Dechlorination of Chlorinated Organic Compounds by Zero-valent Metal and Bimetallic Mixture

© Anwar Kabir

Department of Food Science and Agricultural Chemistry
Macdonald Campus of McGill University
Montreal, Quebec

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ABSTRACT

Many compounds containing chlorine atoms bound to carbon (organochlorine compounds) have been manufactured and released in huge tonnage during the period that post-dates the Second World War. Organochlorine (OC) compounds that include several pesticides as well as an array of industrial chemicals were very efficacious for their intended use but were also characterized by deleterious environmental impacts when released either intentionally or inadvertently. Their lipophilic nature, long persistence in the environment and threat to human health caused all the developed countries to ban the production of these chemicals as well as restricted the use of formulations containing these material for food production.

A number of scientists have become involved in the development of intentional degradation methods/techniques for these compounds using zero-valent metals or bimetallic mixtures. To date, there is no single, simple and continuous procedure available to completely dechlorinate lindane or pentachlorophenol (PCP). This work describes the complete dechlorination of lindane and pentachlorophenol by zero-valent Zn, Fe and Fe/Ag bimetallic mixture as well as a supercritical fluid extraction technique for a more efficient mass transfer of the substrates to the surfaces of the metal catalyst. The dechlorination reaction occurs on the surface of metal particles with the removal of all the chlorine atoms from lindane and PCP in a matter of minute, and yields completely dechlorinated hydrocarbon molecules and chloride as products.

Lindane was dechlorinated in the range of 84-99% by Zn^0, 87-100% by Fe^0 and 93-100% by Fe^0/Ag^0. For zinc, the temperature was 110°C whereas for Fe^0 and Fe^0/Ag^0 it was 300°C.

Fe^0/Ag^0 dechlorinated pentachlorophenol at 450°C and 250 atm.of pressure. PCP was totally dechlorinated into phenol, *o*-cresol, *m*-cresol, xylenes, trimethylbenzene and dimethylphenols. The products and dechlorination efficiencies varied as the flow rate of the mobile phase supercritical carbon dioxide (SC-CO_2). The dechlorination was run continuously for 14 hours and found to be very efficient in dechlorination even after 14 hours if the reactor column was washed at an interval of 5 to 6 traps (each 2.5 to 3 hours). The identification of the products was performed by GC/MS. A determination of organically bound chlorine was performed by the titration of the reactor eluate with 0.01M $AgNO_3$ solution after digesting with metallic sodium. The research demonstrated the efficiency of dechlorinating the OCs mediated by zero-valent metals or bimetallic mixtures during several hours of continuous operation.

RÉSUMÉ

Beaucoup de produits chlorurés (produits organo-chlorés) ont été utilisés et rejetés en grande quantité durant la période de l'après Seconde Guerre Mondiale. Ces produits organo-chlorés (OC) qui comprennent plusieurs pesticides ainsi que toute une gamme de produits chimiques industriels étaient très efficace mais se caractérisaient également par leurs effets néfastes sur l'environnement lorsque utilisés intentionnellement ou par inadvertance. Leur nature lipophile, leur longue persistance dans l'environnement et leur menace pour la santé humaine ont poussé tous les pays développés à interdire la production de ces produits chimiques et à restreindre leur utilisation pour la production alimentaire.

Un certain nombre de scientifiques sont impliqués dans le développement de techniques ayant pour but la dégradation des OC, en utilisant des métaux ou des composés bimétalliques à valence zéro. À ce jour, il n'existe aucune procédure à la fois simple et continue pour déchlorurer le lindane ou le pentachlorophénol. Cette thèse décrit la déchloruration complète du lindane et du pentachlorophénol (PCP) utilisant le zinc (Zn°) et le fer (Fe°) de même que du composé bimétallique fer/argent (Fe°/Ag°) de valence zéro. L'extraction par fluide supercritique au dioxide de carbone ($SC\text{-}CO_2$) a été utilisé pour son efficacité accrue du transfert de masse des substrats sur la surface catalytique du métal. La déchloruration du lindane et du PCP se produit en quelques minutes à la surface des particules métalliques produisant des molécules d'hydrocarbure complètement déchlorurés et du chlorure comme produits.

Le lindane a été déchloruré de 84% à 99% avec le Zn°, de 87% à 100% avec le Fe° et de 93% à 100% avec le Fe°/Ag°. Une température de 110°C était requise pour le Zn° alors que pour le Fe° et le Fe°/Ag° une température de 300°C fut requise.

Le PCP a été complètement déchloruré par le Fe°/Ag° à 450°C et à une de pression 250 atm produisant du phénol, o-crésol, m-crésol, xylène, triméthylbenzène et diméthylphénol. Les produits formés et l'efficacité de la déchloruration variait en fonction du débit du fluide supercritique (CO_2). La déchloruration a été activée en continu durant 14 heures et s'est avérée efficace si la colonne (réacteur) était nettoyé à intervalle de 2.5 à 3 heures. L'indentification des produits a été effectuée par chromatographie gazeuse en spectrométrie de masse (GC/MS). La détermination du chlore a été réalisée par titrage de l'éluat de la colonne (réacteur) avec une solution de nitrate d'argent ($AgNO_3$) 0.01 M après une digestion avec du sodium métallique. Les résultats ont démontrés l'efficacité de la déchloruration des OC en utilisant des métaux ou des composés bimétalliques de valence zéro durant plusieurs heures d'opération en continu.

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ABBREVIATIONS

AcA	Acetic anhydride
DDT	Dichlorodiphenyltrichloroethane
DGDE	Diethyleneglycol diethylether
EPA	Environmental Protection Agency of the U.S.A
GC	Gas chromatography
GC/MS	Gas chromatography - mass spectrometry
HCB	Hexachlorobenzene
HCH	Hexachlorocyclohexane
HPLC	High performance liquid chromatography
MIBK	Methyl iso-butyl ketone.
OC	Organochlorine
PCB	Polychlorinated biphenyl
PCDD	Polychlorinated dibenzodioxin
PCDF	Polychlorinated dibenzofuran
PCP	Pentachlorophenol
SF	Supercritical fluid
SFE	Supercritical fluid extraction
TCH	Trichloroethylene
THF	Tetrahydrofuran
VC	Vinyl chloride

Chapter I

1.0 Introduction and Literature review

Advances in science and technology have provided numerous innovations that have benefited mankind appreciably in terms of their health and welfare. At the same time, these innovations can cause deleterious impacts on the environment in ways that were never envisaged during the development and initial implementation of these technological improvements. Several of these problems can be traced to the increased release of xenobiotic materials - synthetic chemicals that for the most part, were foreign to the environment. Implied by the term xenobiotic is the concept that living systems haven't been exposed for a time sufficient to develop defense mechanisms so to be able to deal with these materials. Many compounds containing chlorine atoms bound to carbon (organochlorine compounds) have been manufactured and released in huge tonnage during the period that post-dates the Second World War. Organochlorine (OC) compounds that include several pesticides as well as an array of industrial chemicals were very efficacious for their intended use but were also characterized by deleterious environmental impacts when released either intentionally or inadvertently. Although organohalogen compounds are known to be elaborated naturally, (Jong and Field, 1997), most OC compounds do not occur naturally, are very non-polar and rather recalcitrant. In consequence, they tend to accumulate in lipophilic tissues and are lost from living systems only very slowly.

The rate of loss of a particular chemical from a particular micro-environment is often expressed in terms of half lives ($t_{1/2}$), the time taken for the concentration of that chemical to be reduced to one-half of it's initial concentration. Representative half-lives for individual OCs varies widely as suggested by Table 1.

Table 1: Approximate half-lives of OCs.

		Air	Water	Soil	Sediment
1	Endrin[a]	5 hrs	3 wks	2 mths	8 mths
2	Lindane[a]	2 days	3 wks	2 mths	8 mths
3	HCB[a]	2 yrs	6 yrs	6yrs	6 yrs
4	DDT[a]	2 yrs	6 yrs	6 yrs	6 yrs
5	PCP	3 mths to 1 yr in environmental samples			
6	PCB[b]	8 to15 yrs in environmental samples			

a = Ramamoorthy, S, 1997; b = Grittini, C, 1997.

