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Dechlorination of Environmentally Recalcitrant Chlorinated Aromatic Compounds

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Abstract

Chlorinated aromatic compounds are an important group of compounds. Many of them have been produced in large quantities and they are indispensable to technological and societal benefits. But regulatory agencies have tightened regulations on the use and release of chlorinated aromatic compounds because of the scientific understanding of their toxicity, persistence, behavior in the environment and their potential to cause adverse effects on the ecosystem and human health.

Pentachlorophenol (PCP), octachloronaphthalene and decachlorobiphenyl are all highly chlorinated aromatic compounds, of which, PCP has been used mainly as a biocide. Octachloronaphthalene and decachlorobiphenyl don't have practical use, but their congeners have been used widely as chemicals in industry. These compounds are toxic, recalcitrant and bio-accumulated within organisms. As the conventional treatment, incineration of these compounds can cause more serious problems, so that suitable alternatives need to be developed for their detoxification.

When compared with biodegradation or the thermal treatment of these compounds, chemical degradations have several merits. Among them, catalytic reductions by zero-valent bimetallic mixture and catalytic hydrogenation in supercritical CO_2 ($ScCO_2$) have been demonstrated to be highly efficient, safe, rapid and cost efficient.

Pentachlorophenol (C_6HOCl_5, PCP) [5 mg/min in water-methanol (1+4,v/v) merged with 1.5 ml/min of $ScCO_2$] was dechlorinated efficiently (>99.5%) during continuous operation when passed over 2% (w/w) Pd° on Mg° at 400 °C during 6 hours. The principle product was phenol (>73%). There were also small amount of methylated products and only traces of chlorinated products (monochlorinated species). Also, the total hydrodechlorination of PCP (0.365 μmol) was achieved at 70 °C and 8.3 MPa in H_2 (~750 μmol) mixed with $ScCO_2$ in the presence of 25mg Pd°/γ-Al_2O_3 for 1 h. The principle products were cyclohexanol and cyclohexanone with lesser quantities of 1,1'-oxybis-cyclohexane. In the presence of 25 mg Pd°/γ-Al_2O_3, octachloronaphthalene and decachlorobiphenyl were also hydrodechlorinated quantitatively at 70 °C in H_2 (~750 μmol) during 0.5 h reaction. All of the hydrodechlorination products were their corresponding cyclic analogs. No C-C bond scission had occurred.

Résumé

Les composés aromatiques chlorés sont un important groupe de composés. Beaucoup de ces composés ont été produits en grande quantité et sont indispensable et bénéfique à la société et aux progrès technique. Mais les organismes de régulation ont resserrés les réglementations sur l'usage et le rejet des composés aromatiques chlorés à cause de notre compréhension scientifique accru sur leur toxicity, persistence, comportement dans l'environnement et leur effet indésirable sur l'écosystème et la santé de l'homme.

Le pentachlorophénol (PCP), l'octachloronaphtaline et le décadiphényle chloré sont tous des composés aromatiques extrêmement chlorés, dont principalement le PCP a été utilisé comme produit biocide. L'octachloronaphtaline et le décadiphényle chloré n'ont pas d'usage pratique. Mais leurs congénères ont été largement utilisés comme produits chimiques dans l'industrie. Tous ces composés sont toxiques, récalcitrants et bio-accumulés dans les organismes présent dans l'environnement. Comme le traitement conventionnel, l'incinération de ces composés peut causer de sérieux problèmes, d'autres alternatives convenables ont besoin d'être développé pour leur detoxification.

En comparaison avec dégradation biologique ou au traitement thermique de ces composés, la dégradation chimique a plusieurs mérites. La réduction catalytique avec un mélange bimétallique à valence zéro et avec l'aide du fluide supercritique bioxide de carbon ($ScCO_2$) a démontré être extrêmement efficace, sûr, rapide et rentable.

Le pentachlorophénol (C_6HOCl_5, PCP) [5 mg/min dans l'eau-méthanol (1+4,v/v) en combinaison avec 1.5 ml/min de $ScCO_2$] a été efficacement déchloré (>99.5 %) durant l'opération en continue avec un mélange bimétallique de Pd° et Mg° à 2% (w/w) pendant 6 heures à 400 °C. Le produit principal était le phénol (>73%). Une faible quantité de produits méthylés a été détecté et seulement des traces de produits chlorés (monochlorés) furent détectés. De même, l'hydrodéchloration total du PCP (0.365 μmole) a été atteint à 70 °C et avec 8.3 MPa d'hydrogène (H_2) (~750 μmol) mélangé avec le $ScCO_2$ en présence de Pd°/γ-Al_2O_3 pour 1h. Les principaux produits furent le cyclohexanol et le cyclohexanone avec une plus petite quantité de 1,1'-oxybis-cyclohexane. En présence de 25 mg Pd°/γ-Al_2O_3, l'octachloronaphtaline et le décachlorodiphényle ont été aussi hydrodéchlorés quantitativement à 70 °C avec l'H_2 (~750 μmol) pendant 0.5 h. Tout les produits d'hydrodéchloration étaient leurs analogues cycliques représentatifs. Aucune réaction de scission n'est apparu au niveau de la liaison C-C.

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List of Abbreviations

ACS	American Chemical Society
DDD	Dichlorodiphenyltrichloroethane
DDT	Dichlorodiphenyltrichloroethane
DDW	Distilled deionised water
DMA	Dimethylacetamide
DMSO	Dimethyl sulfoxide
GC	Gas Chromatography
HPLC	High Performance Liquid Chramatography
i.d.	Inner diameter
In.	Inch
MS	Mass Spectrometry
NIST	National Institue of Standanrds and Technology
OC	Organochlorine
PCBs	Polychlorinated biphenyls
PCDDs	Polychlorinated dibenzo-*p*-dioxins
PCDFs	Polychlorinated dibenzofurans
PCP	Pentachlorophenol
RSD	Relative Standard Deviation
$ScCO_2$	Supercritical carbon dioxide
SCF	Supercritical fluid(s)
ss	Stainless steel
TCDD	Tetrachlorinated dibeno-*p*-dioxin
TCE	Trichleroethylene
THF	Tetrahydrofuran
TMEDA	N,N,N,N-tetramethyl-1,2-ethylenediamine
ZV	Zero valent
atm	Atmosphere (pressure)
cm	Centimeter
h	Hour

mg	Miligram
min	Minute
ml	Mililiter
mm	Milimeter
MPa	Megapascal
ppm	Part per million
psi	Pounds per square inch
µmol	Micromolar
v/v	Volume per volume
wt %	Weight percent
w/w	Weight per weight
w/v	Weight to volume ratio

Chapter 1
Introduction

1.1 Environmental pollution

We live on a planet that can be characterized as a group of interconnected micro-environments that are in states of delicate equilibria so that perturbations to one of the micro-environment will cause changes to other (or all) microenvironments. Moreover these micro-environment are in states of constant flux that result from the myriad of natural environmental pressures. In consequence, no change is completely good or completely bad. It is also considered to be impossible to return to a "pristine" world that pre-dated human activities.

Although natural processes continue to impact our environment, anthropogenic (human) activities have become dominating factors that influence the health of our ecosystem. This results from the virtual explosion in the human population and an increasing reliance on efficient technologies to exploit non-renewable resources.

Because of the pollution that results from agricultural and industrial activities, the deterioration of the ozone layer and global warming, society has begun to speculate on the continued sustainability of the human race unless concerted actions are taken to mitigate these adverse effects.

One of the greatest challenges remains our continued generation of hazardous wastes that, for the most part, remain an unanticipated by-product of technological innovations. The types and sources of pollutants are as diverse as their potential effects and fates within the environment. Opportunities exist for the release of potentially hazardous compounds at every stage of product manufacture, use and disposal. In addition to the manufacturing industries, pollutants can enter the environment as a result of agricultural practices, food processing and transport. Some releases are intentional, such as the use of pesticides or the discharges of waste effluent produced during manufacturing processes. Others are unintentional, for example, the releases resulting from accidents.

In the era after the world war II, wastes and hazardous by-product of manufacturing have increased markedly from sources such as chlorinated solvents manufacturing, pesticides synthesis, polymer manufacture, plastics, paints and wood preservatives (Manahan, 2000). Among them, aromatic organochlorine (OC) compounds, which have been exploited mostly as industrial chemicals, have caused public concern due to their toxicity to organisms and human health and the fact that, for the most part, they are refractory and persistent in the environment.

1.2 Chlorinated aromatic compounds

Chlorinated aromatic compounds represent an important group of compounds that have been produced in large quantities. They include the most poisonous synthetic chemicals to the bio-environment. Many of them are characterized chemically by aromatic rings substituted with chlorine atom(s) and a general lack of polar functional groups, which not only can increase aqueous solubility (and thereby augments physical dispersal processes), but also can act as reactive sites for metabolic transformations. Because of this lack, they are environmentally stable and resistant to biologically mediated degradation.

Sometimes they have been perceived as indispensable to technological activities. As a society, we have become dependent to these compounds. They can be released during production and use in a variety of ways, and can contaminate the environment unintentionally or as unwanted by-products of chemical production and combustion processes, e.g. chlorinated dibenzodioxins and dibenzofurans. Natural processes also contribute to the environmental load of chlorinated aromatic compounds. Regulatory agencies have tightened regulations on the use and release of chlorinated organic compounds from production to disposal.

Chlorinated aromatic compounds can be classified into chlorinated aromatic hydrocarbons, chlorinated phenols and chlorinated dibenzodioxins and dibenzofurans and certain chlorinated biocides.

1.2.1 Chlorinated aromatic hydrocarbons

Chlorinated Aromatic hydrocarbons consist of monocyclic chlorobenzenes and chlorinated polyaromatic hydrocarbons such as polychlorinated biphenyls (PCBs) and polychlorinated naphthalenes.

1.2.1.1 Chlorobenzenes

Chlorination of the benzene ring yields 12 different compounds: 1 mono-, 3 di-, 3 tri-, 3 tetra-, 1 penta- and 1 hexa-chlorobenzenes. Most of these compounds are colorless liquids with a pleasant odor. An increase in the number of chlorine atoms in the benzene molecule increases the lipophilicity of the chlorobenzene.

Chlorobenzenes have a wide range of uses from biocides to dielectic fluids, for styrene rubber production and as intermediates. Anthropogenic sources for the release of chlorobenzenes into the environment include production and transport, use in various products or from industrial wastes in the manufacture of chlorobenzene-contained products.

Toxicities of chlorobenzenes to aquatic plants is extremely variable, depending on the species, compound, and the environmental conditions. Chlorobenzene is only slightly toxic but increased chlorine substitution leads to an increased toxicity to algae. The acute toxicity of chlorobenzenes to invertebrates generally parallels their toxicity to aquatic plants. Chlorobenzenes cause lethality through tissue narcosis. Hence, they can be considered as a class of compounds termed narcosis agents.

1.2.1.2 Polychlorinated biphenyls (PCBs)

PCBs are a family of synthetic chemicals that contain 209 individual compounds (congeners) of varying toxicity, that range from three monochlorobiphenyls to one fully chlorinated biphenyl (decachlorobiphenyl). Their molecule structures are summarized as Figure1.1.

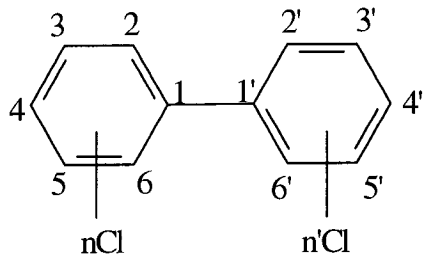


Figure 1.1 General structure of polychlorinated biphenyls (where n and n' may range from 1 to 5)

Aroclors (the trade name of Monsanto's PCB formulations) possess properties different from their individual chlorobiphenyl compounds. The individual compounds are solids at room temperature, whereas, the technical formulations (Aroclors) are either viscous liquids or sticky resins. PCBs are sparingly soluble in water, and aqueous solubility is decreased with increasing chlorine content. Selective solubilization should be considered in evaluating environmental behavior of PCBs technical formulations and their toxicity to organisms.

Because of their chemical and thermal stability, inertness, and favorable dielectric properties, PCBs have found widespread industrial and commercial applications over the last 50 years (1929-1979). They have been used as dielectric fluids in transformers and capacitors, as plasticizers in paints, plastics, sealants, resins, inks, printing, copy paper and adhesives and as components in gas turbines and vacuum pumps.

Since 1972, the use of PCBs has been restricted to controllable close systems such as transformers and capacitors. At present, the major source of PCB exposure in the environment seems to be environmental recycling of PCBs from past uses and the consequent releases into the environment including release from landfills containing discarded transformers, capacitors and other wastes; waste incineration of PCB materials, spills and improper disposal in open areas. Also, explosions or overheating of PCB-containing transformers may also release appreciable quantities of PCBs into the surrounding environment.

The evaluation of toxicity profiles of PCBs is complicated by the fact that PCB mixtures present a variety of congeners and impurities, each with its own characteristics. For invertebrates, members of the insect family, such as the dragonfly, damselfly and stonefly, seem to be relatively less sensitive to PCB when compared with other invertebrates. Certain invertebrates such as Daphnia can accumulate PCBs and show no overt signs of adverse effects.

For mammals, mink seem to be more sensitive to exposure to PCBs than other mammalian species in the field, whereas the guinea pig is the most sensitive specie under laboratory conditions. No pertinent data are available for humans.

No teratogenic effects have been reported for most mammalian species, but thyroid abnormalities have been reported. PCBs also have been reported to decrease reproductive ability in most animals under laboratory conditions. Liver is the organ most often implicated in the toxicity of Aroclors in animals. Hepatic effects have been observed in numerous studies involving exposed rats, mice, guinea pigs, rabbits, dogs and monkeys, but rats have been tested most extensively. (Ramamoorthy, 1997)

1.2.1.3 Chlorinated naphthalenes

Chlorinated naphthalenes are formed by substituting 1 to 8 hydrogen atoms of naphthalene with chlorine atoms. There are 75 possible congeners and they are widely used as dielectric fluids, insulating material, flame retardants, fungicides, and pesticides. All 75 congeners of chloronaphthalene are considered to be environmentally recalcitrant and accumulate in the environment with specific dioxin-like toxicities. Their molecular structures are shown in Figure 1.2.

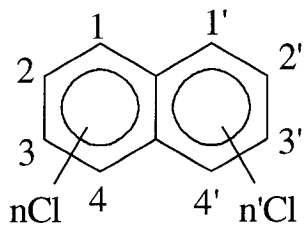


Figure1.2 General structure of chlorinated naphthalenes (where n and n' may range from 1 to 4)

Octachloronaphthalene is a fully chlorinated naphthalene compound. It is a nonflammable, pale yellow, waxy solid containing 70 percent chlorine. Exposure to the chloronaphthalenes causes acne-like lesions that itch severely. Repeated exposures to the fumes of molten chlorinated naphthalenes can cause severe and sometimes fatal systemic poisoning and are especially damaging to the liver (Patty 1963g/Ex. 1-845). Ingestion studies of cattle have shown different toxicities for different naphthalenes, with toxicity increasing with the compound's degree of chlorination (Sikes *et al*). Other chlorinated naphthalene data were not available.

1.2.2 Chlorinated phenols

Phenols are a diverse group of organic compounds with a benzene ring substituted with one or more hydroxyl groups. Chlorophenols are produced by replacing one or more hydrogen atoms on the benzene ring with chlorine atom(s). Their structures are shown in Figure 1.3.

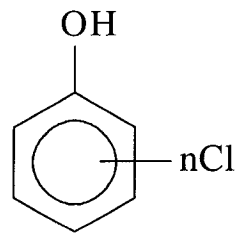


Figure1.3 General structure of chlorinated phenols (where n ranges from 1 to 5)

Chlorinated phenols have been used as disinfectants, biocides, preservatives, pesticides, and industrial organic chemicals.

Monochlorophenols continue to be used as antiseptics and as intermediates in the synthesis of higher chlorinated phenols and chlorocresols for biocide production.

Of the ten isomers of dichlorophenol, only 2,4-dichlorophenol has been used as a primary chemical and chemical intermediate in the production of germicides, temporary sterilants, plant growth regulators, moth proofing agents, seed disinfectants, miticides and wood preservatives.

