this reduction system as the effects of surfactants and humic acid on mass transfer efficiency.

Based on a statistic analysis and the above mentioned affecting mechanisms, the relative importance of the studied factors was in the order surfactants > humic acid > pH > Ni^{2+}. The complex interacting effects of the concerned factors on the reduction of PCB-52 indicate that the improvement on mass transfer is important and effective for the reduction of hydrophobic contaminants by ZVI in aqueous solution.

4.5 Supplementary Information

4.5.1 Data analysis

To understand the individual effect from combination of orthogonal tests, data obtained from experiments were analyzed by SPSS 17.0 for windows system. Results of the analysis are listed below.

Table 4.5 Tests of Between-Subjects Effects for degradation rate.

Dependent Variable: degradation rate

Source	Type III Sum of Squares	df	Mean Square	F	Significance
Corrected Model	1.362[a]	12	0.114	17.57	0.001
	1.415	1	1.415	218.98	0
pH	0.207	2	0.103	16.007	0.004
surfactant	0.748	5	0.15	23.16	0.001
humic acid	0.278	2	0.139	21.542	0.002
Loading of Ni	0.101	2	0.051	7.851	0.021
Error	0.039	6	0.006		
Total	3.297	19			
Corrected Total	1.401	18			

a. R Squared = .972 (Adjusted R Squared = .917)

Table 4.6 Correlations among degradation rate and individual factors.

		degradation	humic acid	EDX(O)	EDX(Fe)	EDX(Ni)
degradation	Pearson Correlation	1	-.489*	.747**	-.672**	.418
	Sig. (2-tailed)		.034	.000	.002	.075
	N	19	19	19	19	19
humic acid	Pearson Correlation	-.489*	1	-.190	.035	-.163
	Sig. (2-tailed)	.034		.435	.887	.504
	N	19	19	19	19	19
EDX(O)	Pearson Correlation	.747**	-.190	1	-.851**	.317
	Sig. (2-tailed)	.000	.435		.000	.186
	N	19	19	19	19	19
EDX(Fe)	Pearson Correlation	-.672**	.035	-.851**	1	-.542*
	Sig. (2-tailed)	.002	.887	.000		.016
	N	19	19	19	19	19
EDX(Ni)	Pearson Correlation	.418	-.163	.317	-.542*	1
	Sig. (2-tailed)	.075	.504	.186	.016	
	N	19	19	19	19	19

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

Table 4.7 Element abundance on ZVI surface affected by concerning factors.

Source	Dependent Variable	Type III Sum of Squares	df	Mean Square	F	Significance
Corrected Model	EDX(C)	883.546[a]	12	73.629	7.680	.010
	EDX(O)	1226.959[b]	12	102.247	2.751	.112
	EDX(Fe)	2918.805[c]	12	243.234	3.884	.053
	EDX(Ni)	4.398[d]	12	.367	2.907	.100
	EDX(C)	2323.149	1	2323.149	242.308	.000
	EDX(O)	2575.490	1	2575.490	69.305	.000
	EDX(Fe)	59587.099	1	59587.099	951.505	.000
	EDX(Ni)	1.679	1	1.679	13.317	.011
pH	EDX(C)	72.079	2	36.039	3.759	.087
	EDX(O)	655.804	2	327.902	8.824	.016
	EDX(Fe)	1120.942	2	560.471	8.950	.016
	EDX(Ni)	.368	2	.184	1.460	.304
surfactant	EDX(C)	720.588	5	144.118	15.032	.002
	EDX(O)	439.390	5	87.878	2.365	.162
	EDX(Fe)	1563.981	5	312.796	4.995	.038
	EDX(Ni)	1.411	5	.282	2.238	.178
humic acid	EDX(C)	26.241	2	13.120	1.368	.324
	EDX(O)	26.164	2	13.082	.352	.717
	EDX(Fe)	1.485	2	.742	.012	.988
	EDX(Ni)	.360	2	.180	1.428	.311
Loading of Ni	EDX(C)	50.212	2	25.106	2.619	.152
	EDX(O)	42.758	2	21.379	.575	.591
	EDX(Fe)	217.891	2	108.945	1.740	.254
	EDX(Ni)	2.035	2	1.018	8.071	.020
Error	EDX(C)	57.525	6	9.588		
	EDX(O)	222.971	6	37.162		
	EDX(Fe)	375.744	6	62.624		
	EDX(Ni)	.756	6	.126		
Total	EDX(C)	5029.511	19			
	EDX(O)	4822.585	19			
	EDX(Fe)	100554.411	19			
	EDX(Ni)	9.181	19			
Corrected Total	EDX(C)	941.071	18			
	EDX(O)	1449.930	18			
	EDX(Fe)	3294.550	18			
	EDX(Ni)	5.155	18			

a. R Squared = .939 (Adjusted R Squared = .817)

b. R Squared = .846 (Adjusted R Squared = .539)

c. R Squared = .886 (Adjusted R Squared = .658)

d. R Squared = .853 (Adjusted R Squared = .560)

4.5.2 SEM-EDX

To shorten the length of article, the raw images of EDX are not displayed in the text. Thus herein presented are the images for accuracy.

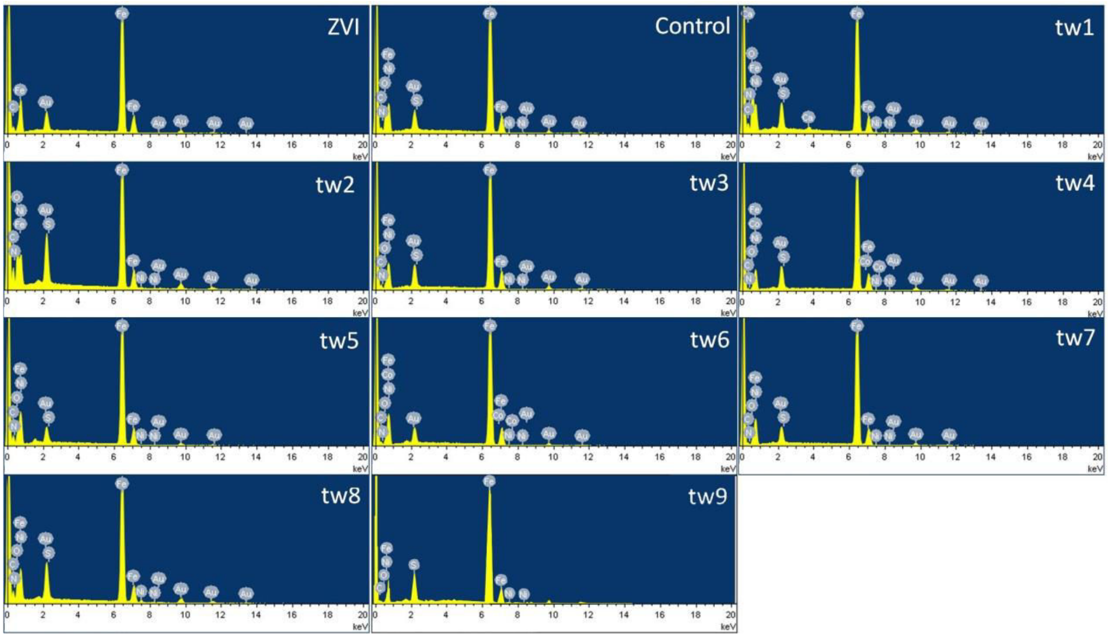

Figure 4.6 EDX spectra of ZVI.
From left to right, top to bottom as: before treatment, control, tw1, tw2, tw3, tw4, tw5, tw6, tw7, tw8 and tw9, respectively.

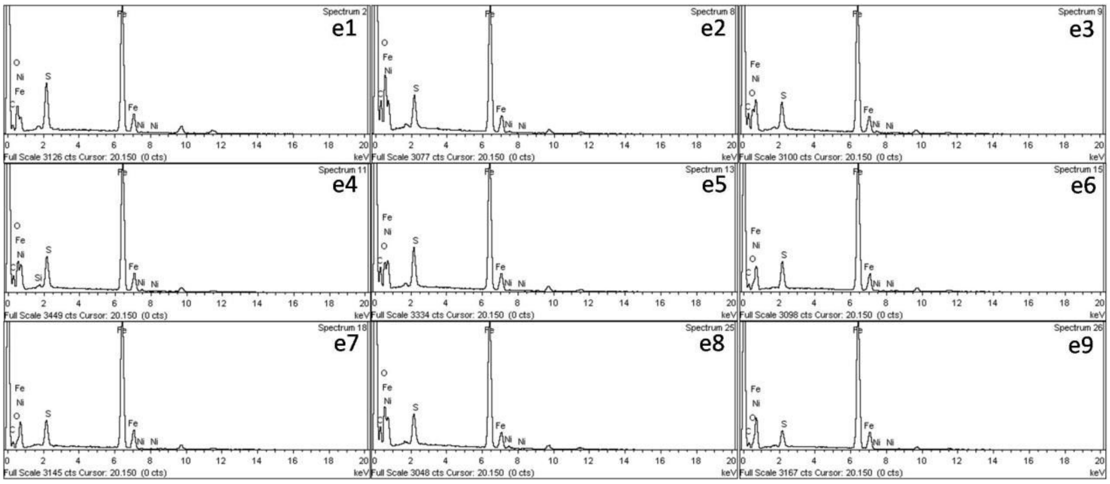

Figure 4.7 EDX spectra of ZVI.
From left to right, top to bottom as: e1, e2, e3, e4, e5, e6, e7, e8 and e9, respectively.

4.5.3 CMC of Envirosurf

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TECHNICAL REPORT

Report No.: IN-01246/2015-E
Pages: 4

PRESENTED SAMPLE

Sample description:

Ref. ENVIRO SURF

Presentation date: 13/05/15

REQUESTED TESTS

- CRITICAL MICELLE CONCENTRATION (CMC).

Performance dates: from 13/05/15 to 27/05/15

Nombre de reconocimiento (DN): c=ES, cn=ALBERT BRIZ AGUILAR, email=abriz@leitat.org, serialNumber=46237530D, sn=BRIZ AGUILAR, givenName=ALBERT, 1.3.6.1.4.1.17326.30.3=G08360232, o=ACONDICIONAMIENTO TARRASENSE, ou=STA, ou=MATERIALES, title=RESPONSABLE TÉCNICO MATERIALES, 2.5.4.13=Qualified Certificate: CAM-PF-SW-KPSC
Fecha: 2015.05.28 11:16:38 +02'00'

Materials Unit Coordinator
Jordi Jamilena

Materials Unit Technical Manager
Albert Briz

Terrassa, May 28th, 2015.

The test/s herein contained has or have been performed under the criteria of Good Environmental Practices, considering the minimization of natural resources consumption, reduction of waste generation and emission of pollutants into water and air as well as the implementation of the best available techniques within our Laboratory's reach.

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CRITICAL MICELLE CONCENTRATION (CMC).

According to: internal method

Scope: This test is intended to determine the Critical Micelle Concentration (CMC) of a surfactant. The CMC (Critical Micelle Concentration) is the concentration of a surfactant in a bulk phase, above which aggregates of tenside molecules, so-called micelles, start to form. The CMC is an important characteristic for surfactants.

Equipment used: KRÜSS Processor Tensiometer K100, no.EQ0005

Conditioning of the specimens: Not required

Test conditions:

Prepare a solution of 1g/L of the surfactant sample.
Measure the contact angle of this solution.
From the solution of 1g/L prepare other solutions, with known concentrations, and measure the contact angle of each others.
Carry out 3 repetitions for each solution.
Graph representation of the values and calculate the critical micelle concentration (CMC).
Liquid used: - MilliQ water to prepare different solutions
Date of performance: May 26th – 27th, 2015

Presented material:

Report No.: IN-01246/2015-E
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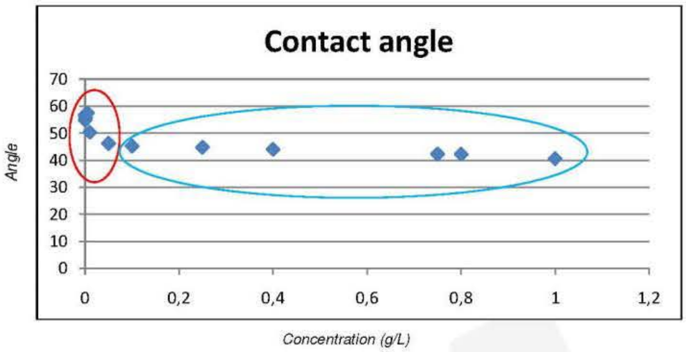
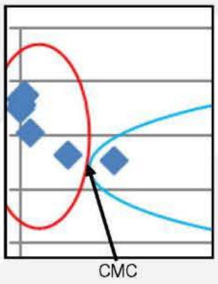
Results:

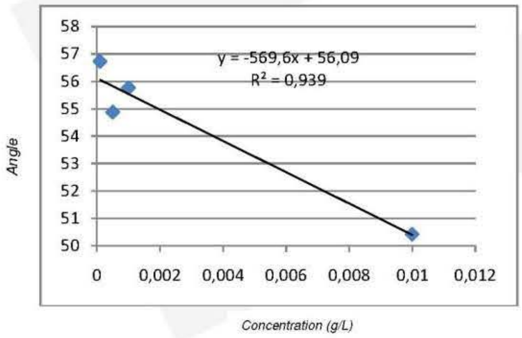
Graphic representation of the contact angle values for each surfactant solution:

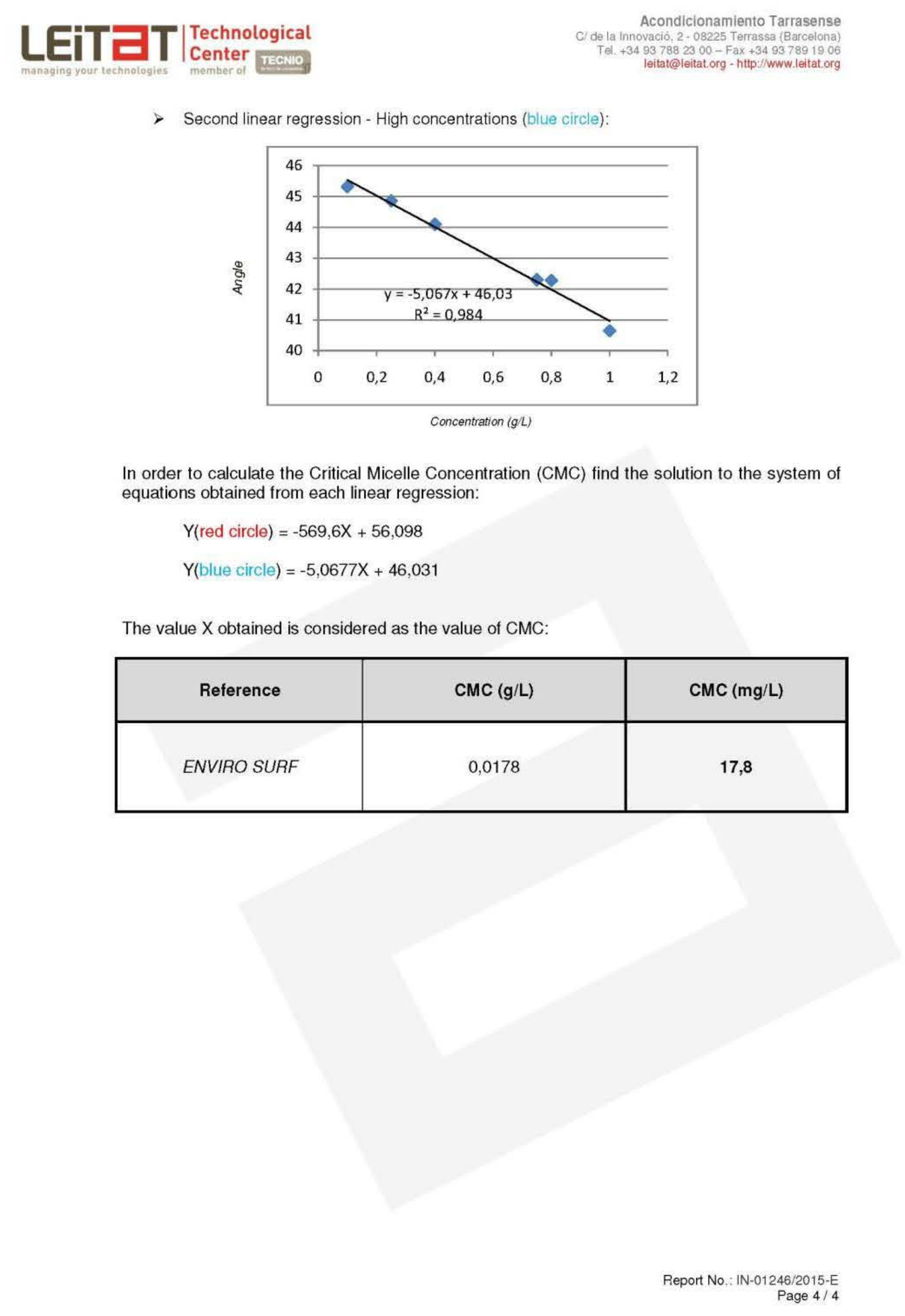


Two different linear regressions are represented, in order to calculate the intersection point of both (CMC):



- First linear regression - Small concentrations (red circle):





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- Second linear regression - High concentrations (blue circle):

In order to calculate the Critical Micelle Concentration (CMC) find the solution to the system of equations obtained from each linear regression:

Y(red circle) = -569,6X + 56,098

Y(blue circle) = -5,0677X + 46,031

The value X obtained is considered as the value of CMC:

Reference	CMC (g/L)	CMC (mg/L)
ENVIRO SURF	0,0178	**17,8**

Chapter 5.

Surfactant-assisted PCBs reduction by ZVI in contaminated sediment

5.1 Introduction

Zerovalent iron (ZVI) is an active material to remove a variety of contaminants. In terms of PCBs removal, it was demonstrated effective by chapter 3 in a stepwise dechlorination process occurred on the surface of ZVI, and the presence of Ni^{2+} ion is able to accelerate the dechlorination without changing its pathway.

Besides groundwater cleanup processes, the introduction of ZVI to soils/sediments remediation has been progressively realized. The removal of Cr(VI), TCE, chlorinated pesticides *etc.* in contaminated soils has been achieved at field scale [200-202]. Nevertheless, the cases of soil decontamination are still limited compared to those of groundwater remediation. Constraints rest on the ineffective contact between ZVI and target pollutant, as well as the passivation of iron in soils.

A possible solution to the problem may be the employment of surface active agents (*i.e.* surfactants). As illustrated in chapter 4, surfactants are able to enhance the mass transfer of PCBs onto the iron surface and alleviate the adverse effect brought by humic acid. In addition, it may also prevent the passivation of iron particles to some extent.

Based on the understandings obtained from chapters 3 and 4, it is possible that surfactants assist the ZVI-mediated dechlorination of PCBs in soils/sediments. The aim of this chapter is to investigate the feasibility of ZVI as a cleanup material for PCBs contaminated sediment with the assistance of surfactants. Also the effect of coexisting Ni in contaminated sediment on PCBs removal is investigated. Two approaches of cleanup process are proposed as table 5.1, with the descriptions on their advantages and disadvantages.

Table 5.1 Two approaches for PCBs removal by ZVI assisted by surfactant in contaminated sediment proposed by this study.

Approach	A	B
Operation	Surfactant desorption followed by ZVI treatment in solution.	Mixture of ZVI and contaminated sediment in surfactant solution
Advantage	Avoid matrix effect on ZVI reduction; optimize individually in separate unit to obtain the best efficiency of each process.	One-step reaction that is more simple and less required on reactor design; less content of surfactants is consumed.
Disadvantage	Dechlorination is subject to desorption; high contents of surfactants may enhance desorption but inhibit dechlorination.	Matrix effect on ZVI reaction; difficulty to separate iron and sample at the end of treatment.

5.2 Experimental

5.2.1 Chemicals

Details of chemicals are available in sections 3.2.1 and 4.2.1.

5.2.2 Contaminated sediment

An aged PCB-contaminated sediment was sampled by hand auger between 0.5 and 1 m from the surface on a former industrial site in Douvaine (France) not far from the Leman Lake. Contamination was due to former electric transformers. More generally, all the area near the city of Lyon in Rhône River basin, France (figure 5.1) has been one of the most important industrial centers in France. A PCB-making plant was located in this area, which contaminated the Rhône basin.

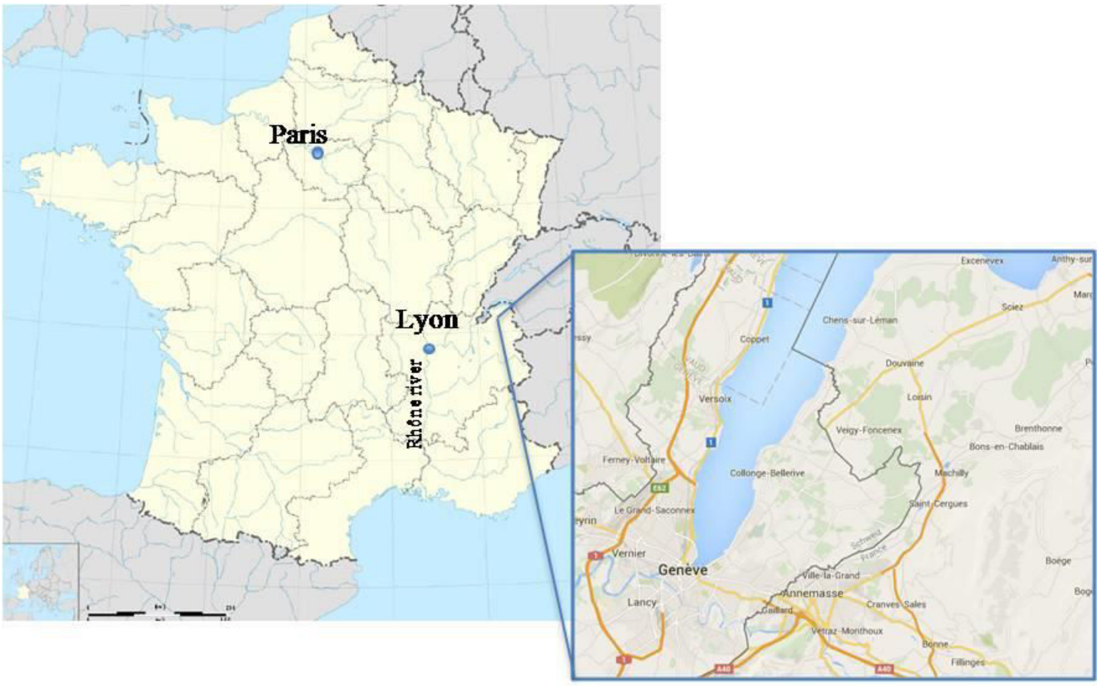


Figure 5.1 Map of Douvaine in France.

After collection, the samples were frozen dried and pre-sieved with a 20-mesh sieve to remove stones. To investigate the potential of simultaneous removal of both PCBs and heavy metals, Ni was spiked in the sediment at a content comparable to the contamination status in Chinese e-waste sites. Hence, 1.0 kg of sieved sediments was stirred by an agitator at 120 rpm with 500 mL 10.0 g/L $NiSO_4$ solution for 48 h. Afterward, the samples were air dried by exposing to ambient air at dark for 30 d with occasional agitation. After 30 d of aging, sediments were frozen dried and then stored at dark in a glass container. Physicochemical properties of the contaminated sediment, including pH, cation exchange capacity (CEC) and contents of organic matters are listed in table 5.2, together with the contents of pollutants.

Table 5.2 Physicochemical properties of the contaminated sediment, data obtained from laboratoire d'Analyses des Sols d'Arras, INRA*.

Soil Property		Value	Soil contamination		Value
Particle size distribution (%)	Clay (< 2 µm)	29.40	PCBs (mg/kg dw)	PCB-28	0.13
	Fine silt (2-20 µm)	33.80		PCB-52	5.21
	Coarse silt (20-50 µm)	10.10		PCB-101	14.10
	Fine sand (50-200 µm)	11.00		PCB-118	6.73
	Coarse sand (200-2000 µm)	15.70		PCB-138	20.40
Organic matter (OM) (g/kg dw)		8.19		PCB-153	23.15
pH (0.1mol/L KCl)		8.19		PCB-180	16.75
CEC (cmol+/kg dw)		6.44		Σ_7PCBs	86.45
Exchangeable Fe (g/kg dw)		3.39			

Heavy metals (mg/kg dw)	Cd	Zn	Pb	Cr	Cu	Ni
	0.256	69.32	177.98	86.48	24.06	4210

* Analysis details are listed in supplementary information.

5.2.3 Batch experiments of approach A

Two surfactants, Tween-80 and Envirosurf, were selected to investigate their performances by approach A, based on the knowledge of their influences on ZVI dechlorination that both of the surfactants are able to affect the dechlorination rates (chapter 4), while they are promising to effectively desorb PCBs from contaminated sediments.

Desorption. To determine the equilibrium time of desorption experiment, a series of batch experiments was conducted at different time intervals from 0.5 h to 32 h. A mixture of 0.50 g (dw) sediment with 10.0 mL surfactant solution (Tween-80/Envirosurf) was agitated at 180 rpm (25±2 °C). In each time interval, the reaction was terminated by filtration (0.45 µm glass fiber filters) to separate the aqueous and solid phases. The contents of Ni^{2+} and PCBs in solution were then detected to determine the equilibrium time. Subsequently, the influence of surfactant contents was investigated on the removal of both Ni and PCBs at equilibrium time. The contents of surfactants tested are listed in table 5.3. All tests were done in duplicate, and treatments with deionized water were set as control.

Dechlorination. The ZVI treatments were performed in 30-mL centrifuge tubes with screw caps, all of which are made of PTFE. A quantity of 0.050 g ZVI was added to 5.0 mL filtered solution after desorption experiment, in the anaerobic workstation. Solution pH was not adjusted. Tubes were tightly sealed, placed in the dark at 25 ± 2 °C and agitated at 200 rpm before set time point. The reaction was terminated by filtration (0.45 µm glass fiber filters) to separate the aqueous and solid phases. A series of kinetic experiments was performed to understand the reduction process of PCBs at different time intervals.

Table 5.3 Contents of surfactants investigated in the experiments of approach A and B.

Approach		A			B		
surfactant	Tween-80	0.08%	1%	2%	0.04%	0.20%	1%
content	Envirosurf	1%	2%	5%	0.04%	0.20%	1%

5.2.4 Batch experiments of approach B

The batch experiments were performed in 30-mL centrifuge tubes with screw caps, all of which are made of PTFE. A 0.10-g of ZVI and 0.50-g of contaminated sediment were added to 10 mL of a thoroughly mixed solution containing surfactants, which was performed in the anaerobic workstation. The contents of surfactants (as displayed by Table 5.3) investigated in this section were determined based on the results of chapter 4 and approach A. Solution pH was not adjusted. Tubes were tightly sealed, placed in the dark at 25 ± 2 °C and agitated at 200 rpm before set time point. The reaction was terminated by filtration (0.45 µm glass fiber filters) to separate the aqueous and solid phases.

According to the results of approach A, a reaction time was set to compare the impacts of surfactants at different contents. To get insight of the mechanisms, kinetic experiments were conducted with low contents of surfactants, following the above mentioned protocol.

5.2.5 Analysis and characterization

The extraction and measurement protocols of PCBs, Ni, Fe and surfactants in washing solution could be referred to sections 3.2 and 4.2. The overall PCBs desorption efficiency by washing solutions was represented by the desorption efficiency of seven selected PCB congeners (as listed in table 5.2), which are the most abundant in contaminated environments. To obtain details of dechlorination, a semi-quantification of each chlorinated biphenyl (mono- to octa-) and biphenyl in each treatment at each predetermined time was calculated as the ratio of the responding peak area of the measured congener to that of PCB-82 in the system.

ZVI characterization was described previously in section 4.2.5. Data analysis was conducted by excel 2013, SPSS 17.0 and origin 8.0 for windows.

5.3 Results and discussions

5.3.1 Approach A

Approach A is a treatment process with two separate operations in sequence. As described in table 5.1, the dechlorination efficiency is highly dependent on the desorption efficiency and the contents of surfactants in the solution. Hence, careful investigations in both processes are necessary to evaluate the performance of this approach.

5.3.1.1 Desorption kinetics

The behaviors of heavy metals and hydrophobic POPs in soils and sediments are not quite similar and either are their behaviors during desorption process by surfactants. Details of the desorption kinetics were discussed in the supplementary information. Briefly, equilibrium of Ni desorption could be obtained rapidly in 4-8 h, and equilibrium of PCBs desorption in 12 h.

To ensure the thorough desorption of both Ni and PCBs in the subsequent tests, 24 h was selected as the equilibrium time for desorption batch experiments.

5.3.1.2 Impacts of surfactant contents on desorption

As illustrated by figure 5.2, the desorption pattern of PCBs is not similar with that of Ni considering different contents of surfactants, implying separate desorption pathways of the two contaminants.

Ni desorption from contaminated sediment was not influenced by the content of Tween-80 in the present study, which is in accordance with the study by Khodadoust *et al.* (2005) concerning the removal of Zn by Tween-80 [143]. An increase of the contents of Envirosurf led to higher desorption of Ni from 2.12 to 13.03%, with a positive correlation between Ni removal and the content of Envirosurf (r^2 = 0.9893). The improvement induced by Envirosurf is attributed to the elevated content of SDBS in mixture for the removal of metals through ion exchange with sodium cations and electrostatic attraction of negatively-charged micelles [262, 263].

On the contrast to Ni, the desorption of PCBs by Tween-80 was dramatically increased at 1% comparing to 0.08% (50 CMC). The ineffective desorption of PCBs by 0.08% Tween-80 could be attributed to surfactant adsorption by sediments. The remaining aqueous Tween-80 was not sufficient to form micelles, leading to lower enhancement on PCBs solubility. Hence, a larger aqueous content of Tween-80 led to larger amount of micelles, and facilitated greater desorption of PCBs without changing the congener profiles in micelles.