The lipophilic character of a chemical has often been characterized in terms of its octanol-water partition coefficient (K_{OW}) that provides a measure of that chemical's tendency to partition between an aqueous phase and a non-polar phase such as 1-octanol. It is presumed that the octanol phase represents a suitable surrogate for fatty tissues. The K_{OW} values for the representative OCs are presented in Table 2. In general, lipophilic character is correlated with the general absence of polar functional groups within the chemical structure of the compounds.

Table 2: Log K_{OW} values of different OCs

CCl_4	TCE	VC	Endrin	Lindane	DDT	PCP	PCBs
2.64	2.49	1.36	5.6	3.61	6.19	5.01	4.3 - 8.26

Most hazardous halogenated aliphatic compounds released from industrial, commercial and agricultural sources are brominated and/or chlorinated aliphatics. There are some compounds in a cyclic form, e.g.γ-hexachlorocyclohexane (lindane). Organochlorine compounds are in common use as cleaning solvents, in dry cleaning operations as well as in semiconductor manufacture. The production and use of these halogenated aliphatic compounds and their apparent hazard to human health have prompted investigations concerning their fate in the human body, in surface water and in treatment facilities as summarized in Table 3, (Vogel, 1987).

Table 3: Production, proposed maximum contaminant levels and toxicity rating of Common halogenated aliphatic compounds[1].

Compound	Production Million Lb/yr.	Contamination level ppm	Carcenogenity[a] EPA/IARC
Trihalomethanes	100	-	-
Vinyl chloride	7000	1	1
1,1-dichloroethylene	200	7	3
Trichloroethylene	200	5	3
Tetrachloroethylene	550	-	3
1,2-dichloroethane	12000	5	2
1,1,1-trichloroethane	600	200	3
1,,2-dichloromethane	332	-	1
Hexachlorocyclohexane	-	-	2

[a] Carcinogenity: 1= carcinogenic; 2 = probably carcinogenic; 3 = cannot be classified.

1.1 Lindane (γ-hexachlorocyclohexane)

The γ-hexachlorocyclohexane (HCH), lindane, has the chemical formula $C_6H_6Cl_6$ (Figure 1) and formula weight of 290.83 g/mol. It is white crystalline solid that is volatile in air and insoluble in water. Its vapor is colorless and has a musty odor with limit of 12ppm (Public Health Service, 1992). The vapor pressure for lindane is 9.4×10^{-6} mm Hg at 20°C. Faraday first synthesized lindane in 1825 but its insecticidal properties were not recognized until the early 1940s, about the same time, as DDT was developed. It is used typically for the treatment of head lice and body scabies.

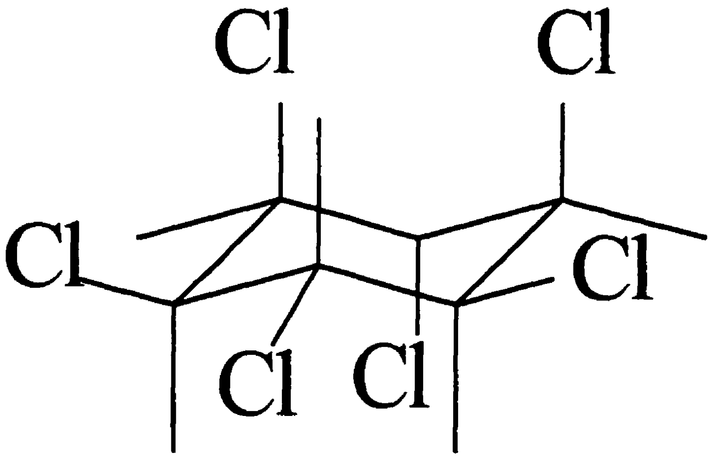


Figure 1: Structure of lindane (HCH)

It is also used as an insecticide on fruit and vegetable corps, for seed treatment, in forestry as a wood preservative and as a dipping solution for livestock. Table 4 presents the annual usage of lindane in North America in 1980 and 1990 (Walker et al., 1999). Non-agricultural approvals for lindane have been restricted mainly to timber treatment where its use has been declining. Minor uses include insecticide to combat ants, moths, fleas and other insects. This compound has been detected in air, surface and ground water, sediment, soil, fish and other aquatic organisms, wildlife, foods and humans.

Table 4: Estimated annual usage of lindane in North America, (tons/year).

Country	1980	1990
United States	268	114
Canada	200	284
Mexico	23	261

It is no longer manufactured in North America and is not permitted to apply aerially in the USA. However technical formulations containing α, β and γ lindane remain in common compounds used in large quantities in India, China, Africa and South America.

Table 5: Concentration of lindane in air samples (pg/m^3)

Location	Time	Range	Mean
Southern England	1987 – 1990	-	39
South Norway	1993	12 – 283	43
Central Norway	1992	13 – 487	77
North Norway	1992	10 – 194	46
South Sweden	1990	87 – 182	134
Central France	1989 – 1990	300 – 3500	1500
North Atlantic	1990	22 – 331	79
Southern Ontario	1988 – 1990	-	145
Bay of Bengal	1989 – 1990	-	8600
South China Sea	1989 – 1990	-	810

A table 5 presents the range and mean concentrations of lindane in air around the globe, (Waina, 1998). The south of Asia and China were characterized by very high concentrations of γ-HCH. It was reported by FAO that 37999 tones of this chemical were used only in India alone in 1988.

Table 6: Concentration of lindane in surface and lake water (pg/L), [Waina, 1998].

Location	Time	Concentration
Southern Ocean	1989 – 1990	28
Bay of Bengal	1989 – 1990	610
South China Sea	1989 –1990	380
Mediterranean Sea	1989 – 1990	180
Arctic	1980	5970
Lake Baikal	1991	1100
Grate Lakes	1980	1300
Niagara river	1980 – 1981	2100
Lake Ontario	1983	865 - 1850

Monitoring studies have suggested that lindane migrates to water despite its limited mobility in soils. Its presence in Canadian waters (Niagara River and Lake Ontario) provides evidence of a potential risk to the populations, (Table 6). Lindane is transferred efficiently to plants, vegetables, fishes and humans.

1.1.1 Environmental Exposure

In common with other organochlorine pesticides, lindane is relatively lipophilic and tends to bio-accumulate up the food chain. Residues have been detected in kidneys, livers and adipose tissues of a variety of animals and birds. It is highly toxic to aquatic invertebrates and fish. The presence of lindane in human milk has been reported in countries throughout the world. Lindane residues have also been detected in cow's milk and for this reason children have already been described as being more susceptible to its toxic effect. The most probable route of human exposure to lindane is via oral ingestion of food containing residues of the insecticide. It can be released to the air during the production of the chemical and during the spreading of formulated materials for agriculture applications. A more limited but more direct exposure can also result from formulations that are used for the treatment of scabies and lice.

1.1.2 Lindane toxicity to Humans

Lindane is severely toxic to humans. It represents a potent contact and internal poison that can be absorbed through skin, inhaled when in vapor form or ingested orally. It has teratogenic, immunotoxic and neurotoxic properties. Its lethal dose in human is 125mg/kg-body weight. The time interval between exposure at high dose and the onset of symptoms is generally less than 12 hours if exposure is gradual, through the skin contact. The symptoms of sub-acute poisoning produced by this agent can last for weeks to months, (Table 7). Patients often experience periodic relapses despite adequate therapy because of subsequent redistribution of this chemical from initial lipid storage depots, (Hall, 1999).