Of the six isomers of trichlorophenol, only 2,4,5 and 2,4,6-trichlorophenols have been exploited commercially. The 2,4,5-trichlorophenol was used to manufacture the insecticide, *Ronnel*, which was used on livestock. It was also used in the production of hexachlorophene [2,2'-methylene *bis* (3,4,6-trichlorophenol)], a compound used in disinfectants and sanitation products for hospital, and for veterinary use.

Of three tetrachlorophenol isomers, only 2,3,4,6-tetrachlorophenol is used commercially in the production of wood preservatives.

Pentachlorophenol was the most widely used commercial chlorophenol, which was used primarily in wood preservation specifically to treat wood for utility poles. It was also registered for use by the U.S. EPA as a termiteicide, fungicide, herbicide, milluscide, algicide, disinfectant, and as an ingredient in antifouling paint. Presently, pentachlorophenol is used mainly as a fungicide in the wood industry and as a slimicide in the paper industry.

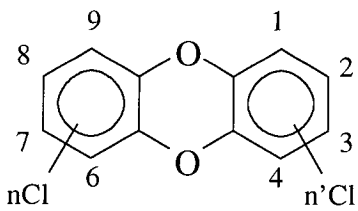
The environmental behavior of individual chlorophenolic compounds is closely influenced by their physical and chemical properties. In general, melting and boiling points increase with the chlorine content of the phenol ring; whereas volatilization and water solubility decrease with increasing chlorination. Because of the fact that chlorinated phenols are weak acids (low dissociation constants), their aqueous solubility increases markedly above their pK_a values, since the corresponding phenolate anion is more water

soluble than the unionized chlorophenol. These properties are also responsible for reduced sorption to sediments and reduced bio-accumulation at pH values appreciably above their pK_a values.

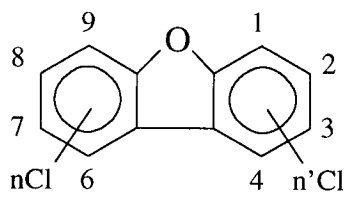
The toxicity of phenols to aquatic organisms (algae, invertebrates and fish) generally increases with increasing chlorine content of the aromatic ring. In general, the para-substituted compounds are more toxic than ortho and meta-compounds. This might be due to relatively faster transport of para-compounds across membranes. (Ramamoorthy, 1997)

1.2.3 Chlorinated dioxins and furans

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are almost ubiquitous in the environment because of the numerous pathways of their formation, including emissions from incineration systems, in various wastewaters, and bleach-kraft pulp mill effluents. There are 75 homologues and isomers of PCDDs, ranging from two monochlorodibenzodioxins to the fully chlorinated octachlorodibenzodioxins. Chlorinated dibenzofurans are a class of compounds in which one to eight chlorine atoms are attached to the aryl ring positions of a dibenzofuran structure. There are eight homologues from monochlorinated to octachlorinated PCDFs and 135 possible PCDF isomers. Figure 1.4 shows their general structures.



PCDDs



PCDFs

Figure 1.4 General structures for Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated debenzofurans (PCDFs) (where n and n' range from 1 to 4)

PCDDs and PCDFs are not produced commercially and have no direct use. They are formed inadvertently during production of 2,4,5-trichlorophenol from 1,2,4,5-tetrachlorobenzene. PCDFs are also produced as undesirable side products during the manufacture, pyrolysis and photolysis of PCBs, polychlorinated phenols and phenoxy herbicides. Municipal and industrial incinerators also produce PCDFs.

As to the properties of the homologs of PCDDs from mono- to octachloro dibenzo-dioxins, both vapor pressure and aqueous solubility decrease with increases in the chlorine content of PCDDs, whereas the log octanol/water partition coefficient ($\log K_{ow}$) increases.

PCDFs are relatively stable to both acid and alkali attack, but they begin to decompose at 700 °C. In general, the melting points increases and vapor pressures and water solubilities of PCDFs decrease with an increase in chlorination. These hydrophobic compounds are generally colorless solids and are soluble in non-polar organic solvents.

Toxicities vary substantially among the different PCDD and PCDF isomers and congeners. The most toxic isomer is 2,3,7,8-tetrachlorodibenzodioxin (-T4CDD) and it has been studied most extensively. In humans, 2,3,7,8-T4CDD causes chloracne, a severe skin lesion, most commonly on the head and upper body.

The 2,3,7,8-T4CDD congener is not acutely toxic to aquatic invertebrates. For fish, exposure to 2,3,7,8-T4CDD and PCDFs has been demonstrated to increase the activity of the enzyme EROD (7-ethoxy resorufin-O-deethylase), to increase cytochrome 450 activity and other overt the chronic effects prior to lethality. (Ramamoorthy, 1997)

1.2.4 Chlorinated biocides

Chlorinated biocides are a small but diverse group of synthetic chemicals characterized by a cyclic structure and a variable number of chlorine atoms. DDT (dichlorodiphenyltrichloroethane) was first synthesized in 1874 but its insecticidal properties were reported only in 1939. Pesticides developed during the 1940s and 1950s

were chlorinated cyclic hydrocarbons. These pesticides were inexpensive to produce, provided control of target organisms, and were characterized by minimal acute mammalian toxicities. During and after World War II, these pesticides were effective in controlling insect-generated and insect-transmitted diseases such as malaria. Thousands of lives have been saved by controlling this insect borne vector.

Most chlorinated insecticides are relatively less soluble in aqueous media and are characterized by a relatively low vapor pressure. They were released into the environment mainly from agricultural or vector control applications, or during manufacture, formulation, storage or disposal.

Chlorinated aromatic pesticides are known to bio-accumulate within organisms that are higher on the food chain, as well as to persist in the environment. These physical attributes account for their accumulation in aquatic and terrestrial wildlife and the resultant chronic toxicity, including reproductive toxic effects.

New pesticides are being developed with the goal of increasing the specificity to target pests, reducing the potential adverse effects on non-target organisms and greatly reducing environmental persistence by designing active molecules that are biodegraded rapidly after their intended use. (Ramamoorthy, 1997)

1.3 Hazardous waste treatments

Given current concerns regarding the general health of our environment, the public and government have begun to take decisive action to prevent the problem from getting worse. Not only has legislative control become increasingly restrictive with regard to the generation of pollution, but also, actions have been taken to remediate the existing damages.

There is a vast array of technologies that can be employed by the pollution control and remediation industries. But to date, techniques remain unproven for the most part. Those

procedures that are employed routinely are ones based predominantly on physico-chemical processes in particular physical containment (bury it) or incineration (burn it).

The application of novel technologies is seen as the way to solve the environment problems of today. Indeed, a look at the vast array of technologies employed by the pollution control industries supports this view. The technologies can be classified into physical, chemical or biological techniques. (McEldowney, 1993)

1.3.1 Physical methods processes

With physical treatments, hazardous wastes are transferred/concentrated from one phase to another or are concentrated from their original medium or immobilized within an isolated site. There are many methods that can be applied in physical treatments, such as filtration, extraction, precipitation, adsorption or evaporation. In practice these processes have been exploited successfully. But they are not final treatments of wastes because they do not detoxify the toxicants. The toxicants can still remain to become a future problem. The process of detoxification must involve making the toxicants less available to contacting organism or to isolating biological processes.

1.3.2 Biological techniques

Biotechnology for hazardous waste treatment can be defined as those processes that use biological organisms (or products derived from them) to degrade, detoxify or accumulate environmental pollutants.

Environmental biotechnologies have become an integral part of the progressive development of pollution control strategies. Firstly, in the remediation of environmental pollution, bioremediation has provided a cost-effective technology for independent application or for use as part of a mixed technology approach. Secondly, with the increased emphasis on waste minimization, bioadsorption and accumulation have shown their worth in recovery and recycling. (McEldowney, 1993)

Biotreatment has advantages for many aspects of waste treatment. It has the potential to transform organic pollutants into innocuous products rather than merely transferring the pollutant from one medium to another. At the same time, bioprocessing is generally cheaper and enjoys a greater degree of public acceptance. But biotreatment technologies need to increase the removal efficiencies of pollutants and to decrease the time required to achieve target levels.

1.3.3 Thermal treatment

Thermal treatment usually refers to high temperature incineration. Actually, it is a chemical oxidation process. Incineration has been demonstrated to be an effective treatment strategy that offers the "nine-nines" efficiency required by the waste treatment industry.

However, over the last few years increasing concerns have been expressed over the destructive efficiency of commercial incinerators. Whereas it is recognized that this disposal technology is intrinsically safe, operational inadequacies have led to incomplete combustion of the waste materials. Emissions (from smoke-stacks) of compounds like dibenzodioxins, dibenzofuranes and polyaromatic hydrocarbons that can result from incomplete combustion, and heavy metal pollution of the surrounding environment, have all been recorded. (McEldowney, 1993)

1.3.4 Chemical treatment processes

Chemical methods are an economically effective alternative for the rapid treatment of large amount of highly concentrated wastes. These processes use chemical oxidation or reduction reactions to decompose hazardous wastes to innocuous products. Technologies used in chemical treatment can include photolysis, hydrolysis, chemical oxidation and reduction.

In this thesis, the methods of dechlorination of chlorinated aromatic compounds will focus on the chemical reductions, specifically on zero valent metal reductions and catalytic hydrogenation.

1.4 Dechlorination of chlorinated organic compounds

Several techniques have been exploited in the development of degradation strategies for chlorinated compounds, especially chlorinated aromatic compounds. These degradation techniques may be classified into the following categories:

1.4.1 Biodegradation of chlorinated organic compounds

In 1951, Young and Carrol had postulated that the biodegradation of pentachlorophenol (PCP) might be an explanation for the loss of this preservative from soil. Since that time, numerous investigators have reported the isolation of fungi and bacteria capable of degrading PCP. Seigle-Murandi and Steiman (1993) examined the action of 999 fungal strains on 100 mg/L PCP. The *taxonomic* groups that showed the maximum degradation of PCP were the *Zygomycetes*, with the *Yeasts* and *Basidiomycetes* having the least efficient conversion of PCP to other products. Most of the *Zygomycetes* strains showed greater than 40% degradation of this compound after 12 days.

Bacteria, in the presence of organic matter in the water column, have been reported to have mineralized 3,4-dichlorophenol, 2,4,5,-trichlorophenol and PCP. Chlorophenols are metabolized microbially in water, sediments, and soils and the rate of degradation, whether aerobic or anaerobic, depends on the type of microbes present, the quantities of substrate, the degree of chlorination and isomeric positions of chlorine atoms on the phenol ring, soil type, moisture content, temperature, minerals and nutrients and percent of organic matter. (Ramamoorthy, 1997)

Laboratory studies have demonstrated that a) two strains of *Rhodococcus* aerobically degraded chlorinated phenols in pulp bleaching effluents; b) Laccase enzymes from the fungus *Trametes versiclor* partially dechlorinated a variety of chlorophenols. Generally, microbial degradation of chlorinated phenolic compounds occured more rapidly and more extensively in sediments than in the water column. Chlorophenols were biotransformed via reductive dechlorination to simpler chlorophenols. (Ramamoorthy, 1997)

The chemical structure of the chlorinated pesticides makes them poorly susceptible to biotransformation reactions, especially under aerobic conditions. The chlorine substituents and the extensive branching block the normal sites for enzyme attack. Half-lives in active aerobic systems usually are measured in weeks to months. While chlorinated pesticides are highly resistant to transformations under aerobic conditions, anaerobic conditions are more favorable. An interesting observation with DDT was that it was reductively dehalogenation rapidly to DDD, and DDD disappeared as well, but much more slowly. Commonly recognized reductive dehalogenation occured with strongly reducing anaerobic conditions for essentially all chlorinated aromatic and aliphatic compounds. While this observation is interesting (and at times of importance), strongly reducing conditions do not occur frequently in the environment and so cannot be counted on to mediate detoxification of chlorinated compounds in general. The other aspect is that reductive dehalogenation does not necessarily result in the complete destruction of the chemical. Indeed, it might create products that are equally hazardous to humans and the environment. The formation of DDD from DDT is an example. (Rittmann and McCarty, 2001)

In spite of their highly resistant nature, polychlorinated biphenyl (PCB) compounds can be biodegraded when the right microorganisms and environmental conditions occur. PCB degradation can occur under either aerobic or anaerobic conditions. Under aerobic conditions, the biphenyl molecule is degraded in a manner similar to other aromatic hydrocarbons: oxygenase mediated addition of molecular oxygen to one of the aromatic rings, resulted in the generation of hydroxyl groups. Further oxidation leads to the cleavage of one ring and subsequent degradation lead eventually to benzoic acid. Benzoic acid then undergoes ring oxidation, ring cleavage, and further oxidation through the usual pathways for aromatic hydrocarbons. PCBs with only a few chlorine atoms on the molecule can readily enter the aerobic pathway for biphenyl oxidation, but increased chlorination makes enzymatic attack on the ring difficult. PCBs most susceptible to aerobic degradation are those containing one to three chlorine atoms per molecule. The most resistant to degradation are PCBs with chlorine atoms in the *ortho* (or 2) position on the molecule. (Rittmann and McCarty, 2001)

Dioxins and related compounds are highly resistant to biodegradation, but microorganisms can bring about their conversion under aerobic and anaerobic conditions. In many studies of aerobic biodegradation, only limited biotransformation of dioxins has been observed. It generally involved the addition of oxygen with oxygenase enzymes, resulting in the unproductive formation of mono-and di-hydroxylated analogs, which tend to accumulate with no further degradation. (Rittmann and McCarty, 2001)

Reductive dechlorination of dioxin has been reported under anaerobic conditions. Interestingly, the TCDD congener can be formed through reductive dehalogenation of other congeners, as well as being dechlorinated itself. As with PCBs, dehalogenation of dioxins has been reported to be a slow process, Very low solution concentrations and the high tendency to partition to sediments reduces biological availability. Biodegradation studies suggest that natural attenuation of dioxins through biotransformation might be possible, but much needs to be learned about factors affecting their movement, fate and effects in the environment. (Rittmann and McCarty, 2001)

1.4.2 Thermal processes of dechlorination

Thermal treatment to achieve dechlorination includes incineration, microwave and plasma treatments.

Incineration has provided the ultimate answer to the disposal of the chlorinated waste materials. There are incineration systems operating today in which chlorinated waste materials are being disposed in an efficient manner. The objective in incinerating residues containing chlorine is to convert as much the chlorine content as possible to hydrogen chloride. Chlorinated organic compounds tend to be slow-burning and soot-forming. As a result, many systems have operated with high excess air to promote mixing of oxygen with the chlorinated organic wastes in an effort to minimize soot formation. This has necessitated a series of requirement such as high combustion temperature and increased combustion turbulence for the incineration system. (Harry, 1989)

Incinerators not employing the best available technologies with respect to operating conditions and emission treatment trains were demonstrated to release significantly higher concentrations of PCDDs and PCDFs in stack emissions and fly ash. (Ramamoorthy, 1997)

PCB detoxcification by microwave plasma was reported by Bailin *et al,* in 1977. Monsanto's Aroclor 1242 liquid was passed through a 250 w plasma arc at 100 torr mixed with oxygen. All the products of decomposition were gases. Mass balance showed no starting material and percent conversion was greater than 99.9%. Gaseous products were identified as CO_2, CO, H_2O, HCl and Cl_2 with minor amount of Cl_2O and $COCl_2$.

1.4.3 Chemical dechlorination of chlorinated organic compounds

1.4.3.1 Photolysis

Photolytic reactions are most useful in breaking chemical bonds in refractory chlorinated aromatic compounds.