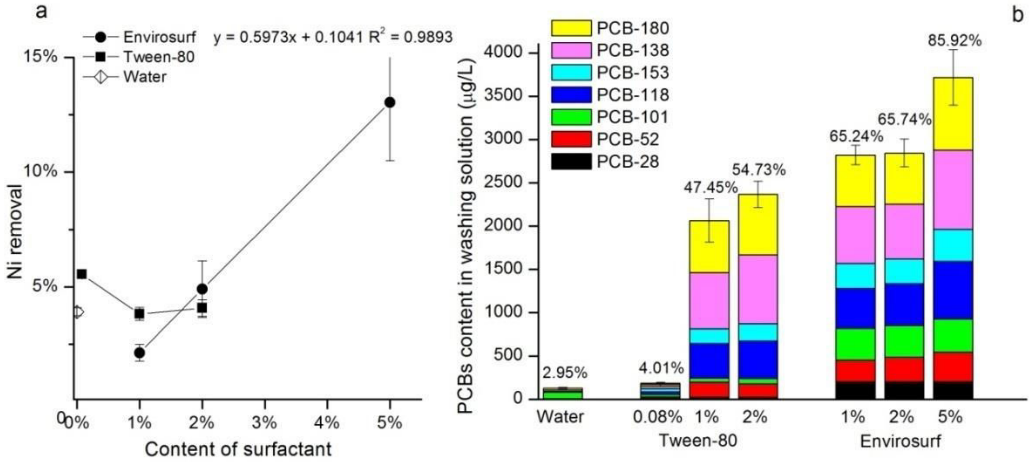


Figure 5.2 Impacts of surfactant contents on desorption: a, Ni removal; b, PCBs removal, average desorption efficiency in each treatment is marked above the stack columns.

In a similar way, no significant differences were recorded between PCB by Envirosurf at 1% and 2%, while 5% of Envirosurf significantly enhanced desorption: the efficiency was larger than 85% without changing the congener profile. It is known that surfactant micelles are spontaneously self-assembled above the CMC usually as spherical shaped. And a more complicated form of micelles could be formed at higher contents, as rod-shaped or even binary, depending on the properties of surfactants and solution [264]. Therefore, the impact on desorption of hydrophobic compounds by larger contents of surfactant, especially surfactant mixtures, could be more complicated. As a result, desorption efficiency is usually not linearly enhanced with elevated applied content of surfactant, as the case of treatment with Envirosurf in this study.

To sum up, considering PCBs desorption from contaminated sediment, 10% of Envirosurf is the best choice among all the tested surfactants, reaching a removal efficiency of 99.91%. Nevertheless, in view of the cost efficiency, 1% of Envirosurf may be more practical by using sequential washing method. Despite the advantage of washing by Envirosurf, the potential ecological risk is unknown for its usage on soils and sediments. Thus sequential washing by 1% of Tween-80 is also recommended for approach A.

5.3.1.3 ZVI treatment

Selected physicochemical properties of washing solution acquired after batch desorption experiments were listed as table 5.4. As the two washing solutions were quite different from each other, except for the similar pH values, results of ZVI treatment in both solutions may be different from each other.

Table 5.4 Properties of washing solutions after desorption experiment.

Properties		washing solution	
		1% Envirosurf	1% Tween-80
pH		6.95	6.76
Content of Ni (mg/L)		89.34	160.78
Content of PCBs (μg/L)	PCB-28	202.02	24.75
	PCB-52	251.65	174.36
	PCB-101	365.70	46.84
	PCB-118	462.77	397.61
	PCB-138	288.32	171.63
	PCB-153	653.53	648.86
	PCB-180	595.86	599.88
	Σ_7 PCBs	2819.85	2063.95
Surfactant content (mg/L)	Nonionic	2148.96	8377.08
	Anionic	8894.83	-

A 7-d ZVI treatment shows that the removal of Ni by ZVI was a rapid and complete process, 98.95% and 97.57% of Ni in Tween-80 and Envirosurf solution were removed from washing solutions, respectively. The remaining of Ni in aqueous solution was not attributed to the saturation of reactive sites on the surface of iron as the molar ratio between Fe and Ni was more than 300. A precipitation and dissolution equilibrium in the reaction system was more likely to be the cause.

Figure 5.3 illustrated that contents of PCBs in both washing solution did not significantly change, which means the failure of degradation reaction by ZVI in 7 d. This phenomenon was a result of high content of surfactant in washing solution. As discussed in chapter 4, the amphiphilic property of surfactants facilitates their sorption on the surface of iron and decreases the interfacial tension between the solid and liquid phases, thus enhancing the adsorption of PCBs onto the iron surface. However, the micelles of surfactants in the aqueous phase can also inhibit PCBs adsorption by sequestering it in hydrophobic pseudophases. Although a given amount of surfactants was lost during sediment desorption process, the content of remaining surfactants was high enough to form a large amount of micelles that inhibits the mass transfer of PCBs.

Moreover, severe aggregates of iron particles and coverage by soil organic matters (SOM) on the particle surface were observed in both treatments (figure 5.9), which may also be the reason for the ineffective degradation. Previously, it was observed by SEM (figure 4.2 and 4.3) that high content of surfactants prevented the adsorption of humic acid on the surface of ZVI, which is not in consistence with the case of washing solution. The more severe coverage by SOM may be a result of aggregation promoted by Ca/Mg cations in the solution [265]. The binding with Ca, Mg or Fe cations could lead to a compact conformation of SOM molecules by reducing intramolecular electrostatic repulsions and by forming multidentate complexes with neighboring functional groups on SOM molecules [266]. Another possible cause of the iron agglomeration is the elevated pH value along with the reaction proceeded. As revealed by table 5.5, the pH value of ZVI suspension without surfactant increased significantly, leading to the agglomeration of iron particles (figure 5.9b). Although the pH was buffered in washing solutions, it was still high enough to cause aggregates.

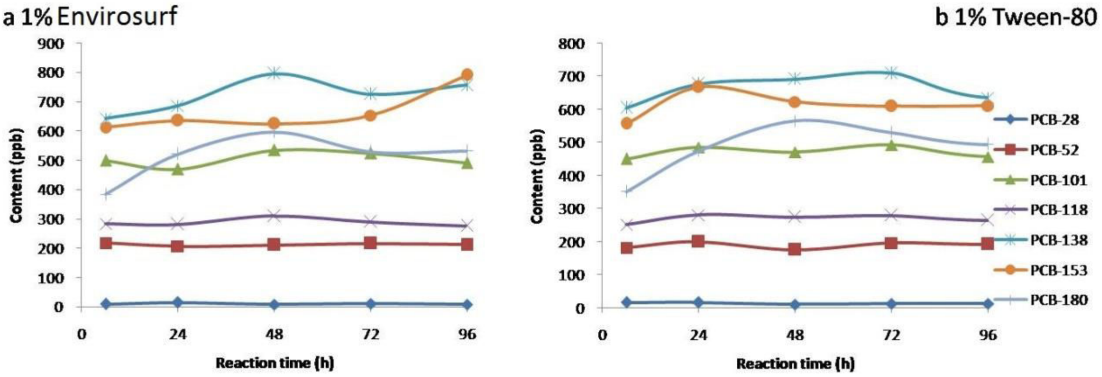


Figure 5.3 Kinetics of PCB congeners during the treatment with ZVI (approach A): a, washing solution with 1% Envirosurf; b, washing solution with 1% Tween-80.

Results demonstrated approach A to be ineffective. Although more than 97% of present Ni could be removed by iron particles, PCBs dechlorination was not effective in washing solutions for a treatment of 7 d (168 h). The high content of surfactants and Ca/Mg ions were ascribed for the ineffective dechlorination.

5.3.2 Approach B

Approach B is a simple operation by mixing ZVI and contaminated sediments in a surfactant solution. In this system, surfactant is able to facilitate the contact between PCBs and ZVI by two processes simultaneously: (1) enhanced desorption of PCBs from sediment; (2) enhanced PCBs adsorption on ZVI. As revealed by chapter 4, the influence of surfactant is dependent on its aqueous contents, thus the contents of surfactants investigated in this section was set accordingly.

5.3.2.1 Impacts of surfactant contents

Effects of different surfactants at different contents are illustrated as figure 5.4, concerning the contents of seven most abundant congeners in the environment and the biphenyl generated during the process. The best degradation was acquired by using 0.04% Envirosurf with a removal efficiency of 76.31% (figure 5.4c).

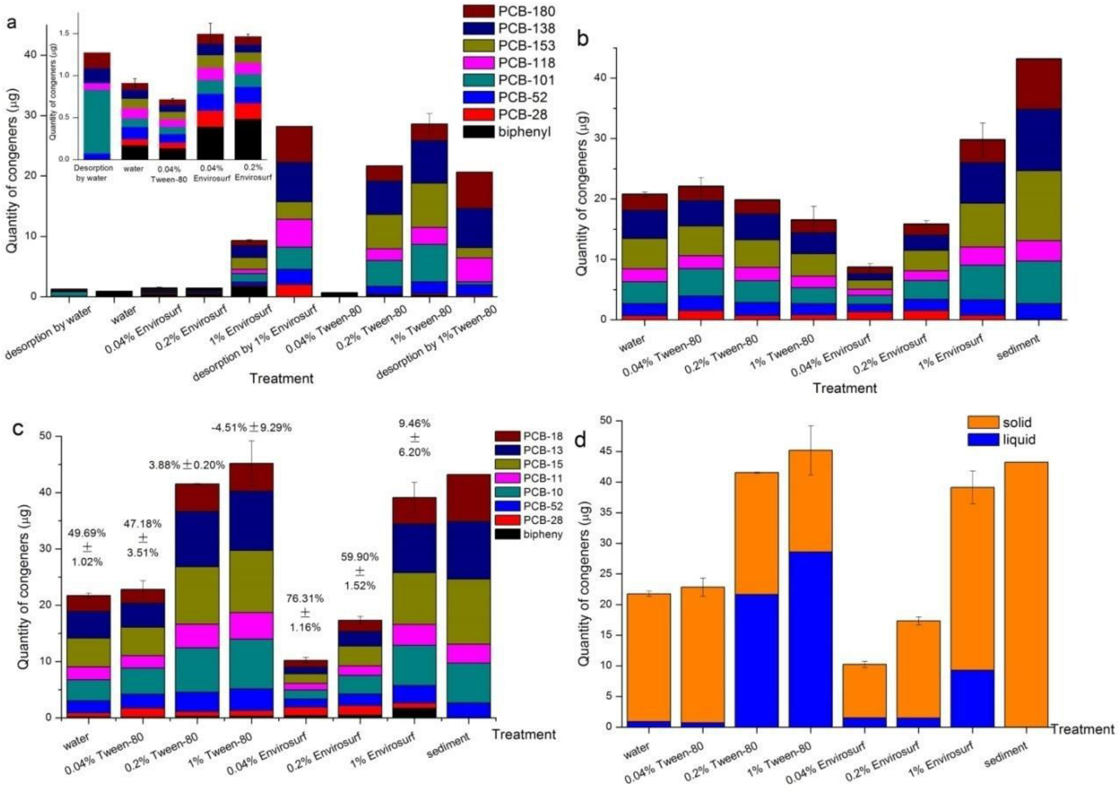


Figure 5.4 Quantity of seven PCB congeners and biphenyl in different treatments for 168 h: a, in liquid phase; b, in solid phase; c, in the whole system (removal rates displayed above columns as mean ± standard error); d, PCBs partition in liquid and solid.

Figure 5.4a depicted the congener profiles among treatments with or without ZVI in liquid phase. 1% of Envirosurf and Tween-80 were efficient to extract PCBs from contaminated sediments by 65.24 and 47.45%, respectively. Although higher solubility of congeners was observed by larger contents of surfactants (figure 5.4a and d), the degradation seems to be negatively related to the contents of surfactants (figure 5.4c). In addition, the abundance of lower chlorinated congeners (CBs) such as PCB-28, PCB-52 and PCB-101 was greater with Envirosurf than Tween-80. An explanation is that the lower CBs in Envirosurf solution were not those desorbed from sediments, but were the dechlorination products of higher CBs. Comparisons at the same contents illustrated the better performance with Envirosurf than with Tween-80, implying the positive effect of anionic SDBS on both improving solubility and degradation.

These results are in accordance with results of chapter 4 on the reaction mechanism in aqueous solution that surfactant micelles inhibit the mass transfer of PCBs onto the iron surface and thus hinder dechlorination. Meanwhile, SDBS in aqueous solution synergistically enhances the ZVI degradation reaction of PCBs by enhancing adsorption of the nonionic surfactant and reducing the amount of aqueous micelles. In the view of PCBs desorption from contaminated sediment, a mixture of nonionic and anionic surfactants has been demonstrated more efficient than individual surfactants [267, 268], thus facilitating mass transfer of PCBs from sediment to ZVI surface.

Although water alone was not feasible to enhance the solubility of PCBs, the effect on degradation by water seems to be comparable with 0.04% Tween-80 concerning the contents of seven PCB congeners, while the accumulation of PCB-28 and PCB-52 during the treatment with 0.04% Tween-80 was significant over the treatment with water. Also the semi-quantification of mono- through octa-CBs (figure 5.5, nona- and deca- was not detectable in the sample) for all the treatments shows higher reduction of octa-CBs and hepta-CBs by 0.04% Tween-80 than water.

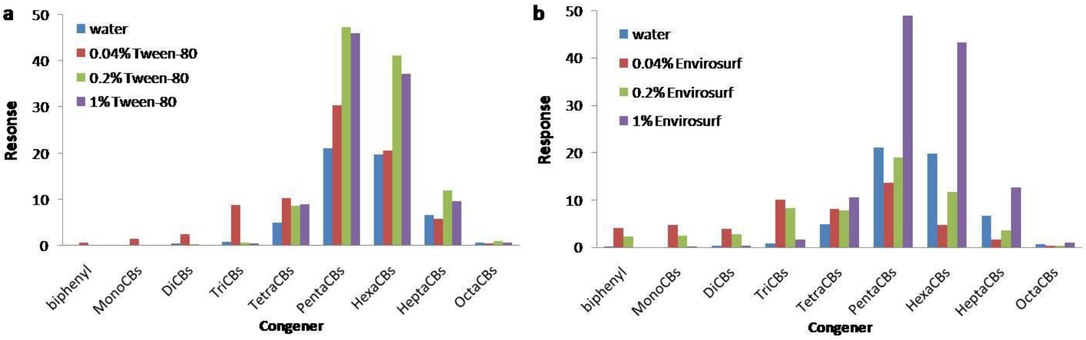


Figure 5.5 Response of mono- through octa-CBs detected by GC-MS SIM mode with different surfactants for 168 h: a, Tween-80 treatment; b, Envirosurf treatment.

This contradiction was attributed mainly to the enhanced solubility and mobility of higher CBs that are more hydrophobic induced by Tween-80. As observed that the congeners in aqueous solution without surfactants were mainly lower CBs, while higher CBs was more abundant in Tween-80 washing solution (figure 5.4a). Another evidence for the greater facilitation by 0.04% Tween-80 over water is that the accumulation from biphenyl through tri-CBs was more significant with 0.04% Tween-80 compared to water. It is noted that the result of semi-quantification could only be compared among different time intervals and treatments with the same PCB species, because the responses of homologues were different from each other through the detection by GC-MS. For the same reason, the semi-quantification could only provide an estimation of degradation extent rather than a precise degradation/generation rate of PCBs.

During the degradation process, all the biphenyls generated in each treatment were distributed in liquid phase (figure 5.10), owing to the relative lower octanol-water partition coefficient (K_{ow}) of biphenyl ($-\log K_{ow}=4.10$) [269]. The distribution of other congeners in liquid phase was also related to the K_{ow} that lower CBs with lower K_{ow} value led to larger distribution in aqueous solution. Besides, the presence of surfactants or SOMs in the aqueous solution enhanced the solubility of PCBs. This phenomenon indicated that PCBs in solid phase can be removed and transferred to liquid phase after ZVI degradation treatment enhanced by surfactants in the form of biphenyls with sufficient reaction time. In that case, the cleanup of soil/sediment could be achieved while the aqueous solution could be recovered and reused after cost-effective biochemical treatments under mild conditions for the removal of biphenyl which is more available to microbes compared to PCBs [270].

In addition, the ZVI-mediated degradation of halogenated organic compounds is a stepwise process that higher halogenated congeners are usually more rapid to be dehalogenated [155, 271], which is in accordance with this study. The higher accumulation of tri-CBs compared to its offspring in 0.04% Tween-80 treatment manifests that 168 h was not sufficient to the degradation reaction mediated by ZVI, thus a subsequent series of kinetic experiments using 0.04% surfactants was conducted to get insight into the influence induced by surfactants.

5.3.2.2 Dechlorination kinetics

The degradation kinetics of PCB congeners were illustrated as figure 5.6(a-c), and 336 h seemed to be sufficient for the equilibriums of degradation in respect of treatments with/without surfactants. In consistence with the 168-h experiments, the best removal of seven PCB congeners was acquired with 0.04% Envirosurf (72.91%), other than with Tween-80 (46.93%) or without surfactants (47.40%) in 14 d (336 h). A pursuant experiment until 28 d did not show significant changes on the contents of selected PCB congeners.

The stepwise dechlorination was reflected in the results of semi-quantification (figure 5.6 d-f). During the course of each treatment, hepta and octa-CBs were efficiently removed within 2 h (64.52-94.01% and 75.52-94.97%, respectively) and hexa-CBs were largely removed within several days (52.58-89.50%), while the changes of lower CBs were distinguished among treatments. Merely a small quantity of biphenyl through tri-CBs was accumulated in the treatment without surfactant, indicating the slow reaction rate. Significant accumulation of tri through penta-CBs were observed in treatments with either surfactant, while the accumulation of offspring was higher with 0.04% Envirosurf within 336 h than with Tween-80. In contrast, the generation of biphenyl to tetra-CBs erupted at 672 h in the treatment with Tween-80.

In order to understand the influence of surfactants on PCBs degradation, the morphologies of iron particles at each time interval and the behaviors of surfactants and metals in the system were studied for all the treatments

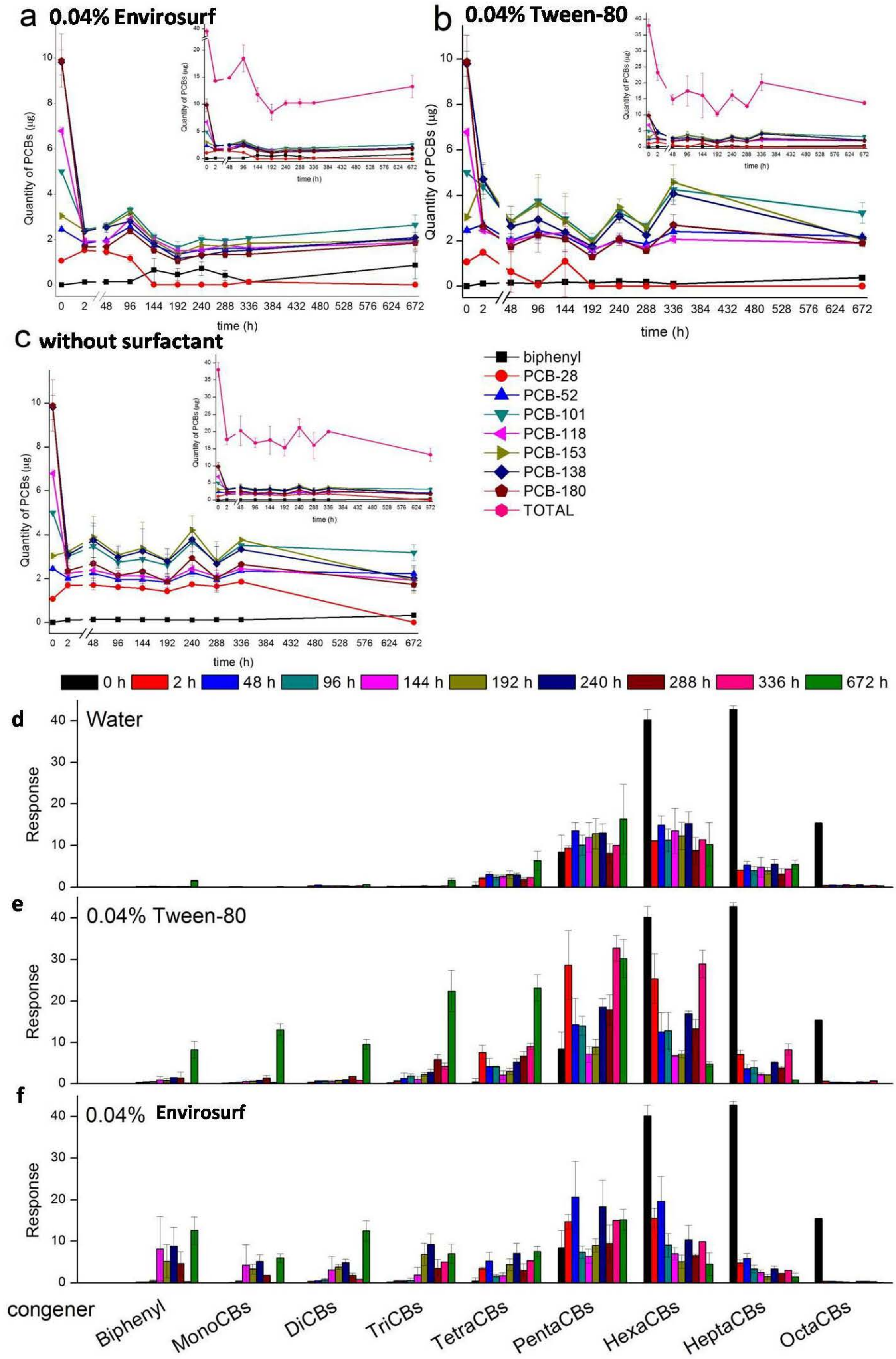


Figure 5.6 Dechlorination kinetics in 28 d (a-c: Σ_7PCBs + biphenyl, e-f: response of mono- through octa-CBs detected by GC-MS SIM mode).

5.3.2.3 Treatment without surfactant

The major dechlorination occurred to hexa-, hepta- and octa-CBs in the treatment without surfactant in the period of 14 d, and the generation/dechlorination of the descendant homologues was limited through the whole course. The relatively less efficiency of water treatment was attributed to the passivation of iron particles, which was displayed by the changes in morphology of iron particles (figure 5.11).

At the early stage of reaction (2 h to 4 d), it was observed that the rough surface of iron particles was adhered by SOM or sediment minerals (confirmed by SEM-EDX in figure 5.11). The slight dissolution of Fe (≈0.08% of ZVI) and Ni (≈1.0% of total content in sediment) as illustrated in figure 5.7a, was in accordance with the observed iron corrosion. The corrosion of iron in the mixture experiment was more significant than that in the 7-d aging experiments without sediment, which is caused by the SOMs such as humic acid (HA) from the sediment. Previous studies confirmed the formation of Fe^{3+}-HA complexes in both the dissolved and solid fractions during the ZVI treatment and the resulted aggregation of HA on the iron surface [272]. HA or other species of SOMs are able to enhance the corrosion of iron serving as an electron shuttle, and to enhance the dissolution of Fe by forming Fe^{3+}-HA complexes. The dissolution of Ni by water could reach as much as 3.91% (data available in figure 5.2a); While merely ≈1.0% of Ni was dissolved in the solution, implying the reductive precipitation of Ni by iron particles and the inhibition of Ni reduction due to the coverage of sediment minerals or SOMs.

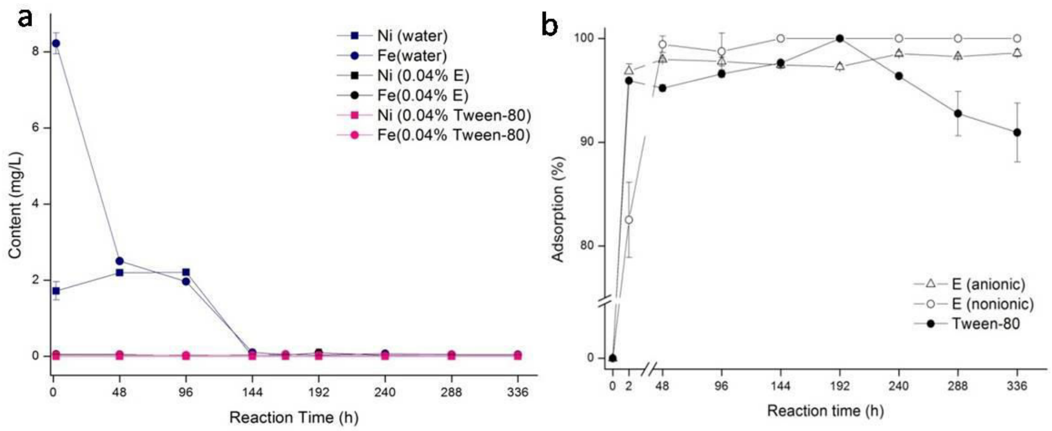


Figure 5.7 a, Contents of dissolved Ni and Fe in treatments with/without surfactants; b, Tween-80 and Envirosurf adsorption during the treatment at 0.04% (E is short for Envirosurf herein).

As the reaction proceeded, the aqueous contents of Ni and Fe decreased to zero and several dozens of μg/L, respectively. The disappearance of metals from solution was supposed to be induced by the elevated pH value along the process and the coincident precipitation of metals. Moreover, the elevated pH and the alkaline clay minerals in the sediment were the causes of iron aggregation (as indicated by figure 5.11) and passivation. A mixture of ZVI and contaminated sediments in aqueous solution without any surfactant was able to trigger the dechlorination of PCBs, primarily of octa-, hepta- and hexa-CBs that are more reactive homologues than their offspring. This fact implies the facilitation of ZVI reaction was improved by enhanced mass transfer (mobilization) of target compounds.

5.3.2.4 Treatment with surfactants

An accumulation of tetra- and penta-CBs was chronologically followed by that of di- and tri-CBs, then the accumulation of mono-CB and biphenyl and their removal in the treatments with 0.04% of both surfactants. The re-emerging accumulation of tetra- and penta-CBs at the latter stage was attributed to the degradation of their parental homologues, *i.e.* hexa- to octa-CBs with weak mobility. It was previously observed that the presence of surfactant is able to prevent iron aggregation and the adherence of SOM on iron surface (chapter 4), thus enhancing the reactivity of ZVI in long term.

Unlike the treatment without surfactant, the dissolution of Fe in the treatment with 0.04% Envirosurf or Tween-80 was very limited, which seems to be incompatible with the morphology observations (figures 5.13 and 5.14) that the iron particles were shattered during the reaction. Ni removal was proved to be ineffective by low contents of surfactants in the preceding study. The behaviors of surfactants in both treatments also differed from each other (figure 5.7b).

In the treatment enhanced by 0.04% Tween-80, the extensive observation of shattered iron particles had begun since 144 h, suggesting the dramatic reaction on iron particles. The scarce release of Fe to aqueous phase probably resulted from the aggregation and precipitation of Fe^{3+}-HA complexes on solid phase and the formation of iron hydroxides or iron oxides induced by higher pH. As it is known that the dissolution of SOMs from soils/sediments could be remarkably improved by the presence of surfactant [273], the released quantity of SOMs was supposed to be larger in treatments with surfactants than without, leading to more facilitation to the formation of Fe^{3+}-HA complexes. The adsorption curve of Tween-80 during the degradation process was rather different from that of nonionic surfactant in treatment with Envirosurf. A gradual complete adsorption of Tween-80 until 192 h was followed by a gradual desorption, which may be related to the changes on solid phase, such as hydrophilicity.

In the treatment with 0.04% Envirosurf, corrosion and shattering of Fe particles was observed after 96 h, even earlier than with Tween-80. Although it was identified that ZVI participated in a fierce reaction, limited content of Fe was dissolved for the same reason with Tween-80 treatment, except for the slightly higher dissolution at 196 h. In addition, the anionic surfactant, SDBS, is able to form complex with metal ions such as Fe^{2+}/Fe^{3+} by ionic linkage, which is an attribution to the low release of iron ions and the high adsorption of SDBS on solid phase. Conform to Fe dissolution, the adsorption of SDBS was slightly depressed compared to other time interval, which could be caused by the changes on the surface of solid phase.

To sum up, it was shown that surfactants at low contents are able to enhance the stepwise dechlorination of PCBs in a ZVI-sediment suspension. Approach B is promising to clean up PCBs contaminated sediments with a reaction time of 28 d.

5.4 Conclusions

Two approaches of surfactant-assisted ZVI dechlorination in PCBs contaminated sediments were investigated in this study.

Surfactant-enhanced desorption followed by ZVI treatment in solution (approach A) was ineffective to remove PCBs because of the high content of surfactants and Ca/Mg ions present in the solution, although the desorption of PCBs from sediments was considerably effective by both Tween-80 and Envirosurf at 1%.

While a mixture of ZVI and sediment in surfactant solution (approach B) was effective for PCBs dechlorination. With 0.04% Envirosurf or Tween-80, the removal of Σ_7PCBs achieved 76.31% and 47.16%, respectively in 7 d. The enhancement by surfactants at low content was attributed to the improved contact between ZVI and PCBs, and also the prevention from passivation.

5.5 Supplementary Information

5.5.1 Desorption kinetics

The behaviors of heavy metals and hydrophobic POPs in soils and sediments are not quite similar and either are their behaviors during desorption process by surfactants. To acquire the optimized contact time for both Ni and PCBs, a series of kinetic experiments was conducted.

Figure 5.8 (a and b) indicates that desorption kinetics of both Ni and PCBs are two-step processes, which consist of a rapid desorption process and a subsequent gradual release process. Equilibrium of Ni desorption could be obtained rapidly in 4-8 h, and equilibrium of PCBs desorption in 12 h. The low extraction efficiency of Ni by water indicates sufficient aging period during the preparation process.