Table 7: Classification of patient symptoms induced by lindane poisoning

Muscarinic[a] (Muscular disorder)	Nicotinic[a] (Drag Effect type)	Central[a] (Nervous system)
Nausea - M	Muscle weakness - S	Confusion - M
Diarrhea - L	Muscle spasm and imbalance - L	Seizure - M
Abdominal pain - L	Myoclonic jerks - L	Fatigue - L
Urinary incontinence - L	Tachycardia - M	Anxiety/Depression - L
Fecal incontinence - L	Pallor - S	Visual disorder - L
Diaphoresis - I		Musical hallucinations - L

[a] I = immediate; S = short-term (days); M = mid-term (weeks); L = long-term (months)

Lindane poisoning is also characterized by long-term psychological and neurological complications. A 37 years old lady was exposed to lindane by the application of a lotion to combat scabies. She experienced myoclonic jerking and twitching, unusual taste, sensations, auditory and visual hallucination, projectile vomiting, diarrhea, discontinued thoughts and loss of control of bladder and bowels, (Hall, 1999). She was treated for several months with high doses of diazepam and apparently recovered fully after 20 months post the poisoning episode.

Recently scientists reported another case of central nervous system toxicity induced by lindane, (Nordt and Chew, 2000). They reported the accidental oral ingestion of lindane by three children (3 years, 4 years and 17 months). Their symptoms included listlessness, nausea, pallor, vomiting and hyperventilation. They were treated with lorazepam and finally were cured.

1.1.3 Carcinogenic behavior

A number of women suffering from breast cancer were treated with lindane in different forms. Due to its lipophilic nature lindane persists in the breast and can itself induce tumors. In Lincolinshire, England where lindane was used extensively on sugar beet crops, the rate of breast cancer was 40% higher than the national average, (Fact sheet, 1995). A man developed stomach cancer due to the use of a lotion (containing lindane) to prevent scabies. A study reported, (Table 8), the characteristics of recipients of lindane who developed cancers of the breast, larynx, stomach, prostate, thyroid, nervous system and connective tissue, (Friedman, 1997).

Table 8: Characteristics of recipients of lindane who developed cancers.

		Cases	Other Lindane users
	Number	31	74
Sex	Female	38.7%	27.0%
	Male	61.3%	73.0%
Race	White	87.1%	73.0%
	Black	6.5%	9.5%
	Other	6.5%	17.6%
Reason for prescription	Scabies	48.4%	36.5%
	Pediculosis pubis	25.8%	48.5%
Form of Lindane	Lotion	71.0%	56.8%
	Shampoo	19.4%	29.7%
	Cream	9.7%	13.5%

EPA considers lindane to be a possible human carcinogen and has ranked this chemical among EPA's group $B_{2/C}$. There is limited information available regarding the reproductive or developmental effects of lindane induced carcinomas in humans, (EPA web page, March 22, 2000).

Because of a number of deleterious effects associated with exposure to lindane, all developed countries have banned the production of this chemical. Concurrently, the use of formulations containing this material for food production has been restricted. The European Community has restricted the use of lindane in seed treatments in 1999, (AWCPN, 1999). Very recently, Co-Operative farms in UK have banned lindane totally and five other companies were said to no longer offer its distribution (Pesticide news, 2000). The Canadian Government banned the incorporation of lindane into seed treatments for canola in 1999; the registration of these materials was cancelled with a phase-out of existing stocks being permitted until July 1st 2000, (AWCPN, 2000).

1.2 Pentachlorophenol (PCP)

Pentachlorophenol (PCP), C_6HOCl_5 (Figure 2) is non-flammable solid, that does not volatilize readily. It exists in two forms: a) the pentachlorophenylate form that dissolves readily in water and b) the other form that does not, (Environment writer, 1997). The latter form is readily soluble in alcohol, benzene and slightly soluble in cold petroleum ether. PCP migrates rapidly in air, on land and in water. It possesses a broad range of biocidal activities and has been used extensively as a wood preservative, as a herbicide and insecticide in agriculture and in a variety of manufacturing processes.

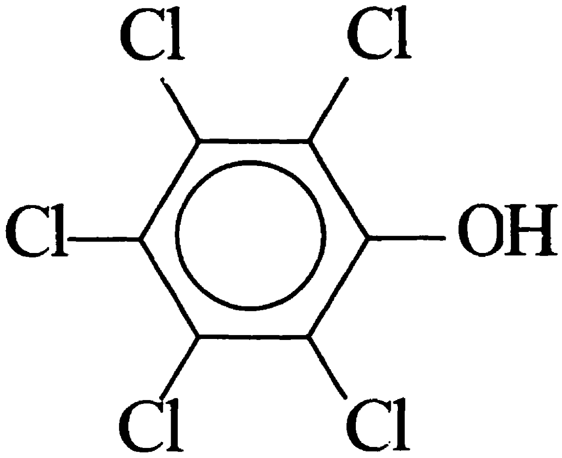


Figure 2: Structure of Pentachlorophenol.

It has been manufactured continuously since 1936 when it was introduced for timber preservation to control of termites and for protection against fungal rots and wood-boring insects. The use of PCP has been restricted severely in both United States and Canada, with only a number of certified applicators permitted to apply this material in industry as a wood preservative for power line poles, railroad ties, cross arms and fence post. It is totally restricted for wood preservative solution or in insecticidal formulations destined for household or garden use.

1.2.1 Pentachlorophenol Exposure

Segments of the populations that potentially are at high risk of exposure to PCP are people involved in wood preservation, lumber-mill, workers and pesticide applicators. Residents near PCP manufacturing plants, cooling towers, and wastewater treatment sludge disposal sites can also be exposed to the chemical at higher levels than the general public, (Environment writer, 1997). The extensive contamination of water, food and air by PCP remains a threat, owing to its persistence and potential for bio-magnification. Epidemiological studies in the USA have detected residues of PCP in over 80% of the general population. PCP continues to vaporize from treated wood even several years after its application to the wood surface. Neither oil nor water-based paints totally eliminate the volatilization of PCP from pressure-treated wood, (Roberts, 1997). After its release into the environment, PCP interacts with soil and organic matter. Adsorption of PCP decreases with increasing pH and for this reason PCP is more mobile in mineral soil than acidic clay, sandy clay and soils with high organic content.

1.2.2 Effect of PCP on Human

Roberts (1997) reported an incident of a five-member family from Alabama, USA, who had been exposed to PCP-treated lumber for 14 months from the siding of their home that had built in 1992 and the burning of PCP-treated logs in the fireplace. In addition to intense irritation of the eyes and respiratory tract, they had recurrent infections, neuropsychiatric symptoms as well as abnormalities in their laboratory blood analyses.

A Caucasian woman born in 1952 had three successive miscarriages between April 1991 and January 1992. An investigation found an old piece of furniture in her room had been treated with a timber preservative containing PCP. In October 1991, another investigation recorded the PCP level in the woman's serum was 62 μg/ml. That level dropped to 24 μg/ml one month after the removal of the piece of furniture. Finally she became pregnant in December 1992, and gave birth a healthy baby, (Maeyer et al, 1995).

Another lady from Caucasus had the similar disorder of three miscarriages from September 1989 to June 1990. A subsequent investigation noted that her house had been built with timber treated with PCP containing preservative. The woman's serum level of PCP was 31 μg/ml. The wood was subsequently treated with polyurethane coating in October 1990. Shortly after that the woman became pregnant and gave birth a healthy baby at full term, (Maeyer et al, 1995).

A long-term low dose exposure to wood-preserving chemicals, (WPC), (containing PCP and lindane) caused the alteration of neurobehavioral performance in 15 women. The exposed women described subjective complaints in attention, mood and motivation, (Peper et al, 1999). The behavioral pattern was a reduced working memory performance under distracting conditions. The mean exposure duration was 10years (5-17 years). Their mean PCP serum level was 43.6μg/l (range 9.4 to 144.5 μg/l) and lindane level was 0.085 μg/l (0.006 to 0.290μg/l). The control levels of PCP and lindane in blood are 11.8μg/l and 0.043μg/l respectively.