Ultra violet (UV) photolysis combined with heating was reported as an alternative route to decomposition of chlorinated hydrocarbons. The photo dissociation of the C-Cl bond by active radical pathways to hydrocarbons and HCl, has demonstrated the potential to dechlorinate polychlorinated hydrocarbons under mild conditions. Photolysis of four chloromethanes (chloromethane, dichloromethane, trichloromethane, and tetrachloromethane) in the presence of H_2 at a reduced pressure in a static reactor using a broadband UV source demonstrated substantial decomposition to hydrocarbons. (Poulos *et al*, 1990)

Dechlorination and detoxification of harmful chlorinated compounds including environmentally recalcitrant PCBs, chlorinated dioxins and furans can be effected photolytically at high efficiency (without producing harmful byproducts) by the action of UV at ~400 nm wavelength. (Tajima *et al*, 2000)

1.4.3.2 Degradation (oxidation) in subcritical water

In recent years, dechlorination of chlorinated organic compounds using subcritical water as an aqueous medium has also become popular. In supercritical water, oxidation of chlorinated organic compounds was carried out in the presence of a high content of air or oxygen at temperatures and pressures above the critical-point values for this medium. Under supercritical conditions (>374 °C and >218 atm) the dielectric constant of water is less than 10 (at ambient conditions, the dielectic constant is ~80) and is similar to that of dichloromethane. But under these conditions, supercritical water is very corrosive.

Polychlorinated biphenyls (PCBs) were made harmless using supercritical water hydrolysis with an alkali catalyst such as sodium hydroxide. PCBs over a wide concentration range from 2% (w/v) in transformer oil to pure state were dechlorinated to biphenyl and decomposited to phenol and other small molecules at 30 MPa, 653-723 K, and 20-100 min of reaction time. Furthermore, no dioxins were detected in either the gaseous and liquid. (Sako *et al.* 1999)

Dechlorination under subcritical conditions in the presence of a sacrificial metal in its element form has been reported. (Marshall *et al*, 2001) In this case, dechlorination was a reduction reaction. Kluyev *et al,* (2000) observed hydrothermal decomposition of polychlorinated dibenzodioxins (PCDD) by Fe° at 200-300 °C in subcritical water with simultaneous extraction of PCDD from soil. Yak *et al* (2000) studied reduction efficiencies of isomers of polychlorinated biphenyls (PCBs) by 100-mesh Fe° in subcritical water at 250 °C and 10 MPa. The reaction efficiencies for *meta* and *para* isomers were significantly higher than that of the *ortho* isomer.

1.4.3.3 Catalytic reduction

Zero-valent metal and bimetallic mixtures have become popular for dechlorinations in recent years. The metals (with specific reductive and catalytic activity) that have been used to dechlorinate chlorinated organic compounds are usually transition elements such as Fe, Pd, Cu, Ag, Pt, Ni, Ti and Rh. Less often, alkaline metal Na, Mg have also been reported for dechlorinations. Ag°/Fe°, Pd°/Fe°, Pt°/Sn°, Pd°/Rh°, Ag°/Ni°, Pd°/Cu° and

Ag°/Mg° zero-valent (ZV) bimetallic systems have also been evaluated for dechlorinations.

Chemical reduction for the dechlorination of polychlorinated aromatic compounds have the advantage of avoiding the formation of PCDDs or PCDFs that can accumulate in partly dechlorinatin reaction mixtures during chemical oxidation.

Kabir and Marshall (2001) examined the dechlorination of pentachlorophenol (PCP) by zero-valent silver-iron (Ag°/Fe°) bimetallic mixture. A continuous stream of PCP (10-20 mg/min) in supercritical carbon dioxide ($ScCO_2$) was dechlorinated efficiently by Ag°/Fe° in a heated column (25 ×1cm i.d.) at ~450 °C. No PCP substrate or chlorinated aromatic compound was found among the products.

Wu *et al* (2000) studied zero-valent metal Fe, Ni, Zn, Cu and Ag°/Fe° and Ag°/Ni° bimetallic mixture in PCB dechlorination using $ScCO_2$ as the medium. Polychlorinated biphenyl mixtures (Aroclor 1242 and 1248) were dechlorinated efficiently (but not quantitatively) with heated columns of zero-valent metal or bimetallic mixture in a continuous process. The dechlorination efficiency was influenced appreciably by the identity of the ZV metal in a order of Fe>Ni>Zn>Cu, and by the temperature 400>300>200 °C with a pressure of about 4500 psi within the heated reactor column(s). The composition of the feedstock had an appreciable effect on the efficiency of dechlorination. Extracts of PCBs from a spiked (approximately 600 ppm) sandy loam soil were dechlorinated efficiently.

Liu *et al* (2001) reported dechlorination of PCP by Pd°/Fe°. Three isomers of mono-chlorophenol, *o*-, *m*-, *p*-chlorophenol, were dechlorinated by Pd°/Fe°powder in water via catalytic reduction. The dechlorinated reaction was considered to take place on the surface of the catalyst in a pseudo-first-order reaction. The reduction product for all the three isomers was phenol. The dechlorination rate increased with increased bulk loadings of palladium due to the increase of both the loading of palladium and the total surface

area. The molecular structure of the substrate also had an effect on the dechlorination rate.

Graham *et al* (1998) has also demonstrated the similar dechlorination of *p*-chlorophenol to phenol in aqueous solutions by Pd°/Fe° in less than 1 h in an acidified solution. The difference was that he used beads made from polymerized alginate as the Pd°/Fe° catalyst support and chlorine removal was efficient. The integration of a magnetically stabilized fluidized bed (MSFB) with these beads provides a novel engineering method for handling these toxic chlorinated compounds.

Ukisu *et al* (1996) reported that Pd°/C or Rh°/C efficiently dechlorinated polychlorinated biphenyl compounds (PCBs) to biphenyl and phenylcyclohexane in a 2-propanol solution of NaOH at <82 °C. Total amounts of the dechlorinated aromatic products and chloride ion after the complete dechlorination were in good agreement with predicted values.

Subsequently, Ukisu *et al* (1998) reported the Rh-based catalytic dechlorination of chlorotoluene to toluene in a solution of NaOH at ambient temperature. A carbon-supported Rh catalyst (Rh°/C) displayed high catalytic activity, although an induction period was necessary for the reaction and the activity of the catalyst was reduced during storage in air. The addition of Pt on the Rh catalyst was effective in overcoming the activity reduction by exposure to air and resulted in reactions without any induction period. The composite Rh-Pt catalyst supported on TiO_2 as well as on C was much more active for dechlorinations than the catalysts supported on SiO_2, MgO and Al_2O_3.

Ukisu *et al* (2000) also have used Rh°-Pt°/C catalyst to dechlorinate aromatic organochlorine compounds. Dechlorination was carried out in a solution of NaOH in 2-propanol with a C-supported Rh-based catalyst at <35 °C. It was observed that the dechlorination rate of aromatic chlorocompounds (chlorobenzene, *p*-chlorotoluene, and 4-chlorobiphenyl) was strongly dependent upon the position of the substituents. The dechlorination rate was hardly affected by the presence of water (approximately 10%), although the catalytic activity was suppressed appreciably in the presence of acetone

(approximately 5%) and under aerobic conditions. The catalytic activity decreased gradually with use but could be reactivated by washing with water.

Hinz *et al* (2000) examined dechlorination of a nonachlorobiphenyl congener with Fe° in water under high temperature and pressure and found that temperature was the main influence on the rate of dechlorination. Dechlorination resulted in a variety of lower chlorinated biphenyls. The level of chlorination decreased over time. The amout of PCB molecules decreased to one-third within 90 min at 250 °C and 100 atm.

A Ti catalyst system based on sodium borohydride ($NaBH_4$) also was used to reduce complex mixtures of polychlorinated biphenyls (PCB) to biphenyl in soil under mild conditions. (Liu *et al,* 1995). Catalytic dechlorination of aromatic OC compounds using Grignard reagents in the presence of $(C_5H_5)_2TiCl_2$ was also reported. (Hara at al, 1999)

Shin *et al* (1999) reported Ni°/SiO_2 catalysis for the gas-phase hydrodechlorination of the six dichlorophenol (DCP) isomers over the temperature range 473-573 K.

Na° (Davies *et al*, 1993 and Pittman et al, 2000) or yttrium/NaH system (Penn *et al*, 1996) was also reported to dechlorinate aromatic chlorine compounds. Alkaline catalysts were also used for the dechlorination of chlorinated dioxins. (*Uchida et al*, 1998)

As evidenced by these applications of ZV metals, bimetallic mixtures have shown increased dechlorination efficiency relative to single ZV metals. Especially Pd^0/Fe^0 bimetallic mixture has shown promising practical applications.

Noticeably, in all of these ZV metal dechlorinations, the solvents played an important role, no matter whether in aqueous, organic or SCF media. It was assumed that the solvents provided hydrogen atoms that can favor dechlorinations. The final dechlorination products for these aryl chlorinated compound degradations were usually their correspond parent hydrocarbon. Aromatic rings were not reduced.

There have been also some reports on catalytic hydrodechlorination of chlorinated hydrocarbons with palladium as catalyst. They showed very good dechlorination efficiency within a short time under mild reaction conditions.

Muftikian *et al* (1995) reported the hydrodechlorination of trichloroethylene (1,1,2-TCE), 1,1-dichloroethylene, cis- and trans- 1,2-dichloroethylene and tetrachloroethylene (PCE) in aqueous solutions to C_2H_6 within a few minutes on the surface of palladized iron in batch experiments that were performed in closed vials. No reaction intermediate was detected either in the headspace or in the solution. The chloromethanes, CCl_4, $CHCl_3$ and CH_2Cl_2 were also dechlorinated to CH_4 on palladized iron; the CCl_4 was dechlorinated in a few minutes, the $CHCl_3$, in <1 h and the CH_2Cl_2, in 4-5 h.

Munakata *et al* (1998) also reported the very efficient hydrodehalogenation of supported Pd and H_2 on halogenated hydrocarbons. Ono *et al* (1998) studied Pd°/C in $C_{16}H_{34}$ on hydrodechlorination of PCBs at various reaction temperatures (from room temperature to 210 °C) for 80 min. Dechlorinated with t-BuOK at 210 °C for 10 min were also reported. The principle product was biphenyl and with ≥99.99% dechlorination efficiency.

Also, using Pt-group metals on porous supports to hydrodechlorinate chlorinated aromatic compounds, Kita *et al* (1998) achieved efficient dechlorination under quite mild conditions (temperature >60 °C and pressure ≥11 atm) in a reactor in the presence of an alcohlic compound or carbonyl compound, an alkali agent, a hydrogenation catalyst and a non-polar solvent.

Other types of dechlorination catalysts have also been used. Lingaiah *et al* (1999) reported the action of an iron oxide catalyst system on dehydrochlorination (DHC) of chloroalkanes to their corresponding alkenes. This catalyst was also found to be effective for the removal of chlorine in fuel oil derived from the degradation of PVC [poly (vinyl chloride)]-containing waste plastics.

Polychlorinated benzene reduction with $NaBH_4$, using $PdCl_2$(dppf) [dppf = 1,1'-bis(diphenylphosphino)ferrocene] was tested as the catalyst. A variety of solvents, namely THF, CH_3CN, DMSO, diglyme, DMF and DMA (dimethylacetamide) were examined. A supporting base, TMEDA (N,N,N,N-tetramethyl-1,2-ethylenediamine) was used in certain cases. Catalytic activity was strongly solvent-dependent with DMA and DMF providing the best performance. Addition of TMEDA improved the yields in all cases except for DMSO. In DMA, when TMEDA was used, the catalyst showed appreciable activity even after 2 weeks of reaction. Both solvent and the presence/absence of a base had an appreciable influence on the selectivity of the reaction. (Lassova *et al*, 1999).

1.5 Supercritical carbon dioxide ($ScCO_2$)

From the first reported observation of the phenomena of supercritical phase by Baron Lagniard de la Tour in 1822, supercritical fluid (SCF) technology has experienced continued development albeit at a relatively slow rate. However, a significant development in supercritical fluid aplication was Zosel's work on the decaffeination of green coffee with $ScCO_2$ in 1970.

From then on, SFC technology has been used as a substitute for conventional organic solvents to provide clean extracts in food industries. Examples include the extraction of hops, cholesterol from butter and perfumes and flavors from natural product.

During this period, our understanding of supercritical fluids has been improved greatly in the area of molecular interactions, phase behavior and transport properties. Also, SCF has been applied in remediation of polluted environments, chemical reactions, synthesises and materials processing. (Arai *et al*, 2002).

Among the various possible SCF solvents, CO_2 is by far the more widely used solvent because it is non-toxic, non-flammable, inexpensive, and readily available in high purity. More importantly, it possesses readily attainable critical parameters for practical use.

1.5.1 Principal and physical properties

A supercritical fluid is a substance under pressure above its critical temperature and critical pressure. Under these conditions, the distinction between gases and liquids becomes more nebulous and the substance can best be described as a fluid. The SCF region can be summarized on the conventional *P versus T* phase diagram (Figure 1.5).

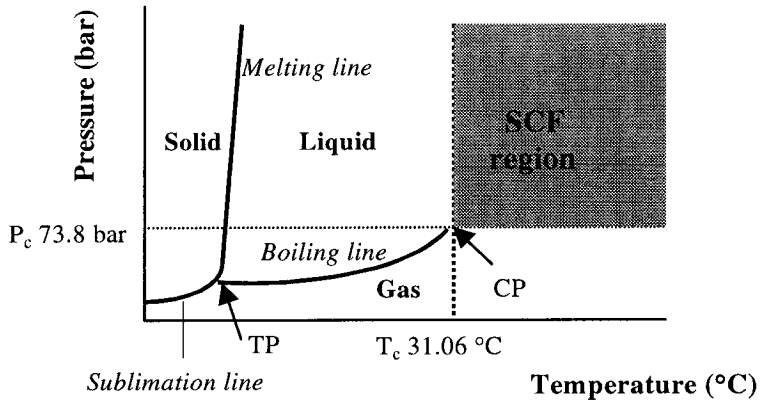


Figure 1.5 Phase (*P v T*) diagram for CO_2 (where CP: critical point, TP: triple point, P_c: critical pressure, T_c: critical temperature). Adapted from Brogle, 1982.

In the SCF state, CO_2 displays the properties which are intermediate between those of the liquid and gaseous state. The main advantages of $ScCO_2$ are that its solvent power is highly dependent on the system temperature or pressure, and can be modified readily. Furthermore, $ScCO_2$ has very good transport properties such as gas-like low viscosity and high diffusivity, which also are pressure and temperature dependent.

Because $ScCO_2$ possesses low polarity, certain miscible polar co-solvents, such as methanol, CH_3CN or THF (tetrahydrofuran), can be added into the $ScCO_2$ to enhance the solubility of more polar solutes.

1.5.2 Applications of $ScCO_2$ for dechlorination

The application of $ScCO_2$ as a solvent in dechlorination not only can decrease the use of organic solvents that are harmful to the environment, but also, when coupled with extraction and transportation, can greatly increase the efficiency of remediation

procedures. Aryl OC compounds can be extracted or concentrated directly from natural media by $ScCO_2$. Fiddler *et al.* (1999) examined the $ScCO_2$ extraction of organochlorine pesticides from liquid whole eggs and the extraction recoveries ranged from 82% to 108%. Wu *et al.* (2000) extracted PCBs from a spiked (approximately 600 ppm) sandy loam soil and efficiently dechlorinated PCBs in $ScCO_2$. Kabir and Marshall (2001) had also reported the dechlorination of pentachlorophenol (PCP) in $ScCO_2$. It is considered that the extraction of OC contaminants from polluted media coupled with an *on line* detoxification sequence would be environmentally benign, more efficient and an economic process of dechlorination.

1.6 Objectives

Because of their toxicity, chemical stability and resistance to degradation, the presence of chlorinated organic compounds in the environment pose a potential health hazard to humans and other organisms. The high degree of public concern and anxiety about chlorinated compounds (especially chlorinated aromatic compounds) persisting in the environment mandate that effective clean-up methods be developed and applied to eliminate their hazard. The factors that lead to the implementation of such techniques are found to vary appreciably according to economic factors, site location, and community perceptions. The disposal of chlorinated aromatic compounds has been researched extensively. Even though the biodegradation of chlorinated aromatic compounds has certain cost advantages and continues to be applied somewhat, it can be unreliable and slow, so that efficient abiotic methods of reducing the chlorinated compounds are required.

Of the various treatment strategies both thermal and chemical, techniques using zero-valent metal or sub-critical water or combination of the two are characterized by its efficient, safe, rapid and economic dechlorinations. It is anticipated that future research can provide reliable alternatives for the dechlorination to refractory chlorinated aromatic compounds.