A more rapid desorption equilibrium of Ni was obtained compared to that of PCBs by surfactants, which may be attributed to the different desorption mechanisms for the pollutants. PCBs are extremely hydrophobic and tend to bond with soil matrix such as soil organic matters. Surfactants enhanced the mobility of PCBs by lowering the interfacial tension between sediment and washing solution and enhanced the solubility by forming micelles in aqueous solutions that trapping hydrophobic components in pseudophases. As for metals, the removal of organic phase-associated metals can be enhanced by surfactants [214], while the removal of other speciation of cationic metals is usually reported to be limited [220].

The PCB profiles in different washing solutions (figure 5.2c) are similar in water and Tween-80 during the whole kinetic experiment. The contents of congeners were comparable probably due to the low solubility of all PCB congeners in water and the indiscriminate solubility induced by Tween-80 micelles. While the treatments with Envirosurf, a mixture of both anionic and nonionic surfactants, showed a preferential desorption for hexa-CB rather than less chlorinated biphenyls, which may be attributed to the presence of anionic SDBS. Anionic surfactant has been reported to facilitate the desorption of soil organic matters, and leading to the enhanced dissolution of organic phase-associated compounds [135]. The more hydrophobic is the compound, the more inclined to bond with organic matters. Hence, the removal of toxic and hydrophobic congeners from soils and sediments could be enhanced by introducing anionic surfactants.

To ensure the thorough desorption of both Ni and PCBs in the subsequent tests, 24 h was selected as the equilibrium time for the subsequent desorption batch experiments.

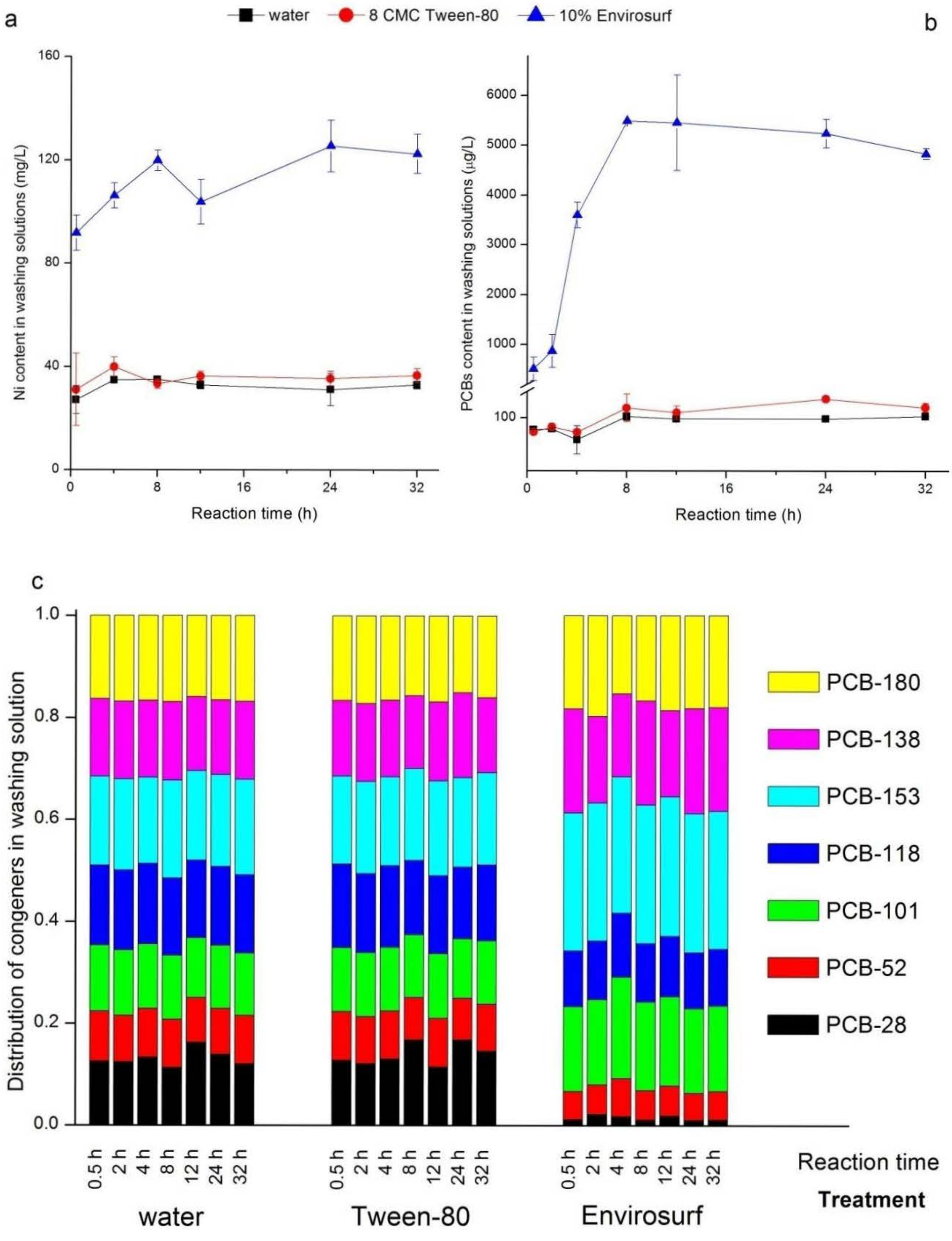


Figure 5.8 Kinetics of extraction with different washing solutions. a: Ni extraction; b: total PCBs extraction; c: distribution of PCB congeners in washing solution.

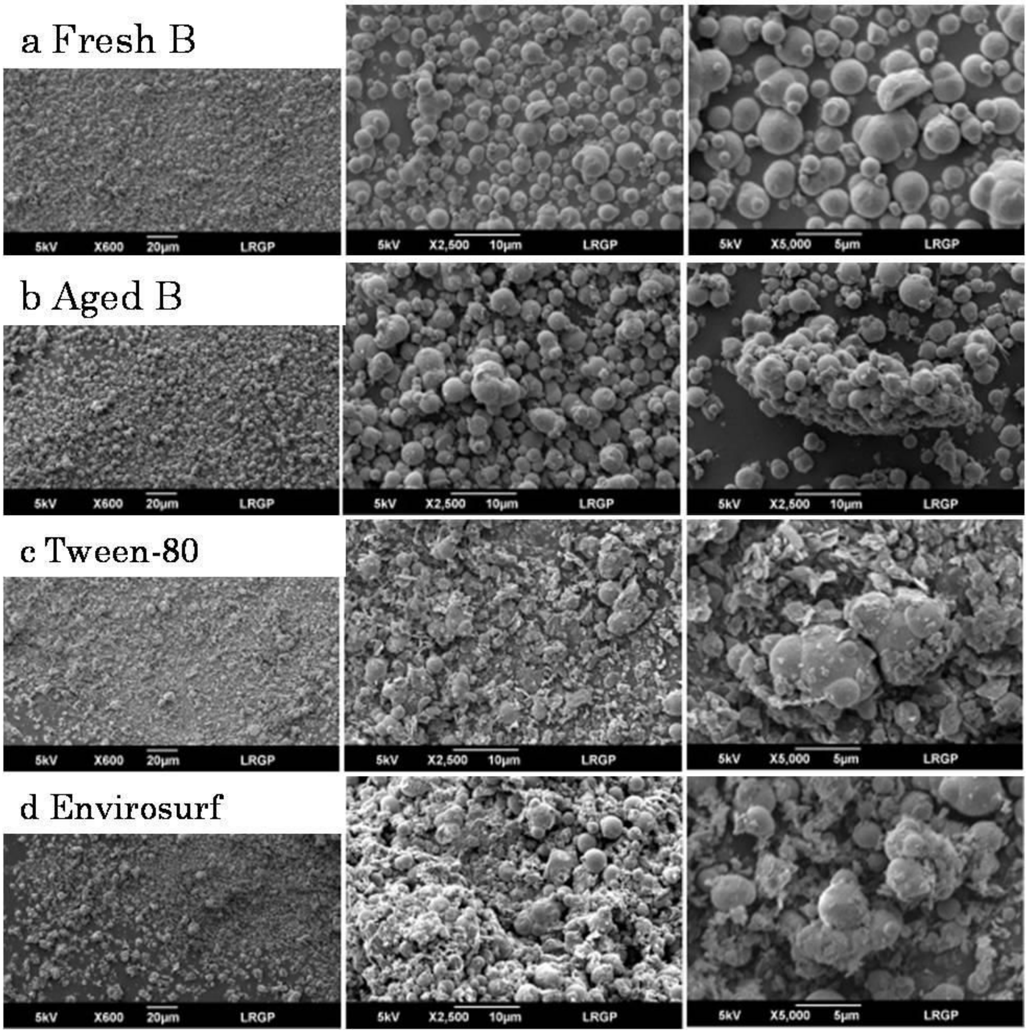


Figure 5.9 SEM images of iron particles: a, fresh particles; b, aged particles; c, particles after treatment in 1% Tween-80 solution; d, particles after treatment in 1% Envirosurf solution.

Table 5.5 pH changes during the ZVI treatments in washing solutions, compared with 168 h aging of ZVI in water.

Treatment	0 h	24 h	48 h	144 h	168 h
Water	7.00	8.74	8.49	9.05	9.17
1% Envirosurf washing solution	6.95	7.95	8.04	7.90	7.85
1% Tween-80 washing solution	6.76	7.72	7.71	7.72	7.78

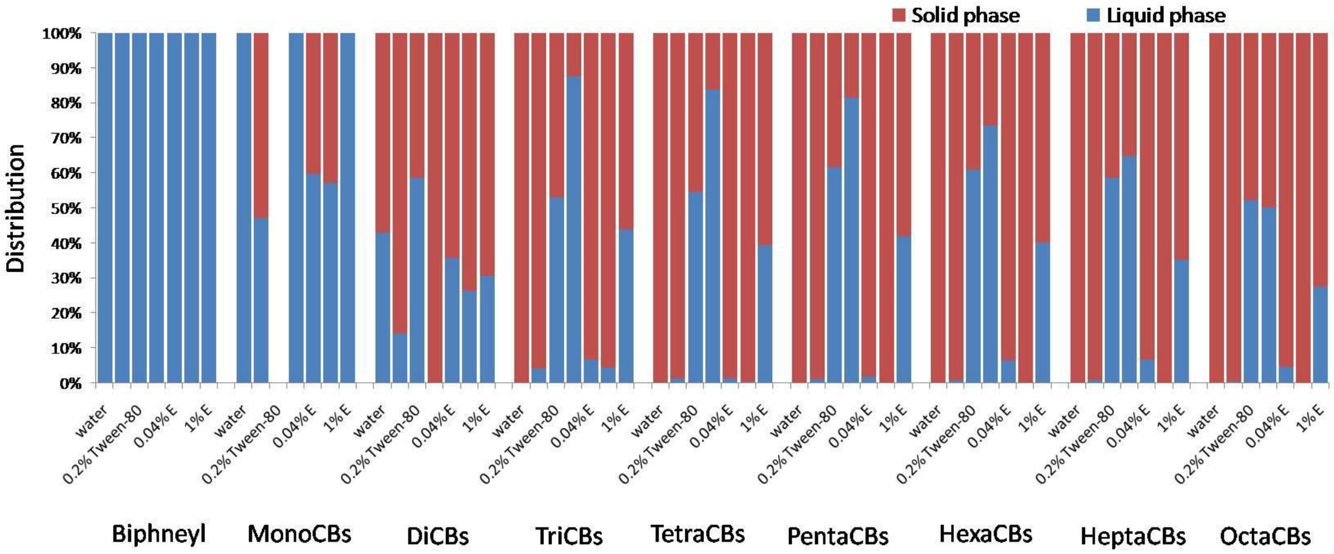


Figure 5.10 Partition of biphenyl and PCBs in liquid-solid phases during the treatment with different contents of surfactants. E is short for Envirosurf.

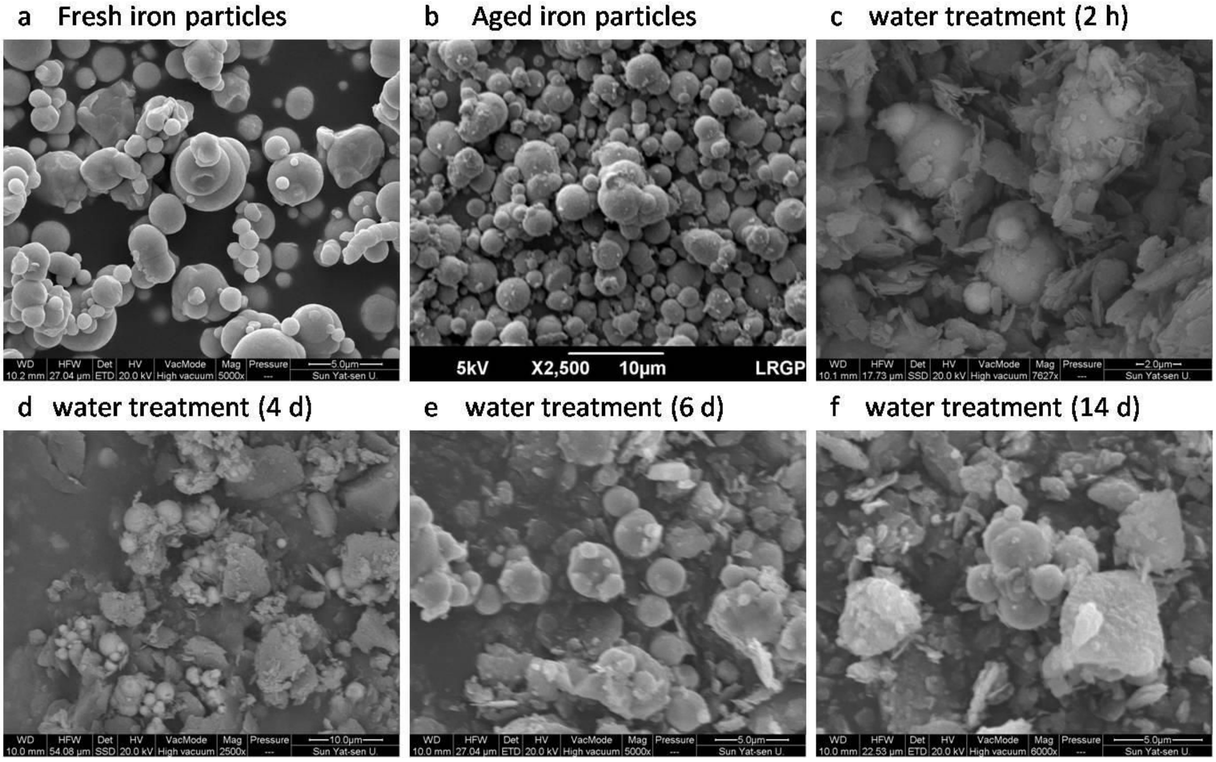
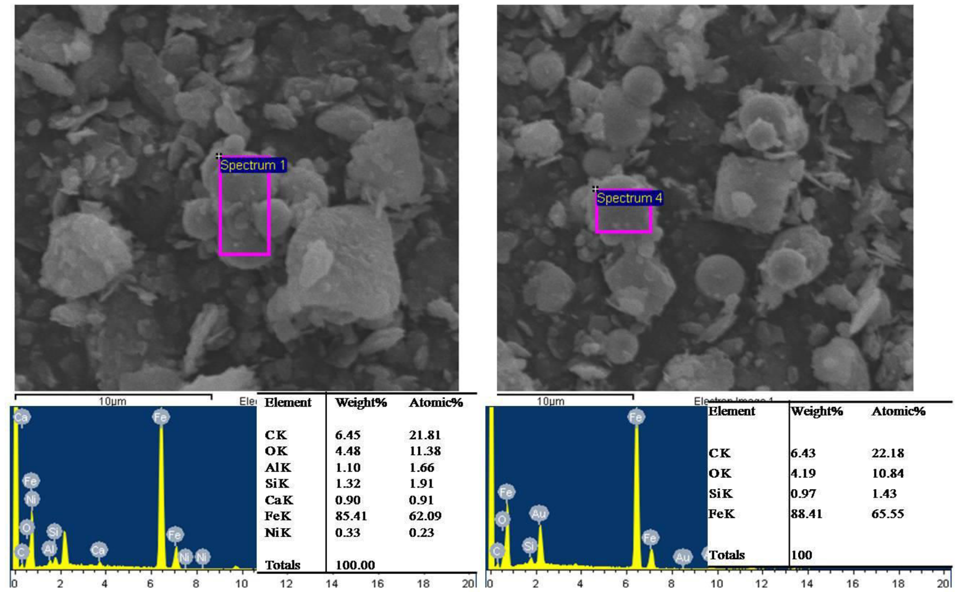


Figure 5.11 Morphology of iron particles: a, fresh iron particles; b, 7-d aging particles; c, water treatment (2 h); d, water treatment (4 d); e, water treatment (6 d); f, water treatment (14 d).

a Treatment without surfactant (14 d)

b Treatment without surfactant (12 d)

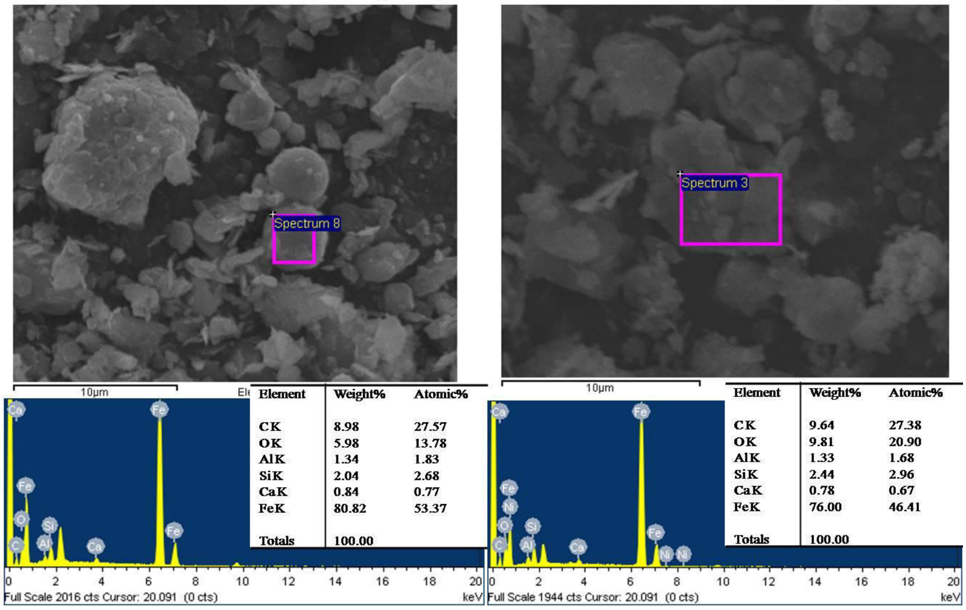


Element	Weight%	Atomic%
CK	6.45	21.81
OK	4.48	11.38
AlK	1.10	1.66
SiK	1.32	1.91
CaK	0.90	0.91
FeK	85.41	62.09
NiK	0.33	0.23
Totals	100.00	

Element	Weight%	Atomic%
CK	6.43	22.18
OK	4.19	10.84
SiK	0.97	1.43
FeK	88.41	65.55
Totals	100	

c Treatment with 0.04% Tween-80 (14 d)

d Treatment with 0.04% E (12 d)



Element	Weight%	Atomic%
CK	8.98	27.57
OK	5.98	13.78
AlK	1.34	1.83
SiK	2.04	2.68
CaK	0.84	0.77
FeK	80.82	53.37
Totals	100.00	

Element	Weight%	Atomic%
CK	9.64	27.38
OK	9.81	20.90
AlK	1.33	1.68
SiK	2.44	2.96
CaK	0.78	0.67
FeK	76.00	46.41
Totals	100.00	

Figure 5.12 SEM-EDX for several spots of interest during different treatment.

a, minerals with Al, Si and Ca were identified on iron surface in treatment without surfactant; b, discrete coverage by SOMs on iron surface in treatment without surfactant; c and d, minerals with Al, Si and Ca were identified on the iron surface in treatment with 0.04% Tween-80 and Envirosurf, respectively.

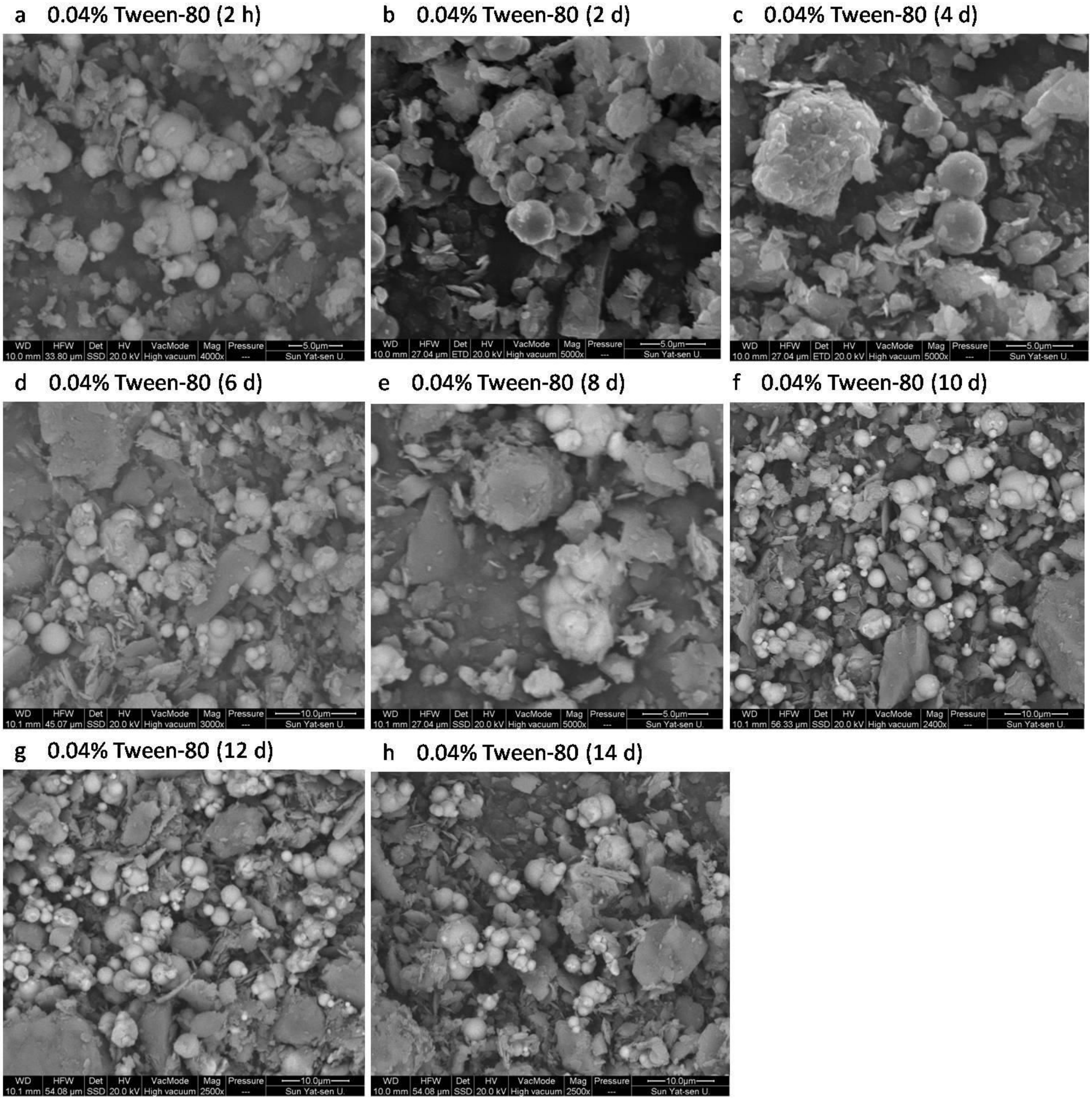
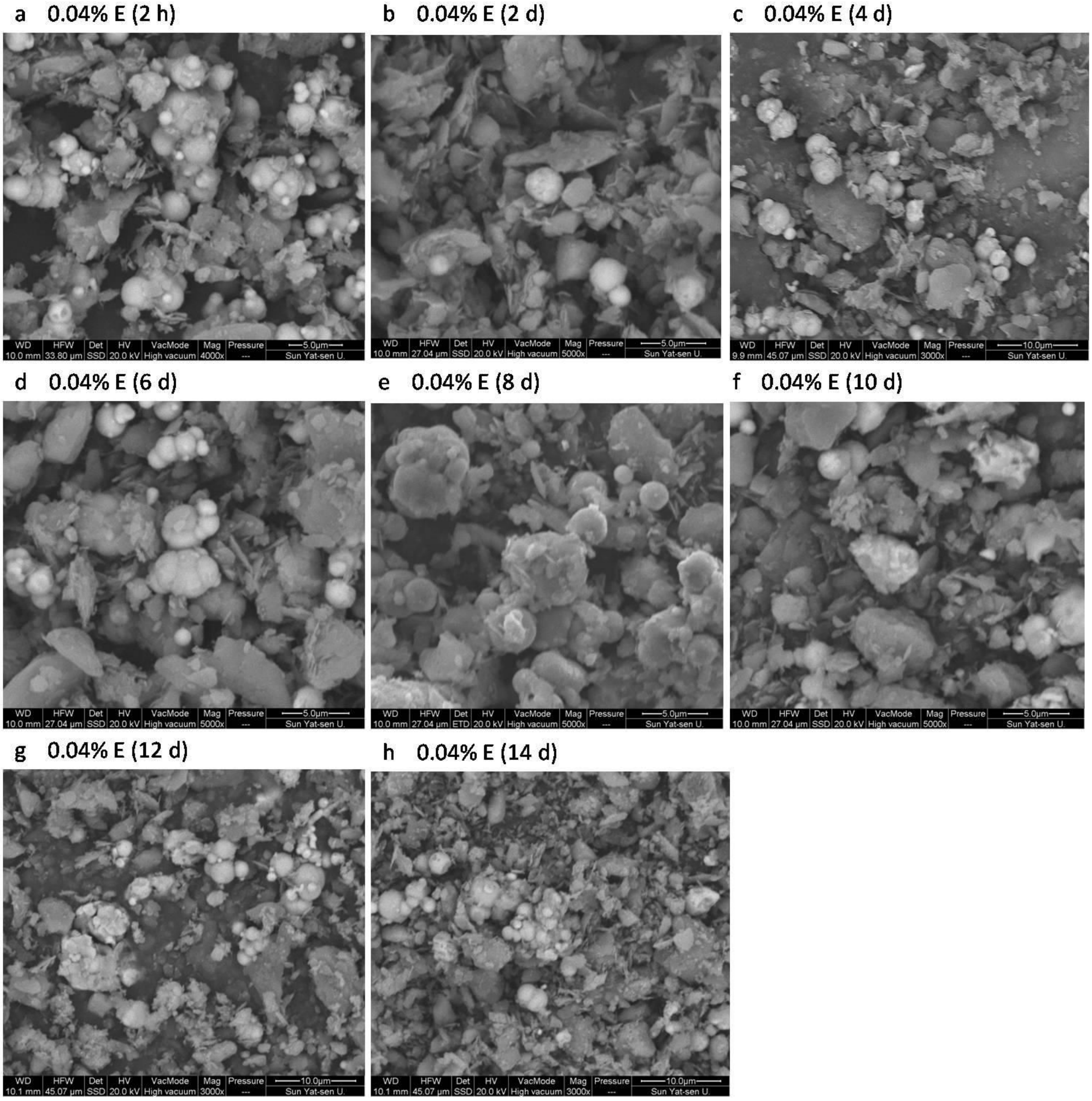


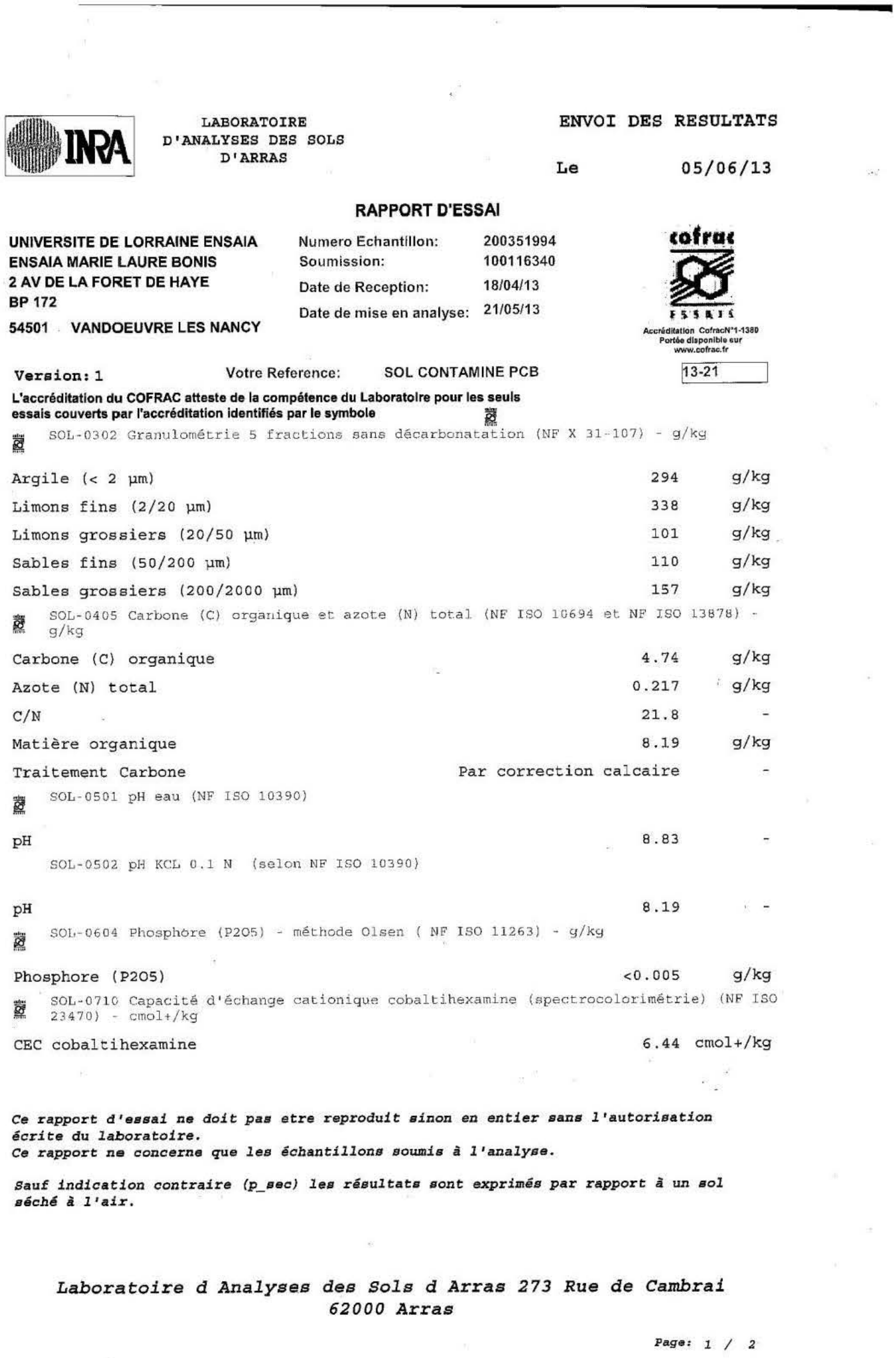
Figure 5.13 Morphology of iron particles in mixture experiment with 0.04% Tween-80.



a 0.04% E (2 h)
b 0.04% E (2 d)
c 0.04% E (4 d)
d 0.04% E (6 d)
e 0.04% E (8 d)
f 0.04% E (10 d)
g 0.04% E (12 d)
h 0.04% E (14 d)

Figure 5.14 Morphology of iron particles in mixture experiment with 0.04% Envirosurf.