Roberts [based on thirty years of his research into the toxicity of PCP] has emphasized the hazards of PCP and its transformation products in his writings and in testimony to EPA (Roberts, 1997). He reported that the most serious complications involve aplastic anemia, red cell aplasia, thrombocytopenic purpura, several types of leukemia, Hodgkin's disease, non-Hodgkin lymphoma and infertility resulting from sperm destruction. Table 9 presents the most common effect of PCP poisoning in human, (environment writer, 1997).

Table 9: Effect of PCP exposure on human.

Short term exposure	Breathing trouble, chest and abdominal pain, sweating, high fever. Damage of kidney, liver, lungs, skin, blood, and nervous system. Irritation of eyes noses and throat.
Long term exposure	Mutation of living cells and can damage developing fetus. Damage of kidney, liver, blood and nervous system. Cause bronchitis and skin rash. Chronic poisoning causing weight loss, weakness and excessive sweating.

The concentration of PCP in water bodies as well as in drinking water must be limited serverly due to its acute and chronic toxicity. The EPA has set the limit of 1ppm for drinking water and recommended a limit of 0.3ppm in children's drinking water. This value is 1ppm in case of an adult.

1.2.3 Extraction of PCP

Pentachlorophenol can be extracted from a contaminated site by a number of extraction protocols. Liquid-liquid extraction (LLE), solid phase extraction (SPE) and supercritical fluid extraction (SFE) have been evaluated by a number of scientists. Aranda and Kruus (1997) compared all three procedures. They reported the statistically significant recovery of PCP by LLE and SFE. They observed that fulvic acids didn't interfere with the recovery by LLE and SPE, but reduced the recovery of PCP by SFE.

Suidan et al (1999) reported the extraction of PCP from soil by water-ethanol mixtures. A mixed solvent containing equal proportions of water and ethanol proved effective in extracting PCP from both spiked and field-contaminated soils. They reported a maximum recovery of PCP within the first hour of contact between the soil and the mixed solvent. Both soxhlet and sonication procedures were used for a comparison study. In batch extractions, 50% ethanol-water mixture proved to be more effective than other ethanol-water mixtures in removing PCP from soil spiked with as much as 99%recovery from spiked as well as field contaminated soils.

The extraction of PCP from pressure treated wood was reported by Endalkachew et al (1997). The extraction was performed with a continuous-flow extractor over pressure treated wood wafers with supercritical carbon dioxide (SC-CO_2). The rate of extraction increased with increases in solvent pressure and decreases in substrate particle sizes. The overall mass transfer coefficient and the rate of extraction increased with an increase in solvent pressure, temperature and a decrease in the flow rate. They reported 80% recovery of PCP with this technique.

1.3 Analysis of Lindane and PCP

Organochlorine compounds have been determined for many years in various media including air, water, sediment and soil. A number of analytical techniques have been applied successfully for the determination of these compounds, including high performance liquid chromatography (HPLC), gas chromatography (GC), GC/MS, and Fourier infrared spectroscopy (FTIR). GC and GC/MS have become the most widely used approaches.

1.4 Degradation Processes

Due to the high toxicity and the persistence of many chlorinated organic compounds, a number of scientists have become involved in the development of intentional degradation procedures. These degradation techniques may be divided into the following categories:

- Biodegradation
- Thermal degradation
- Non-thermal degradation

1.4.1 Biodegradation

The biodegradation techniques use microorganisms and naturally occurring species to promote the transformation and detoxification of chlorinated organics. The treatment system is living and the survival of the microorganisms is paramount to the success of this approach.

Low concentration of lindane can be removed from aqueous solution by adsorption to the surfaces of heat inactivated cell suspensions of the fungus *Rhizopus Oryzae*, (Banks, C.J and Young, E; 1998). However, the efficiency of the system is dependent on temperature, pH of the solution, biomass concentration and biomass age.

Pentachlorophenol can be treated with limited success through microbial degradations. This substrate is considered to be highly resistant to microbial degradation due to the toxicity of highly chlorinated congeners. By contrast, many authors have described aerobic and anaerobic PCP biodegradation. *Flavobacterium spp.* and *Rhodococcus* were employed with success for the treatment of PCP contaminated wastewater and ground water (Beaudet et.al, 1998). They studied an aerobic consortium that degraded PCP by methanogenic fermentation.

Chiang et.al. (1998) investigated the degradation of PCP in municipal sewage sludge by a chlorophenols (CPs) adapted consortium. They observed that, in general, the more concentrated the substrate the lower the rate of degradation. They also reported that anaerobic conditions favored PCP degradation. Brown rot fungi, *Gloeophullum striatum* and *G. trabeum* are other promising degraders of pentachlorophenol and other chlorophenols, (Schlosser, 1999).

Polychlorinated biphenyls undergo biodegradation in a variety of conditions both in the laboratory and in the field. Anaerobic microbes attack more highly chlorinated PCB congeners through reductive dechlorination. These microbially mediate transformations preferentially remove meta and para-substituted chlorines. There is a wide diversity of dechlorinations by microorganisms. In general, microbial populations preferentially dechlorinate meta-substituted substrates in preference to the para-substituted isomers but the ortho substituted analogs are appreciably less reactive.

1.4.2 Thermal Destruction

Thermal treatments involve incineration and/or pyrolysis of the organic compounds at very high temperature. Incineration is the total destruction of materials at very high temperature whereas pyrolysis is the decomposition of the organic compounds using high temperature.

1.4.2.1 Incineration

Incineration is a thermal treatment for the degradation of chlorinated organic compounds. The chlorinated aliphatic compounds are devoid of serious problems in the case of incineration. For the destruction of many chlorinated organic compounds, incineration has remained a permitted technique throughout the world. However, the incineration of chlorinated aromatic substrates is characterized by a number of difficulties.

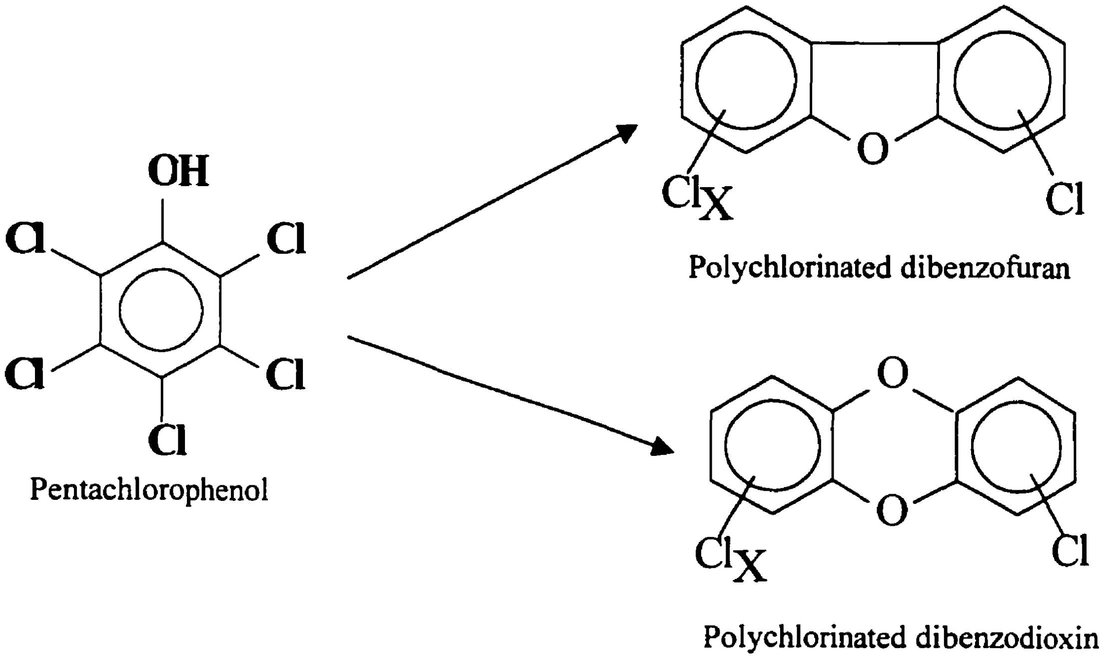


Figure 3: PCDD and PCDF from PCP

The incomplete combustion of PCP and PCBs can produce more toxic products during incineration. The products included polychlorinated dibenzofurans (PCDF), polychlorinated dibenzodioxins (PCDD) and diphenylethers, (Figure 4). PCDDs and PCDFs possess low vapor pressures (6.2×10^{-7} to 7.5×10^{-10} Pa) and water solubilities, along with high octanol-water partition coefficient (log K_{OW} = 6.1 to 8.2), (Harrad, 1996). Toxicity of these compounds includes a wasting syndrome, immune suppression, hepatotoxicity and porphyria, reproductive and development disorders, carcinogenicity, tumor promotion activity and disruptions of endocrine response pathways.