The objective of this research was to identify efficient, economic and safe methods to dechlorinate the aromatic OC compounds and to transform them to innocuous products that are benign to environmental processes. Specifically, the objectives of these studies were:

1. To explore the zero valent bimetallic particles (Pd°/Mg°) as accelerator to dechlorinate PCP;
2. To apply the supercritical carbon dioxide as a medium to replace conventional organic solvent as a reaction medium for the continuous dechlorination of PCP;
3. To investigate the hydrodechlorination of highly chlorinated aromatic compounds such as PCP, octachloronaphthalene and decachlorobiphenyl and to evaluate the suitability of various catalysts in the presence of molecular hydrogen.

Chapter 2

Dechlorination of pentachlorophenol in supercritical carbon dioxide with zero-valent palladium-magnesium bimetallic mixture

2.1 Introduction

Whereas extraction methods can transfer and concentrate target toxicants from one medium to another, they do not detoxify the pollutants *per se*. It would be more efficient to combine the extraction/mobilization of aryl-organochlorine compounds with an *on-line* dechlorination sequence. Such a dechlorination stage that can be combined with an extraction into supercritical carbon dioxide ($ScCO_2$) has been reported for polychlorinated biphenyl (Aroclor 1242 and 1248) mixtures (Wu *et al* 2000, 2001) and for pentachlorophenol (PCP) (Kabir and Marshall, 2001). The principal advantages of the proposed process relative to other remediation techniques include: (i) the process is rapid and non-polluting in that the solvent leaves no residue in either the decontaminated sample matrix or in the extract; (ii) the $ScCO_2$ is inflammable, toxicologically innocuous and does not present any appreciable hazard to the operator or to the environment. The pressures used are those of conventional high performance liquid chromatography and (iii) the process is virtually unique in that it is equally applicable to both non-polar organic contaminants and to metal ions so that both pollutant types can be removed sequentially and recovered in separate fractions. Finally, relative to other solvent extractions, the $ScCO_2$ is no more expensive to purchase/generate than other solvents (organics or aqueous acids) and disposal costs are zero. The feasibility of the process has been demonstrated - the challenge remains to make it as efficient as possible.

The metallic reduction of organic compounds, primarily with zinc or iron powder, is a classical organic reaction that has been utilized for more than a century. Recent research, however, has demonstrated that dramatic improvements in rate and selectivity can be obtained by employing bimetals. (Mallát *et al,* 1991). Zero-valent mixtures of Fe or Mg with palladium have become especially popular. Dechlorination efficiencies with Pd^o/Fe^o (Grittini *et al,* 1996; Kim *et al,* 2000; Korte *et al,* 1997; Wan *et al,* 1999) or Pd^o/Mg^o

(Doyle *et al*, 1998; Engelmann *et al*, 2001, 2000; Marshall *et al*, 2002) can be appreciably greater than with of zero-valent iron alone. (Matheson *et al*, 1994; Helland *et al*, 1995; Orth *et al*, 1996; Johnson *et al*, 1996; Sayles *et al*, 1997) The reaction mechanisms are different and the zero-valent iron reaction is much slower. For example, Pd°/Fe° dechlorinates PCBs at ambient temperature and pressure and retains its reactivity in the presence of alcohols and surfactants (Grittini *et al*, 1995; Korte *et al*, 1995) conditions under which zero-valent iron is essentially unreactive. The enhanced reactivity of palladised iron is believed to be due to hydrogenation (Siantar *et al*, 1995) because Pd has the ability to intercalate hydrogen into its lattice. Thus, the chlorinated organic compound is adsorbed to the Fe surface and reacts with the hydrogen intercalated by the Pd.

Catalytic hydroprocessing over molecular hydrogen, which mediates the reduction of aryl-chlorine substitutents to chloride at relatively low temperatures, has been reported with Ni-, Pd-, Pt-, and Rh-based catalysts. (Suzdorf *et al,*1994; Gioia *et al*, 1994; LaPierre *et al*, 1978; Coq *et al,* 1986; Greghton *et al*, 1995; Hoke *et al,* 1992). The liquid phase catalytic hydrodechlorination of chlorophenols over Pt/C (Chon *et al*, 1991) and in the gas phase over Ni^0/SiO_2 and over Ni^0/zeolite (Shin *et al*, 1998 and 1999) have also been examined. Hydrogen treatment of HOArCl isomers in the range 150-300 °C yielded phenol as the only appreciable product. (Shin *et al*, 1998) Under these conditions, phenol was hydrogenated to cyclohexanol and cyclohexanone with benzene being formed at T>250 °C. The continuous gas phase hydrodechlorination of PCP was studied in H_2 at 200-350 °C over 1.5% or 15.2% Ni/SiO_2 and Ni/zeolite. (Shin *et al*, 1999). With these conditions, dechlorination has been demonstrated (Shin *et al*, 1998; Tavoularis *et al*, 1999) to proceed *via* an electrophilic mechanism involving spillover hydrogen and associated chloroaromatic. There is persuasive evidence (Roessner *et al*,1996; Roland *et al*, 1997) for the co-existence of charged (H^+) and uncharged (H atoms) spillover hydrogen on silica, where the former is considered to be the reactive species in catalytic hydrodechlorination.

Analogous continuous dechlorinations have involved the use of steam or $ScCO_2$. (Wu *et al* 2000; Kabir and Marshall, 2001). In the steam reforming process (Couté *et al*, 2000),

liquid substrate was merged with steam and pyrolysed over a commercial Ni catalyst [$Ni^0/CaAl_2O_4$ (23 wt.%)] or 0.5% $Pt/\gamma\text{-}Al_2O_3$ at 600-800 °C. Aryl organochlorine was converted to CO + H_2 + HCl in a steam reforming reaction and the CO plus water was transposed to CO_2 and hydrogen with a second water gas shift reaction. The current report evaluates the dechlorination of PCP over zero-valent palladium-magnesium bimetallic mixture.

2.2 Materials and methods

2.2.1 Chemicals

Mg° (~20 mesh) was purchased from Alfa Aesar, Danvers, MA, USA. Potassium hexachlorochloropalladiate (K_2PdCl_6), methanol, anisole, *o*-cresol, *p*-cresol, cyclohexanone, phenol, *o*-chloroanisole, *o*-chlorophenol, *p*-chlorophenol, 2,3-dichloroanisole, 2,3-dichlorophenol, 2,4,6-trichloroanisole and 2,4,6-trichlorophenol were purchased from Aldrich Chemical Co., Oakville, ON, Can. All chemicals were ACS Reagent Grade or better and were used as received.

2.2.2 Bimetallic mixture preparation

Pd°/Mg° was prepared from ~20 mesh magnesium granules that had been washed copiously with 0.6M HCl and rinsed with distilled water. Sufficient aqueous K_2PdCl_6 to result in a 2%, 1% or 0.2% (w/w) surface coverage of the magnesium was added to the aqueous magnesium suspension, that was mixed by swirling the vessel containing the reaction suspension under cold running water. After the addition of K_2PdCl_6 was complete, mixing was continued on a rotary evaporator for a further 10 min. Then the particles were recovered by vacuum filtration, rinsed three times with 30 ml of distilled deionised water (DDW) followed by three washes with 30 ml acetone, finally dried at 105 °C and stored in a closed container.

2.2.3 Reactor

The dechlorination assembly (Wu *et al* 2000; Kabir and Marshall, 2001) consisted of a source of compressed CO_2, [pressurized to 1400 psi with He and further pressurized with an SCF pump (Prepmaster, Isco Corporation, Lincoln, NE, USA)], a mixing tee and a

reactor unit. Target substrate chemical in water methanol (1 + 4 v/v), was delivered at 0.1 ml/min to the mixing tee (1/16 in. i.d.), merged with a $ScCO_2$ stream (~1.5 ml min^{-1}) and fed to a stainless steel (ss) HPLC column assembly [10 mm (i.d.) × 25 cm] filled with zero-valent palladium-magnesium mixture, which was encased in an insulating alumina jacket [fashioned from thin walled alumina tube (Alfa Aesar, Danvers, MA, USA), that had been cut lengthwise to provide two semi-cylinders]. The alumina jacketed ss column assembly was heated with an 80-turn coil of high resistance heating wire that was energized from a variable transformer. Pressure within the reactor was maintained with a terminal restrictor made of capillary quartz (25 cm × 0.05-mm i.d.) tubing (Chromatographic Specialties, Brockville, ON, Canada). The reactor system is illustrated schematically in Figure 2.1.

2.2.4 Reactor operation

After a short delay to purge residues of air from the system (during which time only Sc CO_2 was fed to the reactor), feedstock (0.1 ml/min) was added continuously via the HPLC pump to the $ScCO_2$ stream and transported to the reactor. Measurements at the exit of the capillary restrictor indicated a flow rate corresponding to ~1500 ml/min of decompressed gas. The exit tip of the capillary restrictor was immersed in methanol (25 ml) to trap products from the reactor elute. Each experiment was continued for 5 or 6h with successive fractions that corresponded to 30 min of cumulative trapping of reactor elute. The course of the dechlorination was monitored by gas chromatography – mass spectrometry (GC-MS).

Warning: It is imperative to interpose a pressure release valve (upstream from the reactor column) that is configured to release pressure if the pressure within the reactor column becomes excessive.

2.2.5 GC-MS analysis

GC-MS analysis was performed on an Agilent Technologies model 5890 series II gas chromatograph fitted with a model 5970 mass selective detector. The HP-1 capillary column (30 m × 0.25 mm i.d.; 0.25μm film thickness) was eluted with helium at 0.8 ml/

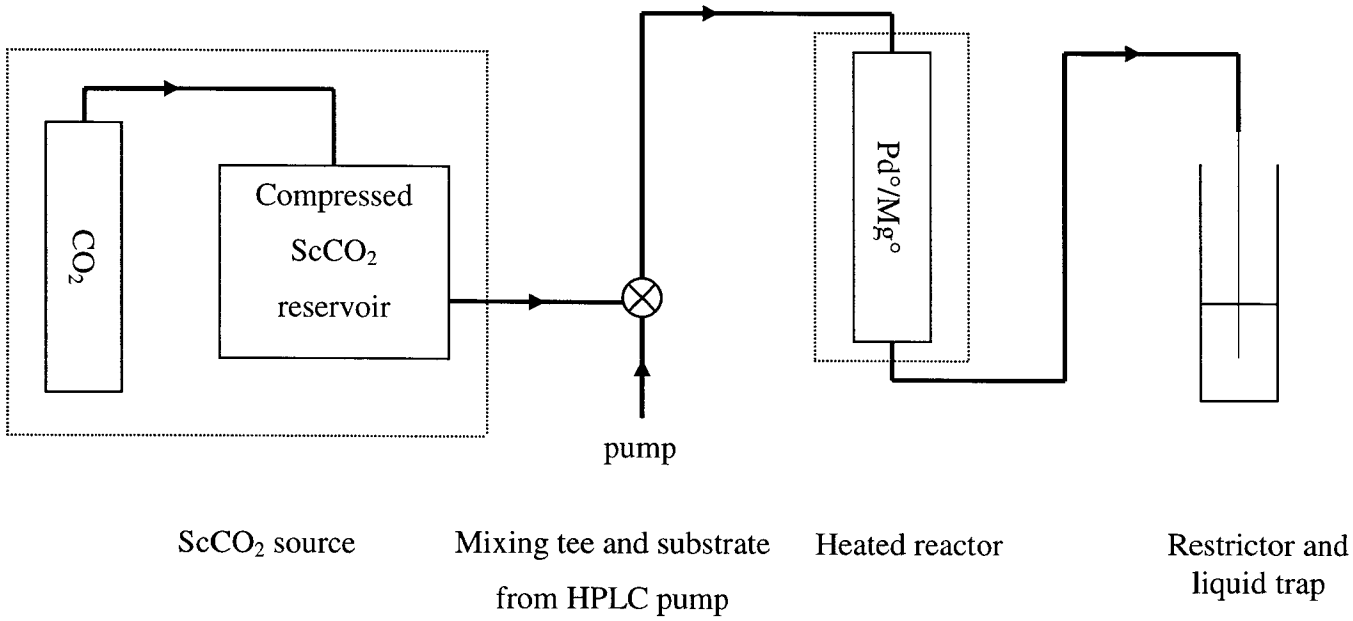


Figure 2.1 Schematic representation of the reactor system for the Pd°/Mg° mediated dechlorination of PCP in $ScCO_2$.

min. After an initial hold for 2 min at 40 °C, the column was ramped, at 10 °C/min, to 250 °C and held for a further 1 min prior to cool down. The temperature of the injector and detector were maintained at 220 and 165 °C respectively. Eluting components were identified tentatively by comparison of experimental mass spectra with spectra catalogued in the National Institute of Standards and Technology (NIST) or Wiley 318 spectral libraries and corroborated by co-chromatography and spectral matching with authentic standards.

2.3 Results and discussion

It was envisaged that the overall process of decontamination of natural media (soils/sediments) would become more appealing if extractions of organochlorine (OC) contaminants from polluted media were to be coupled with an *on-line* detoxification sequence. Generally, OC compounds have been considered to be environmentally recalcitrant due principally to their relatively non-polar nature (that decreases aqueous solubility and hinders physical dispersal processes) and the general lack of functional groups (that can facilitate metabolic transformations). Toxicities of OC compounds can be reduced appreciably by reductive dechlorination to form relatively innocuous hydrocarbon and chloride ion. It was further anticipated that once mobilized into supercritical carbon dioxide ($ScCO_2$), dechlorination might be accelerated further by contact of the solution with zero-valent bimetallic mixture of palladium and magnesium (Pd^o/Mg^o). The reactivity of Mg^o (E^o = -2.02 V) was anticipated to be greater than the reactivity for Fe^o (E^o = -0.44 V); however the reactivity of Mg^o was also anticipated to be moderated by the hydrolysis of its ions (pK_{SP} $[Mg(OH)_2]$ = 11.15) on the metal surface so that it was unclear whether the substitution of Pd^o/Mg^o bimetallic mixture for Pb^o/Fe^o would improve the dechlorination activity of the reactor column. In dechlorination of OC compounds, hydrogen replaces the chlorine atoms of OC compounds to form non-chlorinated product. The hydroxylic solvent (methanol, 2-propanol or water) can serve as the hydrogen source.

The addition of 0.1 ml/min methanolic solution to the $ScCO_2$ mobile phase was considered to result in a single supercritical phase (Cui *et al*, 1991) that possessed

attractive features, including increased solvent strength while the viscosities and fluidities approached those of supercritical carbon dioxide (Sun *et al*, 1991). In preliminary trials, the decrease in the gas chromatography (GC) peak for PCP in the reactor eluate was influenced appreciably by the temperature (Table 2.1) for feedstock dissolved in propan-2-ol. As had been observed for PCBs (Wu *et al* 2000) and PCP (Kabir and Marshall, 2001), higher reactor column operating temperatures in the presence of a hydroxylic solvent favoured the dechlorination of PCP. With a single column of zero-valent palladium-magnesium (Pd°/Mg°) bimetallic mixture and moderate operating temperature, increased quantities of PCP were detected in successive trapping solutions (data not shown). However, at higher operating temperatures, the reaction was more complete and more persistent (shorter range of PCP recoveries in six successive 10 min traps). Increased mobile phase flow rates, that resulted in a decreased contact time of substrate with the metal surface, decreased the dechlorination efficiency somewhat. With 15.6g of ~20 mesh Pd^{o}/Mg^{o} bimetallic mixture required to fill the column completely, the void volume was estimated to be appreciably less than 1 cm^3.

Table 2. 1 Variations in product distribution (mol%) with temperature for a 30 min cumulative trap of reactor elute for PCP delivered (at 10 mg/min in propan-2-ol) to a single reactor column filled with Pd^{o}/Mg^{o}.

Temperature / °C	PCP	TeClP*	TrClP*	DiClP*	MClP*	Sum
250	82.3	8.1	2.1	2.6	N.D*.	95.1
300	30.1	38.7	12.3	6.1	6.8	94.0
350	19.3	34.8	12.6	6.9	5.3	78.9
400	8.0	31.1	18.2	8.0	7.1	72.4
450	7.7	33.5	27.5	8.6	9.8	87.1

*TeClP, tatrachlorophenol; TrClP, trichlorophenol; DiClP, dichlorophenol; MClP, monochlorophenol; N.D., none detected.