5.5.2 Details of contaminated sediments



LABORATOIRE
D'ANALYSES DES SOLS
D'ARRAS

ENVOI DES RESULTATS

Le 05/06/13

RAPPORT D'ESSAI

UNIVERSITE DE LORRAINE ENSAIA
ENSAIA MARIE LAURE BONIS
2 AV DE LA FORET DE HAYE
BP 172
54501 VANDOEUVRE LES NANCY

Numero Echantillon: 200351994
Soumission: 100116340
Date de Reception: 18/04/13
Date de mise en analyse: 21/05/13

Accréditation CofracN°1-1380
Portée disponible sur
www.cofrac.fr

Version: 1 Votre Reference: SOL CONTAMINE PCB 13-21

L'accréditation du COFRAC atteste de la compétence du Laboratoire pour les seuls essais couverts par l'accréditation identifiés par le symbole

SOL-0302 Granulométrie 5 fractions sans décarbonatation (NF X 31-107) - g/kg

Argile (< 2 µm)	294	g/kg
Limons fins (2/20 µm)	338	g/kg
Limons grossiers (20/50 µm)	101	g/kg
Sables fins (50/200 µm)	110	g/kg
Sables grossiers (200/2000 µm)	157	g/kg

SOL-0405 Carbone (C) organique et azote (N) total (NF ISO 10694 et NF ISO 13878) - g/kg

Carbone (C) organique	4.74	g/kg
Azote (N) total	0.217	g/kg
C/N	21.8	-
Matière organique	8.19	g/kg
Traitement Carbone	Par correction calcaire	-

SOL-0501 pH eau (NF ISO 10390)

pH	8.83	-

SOL-0502 pH KCL 0.1 N (selon NF ISO 10390)

pH	8.19	-

SOL-0604 Phosphore (P2O5) - méthode Olsen (NF ISO 11263) - g/kg

Phosphore (P2O5)	<0.005	g/kg

SOL-0710 Capacité d'échange cationique cobaltihexamine (spectrocolorimétrie) (NF ISO 23470) - cmol+/kg

CEC cobaltihexamine	6.44	cmol+/kg

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Sauf indication contraire (p_sec) les résultats sont exprimés par rapport à un sol séché à l'air.

Laboratoire d Analyses des Sols d Arras 273 Rue de Cambrai
62000 Arras

Page: 1 / 2

INRA

LABORATOIRE
D'ANALYSES DES SOLS
D'ARRAS

ENVOI DES RESULTATS

Le 05/06/13

RAPPORT D'ESSAI

UNIVERSITE DE LORRAINE ENSAIA
ENSAIA MARIE LAURE BONIS
2 AV DE LA FORET DE HAYE
BP 172
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Numero Echantillon: 200351994
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SOL-0719 Ca, Mg, Na, K, Fe, Mn, Al échangeables à la cobaltihexammine (ICP-AES/EAF) (NF ISO 23470) - cmol+/kg

Calcium (Ca)	5.76	cmol+/kg
Magnésium (Mg)	2.07	cmol+/kg
Sodium (Na)	0.183	cmol+/kg
Potassium (K)	0.376	cmol+/kg
Fer (Fe)	0.0067	cmol+/kg
Manganèse (Mn)	<0.005	cmol+/kg
Aluminium (Al)	0.0414	cmol+/kg

SOL-0905 Si, Al, Fe méthode Tamm en obscurité (ICP-AES) (méth. INRA) - g/100g

Silicium (Si)	0.094	g/100g
Aluminium (Al)	0.121	g/100g
Fer (Fe)	0.339	g/100g

SOL-0910 Si, Al, Fe méthode Merha-Jackson (ICP-AES) (méth. INRA) - g/100g

Silicium (Si)	0.115	g/100g
Aluminium (Al)	0.115	g/100g
Fer (Fe)	0.773	g/100g

Richard Antoine
pour le Directeur du Laboratoire

Fin du rapport de l'échantillon 200351994

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Sauf indication contraire (p_sec) les résultats sont exprimés par rapport à un sol séché à l'air.

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62000 Arras

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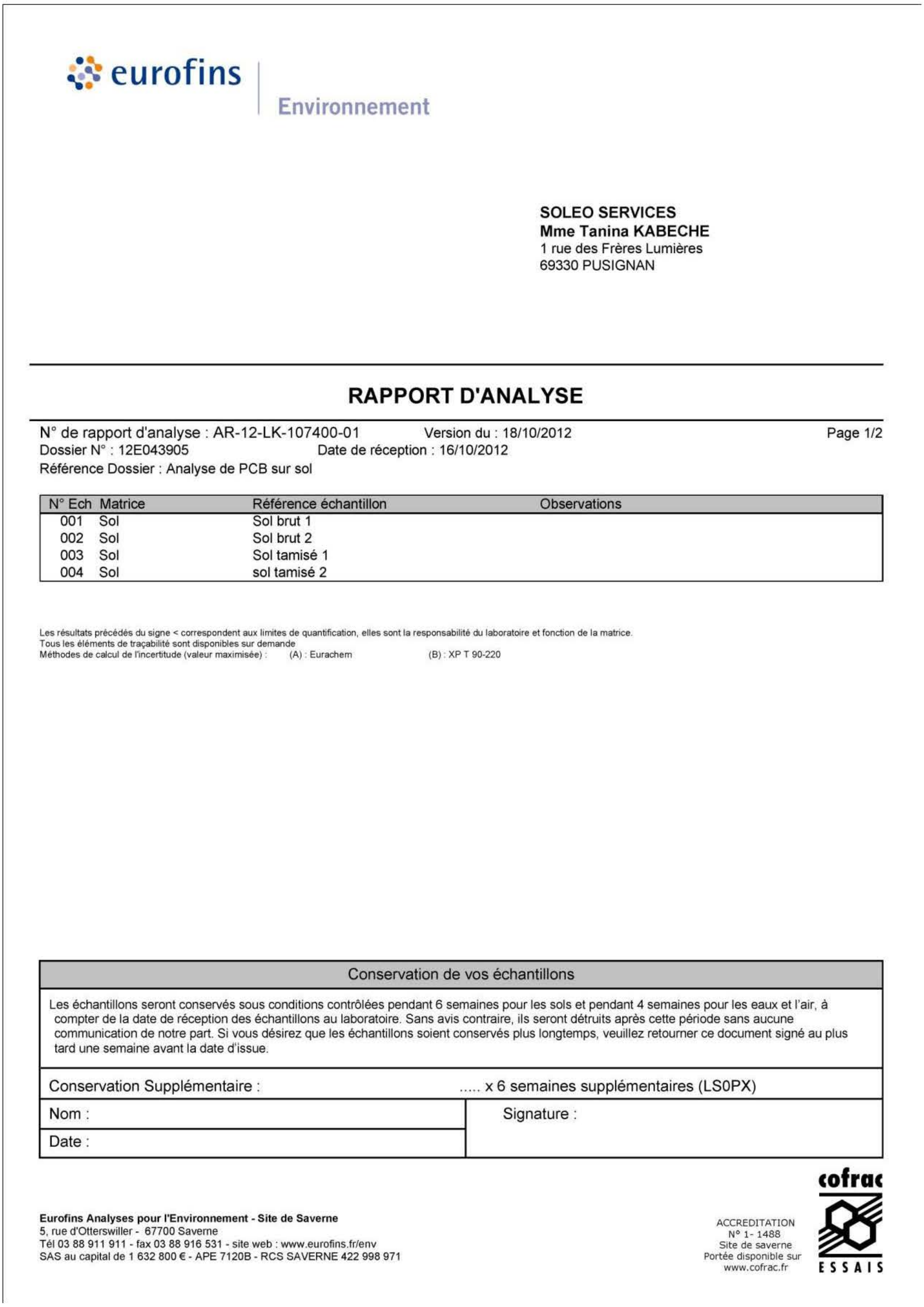

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Environnement

SOLEO SERVICES
Mme Tanina KABECHE
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69330 PUSIGNAN

RAPPORT D'ANALYSE

N° de rapport d'analyse : AR-12-LK-107400-01 Version du : 18/10/2012 Page 1/2
Dossier N° : 12E043905 Date de réception : 16/10/2012
Référence Dossier : Analyse de PCB sur sol

N° Ech	Matrice	Référence échantillon	Observations
001	Sol	Sol brut 1	
002	Sol	Sol brut 2	
003	Sol	Sol tamisé 1	
004	Sol	sol tamisé 2	

Les résultats précédés du signe < correspondent aux limites de quantification, elles sont la responsabilité du laboratoire et fonction de la matrice.
Tous les éléments de traçabilité sont disponibles sur demande
Méthodes de calcul de l'incertitude (valeur maximisée) : (A) : Eurachem (B) : XP T 90-220

Conservation de vos échantillons	
Les échantillons seront conservés sous conditions contrôlées pendant 6 semaines pour les sols et pendant 4 semaines pour les eaux et l'air, à compter de la date de réception des échantillons au laboratoire. Sans avis contraire, ils seront détruits après cette période sans aucune communication de notre part. Si vous désirez que les échantillons soient conservés plus longtemps, veuillez retourner ce document signé au plus tard une semaine avant la date d'issue.	
Conservation Supplémentaire :	..... x 6 semaines supplémentaires (LS0PX)
Nom :	Signature :
Date :	

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5, rue d'Otterswiller - 67700 Saverne
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SAS au capital de 1 632 800 € - APE 7120B - RCS SAVERNE 422 998 971

ACCREDITATION
N° 1- 1488
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RAPPORT D'ANALYSE

N° de rapport d'analyse : AR-12-LK-107400-01 Version du : 18/10/2012 Page 2/2
Dossier N° : 12E043905 Date de réception : 16/10/2012
Référence Dossier : Analyse de PCB sur sol

		001	002	003	004	
N° Echantillon						
Date de prélèvement :						
Début d'analyse :		16/10/2012	16/10/2012	16/10/2012	16/10/2012	

Préparation Physico-Chimique

		001	002	003	004	
LS896 : **Matière sèche** Analyse réalisée sur le site de Saverne Accrédité Cofrac N°1-1488 *Gravimétrie - NF ISO 11465*	% P.B.	* 76.4	* 83.9	* 98.5	* 98.4	

Polychlorobiphenyls (PCBs)

LSA42 : **PCB congénères réglementaires (7)** Analyse réalisée sur le site de Saverne Accrédité Cofrac N°1-1488

Extraction Hexane/Acetone et dosage par GC/MS - XP X 33-012

		001	002	003	004	
PCB 28	mg/kg MS	* 0.05	* 0.05	* 0.13	* 0.12	
PCB 52	mg/kg MS	* 1.14	* 1.01	* 5.31	* 5.10	
PCB 101	mg/kg MS	* 3.96	* 3.67	* 14.2	* 14.0	
PCB 118	mg/kg MS	* 1.56	* 1.38	* 6.89	* 6.56	
PCB 138	mg/kg MS	* 7.13	* 6.92	* 20.9	* 19.9	
PCB 153	mg/kg MS	* 9.20	* 8.67	* 23.2	* 23.1	
PCB 180	mg/kg MS	* 6.88	* 6.22	* 17.2	* 16.3	
SOMME PCB (7)	mg/kg MS	29.9	27.9	87.8	85.1	

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Laboratoire agréé par le ministre chargé des installations classées par arrêté du JO du 07/01/2011. Mention des types d'analyses pour lesquels l'agrément a été délivré sur www.eurofins.fr ou disponible sur demande.

Stéphanie Vallin
Coordinateur de Projets

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Chapter 6.

Environmental implications, conclusions and perspectives

6.1 Environmental implications

The issue -> the feasibility -> lab-scale application

The main goal of the present thesis is to investigate the potentiality of ZVI reduction with the assistance of surfactants as a cleanup method to remove PCBs from contaminated soils/sediments. The thesis begins with a literature review presenting 1) the issue of soil contamination by PCBs , especially in e-waste contaminated sites where other contaminants (heavy metals) are present, 2) cleanup attempts on PCBs contaminated soils and 3) the state of art on the use of ZVI for contaminant reduction. Subsequently, a survey was conducted in two e-waste sites (Guyiu and Qingyuan) of South China, in order to evaluate soil contamination and to find proper samples. After that, the reaction mechanisms of PCB dechlorination in aqueous solution was investigated in order to find the reaction pathway. Also the influence of different parameters affecting dechlorination was studied. Finally, the ZVI dechlorination was applied to sediment contaminated by PCBs, with the assistance of surfactant, based on the understanding of mechanisms.

6.1.1 The issue

Soil contamination by PCBs was recognized by many researchers, in brown sites affected by industrial activities, especially e-waste contaminated sites in south China. To understand the contamination profiles in soils from e-waste sites, a survey (chapter 2) was conducted in Qingyuan and Guiyu, both of which have been involved in such activities for decades. Results show that the contamination by PCBs was not as severe as expected; the most contaminated sample was from a dismantling site. Moreover, the survey confirmed the coexistence of multiple pollutants in different distribution patterns, depending on the nearby recycling activities. Metals such as Ni and Cu were frequently detected together with PCBs. Therefore, it is of necessity and interest to evaluate the influence from the coexisting metals during the soil cleanup process.

A more contaminated sediment sample, coming from the Rhône valley (France) was used instead of samples from e-waste sites in the subsequent studies. To estimate the role of metal during the remediation, it was spiked by Ni and the sample was aged for 30 d before treatment experiments.

6.1.2 Feasibility

As revealed by previous studies, the performance of ZVI is controlled by several parameters and influencing factors. In soil solution or washing solution, the coexistence of many components, such as surfactants, SOM, metal ions, *etc.* may cast an impact on reduction by ZVI. To evaluate the feasibility, series of aqueous experiments simulating soil washing solutions were conducted.

Results confirmed the stepwise reduction of PCBs and the major pathway of dechlorination (regiospecificity), using PCB-52 as representative (chapter 3, summarized as figure 6.1). The degradation of PCB-52 by ZVI was not significantly influenced by Cu ion or humic acid, but could be enhanced by Ni or Tween-80. A synergistic enhancement on degradation was identified in the presence of Tween-80 and Ni. This study suggested that the use of ZVI dehalogenation enhanced by Ni^{2+} and Tween-80 for the post-treatment of PCB-contaminated soil washing solutions is promising; it is also promising to apply ZVI to contaminated soils.

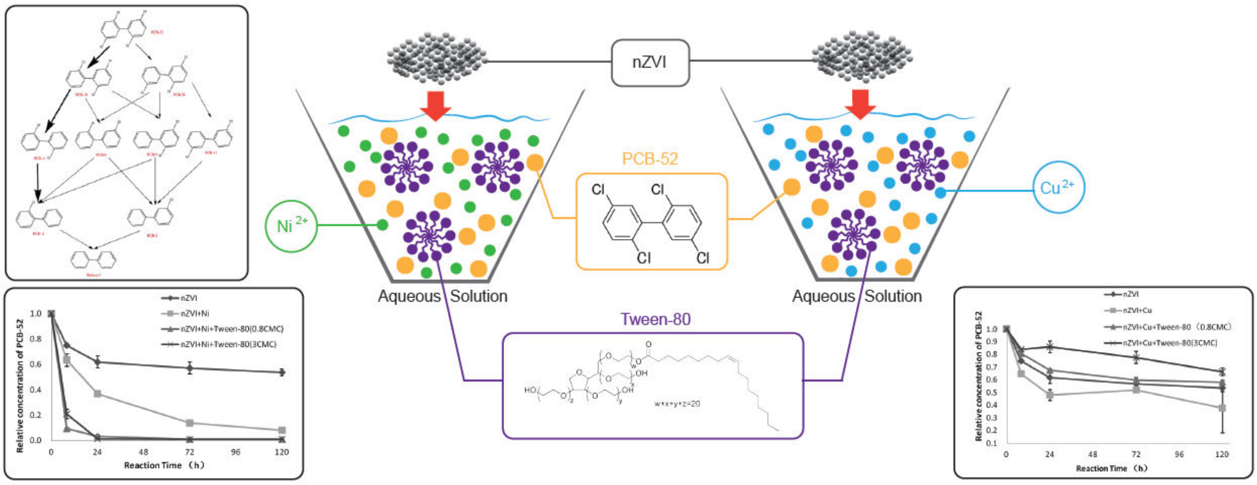

Figure 6.1 Schematic abstract on the effect of Tween-80 and metal ions on the dechlorination of PCBs by ZVI (chapter 3).

The synergistic effect of Ni^{2+} ion and Tween-80 inspired the idea that the combined effect of components in washing solution could be complicated. Previous studies have identified and discussed the influences brought about by various factors, whereas all of which could be explained at the perspectives of mass transfer or/and electron transfer processes. To investigate which of these processes limits reductive dechlorination of PCBs by ZVI, orthogonal experiments testing varying concentrations of Ni^{2+}, H^+, humic acid, and two surfactants (Tween-80 and Envirosurf) were carried out (chapter 4). Mass transfer of PCB-52 onto the ZVI surface was significantly influenced by surfactant type and concentration, being facilitated due to decreased interfacial tension or hindered by micelle sequestration, depending on the extent of surfactant sorption. Anionic surfactant alleviated the adverse impact of high concentrations of nonionic surfactant and humic acid by changing their sorption behavior, which was also influenced by initial pH of the reaction mixture. Electron transfer was accelerated by humic acid acting as a reductant, with generation of $FeCO_3$ as the oxidative product. The concentration of Ni^{2+} was not a significant factor, suggesting that for practical application of ZVI in remediation of hydrophobic organic contaminants in aqueous solution, mass transfer is a greater constraint than is electron transfer. The relative importance of the studied factors was in the order surfactants > humic acid > pH > Ni^{2+}.

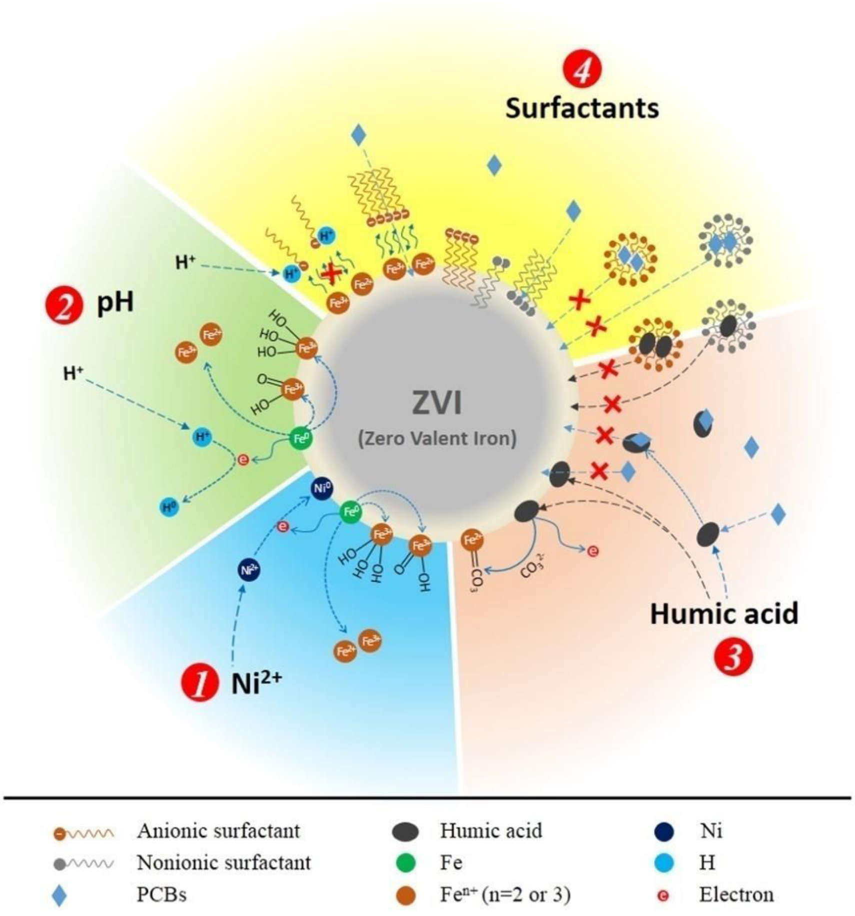

Figure 6.2 Schematic abstract on the influence of surfactant, humic acid, pH and Ni^{2+} on ZVI degradation of PCB-52, in addition with their combined effect (chapter 4).

Results of chapter 4 implicate that it is more cost effective to enhance the efficiency of mass transfer of the hydrophobic target compounds onto the iron surface rather than to improve electron transfer in the remediation system. Many approaches could be employed for this purpose, a simple approach is to introduce surface active agents (*i.e.* surfactants).

6.1.3 Lab-scale application

Based on the findings of chapters 3 and 4, surfactant-assisted PCBs dechlorination by ZVI in contaminated sediment was proposed with two possible approaches: surfactant desorption followed by ZVI treatment in solution (approach A); mixture of ZVI and sediment in surfactant solution (approach B).

The investigation on approach A began with the trial on surfactant enhanced desorption of PCBs. Two commercially available surfactants were selected for the desorption experiment: Tween-80, a nonionic surfactant that has been widely used for soil washing/flushing; and Envirosurf, a mixture of anionic and nonionic surfactant. Comparisons among the performance of all the surfactants recommended the sequential washing by 1% of Tween-80 or Envirosurf as the clean up protocol for the PCBs contaminated sediment. Neither of the surfactants was effective in the removal of Ni.

The subsequent dechlorination of PCBs by ZVI in washing solution containing 1% Envirosurf or Tween-80 was ineffective, as in consistence of the results from aqueous experiments; while more than 97% of coexisted Ni could be removed by iron particles. Aggregates of iron particles and discrete coverage by soil organic matters could be observed during the treatment.

As for approach B, it was demonstrated effective for PCBs dechlorination. It indicates the possibility of remediation for the PCB-contaminated sediment by ZVI in exempt of dehydration. The binding water of sediment is able to facilitate mass transfer of PCBs during degradation. To improve the reactivity of ZVI in the suspension and to accelerate the reaction, the addition of nonionic surfactant or mixture of anionic and nonionic surfactants at low content is recommended. After degradation, less toxic and hydrophobic PCB congeners are dissolved in the aqueous solution to be mineralized by biochemical methods and limited amount of Fe ions in the solution could be utilized by functional microbes as nutrient. The remained iron particles in the sediment could be magnetically separated for reuse or regeneration (figure 6.3).

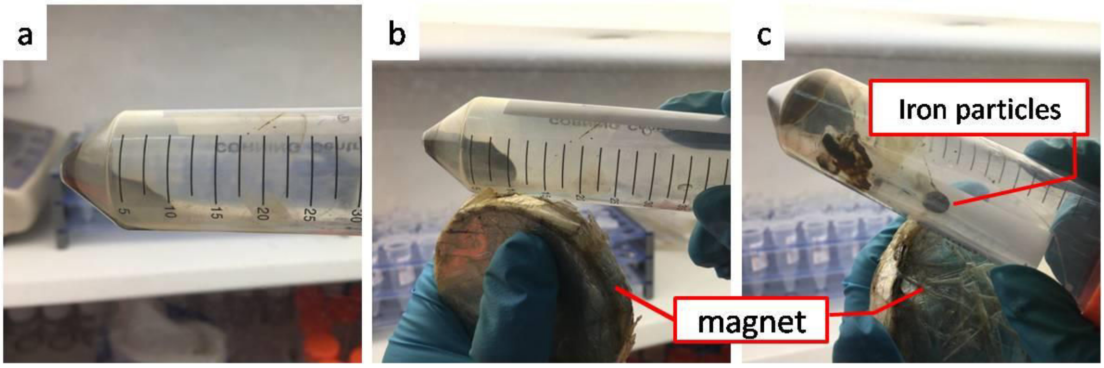

Figure 6.3 Magnetic separation of ZVI from contaminated sediment after mixing treatment: a, the mixture; b, magnetic induction of iron particles; c, separation of iron particles from sediment samples.

6.2 Conclusions

Based on the experimental findings, the following conclusions on the application of ZVI to the remediation of PCB-contaminated sediment are drawn as follows:

1) The coexistence of multiple contaminants was ubiquitous in e-waste contaminated sites located in south China, and the status of contamination was generally related to the disposal activities and the soil properties.

2) Dechlorination of PCB-52 by ZVI in aqueous solution was synergistically enhanced by the presence of Ni^{2+} ions and the nonionic surfactant Tween-80, while the effect of humic acid on degradation was negligible. The PCB-52 degradation pathway exhibited regiospecificity and congener specificity that minimized the generation of environmentally toxic coplanar PCB congeners. The use of ZVI dehalogenation enhanced by Ni^{2+} and Tween-80 for the post-treatment of PCB-contaminated soil washing solutions is promising.

3) A series of orthogonal experiments investigating factors affecting dechlorination of PCB-52 by ZVI particles showed that mass transfer is a crucial process for PCBs reduction by ZVI in aqueous solution; the relative importance of the studied factors was in the order of surfactants > humic acid > pH > Ni^{2+}.

4) Surfactants on iron surface were found to decrease interfacial tension, while aqueous micelles were found to sequestrate PCB-52 and humic acid. The inhibitory effect of a high concentration of nonionic surfactant was attributed to the formation of micelles in aqueous solution rather than to multi-layer adsorption on the ZVI surface. This inhibition was alleviated by the introduction of an anionic surfactant (i.e., SDBS), which enhanced adsorption of the nonionic surfactant and reduced the amount of aqueous micelles. Excessive humic acid hindered mass transfer of PCB-52 by covering active sites on ZVI and binding with PCB-52 in the aqueous phase. Surfactants, especially the anionic surfactant, were able to alleviate the adverse effect of humic acid by reducing its adsorption. The pH value of the system influenced the adsorption behavior of humic acid and the anionic surfactant, and consequently influenced mass transfer.

5) The most important factors affecting surface oxidation of ZVI were pH and surfactant. The participation of humic acid as a reductant was suggested by the fact that the mineral $FeCO_3$ was detected on the iron surface. The influence of surfactants on surface oxidation was related to their influence on mass transfer of oxidants. The acceleration of electron transfer by Ni^{2+} was not as important in this reduction system as the effects of surfactants and humic acid on mass transfer efficiency. The complex interacting effects of surfactants, soil organic matter, pH, and catalytic metal ions on the reduction of PCB-52 indicate the necessity of optimizing these factors for application of the ZVI technique to decontamination of aqueous solutions, including groundwater, industrial effluents, and washing solutions. Improvements in mass transfer are important for effective degradation of hydrophobic contaminants by ZVI in aqueous solution.

6) Desorption isotherms of both Ni and PCBs from contaminated sediment by various surfactants were measured to understand desorption behaviors. To ensure the thorough

desorption of both PCBs, 24 h was selected as the equilibrium time for all the desorption batch experiments. The removal of Ni by surfactants was not effective by either Tween-80 or Envirosurf at tested concentrations. 1% Tween-80 was effective to remove PCBs; while Envirosurf was effective to remove PCBs at the content above 1%, and was more effective to remove Ni than Tween-80 at the content of 2%. Sequential washing by 1% of Tween-80 or Envirosurf is recommended as the clean up protocol for the contaminated sediment.

7) It was demonstrated to be ineffective to treat surfactant-enhanced washing solution with PCBs by ZVI. Although more than 97% of coexisted Ni could be removed by iron particles, the dechlorination of PCBs was not effective in washing solutions with 168 h. Aggregates and coverage by soil organic matters could be observed during the treatment. The high content of surfactants and divalent cations (*e.g.* Ca and Mg) were ascribed for the inefficiency.

8) A series of batch experiments manifested the enhancement of surfactants at low concentrations on the stepwise degradation of PCBs in a ZVI-sediment suspension. Treatment without surfactant was able to degrade PCBs by facilitating the mobility of target compounds yet the further degradation was restricted by the latter passivation of iron particles. Surfactants at the content of 1% were effective to enhance the solubility of PCBs but were ineffective to enhance the degradation due to the wrapping by aqueous micelles. With 0.04% Envirosurf or Tween-80, the removal of Σ_7PCBs achieved 76.31% and 47.16%, respectively in 7 d. The enhancement by surfactants at low content was attributed to the improved contact between ZVI and PCBs, and also the prevention from passivation.

6.3 Deficiencies and perspectives

1) As discussed in chapter 3, further studies are required to understand the mechanisms of the synergetic enhancement by Tween-80 and Ni^{2+} of PCB dechlorination by ZVI and also the optimization of the ZVI degradation technique as the post-treatment for PCB-contaminated soil washing solutions.