1.4.2.2 Pyrolysis

Pyrolysis of PCBs involves high temperature thermal degradation in the absence of oxygen. The pyroplasma system uses a plasma torch to induce temperature up to 15000 ^{0}C and pyrolyze organic liquids producing CO, N_2, H_2 and some hydrocarbons of low-molecular weight (Erickson, 1997). This system prevents the formation of undesirable PCDDs and PCDFs.

1.4.3 Low temperature Degradation

Non-thermal degradation involves chemical, photochemical, radiolytic or the ultrasonic destruction of substrates. Chemical degradation is becoming the most popular technique among them.

1.4.3.1 Chemical Degradation

Reaction with alkali, catalytic dehydochlorination, ozonation, wet air oxidation and reduction by zero-valent metals or bimetallic mixtures are among the common techniques for the chemical transformation of OCs.

Catalytic Degradation

Catalytic degradation of chlorinated organic compounds, 1,2,4-trichlorobenzene and PCP, were achieved by using $NaBH_4$ in tetraglyme at 290-315°C or by $NaBH_4$/LiCl at 125-135°C in glyme, triglyme and tetraglyme, Figure 5, (Pittman and Yang, 1998).

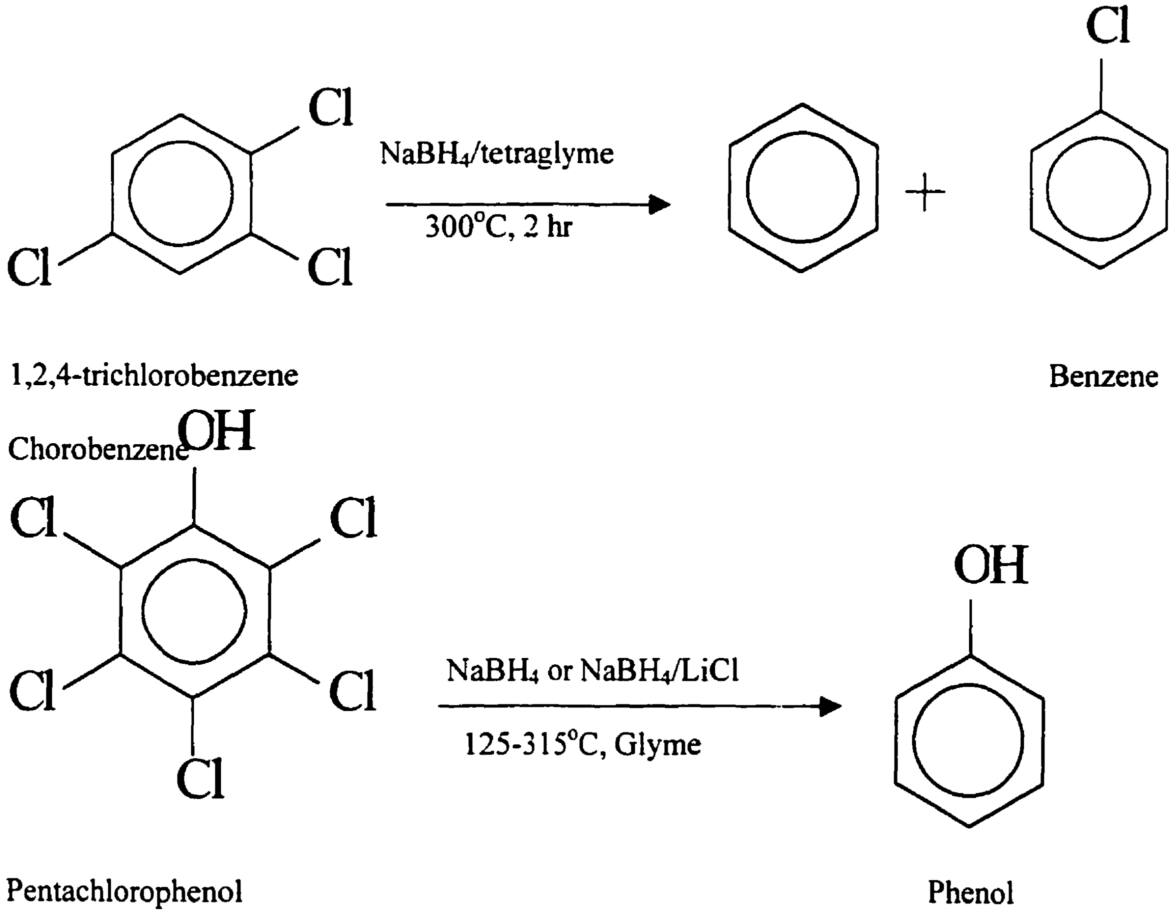


Figure 4. Degradation of Trichlorobenzene and PCP

Schwartz et al. (1995) reported the reductive dechlorination of PCB mixtures accomplished with homogeneous catalysis under mild condition. The catalyst for the dechlorination was prepared in situ from a titanium complex (titanocene dichloride), whereas $NaBH_4$ served as the reducing agent.

Recently a gas-phase hydrodechlorination of PCP over supported nickel catalyst (nickel/silica and nickel/Y zeolite) was reported, (Keane and Shin, 1999). The catalysts were 100% selective in cleaving the C-Cl bonds, while retaining both the hydroxyl substituent and the aromatic character of the benzene ring intact. They also observed an increase in the level of dechlorination by increasing the nickel loading on the silica support whereas the use of zeolite support introduced spatial constraints that limited the extent of dechlorination severely. Phenol was formed via both simultaneous and consecutive irreversible steps but the stepwise route predominated.

Photocatalytic Degradation

Hoffmann and Mills (1993) achieved photocatalytic degradation of PCP in TiO_2 particulate suspension. They reported a complete dechlorination of 47 μmole of PCP after 3 hours of illumination at high intensity with apparent quantum efficiencies ranging 1-3%. They also found *o*-chloranil, *p*-chloranil, tetrachlorohydroquinone and hydrogen peroxide as the principal intermediates. Hoffmann and Choi (1995) reported the photoreductive degradation of CCl_4 in TiO_2 particulate suspension in the presence of a variety of organic electron donors such as alcohols, carboxylic acids and benzene derivatives. The rate of CCl_4 dechlorination was enhanced appreciably by the use of alcohols and organic acids as electron donors.

Ultrasonic Degradation

Gondrexon et al. (1999) reported the degradation of aqueous solution of pentachlorophenol (PCP) in a three-stage sonochemical reactor that was operated in the continuous flow mode. The experimental reactor was described as a high frequency ultrasonic unit. They justified the choice of high frequency ultrasound (500 kHz) because the ultrasonic degradation of phenolic compounds involved OH radical attack.

Metal Mediated Treatment

The use of zero-valent iron for remediating contaminated ground water has prompted laboratory and field studies to assess the general application of this treatment process. Two types of treatment schemes have been pursued using either *in situ* reactive barriers or above ground reactors, (Gillham and O'Hannesin, 1994; Weber, 1996). The remediation schemes commonly involve pumping the contaminated ground water to the surface and passing it through a treatment system, that either degrades the chlorinated compounds, as in the case of advanced oxidation systems or transfers them to another medium, (Oarth and Gillham, 1996). The reaction yields relatively harmless alkali salts as products. Sweeny (1979) reported that various combination of Zn, Cu, Al and Fe with sand could be used for the treatment of industrial waste water. The system degraded trihalomethanes, chloroethenes, chlorobenzene, PCBs as well as atrazine, nitrophenols and N-nitrosomethylamine, (Tratnyek and Matheson, 1994).