Somewhat arbitrarily, 400 °C and 22.5 MPa (corresponding to 1500 ml/min of decompressed gas) were chosen as the operating conditions for subsequent studies. The dechlorination efficiency was also influenced appreciably by the composition of the

feedstock solvent (Table 2.2). Although dechlorinations were more extensive on Pd°/Fe° surfaces than on Pd°/Fe° for PCP dissolved in methanol (Table 2.2, trial 3 *vs.* trial 2), dechlorinations proved to be appreciably more extensive in water methanol mixtures (trials 4-7) than in methanol (trial 2 or 3) which, in turn was more efficient than in propan-2-ol (trial 1). Presumably, interactions of water with the Mg^0 surface generated reactive hydrogen species more readily than from hydroxylic solvents and facilitated the hydrodechlorination.

To evaluate the magnitude of thermally induced dechlorinations, a companion experiment was conducted using silica (acid washed sea sand) to fill the reactor column. With somewhat similar reaction conditions (450 °C / 25.3 MPa, 1.5 ml/min $ScCO_2$), a feedstock of 10% (w/v) PCP in 1,2-dimethoxyethane delivered at 0.1 ml/min, served as substrate and six traps of elute were collected. The resulting chromatograms indicated the loss of approximately 50% of the PCP peak area and the formation of 4-chlorophenol, 3,5-dichlorophenol, 2,3,5-trichlorophenol, 2,3,4-trichlorophenol and 2,3,4,5-tetrachlorophenol that comprised the remainder of the products. Only a trace of phenol was detected in any of the eluate solutions. Thus, thermally induced dechlorination was inefficient relative to the action of bimetallic particles.

A variety of products were detected by GC-MS (Table 2.3) from a 6 h trial using a 5% (w/v) PCP feedstock dissolved in aqueous methanol (1 + 4, v/v). Conditions were 0.1 ml/min of feedstock delivered, at 400 °C/ 22.5 MPa to the reactor column containing 2% (w/w) palladium-magnesium bimetallic mixture. Substrate PCP was not detected in any of the 12 trapping solutions. Although the proportions of products in the first trap apparently was anomalous, the contents of traps 2-12 were highly repeatable. Table 2.3, which reports the mean content of analytes from three replicate trials (± RSD), provides a measure of the level of repeatability that was achieved in these trials and indicates that 88.7 ± 2.5% of the substrate PCP (mean mass balance) was accounted for among the products. In addition to the anticipated phenol which accounted for 79.0 ± 3.6% of the substrate PCP (mean of traps 2-12), methylated products, principally anisole (3.8 ± 1.8%) and ring-methylated phenols (3.6 ± 1.5%) were also detected. Traces of cyclohexanone

were also present (mean, 1.2 ± 0.8%) in the mixture of trap 2, but decreased steadily in successive traps and was not detected in trap 12. Chlorinated products (mean, 1.8 ± 2.4%), that represented less than 1.0% of the product mixture in trap 2, gradually increased to ~7% in trap 12. Possibly, other products were not detected because they were co-eluted from the GC together with the solvent. In successive traps, the quantity of O-methylated products, were relatively constant (3.6 ± 0.5%) whereas the quantities of both ring methylated products (*o*- and *p*-cresol) decreased gradually but steadily with continued reactor operation. The mean ratio of *o*- to *p*-cresol over the course of the trial was relatively invariant (5.5 ± 0.4%) in successive traps. The product speciation is summarized in Table 2.4.

With identical conditions of temperature and pressure, a decreased Pd^0 loading on the Mg^0 [1% Pd^0 (w/w)] did change the dechlorination efficiency modestly (Table 2.5 *vs.* Table 2.3); however the dechlorination capacity of the mixture was reduced as demonstrated by a more rapid increase in partially dechlorinated analogs (Table 2.5). In addition to phenol, that accounted for 61.7 ± 8.6% of the elute, anisole (8.3 ± 1.3%), *o*-cresol (4.4 ± 2.3%) and *p*-cresol (0.8 ± 0.6%) and cyclohexanone (0.4 ± 4%) were the other products. Again, O-methylated products were relatively invariant in the successive traps and there was slow but continued decreases in the quantities of ring methylated products. The ratio of *o*- to *p*-cresol over the course of this trial was again relatively constant (6.1 ± 13%) and not appreciably different from the observations at the higher Pd° accelerator loading (5.5 ± 0.4%). Of 35.24 mmoles of organically bound chlorine in the substrate (equivalent to 5 chlorine atoms times the sum of the isolated products), 0.139 mmoles organically bound chlorine was accounted for among the products and the remainder was presumed to be retained on the column as chloride ion. Thus, the dechlorination efficiencies among the products in two trials in traps 2-12 were: (1-0.139/35.24)=0.996 for the 2% Pd° loading and (1-0.44/27.50)=0.984 for the 1% Pd° loading on the Mg°.

Differences in the course of the reactions between trials conducted at the two Pd° loadings (2% *vs.* 1%) were not evident. However the distribution of products in these

trials was somewhat different from previous observations for methanolic PCP reacted with Ag°/Fe°. In the earlier study (Kabir and Marshall, 2001), during which the reactor was run for 2.5 h at 450 °C, methylated phenols accounted for 47.5 ± 1.5%, phenol for a further 46.9% and methylated benzenes for 5.1 ± 0.5% of the PCP elute. For dechlorinations in propan-2-ol, the distribution was changed to ~13% methylated phenols, ~50% phenol and ~36% methylated benzenes. In the current trials, which were continued for 6 and 5 h respectively, methylated benzenes were not detected; phenol accounted ~79 ± 4% and ~62 ± 9% of the influent PCP (higher and lower Pd° loading respectively) and methylated phenols accounted for a further 7 ± 2% and 15 ± 2%. Seemingly, the loading of higher levels of Pd° on the Mg° surface imparted increased dechlorinating capacity to the bimetal. The addition of water to methanol (1+4, v/v) caused a further shift in product distribution, so that phenol methylation and ring reduction generated minor quantities of transformation products and no deoxygenation (to form substituted benzenes) was observed. In terms of detoxification, the loss of deoxygenating activity and the decrease in O-methylating activity are considered to be beneficial to the overall remediation process, in that more of the phenolic group is retained intact and the resulting products can be anticipated to be more water soluble.

Table 2.2 Products (mol% ± RSD) and mass balance observed for six sequential 10-min traps of reactor eluate for various feed rates of PCP dissolved in test hydroxylic solvent and delivered to a single reactor column filled with Pd°/Mg° or Pd°/Fe° operated at 22.5 MPa / 400 °C.

	Feed rate		Products[a]										
Trials	(mg/min)	Feedstock Solvent	PCP	TrClP	DClP	MClP	Xylenols	Chloroanisoles	Anisole	Phenol	o-Cresol	Cyclohexanone	Mass balance
1	1	propan-2-ol	11.9±26	17.0± 6	12.9±34	9.7±18	5.2±27	N.D. [b]	N.D.	13.6± 7	N.D.	N.D.	65.1 ±13.0
2	1	methanol	N.D.	7.7±12	7.6±13	23.7±8	5.1±2	N.D.	N.D.	13.8±12	11.0±26	N.D.	72.5 ± 7.3
3	1	methanol [c]	N.D.	N.D.	N.D.	12.6±2	2.2± 5	N.D.	N.D.	38.9± 6	16.6±13	N.D.	70.3 ± 7.0
4	5	water methanol (1+49)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	8.6± 9	68.4± 3	3.0±3	N.D.	80.0 ± 1.8
5	5	water methanol (1 + 9)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	5.1± 5	71.4± 1	4.7± 9	1.8 ± 12	82.9 ± 0.7
6	5	water methanol (1 + 4)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	2.1± 7	80.2± 5	3.6 ±9	3.4 ± 10	89.3 ± 4.9
7	10	water methanol (1 + 4)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	2.2±13	82.1± 5	1.8±42	N.D.	86.1 ± 4.4
8	15	water methanol (1 + 4)	N.D.	24.2±6	15.4±24	7.2±14	N.D.	3.9±29	N.D.	2.4±24	N.D.	N.D.	60.0 ±18.0[d]

[a] TrClP, trichlorophenol; DiClP, dichlorophenol; MClP, monochlorophenol;

[b] N.D. = none detected

[c] For this series of trials the reactor column was packed with Pd°/Fe°

[d] For this series of trials, organically bound chlorine in the eluate accounted for a further 32.0 ± 22%

Table 2.3 Dechlorination (mol% ± RSD) with time, of 5% (w/v) PCP in water-methanol (1 + 4, v/v) over 2% Pd°/Mg° in 6 hours

	retention time	Trap numbers (collected during 30 min)											
Products	(min)	1	2	3	4	5	6	7	8	9	10	11	12
cyclohexanone	5.1	2.7±6.2	2.9±2.5	2.1±3.0	1.7±5.0	1.4±4.8	1.1±8.3	0.9±6.7	0.8±2.7	0.7±5.1	0.6±4.7	0.5±4.8	0.4±2.2
phenol	6.8	46.8±0.3	72.7±0.4	77.7±0.5	79.5±0.5	81.0±0.3	82.3±0.5	79.3±0.6	81.5±4.3	83.6±4.3	80.7±0.2	76.9±0.2	72.8±1.7
anisole	5.6	5.6±0.4	3.7±1.3	3.3±1.6	3.3±2.2	3.4±1.9	3.3±1.7	3.5±2.1	4.0±1.5	4.1±1.3	3.4±1.4	2.8±2.0	1.8±2.6
2-cresol	7.9	10.0±0.2	6.3±0.3	4.5±0.4	3.7±0.4	3.2±0.6	2.7±0.2	2.5±0.4	2.6±0.3	2.6±0.3	2.2±0.5	2.0±0.1	1.6±0.5
4-cresol	8.2	1.0±0.7	1.0±1.3	0.8±2.6	0.7±2.7	0.6±5.5	0.5±3.9	0.4±2.7	0.5±2.5	0.5±3.4	0.4±2.3	0.4±3.4	0.3±3.6
Ratio *o-/p*-cresol		10.0	6.3	5.6	5.3	5.3	5.4	6.3	5.2	5.2	5.5	5.0	5.3
4-chlorophenol	6.9	N.D. [a]	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D	2.2±1.8	2.5±3.7	3.1±0.6	3.8±6.0
2-chloroanisole	8.7	1.1±0.3	0.2±0.8	0.1±4.8	0.1±8.5	N.D.	N.D.	N.D.	0.1±86.7	0.2±0.6	0.2±5.4	0.2±3.8	0.3±8.3
2,3-dichlorophenol	9.6	0.7±0.8	0.5±1.5	0.4±0.9	0.4±0.2	N.D.	N.D.	N.D.	N.D.	0.5±1.8	0.9±0.4	1.4±0.4	2.5±9.2
2,4,6-trichlorophenol	12.2	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	ND	N.D.	0.2±16.0	0.5±3.4
Mass balance		67.9±0.1	87.4±0.3	88.9±0.4	89.3±0.6	89.6±0.4	89.9±0.5	86.7±0.6	87.5±0.2	93.8±0.2	90.9±0.2	87.4±0.2	84.0±0.5

[a]N.D., none detected.

Table 2.4 Mean recoveries of products (mol% ± RSD) from 0.5h to the termination of the trial

(a)Overall recovery

Products	2% (w/v) Pd^0/Mg^0	1% (w/v) Pd^0/Mg^0
Non-chlorinated	87.1 ± 4.2	75.2 ± 11.2
Chlorinated	1.8 ± 2.4	8.1 ± 9.0
Phenol	79.0 ± 3.6	61.7 ± 8.6
Cyclohexanone	1.2 ± 0.8	0.4 ± 0.4
O-methylated	3.8 ± 1.8	10.1 ±1.0
Ring-methylated	3.6 ± 1.5	4.6 ± 2.1
o-/p-Cresol ratio	5.5 ± 0.4	6.1 ± 13.0

(b)[a] 30 min traps for PCP in methanol

	Trap number						
Products	1	2	3	4	5	6	Mean
Methylated phenols	49.9	47.8	47.4	45.9	47.0		47.5 ± 1.5
Phenol	45.2	46.9	47.5	47.4	47.6		46.9 ± 1.0
Methylated benzenes	4.5	5.5	5.2	5.6	4.6		5.1 ± 0.5
Chlorinated phenols	N.D. [b]	N.D.	0.5	0.8	1.0		

(c)[c] 30 min traps for PCP in propan-2-ol

Methylated phenols	15.9	10.6	12.3	13.2	13.9	14.1	13.3+1.7
Phenol	48.6	51.1	50.1	51.2	50.9	50.3	50.4+1.0
Methylated benzenes	35.4	38.3	35.8	36.7	36.4	36.4	36.5+1.0
Chlorinated phenols	N.D.	N.D.	N.D.	N.D.	N.D.	1.6	

[a, c], Data from Kabir and Marshall, (2000);

[b] N.D., none detected.

Table 2.5 Dechlorination (mol% ± RSD) with time, of 5% (w/v) PCP in water-methanol (1 + 4, v/v) over 1% Pd°/Mg° in 5 hours

	retention time	Trap number (each collected during 30 min)									
Products	min	1	2	3	4	5	6	7	8	9	10
Cyclohexanone	4.7	1.4±13.1	1.1±16.7	0.8±15.6	0.6±14.7	0.4±10.8	0.3±9.3	0.2±1.7	0.1±5.1	0.1±10.7	N.D.[a]
Phenol	6.34	42.0±19.1	63.4±10.8	66.9±11.1	69.5±13.4	69.8±11.3	67.6±20.1	64.1±22.7	55.9±41.7	53.4±18.5	44.8±10.8
Anisole	5.2	8.9±14.8	9.4±27.9	9.1±24.9	8.4±19.9	9.0±19.0	9.0±11.3	9.3±6.9	8.2±5.0	6.7±10.6	5.7±24.5
2-Cresol	7.4	11.7±14.7	9.1±31.8	6.6±32.1	4.6±29.8	3.5±28.0	2.9±17.4	2.8±15.8	2.6±8.9	2.5±12.4	2.3±0.3
4-Cresol	7.8	1.5±3.6	1.7±35.2	1.4±37.0	0.9±35.2	0.6±31.0	0.5±18.8	0.4±15.7	0.3±10.5	0.5±62.1	0.3±2.7
Ratio *o-/p*-resol			5.35	4.71	5.11	5.83	5.80	7.0	8.6	5.0	7.7
2-Chlorophenol	6.38	N.D.	N.D.	N.D.	N.D.	0.8±173.2	2.0±102.5	3.4±96.0	5.3±91.5	7.6±87.1	7.7±86.6
2-Chloroanisole	8.3	1.2±55.2	0.4±51.6	0.2±48.1	0.2±50.0	0.6±77.3	1.2±44.1	2.0±19.5	2.5±15.9	2.9±5.7	2.8±10.8
2,3-Dichlorophenol	9.2	N.D.	N.D.	N.D.	N.D.	0.2±173.2	0.6±54.4	1.4±37.0	3.0±22.7	5.9±5.5	7.3±2.3
2,3-Dichloroanisole	11.1	N.D.	N.D.	N.D.	N.D.	0.1±173.2	0.3±9.2	0.6±46.6	0.9±61.9	1.5±78.6	1.7±87.8
2,4,6-trichlorophenol	11.4	N.D.	N.D.	N.D.	N.D.	0.1±173.2	0.3±173.2	0.9±90.9	1.6±47.7	2.6±58.7	3.4±47.8
2,4,6-trichloroanisole	12.8	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.1±56.6	0.2±47.4	0.4±49.6
Mass balance		66.8±14.0	85.2±5.1	85.0±6.5	84.2±8.7	85.0±8.5	84.7±9.9	85.0±3.8	80.6±8.8	83.8±0.9	76.3±5.0

[a]N.D., none detected.