2) Although the study presented by chapter 5 depicted the desorption efficiency of Ni and PCBs by surfactants, several deficiencies remained to be improved afterwards. First of all, the mechanisms of desorption for both contaminants were not intensively understood. Secondly, it is difficult to simultaneously remove both Ni and PCBs by one commercial surfactant product, while a combination of surfactants could achieve better desorption rate. Optimization is needed for better desorption performance. Finally, the properties of sediments after washing should be measured, especially the potential risk after washing.

3) The ineffectiveness of PCBs degradation by ZVI in washing solution was identified, but the attributions of which were merely deduced without investigation. To improve the feasibility of ZVI application, it is of necessity to understand the mechanisms herein.

4) For the contaminated sediment with various PCB congeners, it is of difficulty to quantitively evaluate the degradation. The reduction pathway of PCBs is a stepwise dechlorination course that includes the elimination of parental congeners and the generation of offspring congeners at the same time. A quantification method should be established for a more precise description of degradation degree.

5) The biochemical mineralization of solutions after ZVI-mixture treatment should be studied, to establish an integrated process for the remediation.

Résumé étendu en français

1 Introduction générale

La contamination des sols et des sédiments par des polluants organiques hydrophobes, comme les polychlorobiphényls (PCB) pose un problème sanitaire et environnemental majeur, puisque ces composés sont très toxiques et très difficiles à éliminer.

Au cours des dernières décennies, une méthode relativement douce a été introduite pour réduire (déchlorer) les polluants organiques chlorés, elle consiste à introduire du fer zérovalent (Fe^0) dans les sols, sédiments ou eaux contaminés [17]. Le fer zérovalent a été beaucoup utilisé pour la remédiation des eaux souterraines, tandis que son application pour la remédiation des sols et sédiments est relativement récente. Elle se pratique *in situ*, sans excavation, par injection dans le sol ou malaxage, ou encore *ex situ*, après excavation. L'efficacité du Fe^0 a été démontrée pour la réduction de métaux et métalloïdes (*e.g.* chrome, arsenic *etc.*) et pour le traitement d'hydrocarbures halogénés (*e.g.* éthylènes chlorés, méthane chloré, PCB, PBDE) [18]. Ainsi, ce traitement apparaît comme prometteur pour la remédiation de sols et sédiments contaminés par les PCB, et notamment pour les sites contaminés suite au recyclage de déchets électroniques. Ces milieux contaminés contiennent aussi des métaux, comme le nickel (Ni) et le cuivre (Cu), qui peuvent être immobilisés par réaction avec le fer, et/ou servir de catalyseur à la surface des particules de fer, accélérant ainsi la dégradation des PCB.

En plus du traitement par réduction chimique, le lavage de sol est aussi une technologie prometteuse pour traiter les sols et sédiments contaminés par les PCB. C'est un procédé assez fréquemment utilisé, rapide et flexible. Toutefois, il consiste à transférer les polluants vers la phase aqueuse et il faut ensuite traiter les solutions de lavage [19]. D'après les connaissances sur la dégradation des PCB par le fer zéro, on peut supposer que la solution de lavage peut être traitée de cette manière pour dégrader les PCB, de manière à pouvoir recycler l'eau pour le lavage.

Pour mettre en œuvre la réduction chimique pour traiter les sols et sédiments ou les eaux de lavage, il est important de comprendre les mécanismes et les limites de la méthode. L'efficacité d'élimination par le Fe^0 des polluants ciblés est limitée par le transfert de matières et le transfert d'électrons. Ces transferts jouent des rôles essentiels sur les cinétiques globales des réactions. Or, ils sont influencés par de nombreux paramètres : le pH, le potentiel redox, les concentrations en matière organique du sol (MOS) ou matières organiques naturelles (MON), l'état de surface des particules de Fe^0 et les ions métalliques présents. La complexité des solutions et des matrices sols et sédiments augmente encore la difficulté d'application du traitement au fer zérovalent.

L'objectif de cette thèse est d'apporter des connaissances dans le domaine du traitement de sols et sédiments contaminés par des PCB, en étudiant particulièrement la réduction chimique par le Fe^0 combinée au lavage à l'aide de tensioactifs. Les objectifs spécifiques sont les suivants :

1) Etudier la contamination des sols de sites dédiés au recyclage des déchets électroniques, comme Guiyu et Qingyuan (Chine) en s'intéressant plus particulièrement aux PCB et métaux lourds. Les paramètres des expérimentations présentées par la suite seront basés sur les résultats des concentrations mesurées sur ces sites.

2) Evaluer le potentiel du Fe^0 pour éliminer les PCB et métaux d'une solution aqueuse et comprendre les mécanismes et itinéraires réactionnels.

3) Déterminer les paramètres qui influencent la déchloration des PCB par leFe^0 et les mécanismes correspondants. Le facteur limitant le plus important devra être identifié et ajusté pour concevoir un procédé de remédiation intégré.

4) Evaluer la faisabilité de tensioactifs commerciaux choisis pour éliminer simultanément les PCB et métaux lourds de sédiments contaminés. Les conditions opératoires optimales incluent aussi le temps de contact et les concentrations des réactifs.

L'objectif global est de combiner la désorption assistée par les tensioactifs et la réduction à l'aide de particules de Fe^0. Les expériences de laboratoire seront effectuées selon deux approches principales : a) étudier la désorption des PCB des échantillons de sols/sédiments puis la réduction chimique des PCB transférés en solution et b) combiner les deux opérations en mélangeant directement les échantillons de sol, les surfactants et le fer zérovalent.

La thèse s'organise de la manière suivante :

Partie 1: problématique, enjeux, état de l'art

Chapitre 1 : synthèse bibliographique

Chapitre 2 : diagnostic de la contamination de sites pollués suite au recyclage des déchets électroniques

Partie 2 : mécanismes de réduction chimique des PCB par le fer zérovalent

Chapitre3 : mécanismes de réduction avec/sans tensioactifs, acide humique, métaux

Chapitre4 : paramètre et processus influençant la réduction par le fer zérovalent

Partie 3 : procédés de traitement à l'échelle du laboratoire

Chapitre5: réduction de PCB contenus dans un sédiment contaminé, assistée par tensioactif

Partie 4:discussion générale& conclusions/perspectives: de la réalité aux mécanismes puis à l'application.

La synthèse de la démarche générale est présentée en figure 1.

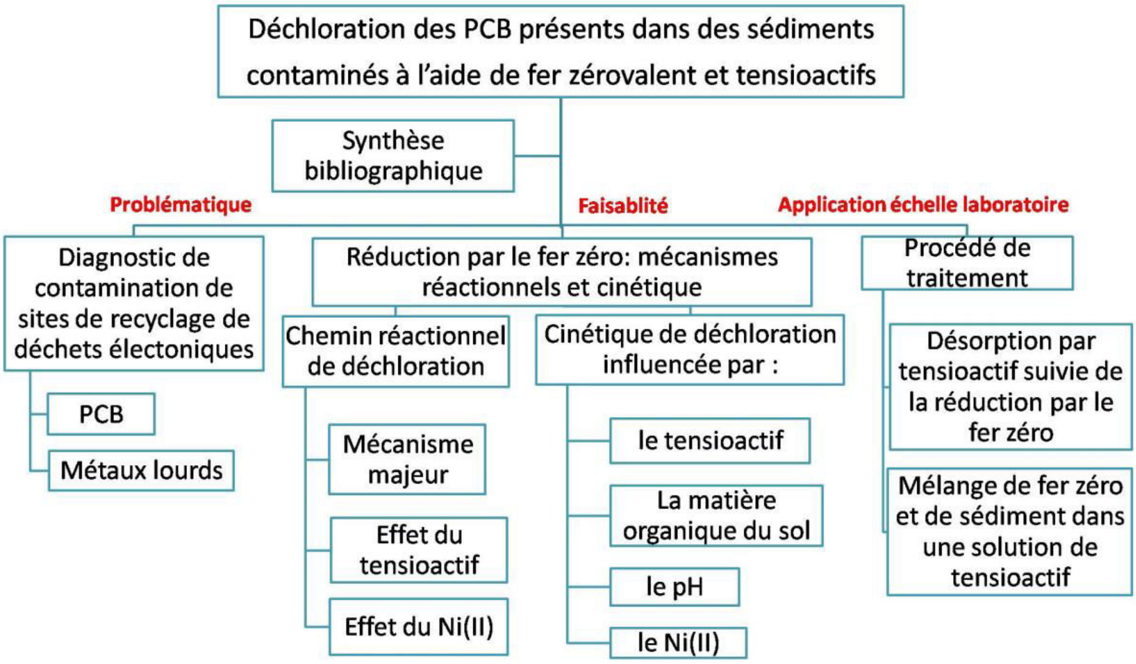

Figure 1. Structure de la thèse

2 Synthèse bibliographique

Le chapitre 1 donne une vue globale de l'état de l'art de la recherche sur la contamination des sites de recyclage de déchets électroniques en Chine, la question des PCB et le traitement par le fer zérovalent.

2.1 Contamination des sols et sédiments due à la gestion inadaptée de la fin de vie des déchets électroniques

Selon la convention de Bâle et la coalition contre les produits toxiques de la SiliconValley, les déchets électroniques et électriques (« e-wastes ») sont définis comme les différents appareils électroniques en fin de vie, contenant des commandes numériques et/ou provenant d'appareils ménagers de grandes tailles. Ils incluent les réfrigérateurs, les appareils à air conditionné, les téléphones portables, les équipements permettant d'écouter de la musique, les composants d'ordinateurs *etc.* [3]. La production de ce type de déchets a énormément augmenté dans les dernières années, or ces déchets contiennent des métaux et autres composés ayant de la valeur. Par conséquent, leur recyclage est nécessaire et génère du profit [21].

Toutefois, le coût élevé du recyclage par filières appropriées légales a motivé l'exportation illégale de ces déchets vers des pays en développement d'Amérique Latine, d'Asie et d'Afrique. Dans ces pays, les déchets sont traités sans les précautions ni les conditions de sécurité requises, ce qui donne lieu à des problèmes environnementaux majeurs au niveau des sites de traitement et aux alentours.

Les déchets électroniques contiennent plus de 1000 espèces chimiques, la plupart d'entre elles toxiques envers les organismes [2]. Parmi elles, on recense les métaux lourds comme le plomb (Pb), le zinc (Zn), le cuivre (Cu), le cadmium (Cd) et le nickel (Ni) dont certains sont cancérigènes. On trouve également des polluants organiques comme les PCB ou les retardateurs de flammes bromés ; la plupart d'entre eux appartiennent à la famille des Polluants Organiques Persistants (POP). De plus, des contaminants dangereux peuvent se former, surtout lorsque les déchets électroniques sont brûlés, comme les hydrocarbures aromatiques polycycliques (HAP), les dioxines et composés voisins (dibenzo-p-dioxines polychlorés/dibenzofurane (PCDD/F) et dibenzo-p-dioxines polybromés/dibenzofurane (PBDD/F)). Suite à l'incinération en plein air, ces composés sont transportés par des gaz ou des particules.

Comme illustré sur la figure 2, des eaux contaminés, des gaz et des résidus contenant des composés toxiques sont formés et rejetés vers les environnements avoisinants lors du recyclage mené en conditions non sécurisées et conduisent à des effets désastreux. L'effet de ces activités sur les populations locales et sur les écosystèmes a été prouvé etlargement étudié ces dernières années.

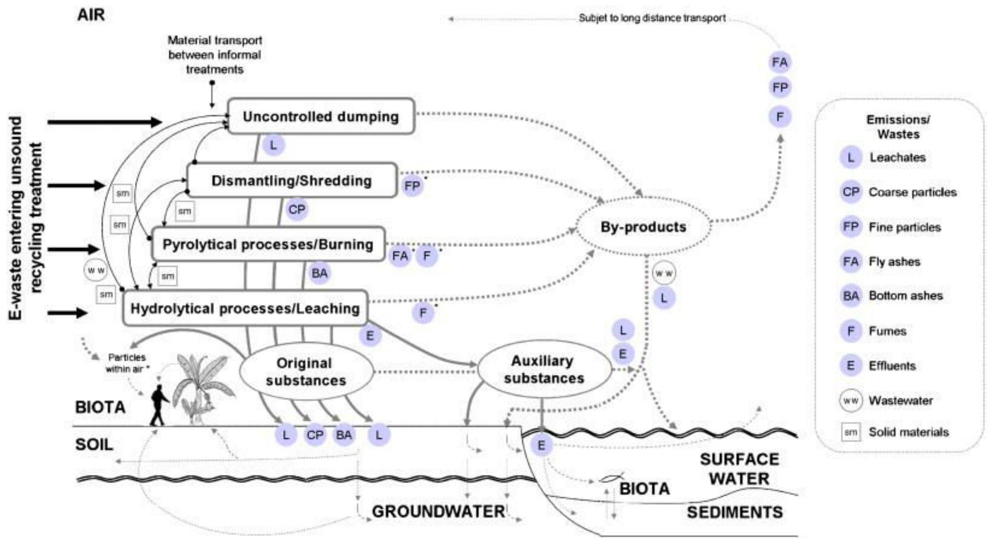

Figure 2.Flux de déchets émis suite au démantèlement et traitement des déchets électroniques en Chine et en Inde [2].

La Chine est l'un des pays les plus impliqués dans le traitement des déchets électroniques [3, 64]. De nombreuses publications ont montré la forte pollution résultant du traitement non sécurisé des déchets électroniques [4, 65]. Les sols et sédiments constituent un réservoir important dans lesquels s'accumulent les contaminants provenant du traitement, conduisant à la perte de fonctions écologiques et à des impacts négatifs sur la chaîne alimentaire. La contamination des sols et sédiments est complexe puisqu'elle implique à la fois les métaux lourds (Ni, Pb, Zn, Cu, Cd, Cr, *etc.*) et les polluants organiques persistants (PCB, BFR, PCDD/F, PBDD/F, *etc.*).

2.2 Les PCB dans les sols et sédiments

Les PCB sont parmi les composés qui posent le plus de problèmes en raison de leur toxicité élevée, leur bioaccumulation, leur bio-amplification, leur récalcitrance et leur persistance [46, 78]. Les fuites accidentelles de PCB qui ont eu lieu dans le monde ont démontré les risques pour la santé et les écosystèmes. Par conséquent, la contamination aux PCB représente un problème global.

La toxicité et le devenir des PCB dans l'environnement sont gouvernés par leurs propriétés : ils sont stables, avec une faible solubilité dans l'eau ($-\log S_w$=5.26-10.49) et un coefficient de partage eau-octanol assez élevé ($\log K_{ow}$=4.66-8.02) [83]. En raison de leur hydophobicité et lipophilicité, ils sont retenus sur les sols et sédiments par sorption et/ou partage avec la matière organique. Ils sont d'autant plus persistants que la teneur en matière organique du sol est élevée [92, 93].

Selon un rapport sur la liste nationale des priorités de l'US EPA, près d'un tiers des sites militaires aux Etats-Unis étaient contaminés par des PCB [103]. De même, d'autres zones industrielles dans des pays développés ou en développement ont aussi été touchéespar cette contamination [102, 104, 105].

2.3 Remédiation des sols des sites de recyclage de déchets électroniques et de sols co-contaminés

La remédiation de sites contaminés par les activités de recyclage de déchets électroniques est compliquée en raison de la co-contamination par des métaux lourds et des composés organiques. Des efforts ont été faits pour chercher des techniques qui s'adressent aux deux types de polluants, elles incluent la phytoremédiation, la remédiation électrocinétique, le lavage de sols *etc.*

Le lavage de sols est utilisé depuis longtemps, c'est un traitement rapide et relativement facile à mettre en œuvre. Il s'agit de mettre en contact le sol (plutôt la fraction fine) avec de l'eau contenant ou non des additifs pour désorber les contaminants des sols, ce qui est efficace avec des sols sableux. Cette application peut être flexible et efficace, selon les propriétés du sol et le type de contaminants [131].

Pour les composés hydrophobes fortement fixés par la matrice du sol, les surfactants améliorent la désorption et la solubilisation [135]. Les métaux peuvent aussi être éliminés, surtout par des tensioactifs anioniques, avec des mécanismes d'échange d'ions, de complexation, de dissolution, *etc.* [137]. Ainsi, le lavage avec des tensioactifs apparaît comme une solution prometteuse pour des sols co-contaminés.

Cependant, le lavage provoque le transfert de contaminants d'un sol vers une solution aqueuse qu'il faudra traiter par la suite. Un des post-traitements possibles est la réduction chimique à l'aide de fer zérovalent.

2.4 Réduction par le fer zérovalent (Fe^0)

Le Fe^0 a été utilisé pour la décontamination d'eaux souterraines et de sols. Les mécanismes réactionnels, les paramètres influençant l'efficacité de la réduction et les applications ont été beaucoup étudiés. Le Fe^0 est un réducteur fort, prêt à être oxydé, qui réagit avec toute une variété de contaminants (métaux, polluants organiques persistants, solvants chlorés *etc.*) [145].

Il réagit avec les composés organiques chlorésparhydrogénolyse progressive (remplacement d'un halogène par un hydrogène) [180-182]. Lors de l'hydrogénation réductive, le fer et l'hydrogène sont des donneurs d'électrons et les composés chlorés, des accepteurs. La réduction a lieu en phase hétérogène, entre le Fe^0 solide et la solution. Les produits finaux sont des hydrocarbures non halogénés ou portant moins d'halogènes.

En plus des mécanismes de réduction chimique, le Fe^0 favorise la dégradation de composés par des microorganismes anaérobies [184-186]. Les processus chimiques et biologiques sont souvent simultanés et difficiles à distinguer.

La cinétique de réduction dépend des propriétés de surface du fer (surface spécifique, nombre de sites catalytiques, état d'oxydation) et de l'efficacité du transfert des polluants du sein de la solution à la surface des particules.

L'application du Fe^0 peut se faire *in situ* ou *ex situ*, sur les eaux ou les sols [188]. Les microparticules de Fe^0 ont d'abord été utilisées dans les barrières réactives perméables (BPR) pour le traitement des eaux souterraines, ceci depuis près de 20 ans [189]. Une enquête menée en 2002 aux Etats-Unis a montré que le Fe^0 était un matériau efficace dans 55% des BPR [190].

L'application au sol (sous forme de micro ou nano particules) est plus limitée, probablement en raison de la vitesse de réaction plus faible que dans l'eau. De plus, la longévité du Fe^0 décroît significativement en raison de la passivation de la surface. De plus, la faible disponibilité des polluants cibles (hydrocarbures, métaux) limite l'application[199].

Pour ces raisons, il est nécessaire de mieux comprendre et optimiser les conditions opératoires pour le traitement direct des sols et sédiments ou de la solution après lavage.

3 Diagnostic de contamination de sols de sites de recyclage de déchets électroniques

Un diagnosticde la contamination des sites de recyclage des électroniques a été mené en Chine du Sud, à Guiyu et Qingyuan, en vue de comprendre les distributions de contaminants dans les sols. Ces données sont importantes pour choisir les stratégies de remédiation.

Malgré plusieurs investigations, peu de données ont pu être acquises à Qingyuan. En plus des PCB, d’autres contaminants organiques et métalliques sont présents [54, 62, 203]. Le diagnostic a aussi porté sur les métaux.

Des prélèvements ont été effectués à Guiyu et Qingyuan, villes très impliquées dans le recyclage des déchets électroniques depuis des décennies (figure 3). Pour bien comprendre la localisation des contaminants, des échantillons ont été pris près des ateliers de démantèlement, de lavage acide et d’incinération en plein air respectivement.

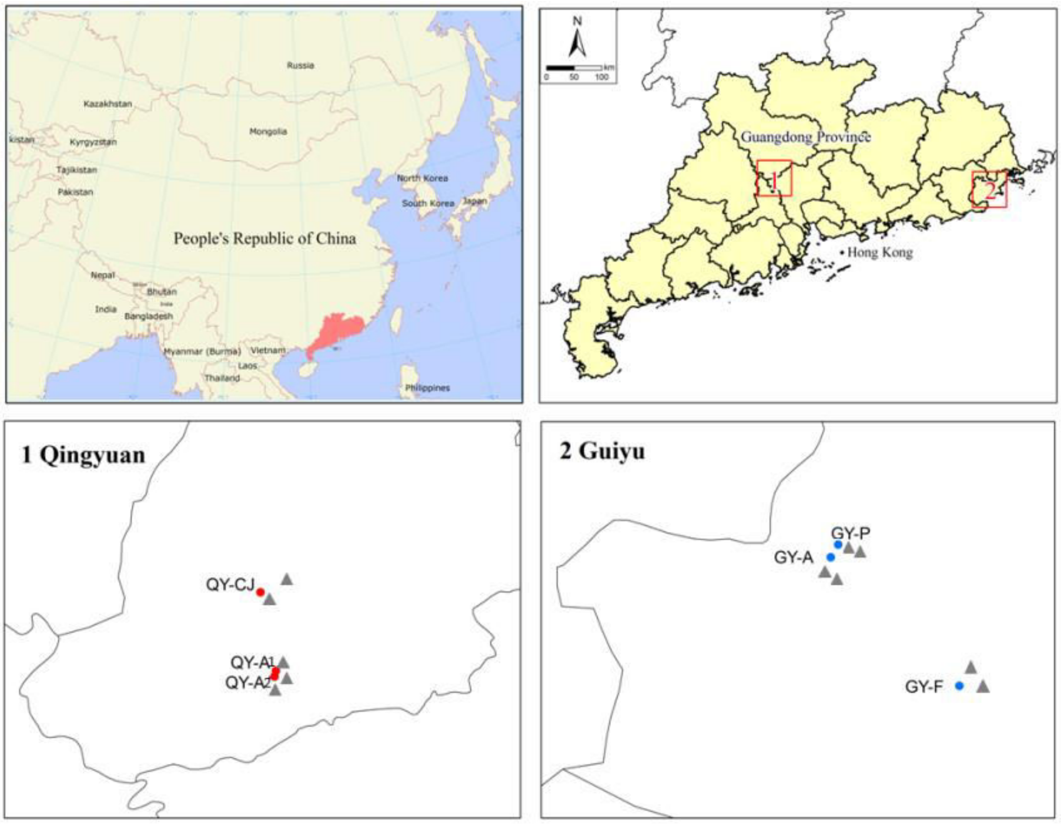

Figure 3. Localisation des points de prélèvements et des ateliers: 1 Qingyuan; 2 Guiyu. Triangles: ateliers. Points: sites de prélèvement.

Les résultats montrent que la contamination par les PCB n’estpas aussi grave que prévu sur les deux sites. L'échantillon le plus contaminé correspond à des sols à proximité d'un site de démantèlement (Σ_7PCB = 37,1 mg/kg$_{MS}$), tandis que les 7PCB dans d'autres échantillons variaient de 0,932 à 8,63 mg/kg$_{MS}$. Aucune des teneurs ne dépassait les valeurs d'intervention néerlandaise (Σ_7PCB = 1000 mg/kg$_{MS}$) [36], donc aucun échantillon n’était gravement contaminé. D’après les comparaisons avec les études précédentes, la situation s’est améliorée.

Le profil de contamination montre aussi des différences entre échantillons. Les congénères dominants au niveau du site de démantèlement sont les PCB-28 et PCB-52, ainsi, le mélange commercial Aroclor 1242 pourrait être l'origine majeure de la contamination lors du recyclage des condensateurs électriques ou des transformateurs [34]. Pour les autres, la distribution des congénères était assezsimilaire entre eux, ce qui suggère de multiples sources de contaminants.

L'enquête a également confirmé la coexistence de différents polluants selon les activités de recyclage. Les métaux tels que Ni (de 21,88 ± 1,05 à 106,13 ± 0,47 mg/kg$_{MS}$) et Cu (de 36,46 ± 5,76 à 578,83 ± 29,82 mg/kg$_{MS}$) ont été détectés en même temps que les PCB. Parmi tous les échantillons, les sols et sédiments provenant de sites de lavage acides étaient les plus contaminés en métaux.

La comparaison entre les deux villes montre que les sites de Qingyuan sont bien plus contaminés en métaux que ceux de Guiyu. D'après la norme environnementale sur les sols en Chine [37], la teneur en Cd dans les échantillons de Qingyuan et en Cu dans des échantillons provenant de sites de lavage acide dépassent la limitation de niveau 3 relative aux sols agricoles (1,0 et 400 mg/kg$_{MS}$, respectivement). Les teneurs en Zn et Ni dans les échantillons de sites de lavage acide dépassentcelle de niveau 2, tandis que celles de Pb et de Cr restent en-dessousdes normes. Ces résultats montrent la sérieuse pollution et la menace grave pesant sur les sols agricoles aux alentours de Qingyuan. A Guiyu, sur le site de lavage acide, seul la teneur en Ni est critique.

En bref, la contamination en PCB dans les sites de recyclage des déchets électroniques à Qingyuan et Guiyu ne sont pas aussi graves qu'ils étaient dans le passé, probablement à cause de l'attention portée sur la question et à l'effort entrepris pour arrêter la pollution, surtout à Guiyu. Toutefois, la co-contamination par des PCB et métaux représente une menace potentielle pour les populations locales et les écosystèmes, et augmente la difficulté de la remédiation.

4 Déchloration des PCB par le fer zérovalent et influence du Tween- 80, des acides humiques et d'ions métalliques

En vue d'appliquer la déchloration réductive à la décontamination de sols de sites de recyclage de déchets électroniques, nous avons étudié les effets d'un tensioactif non ionique, de la MOS, et d'ions métalliques sur la réduction par le Fe^0 du 2,2', 5, 5' tétra chloro-biphényle (PCB 52), en utilisant une solution modèle. Le Tween-80 (polyoxyéthylène (20) sorbitanmonooléate, polysorbate 80), tensioactif non ionique couramment étudié et utilisé [38-40] a été choisi comme modèle. L'acide humique a été choisi comme modèle de MOS. L'objectif était d'obtenir l'itinéraire réactionnel de déchloration réductive du PCB-52 par le Fe^0. Cette étude est synthétisée par la figure 4.

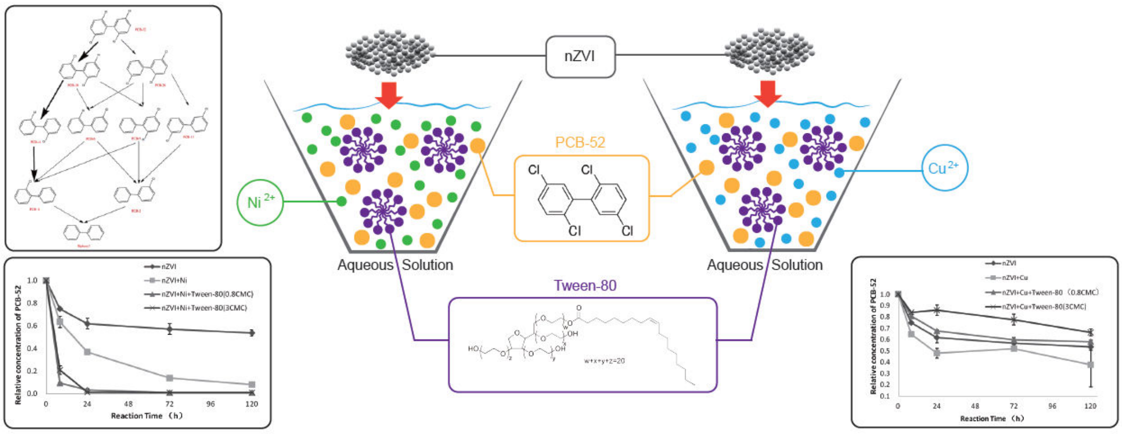

Figure 4. Schéma de la démarche d’étude de l’effet duTween-80 et d’ions métalliques sur la déchloration réductive des PCB en solution aqueuse par le Fe^0

4.1 Itinéraire réactionnel de déchloration

La connaissance de l’itinéraire réactionnel de déchloration est cruciale, car des intermédiaires peuvent être plus toxiques que la molécule mère. Lors d’expériencesen réacteurs fermés (7 jours), l'abondance relative des biphényles mono à tétra chlorés (BC) et des biphényles a démontré que la dégradation du PCB-52 par le Fe^0 et Ni^{2+} se faisait par étapes. En 168 h, plus de 95% du PCB 52 se dégrade en mono-tri BC et biphényles.

La spécificité des congénères a été mise en évidence : la formation de congénères contenant du chlore en ortho sans structure coplanaire est favorisée. Comme les congénères coplanaires ont une toxicité plus élevée dans l'environnement [41], l'utilisation de Fe^0 et Ni^{2+} pour traiter l'eau ou des sols contenant des PCB réduirait le risque environnemental.

Pour comprendre l'effet du tensioactif sur l’itinéraire réactionnel de déchloration, les produits de réaction obtenus lors de la dégradation effectuée en présence de Ni^{2+} et de Tween-80 ont également été déterminés. Les résultats montrent peu de différence sur la voie de dégradation avec ou sans Tween-80, toutefois l’ajout de Tween-80 a provoqué l'accumulation de certains congénères récalcitrants comme les PCB-26 et PCB-9. Le Tween-80 semble avoir amélioré plutôt la dégradation des congénères les plus vulnérables que celle des plus récalcitrants. La tendance observée sur l'accumulation de certains congénères confirme la principale voie de déchloration par le Fe^0.

4.2 Cinétique de déchloration

L’itinéraire réactionnel n’a pas changé en présence des différents paramètres, en revanche, la cinétique a pu être modifiée.

Pour accélérer la déchlorationdes PCB par le Fe^0, on peut utiliser du Ni ou du Cu comme catalyseurs [42]. Ici, on a observé que le Cu était moins efficace que le Ni comme catalyseur, ce qui est en accord avec des résultats précédents [43-45]. Ce résultat peut être attribué au degré de recouvrement du Fe par le Cu. En effet, Ni et Cu peuvent protéger la surface du fer de l'oxydation, bien que leurs mécanismes catalytiques diffèrent. Le Ni joue un rôle catalytique pour les réactions de déshydrogénation, ce qui accélère la déshalogénation par réduction de l'hydrogène, tandis que le Cu accélère la réaction principalement par augmentation du transfert d'électrons [43, 46]. Ici, la masse de Cu déposée en surface était supérieure à celle nécessaire pour former une monocouche, ce qui indique un excès sur plus de 80% de la surface des particules [47]. L'épaisseur de cette couche de Cu peut influencer le transfert des PCB vers la surface et inhiber la réaction si elle n'est pas optimale. Ainsi, le rapport molaire Cu: Fe est à optimiser.