Boronina et al.(1995) reported the transformation of halogenated aliphatic compounds mediated by redox reactions with Mg^o, Sn^o and Zn^o. More recently, they reported (Boronina et al. 1998), the bimetallic enhancement of Zn^o with Pd^o, Ag^o or Au^o to increase the surface activity of the zinc metal towards halogenated organic compounds in water thereby promoting both dechlorination and conversion into hydrocarbons.

For halogenated aromatic compounds, the general reaction pathway is different from their aliphatic analogues. These compounds were dehalogenated to their hydrocarbon analogs by Fe^{o} and Fe^{o}/Pd^{o} bimetallic system at high temperature, (Fernando et al, 1995; Manahan et al, 1997).

Fe

In the last few years the zero-valent Fe was used for the dechlorination of a wide range of chlorinated organic compounds in both batch and column systems, (Gillham and O'Hannesin, 1994; Tratnyek and Matheson, 1994 and Burris et al. 1995). The scientists were successful in dechlorinating TCE (trichloroethylene) and PCE (tetrachloroethylene). They reported that halogenated organic solvents were unstable in the presence of some commonly used well casing materials. Further investigation of this effect indicated that most of the apparent degradation was due to dehalogenation; the reaction occurred in presence of galvanized steel, stainless steel, Al and Fe. Since Fe is relatively inexpensive and nontoxic, it was proposed that Fe might be useful for the *in-situ* remediation of contaminated ground waters.

Recently, reduction of DDT [1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane], DDD [1,1-dichloro-2,2-bis(p-chlorophenyl)ethane] and DDE [2,2-bis(p-chlorophenyl)-1,1-dichloroethylene] were studied by Sayles et al.(1997) for remediation by Fe^{o} powder at room temperature.

A reductive dechlorination of trichloroethylene by Fe^{o} was studied under condition in which the trichloroethylene would exist as a separate phase in water/Fe system, (Oarth et al., 1998).

As reported by Chuang and coworkers (1995), the reaction of a PCB mixture (Arochlor 1221 and a mixture of biphenyl, mono-, di- and trichloro biphenyl congeners) with Fe^o at a temperature range of 200 - 600°C for 1 hour proceeded rapidly. At 200° or below, little reduction of PCBs was observed. Appreciable rates of dechlorination were apparent at 300°C (78% conversion). At 400°C a 95% transformation of PCBs to biphenyl was observed. At temperature greater than 400°C (at 500 and 600°C) the yield of biphenyl in the samples began to fall; the total yield of chlorobiphenyl congeners also decreased (59% to 2% conversion) and the yield of biphenyl also decreased. Therefore, not only dechlorination of PCBs but also other reactions must have taken place at this elevated temperature giving rise to the compounds that were not detected by GC/MS.

Mg, Sn and Zn

As a possible method for degrading halogenated organic compounds in contaminated water supplies, the reactions of metallic Mg, Sn and Zn with CC14/H2O mixtures were studied by Boronina et al. (1995). In the case of Mg, oxidation of the metal catalyst by water overwhelmed the Mg-CCl_4 reaction. The reaction products indicated the formation of $CHCl_3$ and CO_2 in addition to H_2O and CCl_4. The conclusion from the experiments was that the presence of CCl_4 enhanced the rate of the Mg^0/H_2O reaction, yielding $Mg(OH)_2$ and H_2 more quickly. Only a small quantity of CCl_4 was reduced.

For Sn^0 and Zn^0, the degradation of CCl_4 was more successful. In the $Sn^0/CCl_4/H_2O$ system the products were CO_2, CH_4, SnO_2 and HCl with very small amount of $CHCl_3$ and CH_2Cl_2. In case of $Zn^0/CCl_4/H_2O$ system, the products were $ZnCl_2$, $Zn(OH)_2$ and

CH_4 with $CHCl_3$, CH_2Cl_2 and CH_3Cl as intermediate products. This was rationalized as a competing reaction of a possible intermediate Cl_3CMCl, that can be protonated by H_2O to produce $CHCl_3$ or converted to CH_2Cl_2 via elimination.

Roberts and coworkers reported that halogenated ethylene can undergo reductive elimination to alkynes under environmental conditions. They used two different zero-valent metal, Fe^o (Roberts et al 1996) and Zn^o (Reberts et al. 1998), to study the reductive elimination reaction of chloroethylenes that were comparable energetically to hydrogenolysis at normal pHs.

More recently, Boronina et al, 1998 reported the degradation of CCl_4 by Zn^o. Commercial Zn dust converted CCl_4 via $CHCl_3$ and CH_2Cl_2 into CH_3Cl and CH_4, though CH_2Cl_2 was degraded about two orders of magnitude more slowly than CCl_4. They employed Zn^o activated by cryochemical treatment or doping of the metal surface with Pd, Ag and Au in an attempt to, (i) enhance the surface performance towards CCl_4 in water and (ii) to promote dechlorination and conversion into CH_4 and other hydrocarbons. They reported that rates of dechlorination were enhanced by both the bimetallic preparation and by cryo treatment of the Zn surface.

Ni

The U.S. Air Force Center has began testing a permeable nickel-plated iron wall designed to passively clean ground water contaminated with chlorinated compounds. Two walls were built to surround a contaminated plume of ground water at the Massachusetts Military Reserve on Cape Cod, MS. When halogenated methane, ethane and ethene come in contact with zero-valent iron filings of the wall material, they are dehalogenated and ultimately form chloride and nontoxic hydrocarbons. Laboratory tests (Appelton, 1996) have demonstrated that enhancing the Fe^o with Ni^o can degrade organochlorine compounds up to 10 times more rapidly than Fe^0 alone.

Pd/Fe

Palladized iron has been used for the rapid dechlorination of organic contaminants in aqueous solution, (Muftikian et al. 1995). It was reported that 1,1,2-trichloroethylene, 1,1-dichloroethylene, cis and trans-1,2-dichloroethylene and tetrachloroethylene at a concentration of 20 ppm in aqueous solution were converted into ethane on the surface of Pd^0/Fe^0 within a few minutes. No other intermediate, (at level greater than 1ppm) were detected. Chloromethanes were also reduced to methane on Pd^0/Fe^0, although CH_2Cl_2 took four to five hours to react completely. These studies were concerned with only low molecular weight chlorinated aliphatic compounds.

A simple method for dechlorinating commercial mixtures of PCBs (Arochlor 1260 and Arochlor 1254) has been described by Farnando et al. (1995). A methanol-water solution of PCBs was totally dechlorinated into biphenyl and chloride ions at ambient temperature. The PCBs were adsorbed on the Pd^0/Fe^0 surface and hydrogen produced by the corrosion of iron was collected on the Pd surface. This chemical method has the potential to remediate soil and water contaminated with PCBs.

A complete degradation of PCP was achieved by mixing a solution of PCP with palladized iron, (Grittini, 1997). Palladized iron was also effective in mediating the dechlorination of other chlorinated phenols. The principle reaction product was phenol, although the formation of cyclohexanol was also detected.

Other Bimetallic Mixtures

Grittini (1997) also achieved the dechlorination of PCP and other chlorinated phenols with palladized aluminium (Pd^0/Al^0), the process was not as efficient as with palladized iron. Additionally the preparation of Pd^0/Fe^0 is more facile than that for Pd^0/Al^0.

Very recently Kim and Carraway (2000) reported the dechlorination of PCP by iron and several bimetallics like Pd^0/Fe^0, Pt^0/Fe^0, Ni^0/Fe^0 and Cu^0/Fe^0. They found the rate of dechlorination was much slower than previously reported by other scientists. Another very recent report described the total dechlorination of PCBs by Fe^0/Ag^0 using supercritical CO_2 as a carrier of the feedstock solution, (Wu et al., 2000).