Chapter 3
Detoxification of aryl organochlorine compounds by catalytic hydrogenation

3.1 Introduction

The use of mixtures of molecular hydrogen with supercritical carbon dioxide ($ScCO_2$) as a medium to perform reductive dechlorinations has remained less extensively explored, yet this phase possesses several attractive properties. The use of $ScCO_2$ has often been considered to be an ideal phase because of its mild critical properties (T_c=31 °C, P_c=7.4 MPa), non-toxicity, non-flammability, modest cost and a lack of restrictive regulations. Molecular hydrogen is completely miscible in near-critical CO_2 (Tsang *et al*,1981) and can result in a very high initial rate of reaction; up to 1400 mol of formic acid have been produced from CO_2 per mol of catalyst per h (Jessop *et al*, 1994). The same reaction under identical conditions but in liquid organic solvents is much slower principally due to decreased diffusion rates and the limited solubility of H_2 in most organic solvents. Solvent polarity of the reaction medium can be fine tuned with ease in the near-critical region [generally 1.05-1.2 T_c (Subramaniam *et al*, 2002)] by simply changing the pressure. To achieve suitable substrate solubility, the reaction medium can be modified by adding an inert co-solvent. As an example, ethanol can be volume expanded several fold with dense-phase CO_2 in which this solvent become totally miscible. Moreover, the reactants/products can be separated readily from the reaction medium by pressure reduction. Because aromatic hydrogenations are highly exothermic (Song, 1999) reaction is favored and selectivities can be increased by operation at lower temperatures. Yet for hydrogenations on a larger scale, some means of heat dissipation can become necessary. The heat capacities of $ScCO_2$ can also be pressure-tuned to be more liquid-like (Arunajatesan *et al*, 2001) and to minimize product hold up. For porous solid catalysts product selectivity can also be optimized to mitigate pore-diffusion limitations and the accumulation of coke-forming precursors that can inactivate catalytic sites. Clark and Subramaniam (1998) have reported that in $ScCO_2$, 1-butene/isobutane alkylation resulted in virtually steady alkylate (trimethylpentanes and dimethylhexanes) production during two days. The ability of the carbon dioxide based supercritical reaction mixtures to mitigate coking and thereby to maintain better pore accessibilities was evident from the

narrow product spectrum (confined to C_8 products), the lighter color of the spent catalyst samples, and relatively low surface-area of area and pore-volume losses (<25%) in the spent catalysts. For identical 1-butene space-velocity and feed isobutane/olefin ratios in the absence of CO_2, alkylate formation declined continuously with time. At the high temperatures (>135 °C) required for supercritical operation without carbon dioxide, cracking and cooking reactions were dominant.

Catalytic inactivation has been reported during hydrogenations over $Pt°/Al_2O_3$ in near-critical CO_2 (Minder *et al*, 1995) that might have resulted from the possible formation of one or more possible surface species including formates, carbonates and/or CO in the presence of CO_2+H_2. A variety of fats and oils have been reduced successfully in near-critical CO_2 over Ni (Tacke *et al*, 1996), Pd or Pt (King *et al*, 2001). As well, the reduction of double bonds of unsaturated ketones over $Pd°/Al_2O_3$ has been reported (Bretucoo *et al*, 1997). Several insightful reviews (Savage *et al*, 1995; Baiker, 1999; Subramaniam, 2001) have been published recently.

LaPierre et al (1977) reported that a batch process using a supported Ni or Pd catalyst in EtOH/NaOH (as an acid acceptor of the HCl liberated) for the hydrodechlorination of polychlorinated pesticides and related substances. Under certain conditions of temperature (< 150 °C) and H_2 pressures (< 50 atms), they observed a reactivity sequence established on C-Cl bonding where an olefinic Cl was most reactive, aromatic Cl was less reactive and aliphatic Cl was least reactive. Highly bridged and nonplanar molecules such as Aldrin and Dieldrin were the most difficult compounds to hydrodechlorinate due to steric effects. Removal of aromatic Cl was the limiting factor in the hydrodechlorination of DDT and DDE. Yakovlev *et al* (1998) have demonstrated that Pd and Pd-promoted Ni catalysts exhibited activity in the liquid phase hydrodechlorination of chlorobenzene, 1,2,4-trichlorobenzene, hexachlorobenzene, and polychlorinated biphenyl compounds. Experiments were carried out in ethanol containing H_2 (1-50 atm) at 20-70 °C.

The gas phase hydrodechlorination of chlorophenols [(dichlorophenols (DCPs), trichlorophenols (TCPs), and pentachlorophenol (PCP)] in H_2 over Ni (1.5 and 15.2

wt.%) loaded on silica and Ni (2.2%, w/w) exchanged Y zeolite catalysts were evaluated over the temperature range 200-300 °C. In every instance, the Ni catalysts were 100% selective in cleaving the Cl component from the ring, leaving the aromatic nucleus and OH substituent intact (Shin *et al*, 1999). Similarly, the gas phase hydrodechlorination of methanolic and mixed methanol/water solutions of 2-chlorophenol, 2,6-dichlorophenol, 2,4,5-trichorophenol and pentachlorophenol have been studied at 300 °C over Ni/SiO_2 catalysts of varying (1.5-20.3 wt.% Ni) nickel loading (Shin et al, 2000). Each catalyst was again 100% selective in promoting hydrodechlorination.

Hydrogen temperature programmed desorption (TPD) revealed the existence of three forms of surface hydrogen: (I) hydrogen bound to the surface nickel; (ii) hydrogen at the nickel/silica interface; and (iii) spillover hydrogen on the silica support (Tavoularis *et al*, 1999). The spillover hydrogen appeared to be hydrogenolytic in nature and was responsible for promoting hydrodechlorination while the hydrogen that was chemisorbed on, and remained associated with, the surface nickel metal participated in aromatic hydrogenation. Hydrodechlorination proceeded *via* an electrophilic mechanism, possibly involving spillover hydronium ions. The gas-phase hydrogenation/hydrogenolysis of alcoholic solutions of phenol was studied at 150-300 °C using a Y zeolite-suppouted Ni catalyst and a Ni/SiO_2 (Shin *et al*, 2000) catalyst. Phenol hydrogenation proceeded in a stepwise fashion giving cyclohexanone as a reactive intermediate while a combination of hydrogenolysis and hydrogination yielded cyclohexane. Hydrogenolysis to benzene was favored by high Ni loadings and elevated temperatures. The gas-phase hydrogenation of PhOH at 150-300 °C has also been studied over Pd°/Mg° (1%, w/w). Hydrogenation proceeded in a stepwise fashion with cyclohexanone as the partially hydrogenated product and cyclohexanol as the fully hydrogenated product (Claus *et al*, 2000). The catalyst provided 96% selectivity with respect to cyclohexanone at 150 °C, but the cyclohexanone yield decreases at higher temperatures as conversion declined and cyclohexanol was increasingly preferred. Conversion and selectivity were stable with prolonged catalyst use (i.e., time on stream>55h.) The catalytic hydrodechlorination of chlorobenzene in ethanol over Ni°/C, Pd°/C and Ni°/Pd° was studied at 50 °C, 1 atm H_2. All three catalysts had mediated efficient dechlorination after 3h (Yakovlev *et al*, 2000).

Dechlorinations in $ScCO_2$ of polychlorinated biphenyl (PCB) compounds or pentachlorophenol (PCP) have been performed in a flow-through reacter filled with zero-valent metal (Fe° or Mg°) or bimetallic mixture (Ag°/Fe°, Pd°/Fe° or Pd°/Mg°). Substrate (20-30 mg/min) was dechlorinated very efficiently (but not quantitatively) within a 25×1 cm reactor column operated at ~450 °C. The only appreciable products were biphenyl (or phenol) and chloride ion the remained on the ZV metal surface (Wu *et al*, 2000; Kabir *et al*, 2001; Yuan *et al*, 2002). Aikawa *et al* (2000) have studied the Pd catalyzed hydrodehalogenation of 1-chlorooctadecane, 9,10-dichlorostearic acid, and 12,14-dichlorodehydroabietic acid in $ScCO_2$. The objective of the current study were to evaluate mixtures of H_2 with $ScCO_2$ for their ability to mediate the catalytic dechlorination of aromatic organochlorine compounds.

3.2 Materials and methods

3.2.1 Chemicals

Pentachlorophenol (PCP), octachloronaphthalene, decachlorobiphenyl, phenol, naphthalene, biphenyl, cyclohexanol, cyclohexanone, *o*-cholrophenol, *p*-chlorophenol, 2,3-dichlorophenol, 2,3,5- 2,3,6-trichlorophenol, *trans*- and *cis*- decalin, bicyclohexyl, 4-bromobiphenyl, ehthanol and hexane were purchased from Aldrich Chemical Co., Oakville, ON, Canada. Tetrachlorophenols (2,3,4,6- and 2,3,5,6-) were purchased from Supelco Co., Oakville, ON, Canada. Catalysts Ni°/SiO_2-Al_2O_3 (66%±3, w/w), Pd°/γ-Al_2O_3 (5%, w/w) and Pt°/γ-Al_2O_3 (1%, w/w) were purchased from Alfa Aesar, Ward Hill, MA, USA. Ag° (0.3%, w/w) /Fe° (1.7%, w/w) /Al_2O_3, Fe° /Al_2O_3 (0.3%, w/w) were prepared by surface deposition. All chemicals were ACS Reagent Grade or better and were used as received.

3.2.2 Experimental reactor and operation

The dechlorination assembly consisted of a source of pressurized $ScCO_2$, [a K-type cylinder of compressed CO_2 that was further pressurized with an diaphragm compressor (Newport Scientific, Jessop, MD)], hydrogen source, a reactor unit and a sample trap. The

supercritical fluid reactor consisted of a 50 ml high-pressure cylindrical vessel with a demountable top that had been modified with the addition of four stainless steel (ss) tubes (1/16 in. i.d.) that served as gas inlet and outlet. The tubes were each terminated with a high pressure needle valve. At the exit of the reactor, a capillary restrictor (25 cm × 0.05 mm i.d.) was used to release the pressure and a liquid trap was used to collect the reaction products. The hydrodechlorination reactor system is illustrated schematically in Figure 3.1.

In operation, the vesseal was eauilibrated in a water bath to the desired operating temperature of the experiment and then charged with substrate (1 mg) in 0.2 ml hexane, test catalyst (25 mg) and a teflon-coated magnetic stirring bar. After a short purge of residues of air by displacement, the mixture was then pressurized to 690 KPa with H_2 gas. For certain runs, the reaction medium was overpressured with $ScCO_2$ (8.27-30.34 Mpa). Post reaction for 0.5-2h, the pressure was released gradually through a restrictor into ethanolic trapping solvent (10 ml). Sample was collected by combining the wash solution of the vessel and trapping solution in the vial. All trials were performed in triplicate. The course of each trial was monitored by gas chromatography-mass spectrometry (GC-MS).

3.2.3 GC-MS Analysis

GC-MS was performed on a Varian model 3900 gas chromatograph fitted with a model 8400 autosampler and a model 2100T MS detector. The DB-5 capillary column (30 m × 0.25 mm i.d.; 0.25 μm film thickness) was eluted with helium at 1.0 ml/min. After an initial hold for 1 min at 50 °C, the column was ramped, at 10 °C/min, to 300 °C, and held for a further 3 min prior to cool down. The temperature of the injector, transferline and detector were maintained at 250 °C, 250 °C and 150 °C respectively. Eluting components were identified tentatively by comparison of experimental mass spectra with spectra catalogued in the National Institue of Standards and Technology (NIST) or the Saturn mass spectral libraries and corroborated by co-chromatography and spectral matching with authentic standards. (For the quantatitation of 1,1'-oxybis-cyclohexane, the signal response was presumed to be twice that of phenol.)

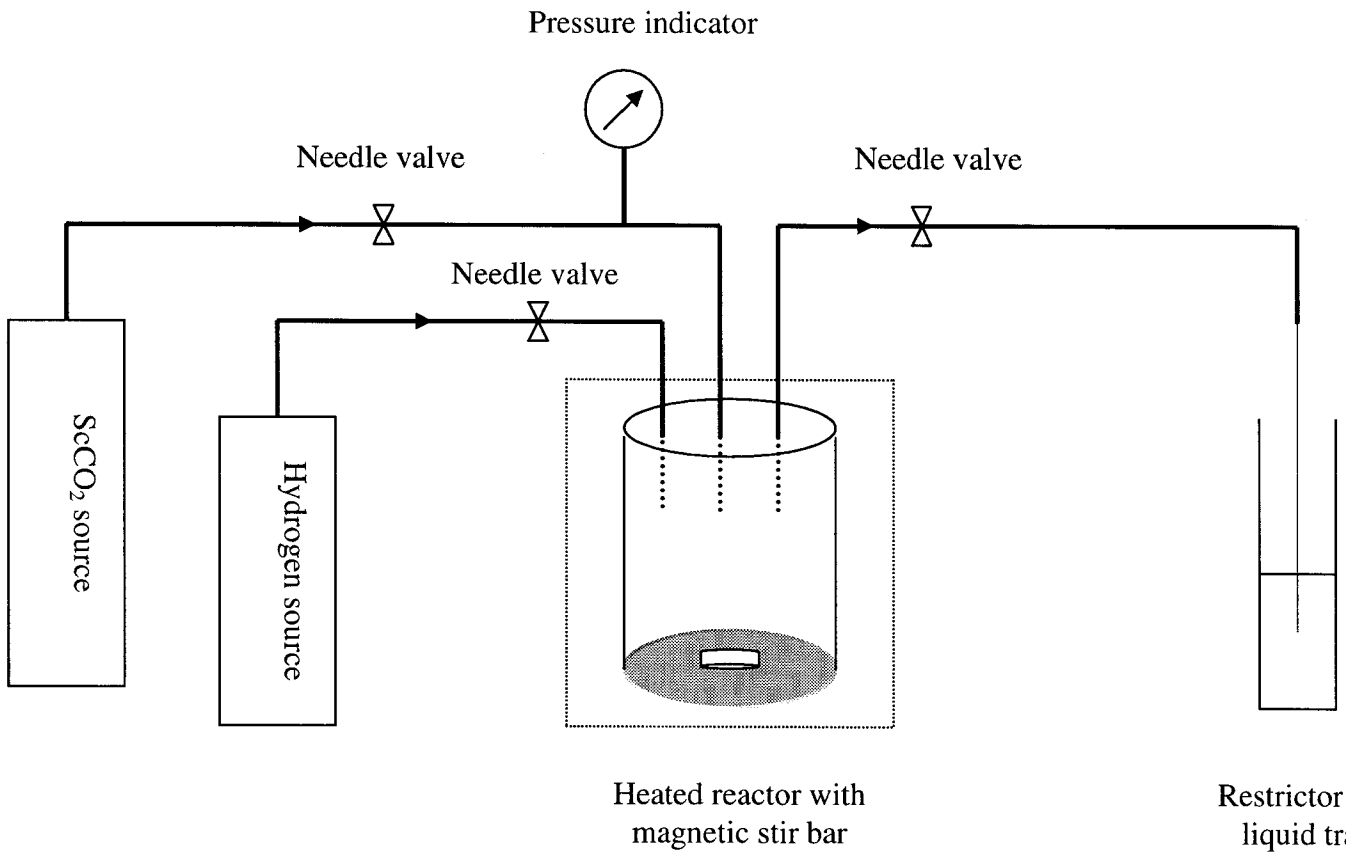


Figure 3.1 Schematic representation of the reactor system for hydrodechlorination of chlorinated aromatic compounds in $ScCO_2$.

3.3 Results and discussion

It was envisaged that the overall process of decontamination of natural media (soils/sediments) would become more appealing if supercritical carbon dioxide ($ScCO_2$) extractions of organochlorine (OC) contaminants from polluted media were to be coupled with an *on line* detoxification sequence. Generally, OC compounds have been considered to be environmentally recalcitrant due principally to their relatively non-polar nature (that decreases aqueous solubility and hinders physical dispersal processes) and the general lack of functional groups (that can facilitate metabolic transformation). Toxicities of OC compounds can be reduced appreciably by reductive dechlorination to form relatively innocuous hydrocarbon and chloride ion. It was further anticipated that once mobilized into supercritical carbon dioxide ($ScCO_2$), dechlorination might be accelerated further by contact of the solution with molecular hydrogen in the presence of a catalyst.