En plus du transfert d'électrons, la cinétique de déchloration peut être limitée par le transfert de matière, surtout pour les PCB ou les PBDE qui sont très hydrophobes. Dans cette étude, une quantité négligeable de co-solvant a été ajoutée en solution pour favoriser la dissolution des PCB. Pour améliorer la désorption, en général, des tensioactifs sont utilisés lors du traitement au Fe^0 [44, 48].

Les résultats montrent que le Tween-80 à des teneurs de 0,8 à 3 fois la CMC accélèrela déchloration du PCB-52 en présence de Fe^0 et Ni^{2+} mais l'inhibe pour le traitement Fe^0 et Cu. En l'absence du Ni ou Cu, la réaction est juste légèrement ralentie. Les effets du Tween-80 et du Ni^{2+} sont synergiques : leur effet combiné est supérieur à la somme de leurs effets individuels. Cette synergie peut être attribué à la non passivation de la surface du Fe.

Un autre facteur potentiellement important est l'influence de la MOS. Des résultats controversés ont été obtenus dans la littérature. L'explication qui fait consensus est que l'acide humique agit comme transporteur d'électrons à faible concentration, tandis qu'il recouvre la surface et inhibe le transfert de matière à forte concentration [43, 49]. Ici, l'acide humique a eu une influence négligeable sur la déchloration du PCB-52 par le Fe^0 en présence de Ni ou Cu, quelles que soient les concentrations appliquées. Ce résultat a étéattribué à l'équilibre des effets positifs et négatifs induits.

Pour conclure, la déchloration du PCB-52 par le Fe^0 en solution aqueuse a été favorisée de manière synergique par la présence d'ions Ni^{2+} et de Tween-80. L'effet de l'acide humique était négligeable, dans les conditions du système étudié. La voie de dégradation du PCB-52 présentait une régiospécificité et une spécificité pour les congénères qui minimise la production de PCB coplanaires toxiques pour l'environnement. Ainsi, l'utilisation du Fe^0 en présence de Ni^{2+} et de Tween-80 est prometteuse pour le post-traitement des solutions de lavage dessols contaminés aux PCB. Le Fe^0 seul peut également être appliquée à des sols contaminés à la fois par des PCB et du Ni.

Par la suite, il faudra étudier les mécanismes plus détaillés pour expliquer l'influence du Tween-80 et du Ni et tester différentes conditions de concentrations et d'autres tensioactifs.

5 Facteurs influençant la déchloration des PCB par le Fe^0 en phase aqueuse

L'effet synergique du Tween-80 et du Ni^{2+} a montré que l'effet combiné des composants en solution aqueuse pouvait être compliqués et non additif. Des études antérieures ont porté sur l'influence de divers facteurs. Elles montrent que ces facteurs jouent sur le transfert de matière de composés – cibles et/ou le transfert d'électrons. Ici, nous avons étudié l'effet de la combinaison de plusieurs paramètres sur la déchloration réductive du PCB-52 par le Fe^0, en vue d'identifier les processus limitants.

Pour cela, un plan d'expérience orthogonal a été réalisé pour étudier les effets des concentrations en Ni^{2+}, H^+, acide humique et de deux tensioactifs (Tween 80 et Envirosurf (Environium)). De plus, les particules de Fe ont été caractérisées par microscope électronique à balayage couplé à un spectromètre à dispersion d'énergie aux rayons X (MEB-EDX) et un diffractomètre des rayons X (DRX).

Les résultats du plan d'expériences et l'analyse statistique montrent que l'importance relative des facteurs étudiés se classe dans l'ordre : tensioactifs> acide humique> pH>Ni^{2+}. Ce résultat suggère l'importance du transfert de masse de PCB-52 dans le système aqueux, étant donné qu'il a été rapporté que les tensioactifs et acides humiques affectent le transfert des contaminants cibles durant la déchloration par le Fe^0 [50]. La formation de minéraux du de fer a été observée par EDX et DRX ; ainsi des mécanismes corrosion/oxydation semblent couplés au processus de déchloration.

Les résultats de l'étude des effets du Ni^{2+}, H^+, acide humique et de deux tensioactifs sont présentés sur la figure 5.

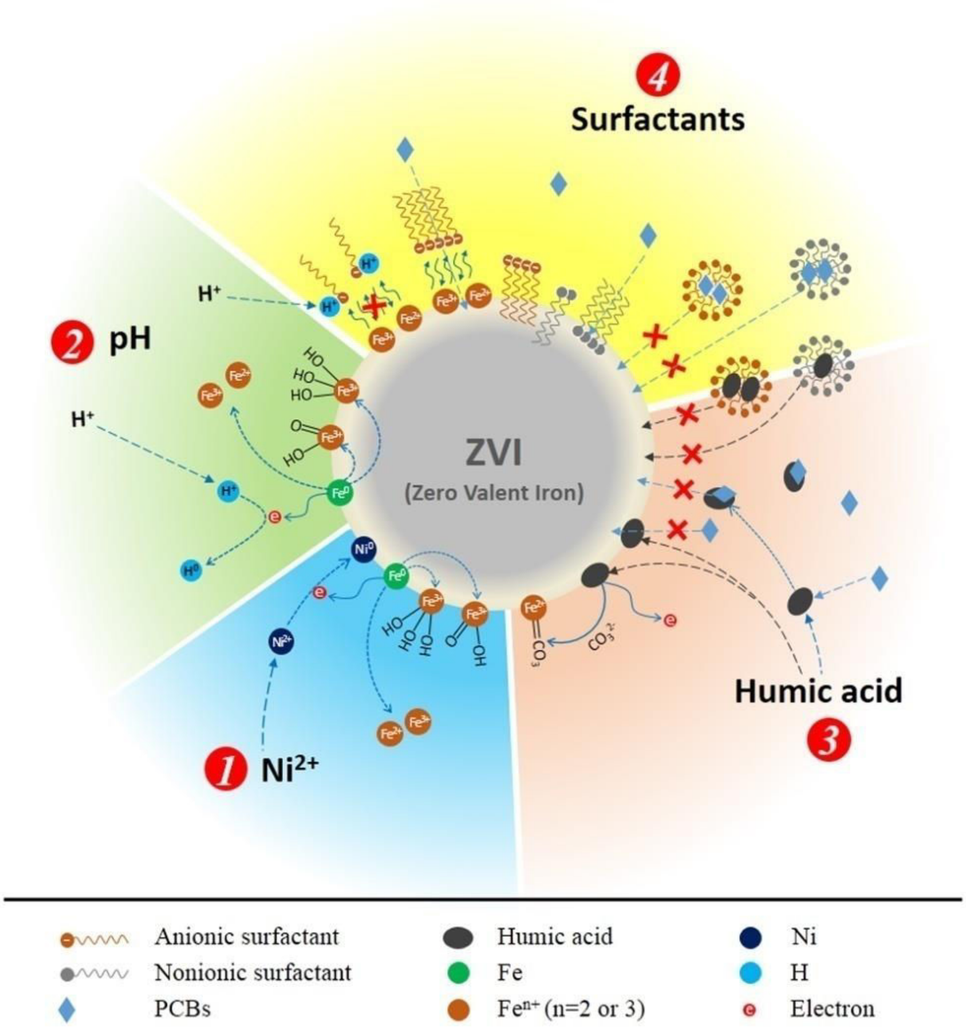

Figure 5. Schéma des influences et effets combinés du tensioactif, de l'acide humique, du pH et de Ni^{2+} sur la déchloration du PCB-52 par le Fe^0.

5.1 Transfert de matière

Le type de surfactant et sa concentration sont les facteurs les plus importants pour le système étudié, car ils jouent sur le transfert de matière du PCB-52 vers la surface des particules de Fe^0.

Lors du plan d'expérience, l'abondance de C était significativement affectée par les tensioactifs, ce qui signifie qu'ils sont adsorbés par les particules de Fe préférentiellement à l'acide humique. Leur caractère amphiphile facilite leur adsorption et réduit la tension interfaciale entre les phases solide et liquide, renforçant ainsi l'adsorption de PCB-52 à la surface du fer. Cependant, les micelles de tensioactifs peuvent inhiber l'adsorption du PCB-52 en le séquestrant dans ces phases pseudo-hydrophobes [51]. Ainsi, l'impact positif ou négatif d'un tensioactif non ionique est gouverné par l'importance relativede ces deux effets.

L'ajout de SDBS (sodium dodécyl benzène sulfonate) anionique améliore la réduction lors des traitements avec une forte concentration de tensioactif non ionique. En effet, il atténue les effets négatifs des concentrations élevées de tensioactif non ionique et d'acide humique en modifiant la sorption, également influencée par le pH initial du mélange réactionnel.

Le deuxième facteur le plus influent est la concentration d'acide humique, négativement corrélée avec le taux de dégradation du PCB-52. L'acide humique est en compétition avec le PCB-52 pour les sites réactifs disponibles à la surface des particules de Fe^0; par conséquent, il diminue le taux de déchloration. De plus, en raison de son caractère amphiphile, l'acide humique peut former des structures micellaires, favorisant encore la solubilisation des composés cibles [52, 53] et limitant leur adsorption à la surface.

Les tensioactifs et l'acide humique ne sont pas indépendants, leurs interactions influencent aussi la réaction. Une concentration plus élevée de tensioactif, surtout de tensioactif anionique, diminue les interférences avec l'acide humique. Cependant, des concentrations trop élevées de tensioactif peuvent limiter la réduction. Par conséquent, l'optimisation de ces deux facteurs est essentielle.

Le pH ne joue pas directement sur le transfert de masse des PCB, mais peut influencer le processus de déchloration par son effet sur l'adsorption des ions en solution, à savoir, l'acide humique et le SDBS.

5.2 Oxydation du fer

L'autre processus crucial dans la réduction par le Fe^0 est l'oxydation/corrosion du fer par transfert d'électrons. Le Fe^0 est le principal donneur d'électrons, qui seront captés par le PCB-52 et par d'autres oxydants comme l'eau et les ions métalliques. Pour accélérer la réduction du polluant cible, il est important d'améliorer l'efficacité du transfert d'électrons, par exemple par la présence de composés bimétalliques, et d'empêcher/limiter les réactions avec d'autres oxydants.

On démontre ici que l'abondance d'oxygène à la surface des particules de fer (reflet du degré d'oxydation) est statistiquement plus affectée par le pH que par les autres paramètres. Ainsi, l'influence du pH initial se manifeste par son action à la surface des particules de fer.

L'influence des tensioactifs sur l'abondance d'oxygène à la surface est négligeable. Le degré d'oxydation du fer relativement faible lors du traitement avec de fortes concentrations de tensioactifs, ainsi que les diffractogrammes X prouvent l'absence d'oxydation par le tensioactif.

Les points de vuedivergent sur le rôle redox de l'acide humique (ou de la MOS) en raison de la diversité des composés organiques et de leur réactivité. Ici, la formation de $FeCO_3$ observée a été attribuée à l'oxydation de l'acide humique, ce qui indique l'implication de l'acide humique dans la réaction redox comme agent réducteur.

La quantité de Ni n'a pas eu d'influenceici, ce qui suggère que pour l'application pratique du Fe^0 pour la dégradation des contaminants organiques hydrophobes en solution aqueuse, le transfert de masse est plus limitant que le transfert d'électrons.

Pour conclure, la déchloration réductive du PCB-52 par le fer zéro en solution aqueuse est principalement gouvernée par le transfert de matière du PCB-52 vers la surface. Aussi, pour l'application de fer zéro en remédiation, c'est surtout ce transfert qu'il faudra améliorer. L'utilisation de tensioactifs est alors indiquée.

6 Traitement de sédiment contaminé par les PCB assisté par tensioactif à l'échelle du laboratoire

En s'appuyant sur les résultats précédents, on propose d'étudier la déchloration d'un sédiment contaminé par les PCB au moyen de Fe^0 et en présence de tensioactifs. Deux approches sont proposées (figure 6): la désorption par un tensioactif suivie d'un traitement de la solution par le Fe^0 (approche A); traitement par le Fe^0 d'un sédiment contaminé en présence de tensioactif (approche B).

Pour ces expériences, un sédiment contaminé aux PCB a été échantillonné près de la surface (profondeur ≤ 20 cm) dans une rivière proche de la ville de Lyon (bassin du Rhône, France). Pour étudier le potentiel d'élimination simultanée des PCB et des métaux lourds, le sédiment a été Ni a été enrichi en nickel à une concentration comparable à celle des sédiments des sites de recyclage des déchets électroniques en Chine.

6.1 Approche A

L'approche A consiste à mener deux opérations en série : la désorption des PCB présents dans le sédiment à l'aide de tensioactifs puis la dégradation des PCB en solution. Deux tensioactifs disponibles dans le commerce ont été choisis: Tween-80 et Envirosurf.

L'étude de la cinétique de désorption en réacteur fermé a montré que l''équilibre de désorption du Ni était obtenu en 4-8 h, et celui des PCB en 12 h. On a donc choisi une durée d'expérience de 24 h. Aucun des tensioactifs n'a été efficace pour éliminer le Ni de sédiments contaminés. L'augmentation de la concentration de tensioactifs n'a eu aucun effet avec le Tween-8, tandis qu'avec Envirosurf, la désorption du Ni est passée de 2,12% à 13,03%, avec une corrélation positive entre l'élimination de Ni et la teneur en Envirosurf (R^2 = 0,9893). L'amélioration induite par Envirosurf est attribuée à la teneur élevée en SDBS dans le mélange pour l'élimination des métaux par échange d'ions avec des cations de sodium et l'attraction électrostatique des micelles chargées négativement [5, 6].

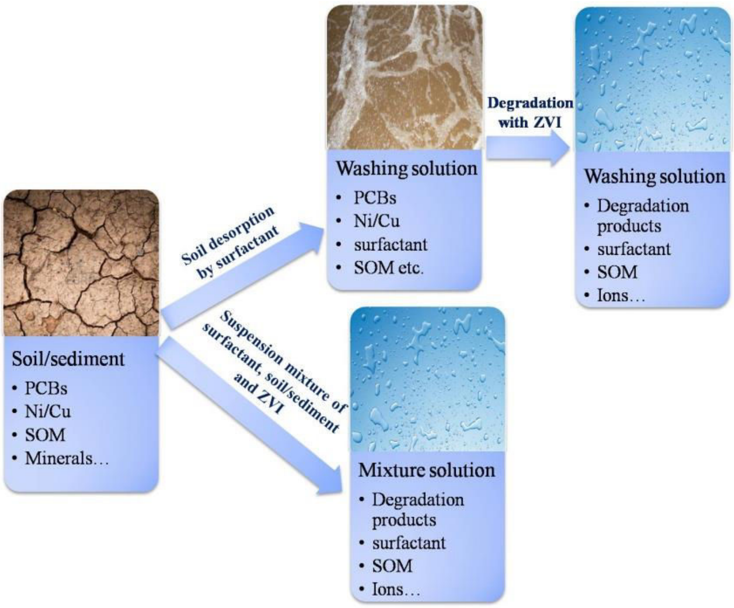

Figure 6. Schéma résumant les expériences de laboratoire pour traiter le sédiment contaminé aux PCB à l'aide de tensioactif et de fer zérovalent

En revanche, la désorption des PCB par Tween-80 a augmenté de façon spectaculaire pour une concentration de 1% par rapport aux traitements à 0,08%, en raison de la plus grande quantité de micelles. Pour Envirosurf, aucune différence n'a été relevée entre 1 et 2%, par contre à 5%, la désorption a atteint plus de 85% sans modifier le profil des congénères.

Avec une concentration de 1% pour chaque tensioactif, l'efficacité de désorption de PCB était de 47,5% pour Tween 80 et 65,2% pour Envirosurf.

La déchloration des PCB par le Fe^0 dans une solution de lavage contenant 1% d'Enviro surf ou de Tween-80 s'est avérée inefficace, ce qui est cohérent avec le résultat des expériences aqueuses; tandis que plus de 97% de Ni a pu être éliminé par des particules de fer. Ceci résulte d'une forte teneur en tensioactif dans la solution de lavage, tel que révélé par la section 5.1. De plus, une forte agrégation des particules de fer et un recouvrement par la MOS a été observé dans les deux cas, ce qui contribue aussi à l'inefficacité du traitement.

6.2 Approche B

L'approche B consiste à mélanger le sédiment contaminé, le tensioactif et les particules de Fe^0. Les meilleurs résultats ont obtenus avec 0,04% Envirosurf ou Tween-80, ils ont abouti à la suppression de Σ7PCBs que 76,31 et 47,16%, respectivement en 7 jours. L'amélioration en présence de surfactants à faible teneur a été attribuée au contact amélioré entre la surface du fer et les PCB, ainsi qu'àl'empêchement de la passivation.

Bien qu'il n'ait pas été possible de désorber les PCB uniquement à l'eau,un mélange de Fe^0 et de sédiments contaminés en solution aqueuse sans tensioactif a pu provoquer la déchloration des PCB, principalement des octa-, hepta- et hexa- qui sont les plus réactifs.

Toutefois, à mesure que la réaction avance, les particules de Fe sont passivées, ce qui conduit à une faible déchloration.

Les comparaisons entre les résultats des deux approches révèlent qu'un mélange de Fe^0 et de sédiments contaminés dans une solution de tensioactif (approche B) est plus efficace et réalisable qu'une désorption de PCB par tensioactif suivie d'un traitement de l'eau (approche A).

Les résultats indiquent également la possibilité de remédier les sédiments contaminés sans ajouter de l'eau. L'eau liée des sédiments suffit pour faciliter le transfert de matière des PCB lors de la dégradation. Pour améliorer la réactivité du Fe^0dans la suspension et accélérer la réaction, l'addition d'un tensioactif non ionique ou d'un mélange de tensioactifs anioniques et non ioniques à faible teneur est recommandée. Après dégradation, les congénères de PCB moins toxiques et hydrophobes sont dissous dans la solution aqueuse à minéraliser par des méthodes biochimiques et une quantité limitée de Fe sous forme ionique ensolution pourrait être utilisée par les micro-organismes comme éléments nutritifs. Les particules de fer restées dans les sédiments pourraient être séparées magnétiquement pour la réutilisation ou la régénération.

7 Perspectives

1) Comme indiqué en section 4, il faudrait approfondir l'étude de la synergie entre le Tween-80 et Ni^{2+}, et l'optimisation du traitement par le fer zérovalent de la solution de lavage contaminée par les PCB.

2) Concernant la section 6, plusieurs pistes restent à explorer. Tout d'abord, les mécanismes de désorption des deux typescontaminants sont à approfondir. Ensuite, t, il est difficile d'éliminer simultanément le Ni et le PCB par un seul tensioactif commercial, tandis qu'une combinaison de tensioactifs pourrait permettre un meilleur taux de désorption. Ainsi, une optimisation est nécessaire. De plus, il faudrait étudier les risques potentiels présentés par le sédiment après lavage.

3) On a montré l'inefficacité de la déchloration des PCB dans la solution de lavage, mais il faudrait progresser dans la compréhension des mécanismes impliqués.

4) Pour le sédiment contaminé par différents congénères, il est difficile d'évaluer quantitativement la dégradation. On a vu que la déchloration provoquait une disparition des congénères parents, mais provoquant une augmentation des concentration des molécules-filles. Il faudrait mettreau point une méthode de quantification pour évaluer le degré de déchloration atteint.

5) Enfin, on pourrait étudier la possibilité de mettre en œuvre un post-traitement biochimique pour un construire une filière intégrée de remédiation.

Reference

1. Terazono A., Murakami S., Abe N., Inanc B., Moriguchi Y., Sakai S., Kojima M., Yoshida A., Li J., Yang J., Wong M. H., Jain A., Kim I.-S., Peralta G. L., Lin C., Mungcharoen T., and Williams E., *Current status and research on E-waste issues in Asia.* Journal of Material Cycles and Waste Management, 2006. **8**(1): p. 1-12.
2. Sepúlveda A., Schluep M., Renaud F. G., Streicher M., Kuehr R., Hagelüken C., and Gerecke A. C., *A review of the environmental fate and effects of hazardous substances released from electrical and electronic equipments during recycling: Examples from China and India.* Environmental Impact Assessment Review, 2010. **30**(1): p. 28-41.
3. Puckett J., Ryan M., Zude B., Simpson S., Hedenrick T., and Network B. A., *Exporting harm: the high-tech trashing of Asia*. 2002: Basel Action Network.
4. Zhang W. H., Wu Y. X., and Simonnot M. O., *Soil Contamination due to E-Waste Disposal and Recycling Activities: A Review with Special Focus on China.* Pedosphere, 2012. **22**(4): p. 434-455.
5. Luo Y., Yu X. H., Yang Z. Y., Yuan J. G., Mai B. X., *Studies on Heavy Metal Contamination by Improper Handling of E-Waste and Its Environmental Risk Evaluation Ⅰ. Heavy Metal Contamination in E-Waste Open Burning Sites*. 2015, 2008(1): p.34-41. (in Chinese)
6. Shen C., Huang S., Wang Z., Qiao M., Tang X., Yu C., Shi D., Zhu Y., Shi J., Chen X., Setty K., and Chen Y., *Identification of Ah Receptor Agonists in Soil of E-waste Recycling Sites from Taizhou Area in China.* Environmental Science & Technology, 2008. **42**(1): p. 49-55.
7. Tang X., Shen C., Chen L., Xiao X., Wu J., Khan M., Dou C., and Chen Y., *Inorganic and organic pollution in agricultural soil from an emerging e-waste recycling town in Taizhou area, China.* Journal of Soils and Sediments, 2010. **10**(5): p. 895-906.
8. Luo Y., Luo X. J., Lin Z., Chen S. J., Liu J., Mai B. X., and Yang Z. Y., *Polybrominated diphenyl ethers in road and farmland soils from an e-waste recycling region in Southern China: Concentrations, source profiles, and potential dispersion and deposition.* Science of The Total Environment, 2009. **407**(3): p. 1105-1113.
9. Srogi K., *Levels and congener distributions of PCDDs, PCDFs and dioxin-like PCBs in environmental and human samples: a review.* Environmental Chemistry Letters, 2008. **6**(1): p. 1-28.
10. Desmet M., Mourier B., Mahler B. J., Van Metre P. C., Roux G., Persat H., Lefèvre I., Peretti A., Chapron E., Simonneau A., Miège C., and Babut M., *Spatial and temporal trends in PCBs in sediment along the lower Rhône River, France.* Science of The Total Environment, 2012. **433**: p. 189-197.
11. Xia H., Chi X., Yan Z., and Cheng W., *Enhancing plant uptake of polychlorinated biphenyls and cadmium using tea saponin.* Bioresource Technology, 2009. **100**(20): p. 4649-4653.
12. Chen Y., Tang X., Cheema S. A., Liu W., and Shen C., *β-cyclodextrin enhanced phytoremediation of aged PCBs-contaminated soil from e-waste recycling area.* Journal of Environmental Monitoring, 2010. **12**(7): p. 1482-1489.
13. Huang H., Zhang S., and Christie P., *Plant uptake and dissipation of PBDEs in the soils of*

electronic waste recycling sites. Environmental Pollution, 2011. **159**(1): p. 238-243.

14. Gao Y. Y. and Zhou Q. X. *Application of Nanoscale Zero Valent Iron Combined with Impatiens Balsamina to Remediation of E-Waste Contaminated Soils*. Advanced Materials Research. 2013. **790**: p. 73-76.
15. Li T., Yuan S., Wan J., Lin L., Long H., Wu X., and Lu X., *Pilot-scale electrokinetic movement of HCB and Zn in real contaminated sediments enhanced with hydroxypropyl-β-cyclodextrin.* Chemosphere, 2009. **76**(9): p. 1226-1232.
16. Khodadoust A. P., Reddy K. R., and Maturi K., *Removal of Nickel and Phenanthrene from Kaolin Soil Using Different Extractants.* Environmental Engineering Science, 2004. **21**(6): p. 691-704.
17. Zhang W., Wang C., and Lien H., *Treatment of chlorinated organic contaminants with nanoscale bimetallic particles.* Catalysis Today, 1998. **40**(4): p. 387-395.
18. Cundy A. B., Hopkinson L., and Whitby R. L. D., *Use of iron-based technologies in contaminated land and groundwater remediation: A review.* Science of The Total Environment, 2008. **400**(1–3): p. 42-51.
19. Villa R. D., Trovó A. G., and Nogueira R. F. P., *Soil remediation using a coupled process: soil washing with surfactant followed by photo-Fenton oxidation.* Journal of Hazardous Materials, 2010. **174**(1–3): p. 770-775.
20. Lu C., Zhang L., Zhong Y., Ren W., Tobias M., Mu Z., Ma Z., Geng Y., and Xue B., *An overview of e-waste management in China.* Journal of Material Cycles and Waste Management, 2014. **17**(1): p. 1-12.
21. Tanskanen P., *Management and recycling of electronic waste.* Acta Materialia, 2013. **61**(3): p. 1001-1011.
22. Sthiannopkao S. and Wong M. H., *Handling e-waste in developed and developing countries: Initiatives, practices, and consequences.* Science of The Total Environment, 2013. **463–464**: p. 1147-1153.
23. Panambunan-Ferse M. and Breiter A., *Assessing the side-effects of ICT development: E-waste production and management: A case study about cell phone end-of-life in Manado, Indonesia.* Technology in Society, 2013. **35**(3): p. 223-231.
24. Ma J., Horii Y., Cheng J., Wang W., Wu Q., Ohura T., and Kannan K., *Chlorinated and Parent Polycyclic Aromatic Hydrocarbons in Environmental Samples from an Electronic Waste Recycling Facility and a Chemical Industrial Complex in China.* Environmental Science & Technology, 2009. **43**(3): p. 643-649.
25. Wang F., Huisman J., Meskers C. E. M., Schluep M., Stevels A., and Hagelüken C., *The Best-of-2-Worlds philosophy: Developing local dismantling and global infrastructure network for sustainable e-waste treatment in emerging economies.* Waste Management, 2012. **32**(11): p. 2134-2146.
26. Luo C., Liu C., Wang Y., Liu X., Li F., Zhang G., and Li X., *Heavy metal contamination in soils and vegetables near an e-waste processing site, south China.* Journal of Hazardous Materials, 2011. **186**(1): p. 481-490.
27. Huo X., Peng L., Xu X., Zheng L., Qiu B., Qi Z., Zhang B., Han D., and Piao Z., *Elevated Blood Lead Levels of Children in Guiyu, an Electronic Waste Recycling Town in China.* Environmental Health Perspectives, 2007. **115**(7): p. 1113-1117.
28. Zheng J., Luo X. J., Yuan J., Wang J. G., Wang Y. T., Chen S. J., Mai B. X., and Yang Z. Y., *Levels and sources of brominated flame retardants in human hair from urban, e-waste, and rural areas in*

South China. Environmental Pollution, 2011. **159**(12): p. 3706-3713.

29. Wu J. P., Luo X. J., Zhang Y., Luo Y., Chen S. J., Mai B. X., and Yang Z. Y., *Bioaccumulation of polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) in wild aquatic species from an electronic waste (e-waste) recycling site in South China.* Environment International, 2008. **34**(8): p. 1109-1113.
30. Wu J. P., Luo X. J., Zhang Y., Luo Y., Chen S. J., Mai B. X., and Yang Z. Y., *Bioaccumulation of polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) in wild aquatic species from an electronic waste (e-waste) recycling site in South China.* Environment International, 2008. **34**(8): p. 1109-1113.
31. Luo X. J., Liu J., Luo Y., Zhang X. L., Wu J. P., Lin Z., Chen S. J., Mai B. X., and Yang Z. Y., *Polybrominated diphenyl ethers (PBDEs) in free-range domestic fowl from an e-waste recycling site in South China: Levels, profile and human dietary exposure.* Environment International, 2009. **35**(2): p. 253-258.
32. Lim S.R. and Schoenung J. M., *Human health and ecological toxicity potentials due to heavy metal content in waste electronic devices with flat panel displays.* Journal of Hazardous Materials, 2010. **177**(1–3): p. 251-259.
33. Klaassen C. D., Liu J., and Diwan B. A., *Metallothionein protection of cadmium toxicity.* Toxicology and Applied Pharmacology, 2009. **238**(3): p. 215-220.
34. Leung A., Cai Z. W., and Wong M. H., *Environmental contamination from electronic waste recycling at Guiyu, southeast China.* Journal of Material Cycles and Waste Management, 2006. **8**(1): p. 21-33.
35. Bernhoft R. A., *Mercury Toxicity and Treatment: A Review of the Literature.* Journal of Environmental and Public Health, 2012. **2012**: p. 460-508
36. Dayan A. D. and Paine A. J., *Mechanisms of chromium toxicity, carcinogenicity and allergenicity: Review of the literature from 1985 to 2000.* Human & Experimental Toxicology, 2001. **20**(9): p. 439-451.
37. Gaetke L. M. and Chow C. K., *Copper toxicity, oxidative stress, and antioxidant nutrients.* Toxicology, 2003. **189**(1–2): p. 147-163.
38. Widmer R., Oswald-Krapf H., Sinha-Khetriwal D., Schnellmann M., and Böni H., *Global perspectives on e-waste.* Environmental Impact Assessment Review, 2005. **25**(5): p. 436-458.
39. Lin C. and Chen T., *Nickel toxicity to human term placenta: In vitro study on lipid peroxidation.* Journal of Toxicology and Environmental Health, Part A, 1998. **54**(1): p. 37-47.
40. Kovacs G., Montalbetti N., Franz M. C., Graeter S., Simonin A., and Hediger M. A., *Human TRPV5 and TRPV6: Key players in cadmium and zinc toxicity.* Cell Calcium, 2013. **54**(4): p. 276-286.
41. Winship K. A., *Toxicity of tin and its compounds.* Adverse drug reactions and acute poisoning reviews, 1988. **7**(1): p. 19-38.
42. Hughes M. F., *Arsenic toxicity and potential mechanisms of action.* Toxicology Letters, 2002. **133**(1): p. 1-16.
43. White P. A. and Claxton L. D., *Mutagens in contaminated soil: a review.* Mutation Research/Reviews in Mutation Research, 2004. **567**(2–3): p. 227-345.
44. Nagasaki H., *Hepatocarcinogenicity of polycheorinated biphenyls in mice(Communication).* Gann, 1972. **63**(6): p. 805.
45. Ito N., Nagasaki H., Arai M., Makiura S., Sugihara S., and Hirao K., *Histopathologic Studies on Liver Tumorigenesis Induced in Mice by Technical Polychlorinated Biphenyls and Its Promoting*

Effect on Liver Tumors Induced by Benzene Hexachloride. Journal of the National Cancer Institute, 1973. **51**(5): p. 1637-1646.