Palladized magnesium was also capable of mediating the reductive dechlorination of PCBs, (Doyle et al, 1998). The authors reported that the action of bimetallic Pd^0/Mg^0 was preferred over the action of Pd^0/Fe^0 due to the ease of the preparation of the former mixture.

1.6 Supercritical Fluid extraction (SFE)

After the first report by Baron Cagniard de la Tour in 1822 (Bruno and Ely, 1992), the Supercritical fluid extraction technique has been used extensively for very useful for the separation and many analytical or industrial purposes. In summary the supercritical fluid extraction technique has become an interdisciplinary field that is utilized by chemical engineers, chemists, food scientists, material scientists, agronomists, and researchers in biotechnology and environmental control. An additional application of this technique is the isolation and purification of novel products. A considerable effort has been devoted to gaining a more complete understanding of the influence of (a) molecular structure, (b) phase behavior, (c) cosolvent effects, (d) the solvation process between solute and fluid phase, and (e) transport properties of supercritical fluids. Since 1980, there has been rapid progress with the supercritical fluid extraction (SFE) technique for the extraction of flavor components from hops, cholesterol from butter, perfumes and flavors from natural products, residual solvents and monomers from polymers, and unsaturated fatty acids from fish oils. More recently, the use of supercritical fluids has also been directed to:

- Remediation of soil,
- Demilitarization of propellants,
- Chemical reaction and synthesis of polymers and organic chemicals,
- Removal of nicotine from tobacco,
- Cleaning of electronic parts,
- Nucleation and particle size regulation, and
- Impregnation and *in situ* deposition of chemicals.

1.6.1 Properties of Supercritical fluids

The phase diagram, (Figure 5), summarizes the physical phases of a substance of fixed composition. The pressure-temperature diagram presents the relationship between the three states of matter, (solid, liquid and gas). Points along the intersections of these states (phases) define the equilibrium between two of the phases. The vapor pressure starts at the triple point (TP) and ends at the critical point (CP). At any temperature or pressure above CP, only one phase exists – the supercritical phase, the compressed gas becomes a supercritical fluid (SF) and exhibits solvating properties those are intermediate between the liquid and the gaseous states. The critical pressure and critical temperature are symbolized as Pc and Tc respectively. SFs possess a density similar to that of liquid and behaves like a liquid solvent. However, because of the low viscosity the fluid diffuse readily like a gas.

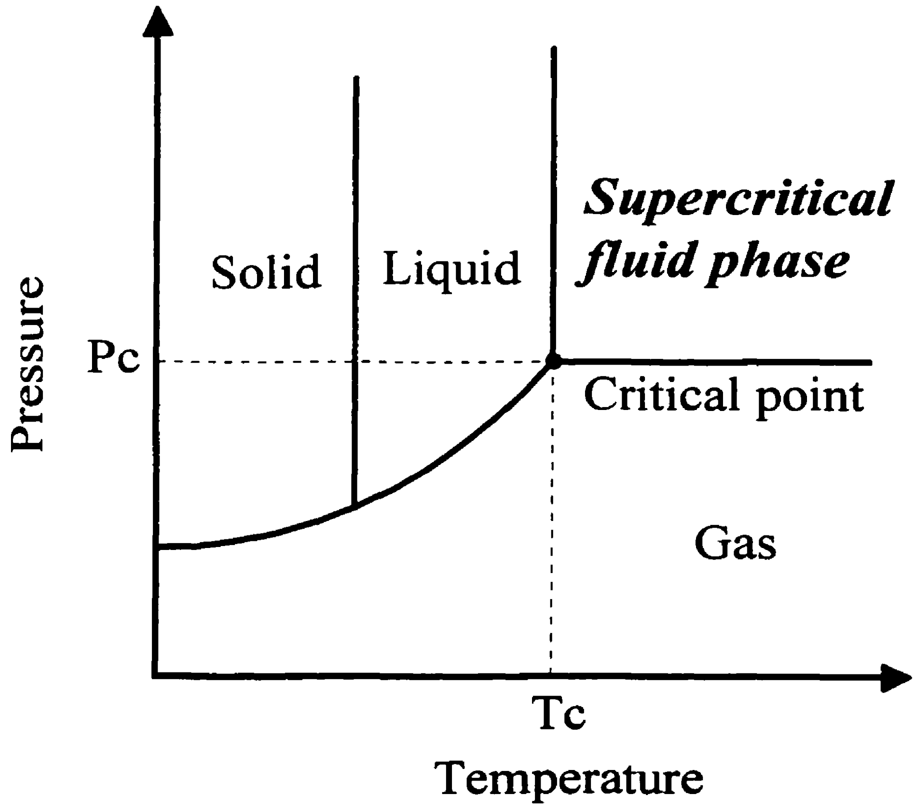


Figure 5: Pressure-temperature phase diagram of a pure substance

The following trends represent a summary of many solubility measurements in the region from ambient conditions up to 1000 bar and 100°C:

- Solvating power of a supercritical fluid increases with density at a given temperature,
- Solvating power of a supercritical fluid increases with temperature at a given density.

For a material at temperature just above the critical temperature of the substance, liquid-like densities are rapidly approached with modest increase in pressure (approx. 0.7-2 times the critical pressure). Higher pressures are required to attain liquid like densities for temperatures further removed from the critical temperature.

Table 10: Characteristics of representative Supercritical Fluids.

Properties	CO_2	NO	NH_3	CH_4	C_2H_4	H_2O
Critical Temperature(°C)	31	36	132	240	32	374
Critical Pressure(atm.)	73	72	112	78	48	227

Inspection of Table 10 reveals that CO_2 is unique among the candidate fluids for effecting supercritical fluid extraction. Its critical temperature of 31°C is close to the room temperature, thereby permitting extractions to be carried out at low temperatures on thermally labile compounds. In general, SC-CO_2 is an excellent solvent for the extraction of lipophilic solutes from a variety of sample matrices. There are several other advantages of CO_2 as a supercritical fluid:

- Low viscosity and low surface tension,
- Inexpensive, abundant and environmentally benign,
- It is non-toxic, odorless, non-flammable and non-explosive.

1.6.2 The use of cosolvent in Supercritical Fluid Extraction

In certain cases, it becomes desirable to add a second solvent to a SF to enhance its solvating power for moderately polar analytes. This second solvent (cosolvent), is usually an organic solvent, that is added to the source of compressed fluid before the pump or compressor, or alternatively, to the extraction fluid after it has been compressed, using a high pressure liquid pump. The addition of a cosolvent to the SF not only enhances the solubility of moderately polar solutes but also, in specific cases, it improves the separation factor between solutes as they are selectively petitioned into the SF phase (King, J.W and France, 1992).

There are several reasons to choose one supercritical fluid over another liquid phase cosolvent system. The choice is governed mainly by:

- The unique solvating and favorable mass transport properties of the supercritical state,
- The ease with which the solvating character of the medium can be varied by adjusting the temperature and pressure of the system.

1.6.3 Critical Parameters for SFE

There are a number of parameters that are of key importance in conducting a supercritical fluid extraction.

- Pressure: at which the desired solute becomes miscible with the supercritical fluid solvent.
- Physical and chemical properties of the solutes that are to be extracted.
- The operating conditions for attaining maximum solute solubility during extraction.

The knowledge of the pressure required to achieve maximum solute solubility in the supercritical fluid has several important applications for analytical SFE. Extractions conducted under these conditions can shorten the extraction time appreciably as well as permitted the processing of larger sample sizes for analysis.

The physical properties of the target solutes including melting point and vapor pressure can also play a role in SFE. Threshold pressures have been demonstrated to be dependent on the melting point of the solute and it has been observed that compounds with melting point in excess of 350°C are not readily solubilized by dense CO_2. In general, it has been observed that the solubility of compounds in a supercritical fluid increases with the increase of temperature. This trend is the result of the substantial reduction in the solute's cohesive energy with increasing extraction temperature that outweighs the commensurate loss of solvating power of the extracting fluid.