It was also considered that operation above the boiling point of hexane would assure a single supercritical phase for the solution. In initial experiments, the capacities of five alumina supported catalysts to accelerate the dechlorination of pentachlorophenol (PCP) were evaluated in the presence of a large excess of hydrogen (Table 3.1). After 2h of reaction at 80 °C, the bare alumina support material had mediated only partial dechlorination to tetrachloropheol species (~5 mol% conversion) that was only marginally more efficient than trials in the absence of either catalyst or hydrogen for which no reaction had been observed. The zero valent iron (Fe°) loaded support was not more efficient at mediating dechlorination than was the bare alumina. Product distributions for reactions in the presence of Ag°/Fe° supported bimetallic mixture contained only totally dechlorinated product that had also been ring reduced to cyclohexanol (~11 mol%) in addition to unreacted substrate (~67mol%). The Pt° and the Ni° supported catalysts did not produce more cyclohexanol (~12 and ~14 mol% respectively) than the bimetallic catalyst but less substrate remained after reaction (~47 and ~37 mol% respectively) and smaller quantities of tetrachlorophenols (~7 and ~18 mol%) and 1,1'-oxybis-cyclohexane (~3 and ~5 mol% respectively) were formed. The Pd°/γ-Al_2O_3 formulation was appreciably more efficient again. Chlorinated materials were absent, cyclohexanol was the one appreciable product (~71 mol%) and small

quantities of cyclohexanone (~2 mol%) and 1,1'-oxybis-cyclohexane (~2 mol%) were also detected. Thus, for this catalyst, dechlorination and de-aromatization were complete and only ~1 mol% of the substrate had lost an oxygen substituent.

In subsequent studies (Table 3.2A), pressure was maintained at 22 MPa while the temperature of the reaction of PCP with H_2 over $Pd°/\gamma\text{-}Al_2O_3$ was varied between 50 and 90 °C without any appreciable change in the product distribution after 2h of reaction. Both the cyclohexanone and the 1,1'-oxybis-cyclohexane were present in the product mixture only at trace quantities so that quantitation was somewhat less repeatable for these products. The reaction mixture was also over-pressured with CO_2 (to 0.69-31.34 MPa) (Table 3.2B) again with no perceptible effect on the product distributions. With these conditions, the $ScCO_2$ functioned as an inert medium for the reaction and apparently did not influence the course of the reaction. Table 3.3A summarizes efforts to detect time pressure interactions. The product distributions remained unchanged by increasing the total pressure from 8.3 to 13.8 MPa and the duration of reaction from 1 to 2h. In subsequent trials (Table 3.3B), the quantity of PCP was increased 10-fold, 3.75 μmol of either PCP in 0.2 ml hexane or 0.2 ml of aqueous phenolate ($NaOC_6Cl_5$) served as the substrate. The dechlorination products of PCP were similar to previous trials with 1 mg substrate but the amount of 1,1'-oxybis-cyclohexane was increased (~20 mol%). By contrast, the reaction was incompleted at this higher loading of phenolate (~33 mol% as cyclohexanone/cyclohexanol, but unreacted substrate ~40 mol%). Apparently, conversion to phenolate influenced the rate of reaction but the course of the reaction was essentially unchanged. It had been anticipated that introducing anionic character to the substrate might have accelerated electrophilic hydrodechlorination but it is also probable that the H_2 was only sparing soluble in this medium so that the rates of substrate reduction were compromised.

The variations among replicate trials, performed under the same operating conditions, was superior (for all three substrates) to the variations among trials at different operating conditions. A possible explanation for the variatiions in recoveries resides in the differences in the total pressure at which the different trials were performed. In general,

the recoveries of products were greater at relatively lower pressure (0.69 MPa) than at higher operating pressures (8.27-30.34 MPa). The products were considered to be somewhat volatile so that trapping efficiencies from the CO_2 were somewhat more efficient when released from lower operating pressures than release from higher operating pressures. A more efficient trapping medium might have solved this problem.

For comparison, the reduction of phenol was tested with H_2 (~570 μmol) at 0.69 MPa and 70 °C for 0.5h in the presence/absence of 25 mg of 5 % *(w/w)* Pd°/ γ-Al_2O_3. The major product was also cyclohexanol (~84 mol%) and only a small amount of cyclohexanone (~14 %mol) was formed. (Table 3.4)

Other highly chlorinated aromatic compounds were also subjected to reaction under the same conditions. Octachloronaphthalene (~70% chlorine by weight) was reacted with H_2 (0.69 MPa) in the presence/absence of 25 mg Pd°/γAl_2O_3 for 0.5 or 2h. Only decalin ($C_{10}H_{18}$) was observed in the crude product mixture (Table 3.5). Interestingly, the ratio of *trans-* to *cis-* product was approximately 3:1 after 0.5h had been decreased to 2.3:1 after 2h of reaction and might have become nearly equal after extended equilibration. In companion trials, reaction to decalin, in the presence of sufficient hexane (5 ml) to cover the catalyst surface completely, was also virtually complete at 80 or at 60 °C but at 50 °C, tetralin was the major product (~75 mol%). The other products were decalin (ratio *trans* to *cis*, 3.2:1) and traces of substrate. A possible explanation is a two-phase system (at 50 °C but perhaps not at 60 °C) that hindered H_2 access to the catalyst surface. A doubling of reaction rate for a 10 degree increase in reaction temperature would seem to be insufficient to account for the observed differences between 50 and 60 °C. Naphthalene also served as substrate for reaction during 0.5h. In this case, the ratio of *trans-* to *cis-* decalin was different again (~0.8:1). There was no tendency for dehydrogenation with these reaction conditions. Neither *trans-* nor *cis*-decalin, when pressurised to 690 kPa with nitrogen in the presence of Pd°/Al_2O_3 and reacted at 70 °C for 0.5–1 h, provided evidence for dehydrogenation to tetralin or naphthalene or for configurational isomerization.

In a final series of trials, decachlorobiphenyl (~71% Cl by weight) served as substrate (Table 3.6). After 0.5h reaction at 70 °C and 0.69 MPa of H_2, only dicyclohexyl (1,1'-dicyclohexane) was observed in the crude product mixture. The reaction was complete; chlorine was removed from the substrate and the product had been de-aromatized but no carbon-carbon bond scission had occurred.

In summary, highly chlorinated aromatic compounds were dechlorinated quantitatively when exposed to alumina supported palladium in hydrogen atmospheres under mild conditions. With these conditions, perchlorinated phenol, naphthalene or biphenyl substrates as well as their hydrocarbon homologs were also smoothly dearomatized to their cyclic analogs but no carbon-carbon bond rupture was observed. The formula structures and the mass spectra of the hydrodechlorination products are shown in Figure 3.2 and Figure 3.3 respectively. In the case of PCP, only small quantities of partial deoxygenation was observed. These observations, under mild reaction conditions, suggest that they might be applied to other aromatic compounds including environmentally recalcitrant polyaromatic hydrocarbons (PAHs).

Table 3.1 Variations in product yield (mol% ± RSD) with catalyst identity for the reaction of 0.375 μmol PCP in the presence of 25 mg catalyst and ~1% H_2 (0.69 MPa, ~570 μmol) in $ScCO_2$ (22.1 MPa) at 80 °C, reaction time of 2 hours.

Products	Ag°/Fe°/Al_2O_3	Pd°/γ-Al_2O_3	Fe°/γ-Al_2O_3	Pt°/γ-Al_2O_3	Ni°/SiO_2-Al_2O_3	Al_2O_3	No Catalyst	No H_2
Cyclohexanone	N.D.[a]	2.0 ±7.6	N.D.	2.5 ±60.7	1.0 ±20.8	N.D.	N.D.	N.D.
Cyclohexanol	11.4 ±1.6	71.1 ±2.6	N.D.	12.2 ±15.8	14.5 ±4.3	N.D.	N.D.	N.D.
1,1-'Oxybis- cyclohexane[b]	N.D.	2.0 ±1.5	N.D.	3.4 ±0.6	4.8 ±13.2	N.D.	N.D.	N.D.
Tetrachlorophenol	N.D.	N.D.	3.8 ±5.9	6.6 ±17.6	17.5± 11.4	4.9 ±21.3	N.D.	N.D.
PCP	66.9 ±5.2	N.D.	76.4 ±2.4	46.9 ±11.7	37.4 ±0.9	71.7 ±8.8	75.5 ±2.2	76.2 ±16.3
Mass balance	78.3 ±4.3	75.1 ±2.7	80.2 ±2.4	71.6 ±5.2	75.2 ±3.6	76.6 ±9.4	75.5 ±2.2	76.2 ±16.3

[a]N.D.: none detected

[b]The results were calculated by assuming that the detector response to this compound was twice that for cyclohexanol

Table 3.2 Variations of product recoveries (mol% ± RSD) with **A**, tempreature (50-90 °C) at 22 MPa or **B**, pressure (0.69-30.3 MPa) at 60 °C for 2 h of reaction of PCP (0.375 μmol) with H_2 (0.69 MPa) in $ScCO_2$ in the presence of 25 mg of $Pd°/\gamma\text{-}Al_2O_3$.

A	Temperature (°C)				
Products	50	60	70	80	90
Cyclohexanone	1.0 ±8.4	2.9 ±7.0	3.6 ±29.3	3.7 ±2.1	7.8 ±10.1
Cyclohexanol	66.8 ±.4	70.1 ±3.3	66.8 ±6.1	78.4 ±0.8	75.1 ±0.2
1,1-'Oxybis- cyclohexane *	5.9 ±6.7	4.7 ±1.4	6.4 ±9.4	7.0 ±0.6	6.8 ±1.2
Mass balance	73.6 ±4.4	77.7 ±3.3	76.8 ±4.8	89.1 ± 0.4	89.8 ± 0.9

B	Pressure (MPa)						
Products	0.69	8.27	13.79	18.62	22.06	26.20	30.34
Cyclohexanone	25.4±0.05	7.0 ±69.8	5.9 ±52.9	1.5 ±0.4	0.8 ±4.3	7.4 ±3.6	4.4 ±81.6
Cyclohexanol	64.7 ±0.2	59.1 ±5.7	59.4 ±2.3	62.9 ±3.6	71.0 ±8.0	58.4 ±1.1	55.7 ±10.1
1,1-'Oxybis- cyclohexane *	6.5 ±0.1	7.2 ±5.9	6.4 ±4.5	6.3 ±0.1	7.2 ±1.0	5.3 ±0.4	5.3 ±6.0
Mass balance	96.6 ±0.2	73.2 ±8.1	71.7 ±3.5	70.8 ±3.4	79.0 ±5.3	71.1 ±2.1	65.4 ±4.6

*The results were calculated by assuming that the detector response to this compound was twice that for cyclohexanol.

Table 3.3 Variations in the distribution of products (mol% ± RSD) for **A**, the reduction of PCP (0.375 μmol) with H_2 (~570 μmol), $ScCO_2$ (8.3 or 13.8MPa) at 60 °C for 1 or 2 h or **B**, with PCP loading (3.75 μmol) and solvent combination with H_2 (~570 μmol) for reactions at 60 °C for in 1 h. Both reactions were with catalyzed with 25 mg Pd°/γ-Al_2O_3.

A.

	Reaction time/hour ($ScCO_2$ pressure/MPa)			
Products	1 (8.3)	1 (13.8)	2 (8.3)	2 (13.8)
Cyclohexanone	9.9 ±1.7	8.6 ±3.7	7.0 ±69.8	5.9 ±52.9
Cyclohexanol	53.2 ±0.05	54.1 ±4.8	59.1 ±5.7	59.4 ±2.3
1,1-'Oxybis- cyclohexane[b]	6.3 ±1.7	6.3 ±3.3	7.2 ±5.9	6.4 ±4.5
Tetra-Cl-phenol	N.D.[a]	N.D.	N.D.	N.D.
PCP	N.D.	N.D.	N.D.	N.D.
Mass balance	69.4 ±5.0	69.3 ±3.9	73.3 ±8.1	71.7 ±3.5

B.

Products	PCP in hexane sol.	PCP sodium salt in water
Cyclohexanone	2.7 ±12.4	23.1 ± 2.6
Cyclohexanol	67.8 ±1.9	9.6 ±0.8
1,1-'Oxybis- cyclohexane	20.1 ±1.9	N.D.
Tetra-Cl-phenol	N.D.	N.D.
PCP	N.D.	39.6 ±12.1
Phenol	N.D.	N.D.
Mass balance	90.6 ±1.5	72.3 ±7.4

[a]N.D.: none detected.

[b]The results were calculated by assuming that the detector response to this compound was twice that for cyclohexanol

Table 3.4 Variations in the distribution of products (mol% ± RSD) for reduction of phenol (1 mg) with H_2 (~570 μmol) at 70 °C for 0.5h in the presence /absence of 25 mg of 5 % *(w/w)* Pd°/ γ-Al_2O_3

Products	with catalyst	no catalyst
Cyclohexanone	13.7 ± 3.4	N.D.[a]
Cyclohexanol	83.9 ± 13.1	N.D.
Phenol	N.D.	94.2 ± 2.0
Mass balance	97.6 ± 11.7	94.2 ± 2.0

[a]N.D.: none detected

Table 3.5 Variations in decalin recoveries (mol% ± RSD) after 0.5 or 2h of hydrogenation (at 70 °C and 0.69 MPa) of 1 mg octachloronaphthalene or naphthalene in the presence/absence of 25 mg of 5 % *(w/w)* Pd°/ γ-Al_2O_3.

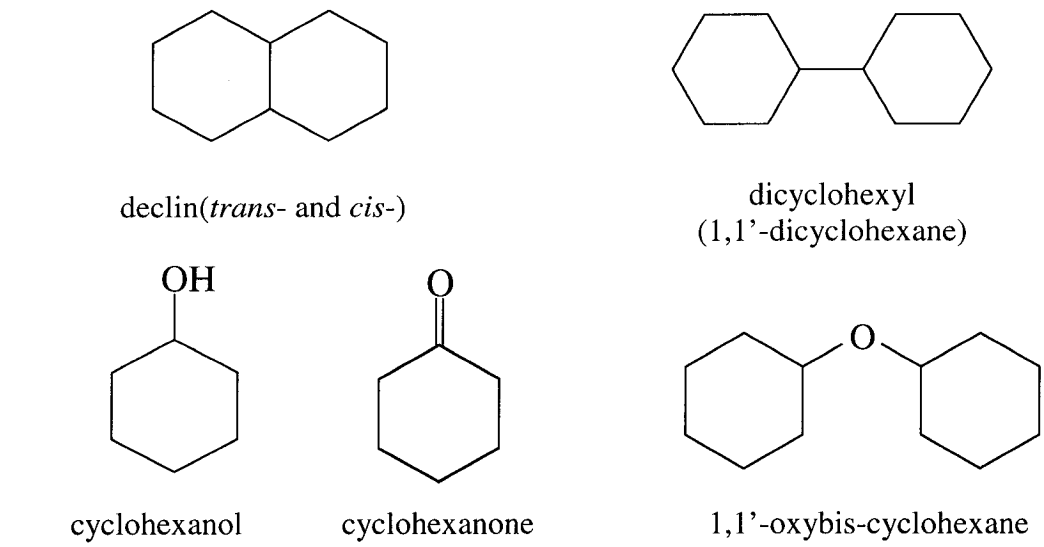
	octachloronaphthalene			naphthalene	
Products	2h without catalyst	0.5h with catalyst	2h with catalyst	2h without catalyst	0.5h with catalyst
Octachloronaphthalene	95.2 ± 5.1	N.D.*	N.D.	-	-
Naphthalene	N.D.	N.D.	N.D.	93.1 ± 5.5	N.D.
Cis-decalin	N.D.	23.3 ± 4.8	29.8 ± 6.6	N.D.	54.6 ± 6.4
Trans-decalin	N.D.	71.7 ± 3.5	67.7 ± 3.4	N.D.	44.5 ± 3.4
Recovery(%)	95.2 ± 5.1	95.0 ± 2.0	97.5 ± 4.2	93.1 ± 5.5	99.1 ± 5.1

*N.D. none detected.