46. Safe S. H., *Polychlorinated Biphenyls (PCBs): Environmental Impact, Biochemical and Toxic Responses, and Implications for Risk Assessment.* Critical Reviews in Toxicology, 1994. **24**(2): p. 87-149.

47. Wan Y., Wiseman S., Chang H., Zhang X., Jones P. D., Hecker M., Kannan K., Tanabe S., Hu J., Lam M. H., and Giesy J. P., *Origin of hydroxylated brominated diphenyl ethers: natural compounds or man-made flame retardants?* Environ Sci Technol, 2009. **43**(19): p. 7536-42.

48. Safe S. H., *Comparative toxicology and mechanism of action of polychlorinated dibenzo-p-dioxins and dibenzofurans.* Annual Review of Pharmacology, 1986. **26**(26): p. 371-99.

49. Shaw S. D., Blum A., Weber R., Kannan K., Rich D., Lucas D., Koshland C. P., Dobraca D., Hanson S., and Birnbaum L. S., *Halogenated flame retardants: do the fire safety benefits justify the risks?* Rev Environ Health, 2010. **25**(4): p. 261-305.

50. Darnerud P. O., *Toxic effects of brominated flame retardants in man and in wildlife.* Environment International, 2003. **29**(6): p. 841-853.

51. Wang J., Tian M., Chen S.-J., Zheng J., Luo X. J., An T. C., and Mai B. X., *Dechlorane Plus in house dust from E-waste recycling and urban areas in South China: Sources, degradation, and human exposure.* Environmental Toxicology and Chemistry, 2011. **30**(9): p. 1965-1972.

52. Dou J., Jin Y., Li Y., Wu B., and Li M., *Potential genotoxicity and risk assessment of a chlorinated flame retardant, Dechlorane Plus.* Chemosphere, 2015. **135**: p. 462-466.

53. Wong C. S. C., Wu S. C., Duzgoren-Aydin N. S., Aydin A., and Wong M. H., *Trace metal contamination of sediments in an e-waste processing village in China.* Environmental Pollution, 2007. **145**(2): p. 434-442.

54. Quan S. X., Yan B., Lei C., Yang F., Li F., Xiao X. M., and Fu J. M., *Distribution of heavy metal pollution in sediments from an acid leaching site of e-waste.* Science of The Total Environment, 2014. **499**: p. 349-355.

55. Alabi O. A., Bakare A. A., Xu X., Li B., Zhang Y., and Huo X., *Comparative evaluation of environmental contamination and DNA damage induced by electronic-waste in Nigeria and China.* Science of The Total Environment, 2012. **423**: p. 62-72.

56. Zhu Z., Han Z., Bi X., and Yang W., *The relationship between magnetic parameters and heavy metal contents of indoor dust in e-waste recycling impacted area, Southeast China.* Science of The Total Environment, 2012. **433**: p. 302-308.

57. Li J., Duan H., and Shi P., *Heavy metal contamination of surface soil in electronic waste dismantling area: site investigation and source-apportionment analysis.* Waste Management & Research, 2011.

58. Fu J., Zhou Q., Liu J., Liu W., Wang T., Zhang Q., and Jiang G., *High levels of heavy metals in rice (Oryzasativa L.) from a typical E-waste recycling area in southeast China and its potential risk to human health.* Chemosphere, 2008. **71**(7): p. 1269-1275.

59. Zhang Q., Ye J., Chen J., Xu H., Wang C., and Zhao M., *Risk assessment of polychlorinated biphenyls and heavy metals in soils of an abandoned e-waste site in China.* Environmental Pollution, 2014. **185**: p. 258-265.

60. Zhang J. H. and Min H., *Eco-toxicity and metal contamination of paddy soil in an e-wastes recycling area.* Journal of Hazardous Materials, 2009. **165**(1–3): p. 744-750.

61. Chen L., Yu C., Shen C., Zhang C., Liu L., Shen K., Tang X., and Chen Y., *Study on adverse impact*

of e-waste disassembly on surface sediment in East China by chemical analysis and bioassays. Journal of Soils and Sediments, 2010. **10**(3): p. 359-367.

62. Tang X., Shen C., Shi D., Cheema S. A., Khan M. I., Zhang C., and Chen Y., *Heavy metal and persistent organic compound contamination in soil from Wenling: An emerging e-waste recycling city in Taizhou area, China.* Journal of Hazardous Materials, 2010. **173**(1–3): p. 653-660.
63. Chinese Environmental Protection Administrator (CEPA), *Chinese Soil Quality Standard (GB15618-1995)*, 1995, Chinese Environmental Press: Beijing. p. 1-5.
64. Chi X., Streicher-Porte M., Wang M. Y. L., and Reuter M. A., *Informal electronic waste recycling: A sector review with special focus on China.* Waste Management, 2011. **31**(4): p. 731-742.
65. Robinson B. H., *E-waste: An assessment of global production and environmental impacts.* Science of The Total Environment, 2009. **408**(2): p. 183-191.
66. Luo Y., Luo X. J., Yang Z. Y., Yu X. H., Yuan J. G., Chen S. J., and Mai B. X., *Studies on Heavy Metal Contamination by Improper Handling of E-Waste and Its Environmental Risk Evaluation Ⅱ Heavy Metal Contamination in Surface Soils on E -Waste Disassembling Workshops within Villages and the Adjacent Agricultural Soils*. Asian Journal of Ecotoxicology, 2008. 3(2): p. 123-129. (in Chinese)
67. Yang Y., Chen F., Zhang L., Liu J., Wu S., and Kang M., *Comprehensive assessment of heavy metal contamination in sediment of the Pearl River Estuary and adjacent shelf.* Marine Pollution Bulletin, 2012. **64**(9): p. 1947-1955.
68. Wen Z., Hui W., Rui Z., Yu X. Z., Qian P. Y., and Wong M. H., *Bacterial communities in PAH contaminated soils at an electronic-waste processing center in China.* Ecotoxicology, 2010. **19**(1): p. 96-104.
69. Yu X. Z., Gao Y., Wu S. C., Zhang H. B., Cheung K. C., and Wong M. H., *Distribution of polycyclic aromatic hydrocarbons in soils at Guiyu area of China, affected by recycling of electronic waste using primitive technologies.* Chemosphere, 2006. **65**(9): p. 1500-1509.
70. de Wit C. A., *An overview of brominated flame retardants in the environment.* Chemosphere, 2002. **46**(5): p. 583-624.
71. Yang Z. Z., Zhao X. R., Zhao Q., Qin Z. F., Qin X. F., Xu X. B., Jin Z. X., and Xu C. X., *Polybrominated Diphenyl Ethers in Leaves and Soil from Typical Electronic Waste Polluted Area in South China.* Bulletin of Environmental Contamination & Toxicology, 2008. **80**(4): p. 340-344.
72. Zhang X. L., Luo X. J., Liu H. Y., Yu L. H., Chen S. J., and Mai B. X., *Bioaccumulation of Several Brominated Flame Retardants and Dechlorane Plus in Waterbirds from an E-Waste Recycling Region in South China: Associated with Trophic Level and Diet Sources.* Environmental Science & Technology, 2011. **45**(2): p. 400-405.
73. Wang J., Chen S. J., Tian M., Ma Y. J., Luo X. J., and Mai B. X., *Polybrominated diphenyl ethers (PBDEs) in indoor and outdoor dust from an electronic waste (e-waste) recycling area in South China: contamination and human exposure.* Environmental Science (Huan Jing Ke Xue), 2010. **31**(1): p. 173-8.
74. Wong M. H., Wu S. C., Deng W. J., Yu X. Z., Luo Q., Leung A. O. W., Wong C. S. C., Luksemburg W. J., and Wong A. S., *Export of toxic chemicals - A review of the case of uncontrolled electronic-waste recycling.* Environmental Pollution, 2007. **149**(2): p. 131-140.
75. Shen C., Chen Y., Huang S., Wang Z., Yu C., Qiao M., Xu Y., Setty K., Zhang J., Zhu Y., and Lin Q., *Dioxin-like compounds in agricultural soils near e-waste recycling sites from Taizhou area,*

China: Chemical and bioanalytical characterization. Environment International, 2009. **35**(1): p. 50-55.

76. Hosoda J., Ofosu-Anim J., Sabi E. B., Akita L. G., Onwona-Agyeman S., Yamashita R., and Takada H., *Monitoring of organic micropollutants in Ghana by combination of pellet watch with sediment analysis: E-waste as a source of PCBs.* Marine Pollution Bulletin, 2014. **86**(1–2): p. 575-581.
77. Asante K. A., Agusa T., Biney C. A., Agyekum W. A., Bello M., Otsuka M., Itai T., Takahashi S., and Tanabe S., *Multi-trace element levels and arsenic speciation in urine of e-waste recycling workers from Agbogbloshie, Accra in Ghana.* Science of The Total Environment, 2012. **424**: p. 63-73.
78. Van Oostdam J., Gilman A., Dewailly E., Usher P., Wheatley B., Kuhnlein H., Neve S., Walker J., Tracy B., Feeley M., Jerome V., and Kwavnick B., *Human health implications of environmental contaminants in Arctic Canada: a review.* Science of The Total Environment, 1999. **230**(1–3): p. 1-82.
79. Ross G., *The public health implications of polychlorinated biphenyls (PCBs) in the environment.* Ecotoxicology and Environmental Safety, 2004. **59**(3): p. 275-291.
80. Agency for Toxic Substances and Disease Registry (ATSDR), *Toxicological profile for polychlorinated biphenyls (update)*, 2000, Agency for Toxic Substances and Disease Registry: Atlanta, GA, USA.
81. Gramatica P., Navas N., and Todeschini R., *3D-modelling and prediction by WHIM descriptors. Part 9. Chromatographic relative retention time and physico-chemical properties of polychlorinated biphenyls (PCBs).* Chemometrics and Intelligent Laboratory Systems, 1998. **40**(1): p. 53-63.
82. Lallas P. L., *The Stockholm Convention on persistent organic pollutants.* American Journal of International Law, 2001: p. 692-708.
83. Patil G. S., *Correlation of aqueous solubility and octanol-water partition coefficient based on molecular structure.* Chemosphere, 1991. **22**(8): p. 723-738.
84. Jones K. C. and de Voogt P., *Persistent organic pollutants (POPs): state of the science.* Environmental Pollution, 1999. **100**(1–3): p. 209-221.
85. Rogan W., Gladen B., Hung K., Koong S., Shih L., Taylor J., Wu Y., Yang D., Ragan N., and Hsu C., *Congenital poisoning by polychlorinated biphenyls and their contaminants in Taiwan.* Science, 1988. **241**(4863): p. 334-336.
86. Kuratsune M., Yoshimura T., Matsuzaka J., and Yamaguchi A., *Epidemiologic study on Yusho, a Poisoning Caused by Ingestion of Rice Oil Contaminated with a Commercial Brand of Polychlorinated Biphenyls.* Environmental Health Perspectives, 1972. **1**: p. 119-128.
87. Burse V. W., Kimbrough R. D., Villanueva E. C., Jennings R. W., Linder R. E., and Sovocool G. W., *Polychlorinated Biphenyls.* Archives of Environmental Health: An International Journal, 1974. **29**(6): p. 301-307.
88. Norback D. H. and Weltman R. H., *Polychlorinated biphenyl induction of hepatocellular carcinoma in the Sprague-Dawley rat.* Environmental Health Perspectives, 1985. **60**: p. 97-105.
89. Brown J. F., *Determination of PCB metabolic, excretion, and accumulation rates for use as indicators of biological response and relative risk.* Environmental Science & Technology, 1994. **28**(13): p. 2295-2305.
90. Mackay D. and Fraser A., *Bioaccumulation of persistent organic chemicals: mechanisms and*

models. Environmental Pollution, 2000. **110**(3): p. 375-391.

91. Campfens J. and Mackay D., *Fugacity-Based Model of PCB Bioaccumulation in Complex Aquatic Food Webs.* Environmental Science & Technology, 1997. **31**(2): p. 577-583.
92. Ayris S. and Harrad S., *The fate and persistence of polychlorinated biphenyls in soil.* Journal of Environmental Monitoring, 1999. **1**(4): p. 395-401.
93. Tucker E. S., Litschgi W. J., and Mees W. M., *Migration of polychlorinated biphenyls in soil induced by percolating water.* Bulletin of Environmental Contamination and Toxicology, 1975. **13**(1): p. 86-93.
94. Harrad S. J., Sewart A. P., Alcock R., Boumphrey R., Burnett V., Duarte-Davidson R., Halsall C., Sanders G., Waterhouse K., Wild S. R., and Jones K. C., *Polychlorinated biphenyls (PCBs) in the British environment: Sinks, sources and temporal trends.* Environmental Pollution, 1994. **85**(2): p. 131-146.
95. Harner T., Mackay D., and Jones K. C., *Model of the Long-Term Exchange of PCBs between Soil and the Atmosphere in the Southern U.K.* Environmental Science & Technology, 1995. **29**(5): p. 1200-1209.
96. Vasilyeva G. K., Strijakova E. R., Nikolaeva S. N., Lebedev A. T., and Shea P. J., *Dynamics of PCB removal and detoxification in historically contaminated soils amended with activated carbon.* Environmental Pollution, 2010. **158**(3): p. 770-777.
97. Brownawell B. J. and Farrington J. W., *Biogeochemistry of PCBs in interstitial waters of a coastal marine sediment.* Geochimica et Cosmochimica Acta, 1986. **50**(1): p. 157-169.
98. Zhou J. L. and Rowland S. J., *Evaluation of the interactions between hydrophobic organic pollutants and suspended particles in estuarine waters.* Water Research, 1997. **31**(7): p. 1708-1718.
99. Brown J., Wagner R., Bedard D., Brennan M., and Carnahan J., *PCB transformations in upper Hudson sediments.* Northeastern Environmental Science, 1984. **3**(3/4).
100. Lake J. L., Pruell R. J., and Osterman F. A., *An examination of dechlorination processes and pathways in New Bedford Harbor sediments.* Marine Environmental Research, 1992. **33**(1): p. 31-47.
101. Wells D. E., *Chapter 4 Current Developments In The Analysis Of Polychlorinated Biphenyls (PCBs) Including Planar And Other Toxic Metabolites In Environmental Matrices*, in *Techniques and Instrumentation in Analytical Chemistry*, D. Barceló, Editor. 1993, Elsevier. p. 113-148.
102. Konat J. and Kowalewska G., *Polychlorinated biphenyls (PCBs) in sediments of the southern Baltic Sea — trends and fate.* Science of The Total Environment, 2001. **280**(1–3): p. 1-15.
103. US Environmental Protection Agency (USEPA), *Final National Priorities List (NPL) sites as of July 31, 2000.*, 2000, US Environmental Protection Agency Office of Emergency and Remedial Response: Washington, DC.
104. Brown M. P., Werner M. B., Sloan R. J., and Simpson K. W., *Polychlorinated biphenyls in the Hudson River.* Environmental Science & Technology, 1985. **19**(8): p. 656-661.
105. Cachada A., Lopes L. V., Hursthouse A. S., Biasioli M., Grčman H., Otabbong E., Davidson C. M., and Duarte A. C., *The variability of polychlorinated biphenyls levels in urban soils from five European cities.* Environmental Pollution, 2009. **157**(2): p. 511-518.
106. Motelay-Massei A., Ollivon D., Garban B., Teil M. J., Blanchard M., and Chevreuil M., *Distribution and spatial trends of PAHs and PCBs in soils in the Seine River basin, France.* Chemosphere, 2004. **55**(4): p. 555-565.

107. Falandysz J., Brudnowska B., Kawano M., and Wakimoto T., *Polychlorinated Biphenyls and Organochlorine Pesticides in Soils from the Southern Part of Poland.* Archives of Environmental Contamination and Toxicology, 2001. **40**(2): p. 173-178.

108. Fromme H., Otto T., Pilz K., and Neugebauer F., *Levels of synthetic musks; Bromocyclene and PCBs in eel (anguilla anguilla) and PCBs in sediment samples from some waters of Berlin / Germany.* Chemosphere, 1999. **39**(10): p. 1723-1735.

109. Brown D. W., McCain B. B., Horness B. H., Sloan C. A., Tilbury K. L., Pierce S. M., Burrows D. G., Chan S. L., Landahl J. T., and Krahn M. M., *Status, correlations and temporal trends of chemical contaminants in fish and sediment from selected sites on the Pacific Coast of the USA.* Marine Pollution Bulletin, 1998. **37**(1–2): p. 67-85.

110. Piazza R., Ruiz-Fernández A. C., Frignani M., Zangrando R., Bellucci L. G., Moret I., and Páez-Osuna F., *PCBs and PAHs in surficial sediments from aquatic environments of Mexico City and the coastal states of Sonora, Sinaloa, Oaxaca and Veracruz (Mexico).* Environmental Geology, 2008. **54**(7): p. 1537-1545.

111. Wilcke W. and Amelung W., *Persistent Organic Pollutants in Native Grassland Soils along a Climosequence in North America.* Soil Science Society of America Journal, 2000. **64**(6): p. 2140-2148.

112. Man Y. B., Lopez B. N., Wang H. S., Leung A. O. W., Chow K. L., and Wong M. H., *Cancer risk assessment of polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) in former agricultural soils of Hong Kong.* Journal of Hazardous Materials, 2011. **195**: p. 92-99.

113. Mamontova E. A., Mamontov A. A., Tarasova E. N., Kuzmin M. I., Ganchimeg D., Khomutova M. Y., Gombosuren O., and Ganjuurjav E., *Polychlorinated biphenyls in surface soil in urban and background areas of Mongolia.* Environmental Pollution, 2013. **182**: p. 424-429.

114. Park S. K., Kim K. S., Kim J. G., *Concentration Distribution of PCBs in Soil Around Industrial Complex and Relationship with PCBs Sources.* Journal of Korean Society of Environmental Engineers, 2007. **29**(5): p. 521-527.

115. Salt D. E., Blaylock M., Kumar N., Dushenkov V., Ensley B. D., Chet I., and Raskin I., *Phytoremediation - A Novel Strategy For The Removal Of Toxic Metals From The Environment Using Plants.* Bio-Technology, 1995. **13**(5): p. 468-474.

116. Pilon-Smits E., *Phytoremediation.* Annual Review of Plant Biology, 2005. **56**(1): p. 15-39.

117. Raskin I. and Ensley B. D., *Phytoremediation of toxic metals : using plants to clean up the environment*. 2000: John Wiley.

118. Baker A. J. M., McGrath S. P., Sidoli C. M. D., and Reeves R. D., *Environmental biotechnology in waste treatment and recycling The possibility of in situ heavy metal decontamination of polluted soils using crops of metal-accumulating plants.* Resources, Conservation and Recycling, 1994. **11**(1): p. 41-49.

119. Cunningham S. D., Berti W. R., and Huang J. W., *Phytoremediation of contaminated soils.* Trends in Biotechnology, 1995. **13**(9): p. 393-397.

120. van Gestel C. A. M., *Physico-chemical and biological parameters determine metal bioavailability in soils.* Science of The Total Environment, 2008. **406**(3): p. 385-395.

121. Chen Y., Tang X., Cheema S. A., Liu W., and Shen C., *β-cyclodextrin enhanced phytoremediation of aged PCBs-contaminated soil from e-waste recycling area.* Journal of Environmental Monitoring, 2010. **12**: p. 1482-1489.

122. Qin H., Brookes P. C., and Xu J., *Cucurbita spp. and Cucumis sativus enhance the dissipation of*

polychlorinated biphenyl congeners by stimulating soil microbial community development. Environmental Pollution, 2014. **184**: p. 306-312.

123. Singer A. C., Smith D., Jury W. A., Hathuc K., and Crowley D. E., *Impact of the plant rhizosphere and augmentation on remediation of polychlorinated biphenyl contaminated soil.* Environmental Toxicology and Chemistry, 2003. **22**(9): p. 1998-2004.

124. Martina M., Petra P., Petr S., Edita R., Ondrej U., Katarina B., Jan R., Veronika K., Katerina D., and Tomas M., *Phyto/rhizoremediation studies using long-term PCB-contaminated soil.* Environmental Science & Pollution Research, 2009. **16**(7): p. 817-829.

125. Dipierro N., Mondelli D., Paciolla C., Brunetti G., and Dipierro S., *Changes in the ascorbate system in the response of pumpkin (Cucurbita pepo L.) roots to aluminium stress.* Journal of Plant Physiology, 2005. **162**(5): p. 529-536.

126. An Y., Kim Y., Kwon T., and Jeong S., *Combined effect of copper, cadmium, and lead upon Cucumis sativus growth and bioaccumulation.* Science of The Total Environment, 2004. **326**(1–3): p. 85-93.

127. Acar Y. B., Gale R. J., Alshawabkeh A. N., Marks R. E., Puppala S., Bricka M., and Parker R., *Electrokinetic remediation: Basics and technology status.* Journal of Hazardous Materials, 1995. **40**(2): p. 117-137.

128. 樊广萍，仓龙，徐慧，周东美，周立祥，*重金属-有机复合污染土壤的电动强化修复研究.* 农业环境科学学报，2010. **29**(6)：p. 1098-1104.

129. Li T., Yuan S., Wan J., Lin L., Long H., Wu X., and Lu X., *Pilot-scale electrokinetic movement of HCB and Zn in real contaminated sediments enhanced with hydroxypropyl-[beta]-cyclodextrin.* Chemosphere, 2009. **76**(9): p. 1226-1232.

130. Li T., Yuan S., Wan J., and Lu X., *Hydroxypropyl-[beta]-cyclodextrin enhanced electrokinetic remediation of sediment contaminated with HCB and heavy metals.* Journal of Hazardous Materials, 2010. **176**(1-3): p. 306-312.

131. Dermont G., Bergeron M., Mercier G., and Richer-Laflèche M., *Soil washing for metal removal: A review of physical/chemical technologies and field applications.* Journal of Hazardous Materials, 2008. **152**(1): p. 1-31.

132. Trellu C., Mousset E., Pechaud Y., Huguenot D., van Hullebusch E. D., Esposito G., and Oturan M. A., *Removal of hydrophobic organic pollutants from soil washing/flushing solutions: A critical review.* Journal of Hazardous Materials, 2016. **306**: p. 149-174.

133. Reed B. E., Carriere P. C., and Moore R., *Flushing of a Pb(II) contaminated soil using HCl, EDTA, and* $CaCl_2$*.* Journal of Environmental Engineering, 1996. **122**(1): p. 48-50.

134. Norvell W. A., *Comparison of Chelating Agents as Extractants for Metals in Diverse Soil Materials1.* Soil Science Society of America Journal, 1984. **48**(6).

135. West C. C. and Harwell J. H., *Surfactants and subsurface remediation.* Environmental Science & Technology, 1992. **26**(12): p. 2324-2330.

136. Rosen M. J., *Surfactants and interfacial phenomena / Milton J. Rosen.* Surfactants & Interfacial Phenomena, 1989(June).

137. Chang S., Wang K., Kuo C., Chang C., and Chou C., *Remediation of metal-contaminated soil by an integrated soil washing.* Soil & Sediment Contamination An International Journal, 2005. **14**(6): p. 559-569.

138. Mulligan C. N., Yong R. N., Gibbs B. F., James S., and Bennett H. P. J., *Metal Removal from Contaminated Soil and Sediments by the Biosurfactant Surfactin.* Environmental Science &

Technology, 1999. **33**: p. 3812-3820.

139. Song S., Zhu L., and Zhou W., *Simultaneous removal of phenanthrene and cadmium from contaminated soils by saponin, a plant-derived biosurfactant.* Environmental Pollution, 2008. **156**(3): p. 1368-1370.
140. Ager P. and Marshall W. D., *Recycle of thermomechanical pulp filtrate after the removal of metals: A study with EDTA.* Journal of Pulp and Paper Science, 2003. **29**(9): p. 303-307.
141. Zeng Q. R., Sauvé S., Allen H. E., and Hendershot W. H., *Recycling EDTA solutions used to remediate metal-polluted soils.* Environmental Pollution, 2005. **133**(2): p. 225-231.
142. Mouton J., Mercier G., and Blais J. F., *Amphoteric Surfactants for PAH and Lead Polluted-Soil Treatment Using Flotation.* Water Air & Soil Pollution, 2009. **197**(1-4): p. 381-393.
143. Khodadoust A. P., Reddy K. R., and Maturi K., *Effect of different extraction agents on metal and organic contaminant removal from a field soil.* Journal of Hazardous Materials, 2005. **117**(1): p. 15-24.
144. Zhang W., Tsang D. C. W., and Lo I. M. C., *Removal of Pb and MDF from contaminated soils by EDTA- and SDS-enhanced washing.* Chemosphere, 2007. **66**(11): p. 2025-2034.
145. Zhang W. X., *Nanoscale Iron Particles for Environmental Remediation: An Overview.* Journal of Nanoparticle Research, 2003. **5**(3-4): p. 323-332.
146. Zhu L., Lin H., Qi J., Xu X., and Qi H., *Effect of H_2 on reductive transformation of p-ClNB in a combined ZVI–anaerobic sludge system.* Water Research, 2012. **46**(19): p. 6291-6299.
147. Agrawal A. and Tratnyek P. G., *Reduction of Nitro Aromatic Compounds by Zero-Valent Iron Metal.* Environmental Science & Technology, 1996. **30**(1): p. 153-160.
148. Matheson L. J. and Tratnyek P. G., *Reductive Dehalogenation of Chlorinated Methanes by Iron Metal.* Environmental Science & Technology, 1994. **28**(12): p. 2045-2053.
149. Li H., Wan J., Ma Y., Wang Y., and Huang M., *Influence of particle size of zero-valent iron and dissolved silica on the reactivity of activated persulfate for degradation of acid orange 7.* Chemical Engineering Journal, 2014. **237**: p. 487-496.
150. 邱心泓，方战强， *修饰型纳米零价铁降解有机卤化物的研究．* 化学进展， 2010. **22**(0203)： p. 291-297.
151. Guan X., Sun Y., Qin H., Li J., Lo I. M. C., He D., and Dong H., *The limitations of applying zero-valent iron technology in contaminants sequestration and the corresponding countermeasures: The development in zero-valent iron technology in the last two decades (1994–2014).* Water Research, 2015. **75**: p. 224-248.
152. Zhuang Y., Ahn S., and Luthy R. G., *Debromination of Polybrominated Diphenyl Ethers by Nanoscale Zerovalent Iron: Pathways, Kinetics, and Reactivity.* Environmental Science & Technology, 2010. **44**(21): p. 8236-8242.
153. Xu Y. and Zhang W., *Subcolloidal Fe/Ag Particles for Reductive Dehalogenation of Chlorinated Benzenes.* Industrial & Engineering Chemistry Research, 2000. **39**(7): p. 2238-2244.
154. Lowry G. V. and Johnson K. M., *Congener-Specific Dechlorination of Dissolved PCBs by Microscale and Nanoscale Zerovalent Iron in a Water/Methanol Solution.* Environmental Science & Technology, 2004. **38**(19): p. 5208-5216.
155. Fang Z. Q., Qiu X. Q., Chen J. H., and Qiu X. H., *Debromination of polybrominated diphenyl ethers by Ni/Fe bimetallic nanoparticles: Influencing factors, kinetics, and mechanism.* Journal of Hazardous Materials, 2011. **185**(2–3): p. 958-969.
156. Gunawardana B., Singhal N., and Swedlund P. *Dechlorination of pentachlorophenol by zero*

valent iron and bimetals: effect of surface characteristics and bimetal preparation procedure. in *Proceedings of the Annual International Conference on Soils, Sediments, Water and Energy*. 2012.

157. Liang D., Yang Y., Xu W., Peng S., Lu S., and Xiang Y., *Nonionic surfactant greatly enhances the reductive debromination of polybrominated diphenyl ethers by nanoscale zero-valent iron: Mechanism and kinetics.* Journal of Hazardous Materials, 2014. **278**: p. 592-596.
158. Tratnyek P. G., Scherer M. M., Deng B., and Hu S., *Effects of Natural Organic Matter, Anthropogenic Surfactants, and Model Quinones on the Reduction of Contaminants by Zero-Valent Iron.* Water Research, 2001. **35**(18): p. 4435-4443.
159. Alessi D. S. and Li Z., *Synergistic effect of cationic surfactants on perchloroethylene degradation by zero-valent iron.* Environmental Science & Technology, 2001. **35**(18): p. 3713-3717.
160. Zhang P., Tao X., Li Z., and Bowman R. S., *Enhanced Perchloroethylene Reduction in Column Systems Using Surfactant-Modified Zeolite/Zero-Valent Iron Pellets.* Environmental Science & Technology, 2002. **36**(16): p. 3597-3603.
161. Li Z., Willms C., Alley J., Zhang P., and Bowman R. S., *A shift in pathway of iron-mediated perchloroethylene reduction in the presence of sorbed surfactant—A column study.* Water Research, 2006. **40**(20): p. 3811-3819.
162. Cho H. H. and Park J. W., *Sorption and reduction of tetrachloroethylene with zero valent iron and amphiphilic molecules.* Chemosphere, 2006. **64**(6): p. 1047-1052.
163. Zhang M., He F., Zhao D., and Hao X., *Degradation of soil-sorbed trichloroethylene by stabilized zero valent iron nanoparticles: Effects of sorption, surfactants, and natural organic matter.* Water Research, 2011. **45**(7): p. 2401-2414.
164. Zhu B. W., Lim T. T., and Feng J., *Influences of Amphiphiles on Dechlorination of a Trichlorobenzene by Nanoscale Pd/Fe: Adsorption, Reaction Kinetics, and Interfacial Interactions.* Environmental Science & Technology, 2008. **42**(12): p. 4513-4519.
165. Loraine G. A., *Effects of alcohols, anionic and nonionic surfactants on the reduction of pce and tce by zero-valent iron.* Water Research, 2001. **35**(6): p. 1453-1460.
166. Bizzigotti G. O., Reynolds D. A., and Kueper B. H., *Enhanced Solubilization and Destruction of Tetrachloroethylene by Hydroxypropyl-β-cyclodextrin and Iron.* Environmental Science & Technology, 1997. **31**(2): p. 472-478.
167. Zhang Z., Cissoko N., Wo J., and Xu X., *Factors influencing the dechlorination of 2,4-dichlorophenol by Ni–Fe nanoparticles in the presence of humic acid.* Journal of Hazardous Materials, 2009. **165**(1–3): p. 78-86.
168. Johnson T. L., Fish W., Gorby Y. A., and Tratnyek P. G., *Degradation of carbon tetrachloride by iron metal: Complexation effects on the oxide surface.* Journal of Contaminant Hydrology, 1998. **29**(4): p. 379-398.
169. Doong R. A. and Lai Y. J., *Dechlorination of tetrachloroethylene by palladized iron in the presence of humic acid.* Water Research, 2005. **39**(11): p. 2309-2318.
170. Doong R. A. and Lai Y. L., *Effect of metal ions and humic acid on the dechlorination of tetrachloroethylene by zerovalent iron.* Chemosphere, 2006. **64**(3): p. 371-378.
171. Dong T., Luo H., Wang Y., Hu B., and Chen H., *Stabilization of Fe–Pd bimetallic nanoparticles with sodium carboxymethyl cellulose for catalytic reduction of para-nitrochlorobenzene in water.* Desalination, 2011. **271**(1–3): p. 11-19.
172. Arnold W. A. and Roberts A. L., *Pathways and Kinetics of Chlorinated Ethylene and Chlorinated*

Acetylene Reaction with Fe(0) Particles. Environmental Science & Technology, 2000. **34**(9): p. 1794-1805.

173. Tan L., Liang B., Fang Z., Xie Y., and Tsang E., *Effect of humic acid and transition metal ions on the debromination of decabromodiphenyl by nano zero-valent iron: kinetics and mechanisms.* Journal of Nanoparticle Research, 2014. **16**(12): p. 1-13.
174. Chiou C. T., Malcolm R. L., Brinton T. I., and Kile D. E., *Water solubility enhancement of some organic pollutants and pesticides by dissolved humic and fulvic acids.* Environmental Science & Technology, 1986. **20**(5): p. 502-508.
175. Tsang D. C. W., Graham N. J. D., and Lo I. M. C., *Humic acid aggregation in zero-valent iron systems and its effects on trichloroethylene removal.* Chemosphere, 2009. **75**(10): p. 1338-1343.
176. Feng J., Zhu B. W., and Lim T. T., *Reduction of chlorinated methanes with nano-scale Fe particles: Effects of amphiphiles on the dechlorination reaction and two-parameter regression for kinetic prediction.* Chemosphere, 2008. **73**(11): p. 1817-1823.
177. Wang Y., Zhou D., Wang Y., Wang L., and Cang L., *Automatic pH control system enhances the dechlorination of 2,4,4′-trichlorobiphenyl and extracted PCBs from contaminated soil by nanoscale Fe0 and Pd/Fe0.* Environmental Science and Pollution Research, 2012. **19**(2): p. 448-457.
178. Dong J., Zhao Y., Zhao R., and Zhou R., *Effects of pH and particle size on kinetics of nitrobenzene reduction by zero-valent iron.* Journal of Environmental Sciences, 2010. **22**(11): p. 1741-1747.
179. Yuan S., Wen H., Wu X., Chen J., and Wang L., *Effect of nonionic and cationic surfactants on the dechlorination kinetics and products distribution of various polychlorinated benzenes by Cu/Fe particles.* Separation and Purification Technology, 2010. **74**(1): p. 130-137.
180. Gillham R. W. and O'Hannesin S. F., *Enhanced degradation of halogenated aliphatics by zero‐valent iron.* Groundwater, 1994. **32**(6): p. 958-967.
181. Fennelly J. P. and Roberts A. L., *Reaction of 1,1,1-Trichloroethane with Zero-Valent Metals and Bimetallic Reductants.* Environmental Science & Technology, 1998. **32**(13): p. 1980-1988.
182. Farrell J., Kason M., Melitas N., and Li T., *Investigation of the Long-Term Performance of Zero-Valent Iron for Reductive Dechlorination of Trichloroethylene.* Environmental Science & Technology, 2000. **34**(3): p. 514-521.
183. Zhuang Y., Ahn S., Seyfferth A. L., Masue-Slowey Y., Fendorf S., and Luthy R. G., *Dehalogenation of Polybrominated Diphenyl Ethers and Polychlorinated Biphenyl by Bimetallic, Impregnated, and Nanoscale Zerovalent Iron.* Environmental Science & Technology, 2011. **45**(11): p. 4896-4903.
184. Son A., Lee J., Chiu P. C., Kim B. J., and Cha D. K., *Microbial reduction of perchlorate with zero-valent iron.* Water Research, 2006. **40**(10): p. 2027-2032.
185. Rysavy J. P., Yan T., and Novak P. J., *Enrichment of anaerobic polychlorinated biphenyl dechlorinators from sediment with iron as a hydrogen source.* Water Research, 2005. **39**(4): p. 569-578.
186. Yu X., Amrhein C., Deshusses M. A., and Matsumoto M. R., *Perchlorate Reduction by Autotrophic Bacteria in the Presence of Zero-Valent Iron.* Environmental Science & Technology, 2006. **40**(4): p. 1328-1334.
187. Zhu L., Jin J., Lin H., Gao K., and Xu X., *Succession of microbial community and enhanced mechanism of a ZVI-based anaerobic granular sludge process treating chloronitrobenzenes wastewater.* Journal of Hazardous Materials, 2015. **285**: p. 157-166.

188. Mueller N. C. and Nowack B., *Nanoparticles for Remediation: Solving Big Problems with Little Particles.* Elements, 2010. **6**(6): p. 395-400.

189. Gomes H. I., Dias-Ferreira C., and Ribeiro A. B., *Overview of in situ and ex situ remediation technologies for PCB-contaminated soils and sediments and obstacles for full-scale application.* Science of The Total Environment, 2013. **445–446**: p. 237-260.

190. Higgins M. R. and Olson T. M., *Life-cycle case study comparison of permeable reactive barrier versus pump-and-treat remediation.* Environmental science & technology, 2009. **43**(24): p. 9432-9438.

191. Wilkin R. T., Puls R. W., and Sewell G. W., *Long-Term Performance of Permeable Reactive Barriers Using Zero-Valent Iron: Geochemical and Microbiological Effects.* Ground Water, 2003. **41**(4): p. 493-503.

192. Scherer M. M., Richter S., Valentine R. L., and Alvarez P. J. J., *Chemistry and Microbiology of Permeable Reactive Barriers for In Situ Groundwater Clean up.* Critical Reviews in Microbiology, 2000. **26**(4): p. 221-264.

193. Phillips D. H., Nooten T. V., Bastiaens L., Russell M. I., Dickson K., Plant S., Ahad J. M. E., Newton T., Elliot T., and Kalin R. M., *Ten Year Performance Evaluation of a Field-Scale Zero-Valent Iron Permeable Reactive Barrier Installed to Remediate Trichloroethene Contaminated Groundwater.* Environmental Science & Technology, 2010. **44**(10): p. 3861-3869.

194. Henderson A. D. and Demond A. H., *Long-Term Performance of Zero-Valent Iron Permeable Reactive Barriers: A Critical Review.* Environmental Engineering Science, 2007. **24**(4): p. 401-423.

195. Gavaskar A., Tatar L., and Condit W., *Cost and performance report nanoscale zero-valent iron technologies for source remediation*, 2005, DTIC Document.

196. Hara S. O., Krug T., Quinn J., Clausen C., and Geiger C., *Field and laboratory evaluation of the treatment of DNAPL source zones using emulsified zero-valent iron.* Remediation Journal, 2006. **16**(2): p. 35-56.

197. Satapanajaru T., Anurakpongsatorn P., Pengthamkeerati P., and Boparai H., *Remediation of Atrazine-contaminated Soil and Water by Nano Zerovalent Iron.* Water, Air, and Soil Pollution, 2008. **192**(1-4): p. 349-359.

198. He F., Zhao D., and Paul C., *Field assessment of carboxymethyl cellulose stabilized iron nanoparticles for in situ destruction of chlorinated solvents in source zones.* Water Research, 2010. **44**(7): p. 2360-2370.

199. Varanasi P., Fullana A., and Sidhu S., *Remediation of PCB contaminated soils using iron nano-particles.* Chemosphere, 2007. **66**(6): p. 1031-1038.

200. Olson M. R., Sale T. C., Shackelford C. D., Bozzini C., and Skeean J., *Chlorinated Solvent Source-Zone Remediation via ZVI-Clay Soil Mixing: 1-Year Results.* Ground Water Monitoring & Remediation, 2012. **32**(3): p. 63-74.

201. Shackelford C. D., Sale T. C., and Liberati M. R., *In-Situ Remediation of Chlorinated Solvents using Zero Valent Iron and Clay Mixtures: A Case History*, in *Waste Containment and Remediation*. 2005. p. 1-9.

202. Shea P. J., Machacek T. A., and Comfort S. D., *Accelerated remediation of pesticide-contaminated soil with zerovalent iron.* Environmental Pollution, 2004. **132**(2): p. 183-188.

203. Liu H., Zhou Q., Wang Y., Zhang Q., Cai Z., and Jiang G., *E-waste recycling induced polybrominated diphenyl ethers, polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins*

and dibenzo-furans pollution in the ambient environment. Environment International, 2008. **34**(1): p. 67-72.

204. Ministry of Housing S. P. A. E., The Netherlands (MHSPEN), *Dutch Target and Intervention Values (the new Dutch list)*, in *ANNEXES Circular on target values and intervention values for soil remediation*2000, Department of soil protection, MHSPEN: Hague.

205. Zhang K., Schnoor J. L., and Zeng E. Y., *E-Waste Recycling: Where Does It Go from Here?* Environmental Science & Technology, 2012. **46**(20): p. 10861-10867.

206. Ministry of Environmental Protection P. R. C., *Environmental quantity standard for soils [S]*, 1995.

207. Li Y., Huo X., Liu J., Peng L., Li W., and Xu X., *Assessment of cadmium exposure for neonates in Guiyu, an electronic waste pollution site of China.* Environmental Monitoring and Assessment, 2011. **177**(1-4): p. 343-351.

208. Wong C. S. C., Duzgoren-Aydin N. S., Aydin A., and Wong M. H., *Evidence of excessive releases of metals from primitive e-waste processing in Guiyu, China.* Environmental Pollution, 2007. **148**(1): p. 62-72.

209. Gotlieb I., Bozzelli J. W., and Gotlieb E., *Soil and Water Decontaminaton by Extraction with Surfactants.* Separation Science and Technology, 1993. **28**(1-3): p. 793-804.

210. Oma K. H., Clarke A. N., Megehee M. M., and Wilson D. J., *Soil Clean-Up by Surfactant Washing. III. Design and Evaluation of the Integrated Pilot-Scale Surfactant Recycle System.* Separation Science and Technology, 1993. **28**(15-16): p. 2319-2349.

211. Delgado-Moreno L., Wu L., and Gan J., *Effect of Dissolved Organic Carbon on Sorption of Pyrethroids to Sediments.* Environmental Science & Technology, 2010. **44**(22): p. 8473-8478.

212. Lee M., Kang H., and Do W., *Application of nonionic surfactant-enhanced in situ flushing to a diesel contaminated site.* Water Research, 2005. **39**(1): p. 139-146.

213. Mulligan C. N., Yong R. N., and Gibbs B. F., *Surfactant-enhanced remediation of contaminated soil: a review.* Engineering Geology, 2001. **60**(1–4): p. 371-380.

214. Mulligan C. N., Yong R. N., and Gibbs B. F., *Heavy metal removal from sediments by biosurfactants.* Journal of Hazardous Materials, 2001. **85**(1–2): p. 111-125.

215. USEPA. *Comprehensive Environmental Response, Compensation, and Liability Act Information System (CERCLIS)*. 2003; Available from: http://www.epa.gov/superfund/sites/cursites/.

216. Shih Y. H., Chen Y. C., Chen M. Y., Tai Y. T., and Tso C. P., *Dechlorination of hexachlorobenzene by using nanoscale Fe and nanoscale Pd/Fe bimetallic particles.* Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2009. **332**(2–3): p. 84-89.

217. Lim D. H. and Lastoskie C. M., *Density Functional Theory Studies on the Relative Reactivity of Chloroethenes on Zerovalent Iron.* Environmental Science & Technology, 2009. **43**(14): p. 5443-5448.

218. He N., Li P., Zhou Y., Ren W., Fan S., and Verkhozina V. A., *Catalytic dechlorination of polychlorinated biphenyls in soil by palladium–iron bimetallic catalyst.* Journal of Hazardous Materials, 2009. **164**(1): p. 126-132.

219. Wang Q., Cissoko N., Zhou M., and Xu X., *Effects and mechanism of humic acid on chromium(VI) removal by zero-valent iron (Fe0) nanoparticles.* Physics and Chemistry of the Earth, Parts A/B/C, 2011. **36**(9–11): p. 442-446.

220. Torres L. G., Lopez R. B., and Beltran M., *Removal of As, Cd, Cu, Ni, Pb, and Zn from a highly contaminated industrial soil using surfactant enhanced soil washing.* Physics and Chemistry of

the Earth, Parts A/B/C, 2012. **37–39**: p. 30-36.

221. Gómez J., Alcántara M. T., Pazos M., and Sanromán M. Á., *Soil washing using cyclodextrins and their recovery by application of electrochemical technology.* Chemical Engineering Journal, 2010. **159**(1–3): p. 53-57.

222. López-Vizcaíno R., Sáez C., Cañizares P., and Rodrigo M. A., *The use of a combined process of surfactant-aided soil washing and coagulation for PAH-contaminated soils treatment.* Separation and Purification Technology, 2012. **88**(0): p. 46-51.

223. Shiu W. Y. and Mackay D., *A Critical Review of Aqueous Solubilities, Vapor Pressures, Henry's Law Constants, and Octanol–Water Partition Coefficients of the Polychlorinated Biphenyls.* Journal of Physical and Chemical Reference Data, 1986. **15**(2): p. 911-929.

224. Alonso F., Beletskaya I. P., and Yus M., *Metal-Mediated Reductive Hydrodehalogenation of Organic Halides.* Chemical Reviews, 2002. **102**(11): p. 4009-4092.

225. Wang C. B. and Zhang W. X., *Synthesizing Nanoscale Iron Particles for Rapid and Complete Dechlorination of TCE and PCBs.* Environmental Science & Technology, 1997. **31**(7): p. 2154-2156.

226. Wu L. and Ritchie S. M. C., *Removal of trichloroethylene from water by cellulose acetate supported bimetallic Ni/Fe nanoparticles.* Chemosphere, 2006. **63**(2): p. 285-292.

227. Cheng S. F. and Wu S. C., *The enhancement methods for the degradation of TCE by zero-valent metals.* Chemosphere, 2000. **41**(8): p. 1263-1270.

228. Cwiertny D. M., Bransfield S. J., Livi K. J. T., Fairbrother D. H., and Roberts A. L., *Exploring the Influence of Granular Iron Additives on 1,1,1-Trichloroethane Reduction.* Environmental Science & Technology, 2006. **40**(21): p. 6837-6843.

229. Ko S. O., Lee D. H., and Kim Y. H., *Kinetic Studies of Reductive Dechlorination of Chlorophenols with NI/FE Bimetallic Particles.* Environmental Technology, 2007. **28**(5): p. 583-594.

230. Zheng Z., Yuan S., Liu Y., Lu X., Wan J., Wu X., and Chen J., *Reductive dechlorination of hexachlorobenzene by Cu/Fe bimetal in the presence of nonionic surfactant.* Journal of Hazardous Materials, 2009. **170**(2–3): p. 895-901.

231. Shih Y. H., Chen M. Y., and Su Y. F., *Pentachlorophenol reduction by Pd/Fe bimetallic nanoparticles: Effects of copper, nickel, and ferric cations.* Applied Catalysis B: Environmental, 2011. **105**(1–2): p. 24-29.

232. Zhu N., Luan H., Yuan S., Chen J., Wu X., and Wang L., *Effective dechlorination of HCB by nanoscale Cu/Fe particles.* Journal of Hazardous Materials, 2010. **176**(1–3): p. 1101-1105.

233. Bransfield S. J., Cwiertny D. M., Roberts A. L., and Fairbrother D. H., *Influence of Copper Loading and Surface Coverage on the Reactivity of Granular Iron toward 1,1,1-Trichloroethane.* Environmental Science & Technology, 2006. **40**(5): p. 1485-1490.

234. Shin M. C., Choi H. D., Kim D. H., and Baek K., *Effect of surfactant on reductive dechlorination of trichloroethylene by zero-valent iron.* Desalination, 2008. **223**(1–3): p. 299-307.

235. Harendra S. and Vipulanandan C., *Degradation of high concentrations of PCE solubilized in SDS and biosurfactant with Fe/Ni bi-metallic particles.* Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2008. **322**(1–3): p. 6-13.

236. Fang Z. Q., Qiu X. H., Chen J. H., and Qiu X. Q., *Degradation of the polybrominated diphenyl ethers by nanoscale zero-valent metallic particles prepared from steel pickling waste liquor.* Desalination, 2011. **267**(1): p. 34-41.

237. Lee C. C. and Doong R. A., *Dechlorination of Tetrachloroethylene in Aqueous Solutions Using*

Metal-Modified Zerovalent Silicon. Environmental Science & Technology, 2008. **42**(13): p. 4752-4757.

238. Holmes D. A., Harrison B. K., and Dolfing J., *Estimation of Gibbs free energies of formation for polychlorinated biphenyls.* Environmental Science & Technology, 1993. **27**(4): p. 725-731.

239. Woods S. L., Trobaugh D. J., and Carter K. J., *Polychlorinated Biphenyl Reductive Dechlorination by Vitamin B12s: Thermodynamics and Regiospecificity.* Environmental Science & Technology, 1999. **33**(6): p. 857-863.

240. Dorathi P. J. and Kandasamy P., *Dechlorination of chlorophenols by zero valent iron impregnated silica.* Journal of Environmental Sciences, 2012. **24**(4): p. 765-773.

241. Su C., Puls R. W., Krug T. A., Watling M. T., O'Hara S. K., Quinn J. W., and Ruiz N. E., *A two and half-year-performance evaluation of a field test on treatment of source zone tetrachloroethene and its chlorinated daughter products using emulsified zero valent iron nanoparticles.* Water Research, 2012. **46**(16): p. 5071-5084.

242. Farrell J., Melitas N., Kason M., and Li T., *Electrochemical and Column Investigation of Iron-Mediated Reductive Dechlorination of Trichloroethylene and Perchloroethylene.* Environmental Science & Technology, 2000. **34**(12): p. 2549-2556.

243. Yin W., Wu J., Li P., Wang X., Zhu N., Wu P., and Yang B., *Experimental study of zero-valent iron induced nitrobenzene reduction in groundwater: The effects of pH, iron dosage, oxygen and common dissolved anions.* Chemical Engineering Journal, 2012. **184**: p. 198-204.

244. Gu C., Jia H., Li H., Teppen B. J., and Boyd S. A., *Synthesis of Highly Reactive Subnano-Sized Zero-Valent Iron Using Smectite Clay Templates.* Environmental Science & Technology, 2010. **44**(11): p. 4258-4263.

245. Luo S., Qin P., Shao J., Peng L., Zeng Q., and Gu J. D., *Synthesis of reactive nanoscale zero valent iron using rectorite supports and its application for Orange II removal.* Chemical Engineering Journal, 2013. **223**: p. 1-7.

246. Shirin S. and Balakrishnan V. K., *Using Chemical Reactivity To Provide Insights into Environmental Transformations of Priority Organic Substances: The Fe0-Mediated Reduction of Acid Blue 129.* Environmental Science & Technology, 2011. **45**(24): p. 10369-10377.

247. Fu F., Dionysiou D. D., and Liu H., *The use of zero-valent iron for groundwater remediation and wastewater treatment: A review.* Journal of Hazardous Materials, 2014. **267**: p. 194-205.

248. Wu Y. X., Wu Z. H., Huang X. F., Simonnot M. O., Zhang T., and Qiu R. L., *Synergistical enhancement by Ni^{2+} and Tween-80 of nanoscale zerovalent iron dechlorination of 2,2′,5,5′-tetrachlorinated biphenyl in aqueous solution.* Environmental Science and Pollution Research, 2015. **22**(1): p. 555-564.

249. Lenore S. C., Arnold E. G., and Andrew D. E., *Standard methods for the examination of water and wastewater.* American Public Health Association. American Water Works Association and World Environment Federation. 20th Edition, Washington DC, 1998.

250. Paria S., *Surfactant-enhanced remediation of organic contaminated soil and water.* Advances in Colloid and Interface Science, 2008. **138**(1): p. 24-58.

251. Yuan S., Zheng Z., Meng X. Z., Chen J., and Wang L., *Surfactant mediated HCB dechlorination in contaminated soils and sediments by micro and nanoscale Cu/Fe Particles.* Geoderma, 2010. **159**(1–2): p. 165-173.

252. Kopinke F. D., Angeles-Wedler D., Fritsch D., and Mackenzie K., *Pd-catalyzed hydrodechlorination of chlorinated aromatics in contaminated waters—Effects of surfactants,*

organic matter and catalyst protection by silicone coating. Applied Catalysis B: Environmental, 2010. **96**(3–4): p. 323-328.

253. Tanaka S., Oba K., Fukushima M., Nakayasu K., and Hasebe K., *Water solubility enhancement of pyrene in the presence of humic substances.* Analytica Chimica Acta, 1997. **337**(3): p. 351-357.
254. Zhang T., Wu Y. X., Huang X. F., Liu J. M., Xia B., Zhang W. H., and Qiu R. L., *Simultaneous extraction of Cr(VI) and Cu(II) from humic acid with new synthesized EDTA derivatives.* Chemosphere, 2012. **88**(6): p. 730-735.
255. Chen J. L., Al-Abed S. R., Ryan J. A., and Li Z., *Effects of pH on dechlorination of trichloroethylene by zero-valent iron.* Journal of Hazardous Materials, 2001. **83**(3): p. 243-254.
256. Lee C. C. and Doong R. A., *Enhanced Dechlorination of Tetrachloroethylene by Zerovalent Silicon in the Presence of Polyethylene Glycol under Anoxic Conditions.* Environmental Science & Technology, 2011. **45**(6): p. 2301-2307.
257. Phillips D. H., Gu B., Watson D. B., Roh Y., Liang L., and Lee S. Y., *Performance Evaluation of a Zerovalent Iron Reactive Barrier: Mineralogical Characteristics.* Environmental Science & Technology, 2000. **34**(19): p. 4169-4176.
258. Roh Y., Lee S. Y., and Elless M. P., *Characterization of corrosion products in the permeable reactive barriers.* Environmental Geology, 2000. **40**(1-2): p. 184-194.
259. Wang X., Chen C., Chang Y., and Liu H., *Dechlorination of chlorinated methanes by Pd/Fe bimetallic nanoparticles.* Journal of Hazardous Materials, 2009. **161**(2–3): p. 815-823.
260. Cwiertny D. M., Bransfield S. J., and Roberts A. L., *Influence of the Oxidizing Species on the Reactivity of Iron-Based Bimetallic Reductants.* Environmental Science & Technology, 2007. **41**(10): p. 3734-3740.
261. Comba S., Di Molfetta A., and Sethi R., *A comparison between field applications of nano-, micro-, and millimetric zero-valent iron for the remediation of contaminated aquifers.* Water, Air, & Soil Pollution, 2011. **215**(1-4): p. 595-607.
262. Shin M. and Barrington S., *Effectiveness of the Iodide Ligand Along with two Surfactants on Desorbing Heavy Metals from Soils.* Water, Air, and Soil Pollution, 2005. **161**(1-4): p. 193-208.
263. Mulligan C. N., Yong R. N., Gibbs B. F., James S., and Bennett H. P. J., *Metal Removal from Contaminated Soil and Sediments by the Biosurfactant Surfactin.* Environmental Science & Technology, 1999. **33**(21): p. 3812-3820.
264. Bergström L. M., *Explaining the growth behavior of surfactant micelles.* Journal of Colloid and Interface Science, 2015. **440**: p. 109-118.
265. Liu T., Tsang D. C. W., and Lo I. M. C., *Chromium(VI) Reduction Kinetics by Zero-Valent Iron in Moderately Hard Water with Humic Acid: Iron Dissolution and Humic Acid Adsorption.* Environmental Science & Technology, 2008. **42**(6): p. 2092-2098.
266. Tipping E., *Cation binding by humic substances*. Vol. 12. 2002: Cambridge University Press.
267. Yang K., Zhu L., and Xing B., *Enhanced Soil Washing of Phenanthrene by Mixed Solutions of TX100 and SDBS.* Environmental Science & Technology, 2006. **40**(13): p. 4274-4280.
268. Yuan S., Shu Z., Wan J., and Lu X., *Enhanced desorption of hexachlorobenzene from kaolin by single and mixed surfactants.* Journal of Colloid and Interface Science, 2007. **314**(1): p. 167-175.
269. Hawker D. W. and Connell D. W., *Octanol-water partition coefficients of polychlorinated biphenyl congeners.* Environmental Science & Technology, 1988. **22**(4): p. 382-387.
270. Higson F. K., *Microbial degradation of biphenyl and its derivatives*, in *Adv Appl Microbiol*1992.

p. 135-64.

271. Kim Y. H., Shin W. S., and Ko S. O., *Reductive Dechlorination of Chlorinated Biphenyls by Palladized Zero-Valent Metals.* Journal of Environmental Science and Health, Part A, 2004. **39**(5): p. 1177-1188.

272. Kim D. G., Hwang Y. H., Shin H. S., and Ko S. O., *Humic acid characteristics and effects on the reactivity of nano-scale zero-valent iron particles during nitrate reduction.* Desalination and Water Treatment, 2012. **49**(1-3): p. 147-156.

273. Wan J., Wang L., Lu X., Lin Y., and Zhang S., *Partitioning of hexachlorobenzene in a kaolin/humic acid/surfactant/water system: Combined effect of surfactant and soil organic matter.* Journal of Hazardous Materials, 2011. **196**: p. 79-85.

Remédiation de sédiment contaminé par des polychlorobiphényls par déchloration réductive au fer zérovalent assistée par tensioactif

Résumé : La contamination des sols et sédiments par les polychlorobiphényls (PCB) pose un problème sanitaire et environnemental à l'échelle mondiale, en raison de la récalcitrance et de la toxicité de ces composés. L'objectif de cette thèse est de chercher un procédé de remédiation de sédiments contaminés aux PCB en utilisant le fer zérovalent (Fe^0). D'abord, une campagne de prélèvement a été menée sur des sites contaminés par le recyclage des déchets électroniques en Chine du sud. La contamination en PCB n'était pas aussi forte que prévue, mais la présence de métaux lourds accentue la difficulté de la remédiation. Ensuite, a été étudiée la déchloration des PCB par le Fe^0 en solution aqueuse, en présence de métaux et surfactants. Les résultats ont montré la déchloration progressive des PCB et révélé l'itinéraire réactionnel avec la spécificité des congénères et la régio-spécificité. L'importance relative des facteurs qui influent se classe selon : tensioactif > acide humique > pH >Ni^{2+}. La décontamination du sédiment a été étudiée par 1) lavage avec une solution aqueuse de tensioactif suivie de la déchloration des PCB en solution et 2) mélange direct avec le Fe^0 et les tensioactifs. La seconde approche s'est avérée prometteuse pour la remédiation.

Mots-clés : sites de recyclage de déchets électroniques, polychlorobiphényls (PCB), fer zérovalent, tensioactif, transfert de matière, réduction chimique

Surfactant-Assisted Zerovalent Iron Dechlorination Of Polychlorinated Biphenyl In Contaminated Sediment

Abstract: Soil and sediment contamination by polychlorinated biphenyls (PCBs) is a global health and environmental concern, since PCBs are toxic and recalcitrant. The aim of this thesis is to find a remediation process to PCBs contaminated sediments by using zerovalent iron (ZVI).To begin the studies on remediation, a survey was conducted on sites contaminated by e-waste recycling activities in south China. PCBs contamination was not as severe as previously, whereas the co-existence of PCBs and heavy metals increases the difficulty of remediation. Afterwards, the feasibility PCBs degradation by ZVI in aqueous solutions was investigated. Results confirmed the stepwise dechlorination of PCBs by ZVI and the major pathway with congener specifity and regiospecifity. The relative importance of the influential factors to ZVI degradation of PCBs was in the order of surfactants > humic acid > pH > Ni^{2+}. Sediment decontamination was studied by 1) washing with an aqueous solution of surfactant followed by ZVI dechlorination of PCBs and 2) direct mixing with ZVI and surfactant solution. The second approach gave promising results for remediation.

Keywords: e-waste sites, polychlorinated biphenyls (PCBs), zerovalent iron, surfactant, mass transfer, chemical reduction