Table 3.6 Variations in dicyclohexyl recoveries (mol% ± RSD) after 0.5h of hydrogenation (at 70 °C and 0.69 MPa) of 1 mg decachlorobiphenyl or biphenyl in the presence /absence of 25 mg of 5 % *(w/w)* Pd°/ γ-Al_2O_3

	decachlorobiphenyl		biphenyl	
Products	0.5h without catalyst	0.5h with catalyst	0.5h without catalyst	0.5h with catalyst
Decachlorobiphenyl	102.7 ± 5.8	N.D.*	-	-
Biphenyl	N.D.	N.D.	93.1 ± 3.4	N.D.
Dicyclohexyl	N.D.	101.6 ± 1.4	N.D.	96.9 ± 9.6
Mass recovery(%)	102.7 ± 5.8	101.6 ± 1.4	93.1 ± 3.4	96.9 ± 9.6

*N.D. none detected.



declin(*trans*- and *cis*-)

dicyclohexyl
(1,1'-dicyclohexane)

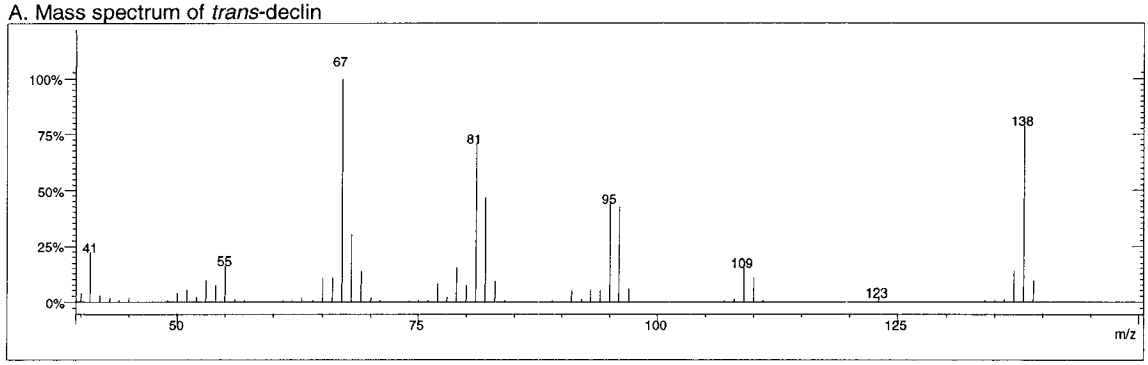
cyclohexanol

cyclohexanone

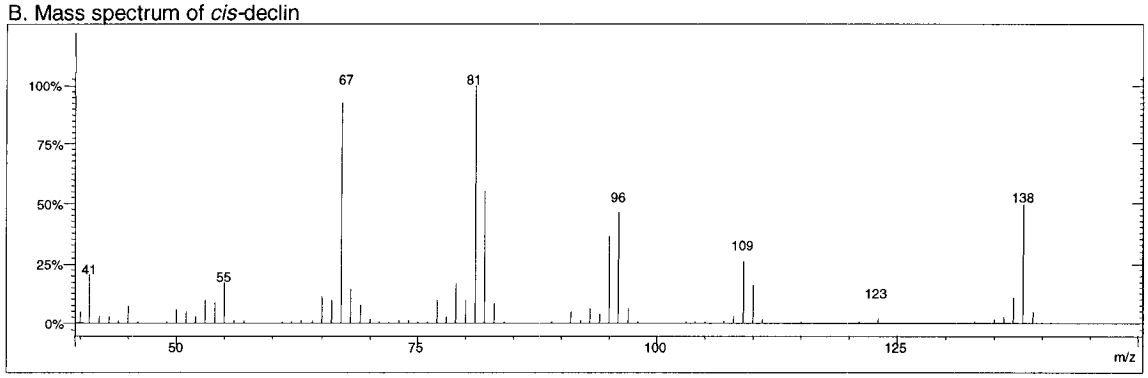
1,1'-oxybis-cyclohexane

Figure 3. 2 Molecular structures of decalin (*trans*- and *cis*-), cyclohexanone, cyclohexanol, 1,1'-oxybis-cyclohexane and 1,1'-dicyclohexane.

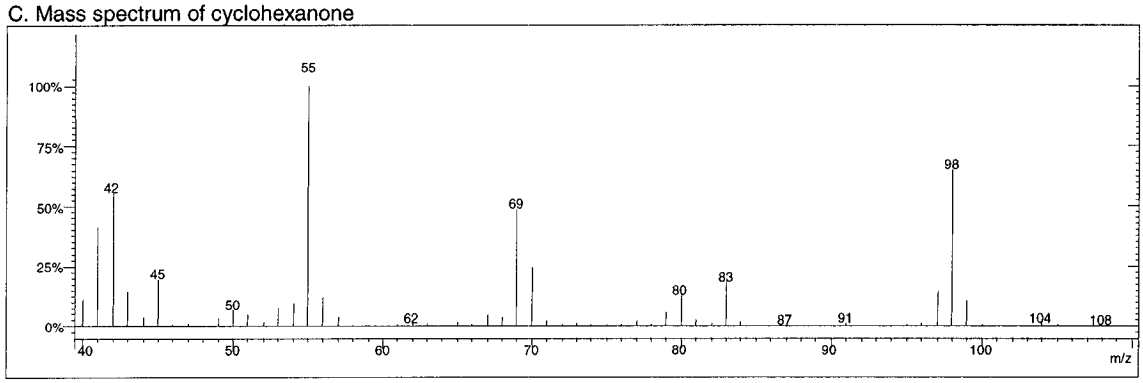
A. Mass spectrum of *trans*-declin



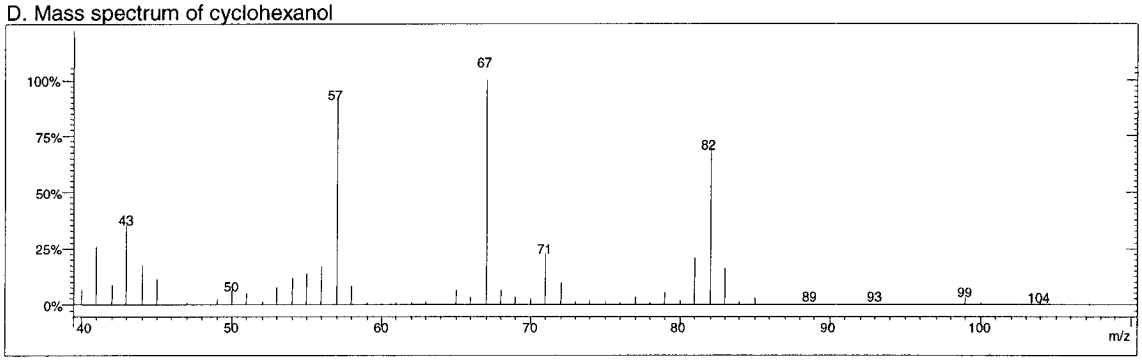
B. Mass spectrum of *cis*-declin



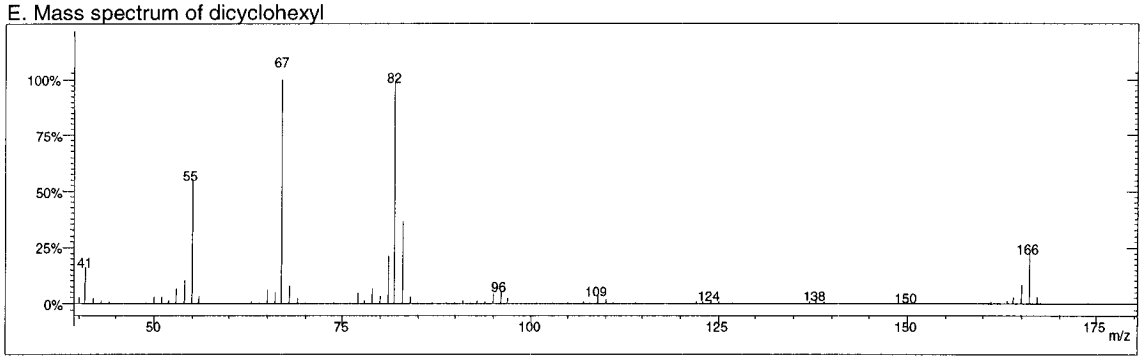
C. Mass spectrum of cyclohexanone



D. Mass spectrum of cyclohexanol



E. Mass spectrum of dicyclohexyl



F. Mass spectrum of 1,1'-oxybis-cyclohexane

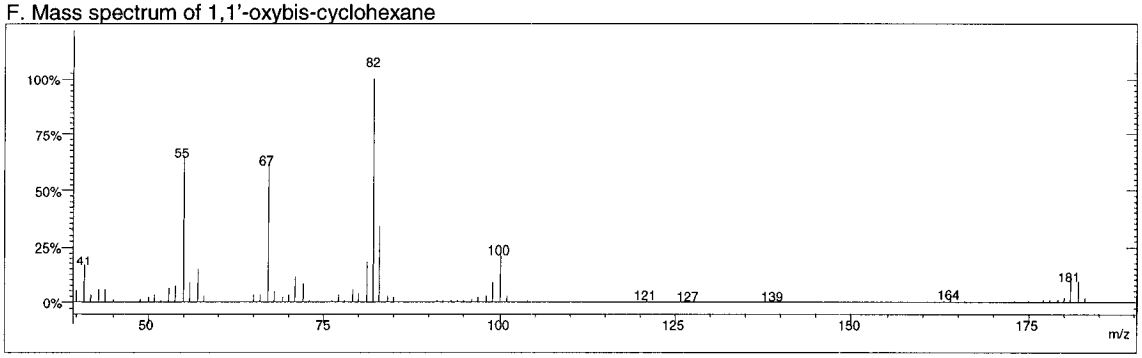


Figure 3.3 Mass spectra of decalin (*trans*- and *cis*-), cyclohexanone, cyclohexanol, 1,1'-oxybis-cyclohexane and 1,1'-dicyclohexane.

Chapter 4
Summary and Conclusion

4.1 Summary

Novel approaches for the dechlorination of chlorinated aromatic compounds have been identified in this research. It has been demonstrated that these new methods of detoxification of organochlorine compounds are efficient, safe for the environment and cost efficient for practical use.

Chlorinated aromatic compounds, as an important group of industrial chemicals, generally lack polar functional groups and possess low aqueous solubility. Their behavior in the environment are often unaffected by physical dispersal processes and biological transformations. Therefore, they are commonly persistent in the environment. Due to their extensive use and the demonstrated deleterious effects on organisms and human health, the disposal of these hazardous compounds has caused both public and governmental concern. Conventional treatments for these chlorinated compounds can cause other problems (like incineration) or still have not been demonstrated to be entirely safe for the environment (biotreatment).

Chemical methods, including catalytic reduction to transform these environmentally undesirable chlorinated compounds into non-chlorinated and essentially non-toxic hydrocarbons and chloride seem to be the best alternatives. In this research, two different approaches to catalytic reduction have been evaluated.

Zero-valent metal reduction, in the presence of bimetallic mixture, has become very popular recently. These bimetals, that usually include a transition metal, possess both reductive and catalytic activity. In the presence of these metallic mixtures and a suitable hydrogen donor, chlorine substituents of OC compounds can be replaced by hydrogen atoms, with the result that the OC is detoxified.

Although $ScCO_2$ served as a reaction medium, it did not detoxify the toxicants *per se*. But when combined with extraction/mobilization methods for aryl-organochlorine

compounds, this solvent has been demonstrated to support an efficient overall process. Compared with other remediation techniques, the principle advantages of using $ScCO_2$ as a reaction medium are: i) it can facilitate the chemical reactions due to desirable transportation characteristics that include high diffusivity and low viscosity; ii) facile post-reaction treatment that leaves no residue of solvent making it environmentally benign; iii) easily achieved near-critical conditions that make it inexpensive in comparison to other conventional solvents. Other merits include readily tuned solvating strength, that can be adjusted readily by moderating pressure. These characteristics of CO_2 have encouraged researchers to make good use of it in many applications besides extraction.

In chapter 2, zero-valent palladium-magnesium bimetallic mixture was evaluated for PCP dechlorination in supercritical carbon dioxide. Compared to other bimetallic mixtures (such as Ag°/Fe°and Pd°/Fe°), Pd°/Mg° was considered to be more reactive and efficient for PCP dechlorination because the reduction potential of Mg^{2+}/Mg° is larger than that of Fe^{3+}/Fe°. This point was demonstrated by the dechlorination of PCP over Pd°/Mg° in $ScCO_2$ at a lower temperature (400 °C compared 450 °C over Ag°/Fe°). PCP, 5 mg/min in water-methanol co-solvent (1:4, v/v) was merged with 1.5ml/min of $ScCO_2$ and delivered to a reactor column (25 × 1 cm, i.d.) of zero-valent Pd°/Mg° mixture. For continuous operation at 400 °C during 6 h, PCP was dechlorinated efficiently. Phenol was the principle product, with lesser quantities of methylated products and only traces of chlorinated products (principally monochlorinated species, no PCDDs or PCDFs were found). PCP deoxygenation was not observed and ring methylation was decreased relative to analogous reactions in hydroxylic organic solvent. This is a desirable characteristic for PCP dechlorination. The lack of deoxygenation activity was regarded as a benefit for PCP detoxification. Oxygen atom in molecule makes organic compounds more polar and more susceptible to metabolism by organisms. With time, the reactor column slowly lost dechlorination activity. Reducing the loading of Pd° on Mg° from 2% to 1% (w/w) apparently did not change the course of the reaction. However, the dechlorination capacity was decreased correspondingly. None the less, over 6 h or 5 h of continued

operation, the dechlorination efficiency was 99.5% for 2% Pd°/Mg° (w/w) and 98.4 for 1% Pd°/Mg°(w/w).

In chapter 3, hydrogen gas was used directly as the H source. Several of catalysts were examined with highly chlorinated aromatic compounds that included PCP, octachloronaphthalene and decachlorobiphenol. Among the tested catalysts Ni°/SiO_2-Al_2O_3, Pd°/γ-Al_2O_3, Pt°/γ-Al_2O_3, Ag°/Fe°/Al_2O_3, Fe°/Al_2O_3 and Al_2O_3 alone, Pd°/γ-Al_2O_3 (5%, w/w) was demonstrated to be the most efficient. During 0.5-2 h with excess hydrogen (~570 μmol) over Pd°/γ-Al_2O_3 (5%, w/w) in the presence/absence of $ScCO_2$ at 50-90 °C and 0.69Mpa, PCP, octachloronaphthalene and decachlorobiphenol (1 mg each) were smoothly converted to cyclohexanol, decalin and dicylohexyl respectively. Under these mild conditions, dechlorinations and dearomatization to their cyclic analogs were completed but no carbon-carbon bond scission was observed and only traces of partial deoxygenation-dimerization of the PCP substrate (to form 1,1'-oxybis-cyclohexane) was seen. For comparison, the parent aromatic compounds of these chlorinated substrates were also tested under the same conditions. They resulted in the same hydrogenation products as their chlorinated homologs. The $ScCO_2$ medium functioned as an inert support for the reactions. Differences in rates of reaction between chlorinated compounds and their aromatic hydrocarbon homologs were not observed.

4.2 Conclusions

In conclusion, the approaches in this research have provided efficient alternative methods for the detoxification of chlorinated aromatic compounds. They have great potential for commercial use in the future. The merits of the techniques include:

1. The treatments of these chlorinated aromatic compounds were demonstrated to be both rapid and efficient.
2. The dechlorination products generated by these methods were considered to be non/less-toxic and safe for the environment and potentially can be recycled.
3. The conditions for the dechlorination of these recalcitrant chlorinated aryl compounds were mild and facile to achieve.
4. These reactions were both virtually quantitative and inexpensive.

4.3 Suggestions for future research

In the future, the following research about these approaches is suggested to improve our knowledge:

1. Research designed to determine the capacity of the catalysts to mediate both dechlorination and dearomatization.
2. Research designed to determine the inactivation of the catalyst with extended use.
3. Research designed to study reactivation of the catalyst.
4. Research on other polychlorinated aromatic compounds or polycyclic aromatic hydrocarbons (PAH) with these approaches.
5. Research the coupling of these detoxification schemes with $ScCO_2$ extraction of these environmentally recalcitrant aromatic compounds so as to achieve mobilization/extraction from natural media (soil/sediment) and detoxification in a single overall process.

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