1.7 Aim of the research

Recent studies on the dehalogination of chlorinated organic compounds by zero-valent metals have been reviewed. From the review it was clear that the rates of degradation of some organic compounds remain slow and certain reactions can yield toxic byproducts. The fundamental mechanisms might not be straightforward, but typical reaction pathways permit the conclusion that intentional degradation can be efficient under favorable conditions. There are limitations associated with some of the reactions, i.e. formation of an oxide layer on the surface of iron in aqueous media as well as precipitation of iron oxides/hydroxides and chloride that can cover up the active sites on the catalyst.

The benefit of OCs decontamination includes a reduction in the risk of human exposure to these toxic compounds. (Reduced exposure results from increased degradability, decreased lipohilicity and reduced persistence of OCs).

The intention was to dechlorinate lindane and PCP by zero-valent metals or bimetallic mixtures using optimized reaction conditions. It is also clear from the review that the rates of dechlorination of organic compounds are increased appreciably when employing bimetallic mixtures. Using supercritical CO_2 to transport the substrates through a column of metal or bimetal particles the research aims were:

i) to identify and optimize an efficient remediation process for lindane and pentachlorophenol

ii) to develop a continuous process that would mediate the dechlorination of OCs to their hydrocarbon analogs.

Chapters 2 and 3 report the materials/methods and the dechlorination of lindane and pentachlorophenol under different reaction conditions and Chapter 4 deals with the continuous dechlorination of pentachlorophenol.

Chapter II

2.0 Introduction

The adverse effects and persistent character of many organochlorine (OCs) compounds has led a number of scientists to try to develop novel techniques to degrade these compounds. A number of techniques have been explored to assess the utility of different reactions for the treatment of contaminated environments. Degradations mediated by zero-valent metals or bimetallic mixtures are currently of broad interest. The general model for such reactions consists of the following steps, (Tratnyek and Matheson, 1994).

- mass transport of the chlorinated substrate to the iron surface from the bulk solution,
- adsorption of the reactant on the surface,
- chemical reaction on the surface,
- desorption of the product,
- mass transport of the products to the bulk solution.

The degradation process, as described by Gillham and O'Hannesin, (1994), appeared to follow a pseudo first-order kinetic with respect to the organic substrates, with the rate constant appearing to be directly proportional to the surface area to volume ratio of the metal particles and increasing with the increasing degree of chlorination. Their column test showed the process (flow through system) to proceed and follow conditions with degradation rates independent of mobile phase velocity and consistent with rates measured in batch test. When normalized to 1 m^2/mL, the t_{50} ranged from 0.013 to 20 hours and were about 5 to 15 orders of magnitude shorter than value reported for rates of natural abiotic degradation.

Most scientists agree that the bimetallic reaction system provides increased efficiency relative to reactions with a single metal. The bimetals are prepared by depositing one metal on the surface of an excess of a second and less reactive metal. A spontaneous redox reaction ensures according to the positive reduction potential. As an example, palladized iron has been prepared by depositing palladium on iron, (Grittini, 1997):

Oxidation	$2Fe^0 \longrightarrow 2Fe^{2+} + 4e^-$	$E^0 = -0.44$ V
Reduction	$PdCl_6^{2-} + 4e^- \longrightarrow Pd^0 + 6Cl^-$	$E^0 = 0.94$ V
	$2\,Fe^0 + PdCl_6^{2-} \longrightarrow 2Fe^{2+} + Pd^0 + 6Cl^-$	$E^0 = 0.50$ V

2.1 Factors affecting the rate of reaction

2.1.1. pH

The reaction kinetics of dehalogenation of the organic compounds mediated by Fe^0 can be influenced by pH. The requirement for H^+ participation in the reaction suggested the possibility that protons can appear in one or more of the steps that influence the reaction rate directly, (Tratnyek and Matheson, 1994). In addition, strong indirect effects are possible due to increased aqueous corrosion at low pH or iron hydroxide precipitation at high pH.

2.1.2 Temperature

The importance of mass transport to the kinetics in dehalogenation of organic compounds comes from the effect of temperature on K_{obs}. Reaction rates that are limited by diffusion typically have low activation energies and therefore, are only weakly depended on temperature as opposed to those reactions that are rate-controlled by a chemical step, (Tratnyek and Matheson, 1994)). The data indicated that K_{obs} was unaffected by temperature over the range from 4 to 35^0C and data that was fitted to the Arrhenius equation resulted in a slope that is not significantly different from zero. This suggested that temperature is an important experimental variable.

Other dehlogenation reactions were reported to be more strongly temperature dependent. The reaction rate of dechlorination of PCBs at 200^0C did not provide an efficient dehalogenation reaction. But at 300^0C the yield was 78% and at 400^0C the yield of biphenyl was virtually quantitative within 10 minutes, (Chuang et al, 1995). For temperatures in excess of 400^0C (500-600^0C), the formation of biphenyl and other chlorobiphenyl compounds were decreased (to 59% and 2% conversion, respectively), that indicated not only the dechlorination but also other reactions had taken place giving rise to compounds undetected by GC/MS under their operating conditions.

2.1.3 Solvent

The successful dechlorination of PCBs required a particular solution ratio for an improved yield. Farnando et al. (1995), reported that a solution of methanol:water:acetone (1:3:1) v/v/v yielded 100% biphenyl in 5-10 minutes using a 0.05% w/w Pd/Fe bimetallic catalyst.

2.1.4 Surface area of metal particles

The surface area of the metal particles influences the dechlorination rate for OCs. Scientists have reported that much of the variability in observed degradation rates for a particular chlorinated compound could be attributed to the effect of iron surface area to mass ratio, (Johnson et al., 1996). Although incorporating the influences of other factors into the kinetic model provided mechanistic insights, the magnitude of these effects is relatively modest over the range of environmentally realistic condition. Thus, initial first-order degradation rate constant normalized to the iron specific surface area (K_{SA}) appeared to offer the most practical, general description of contaminant degradation kinetics. Surface area normalized rate constants for nano-scale Fe^0 particles (1 - 100 nm in diameter) were 10 to 1000 times greater than those of micro-scale commercial Fe particles, (Wang and coworkers, 1997).

The bimetallic reaction was characterized by a more rapid dechlorination relative to the analogous reaction mediated by a mono metallic catalyst. The rate of reaction was observed to depend on the amount of the Pd^0/Fe^0 used, % (w/w) of Pd^0 deposited on the Fe^0 surfaces and on the % (v/v) of water in solution, (Farnando et al. 1995). The higher the percentage of Pd deposited on iron, the more rapid the reaction.

2.2 Materials

2.2.1 Reagents

Iron particles, 40 mesh (nominally 99.5% purity), zinc particles 100 mesh (nominally 99.9% purity), acetic anhydride (AcA), ethylene glycol dimethyl ether (DME), diethylene glycol diethyl ether (DGDE), diethyl ether (Et_2O), methanol (HPLC grade), ethanol (HPLC grade), 2-propanol, butanol, tetrahydrofuran (THF), nitric acid, potassium chromate, sodium bicarbonate and silver nitrate were purchased from Fisher Scientific, Ottawa, ON and used as received. Acid washed sea sand was purchased from ACP Chemicals Ltd., Montreal, QC and used as received. Sodium dispersion (40% w/v in oil) were purchased from Alfa Aesar, Ward Hill, MA and used as received. Lindane (γ-hexachlorocyclohexane, 99%), pentachlorophenol (99%+), 2-chlorophenol (98%), 3-chlorophenol(99%), 4-chlorophenol (98%), and 2,4-dichlorophenol (98%) were purchased from Sigma-Aldrich, Milwaukee, WI. and received as ASC reagent grade. A standard solution containing mixture (2000 μg/ml each) of chlorinated phenols was purchased from Ministry of Environment, Quebec City, QC. High purity CO_2 (1800 psi) and helium were purchased from MEGS, Montreal, QC.

Preparation of Ag^0/Fe^0

The Ag^0/Fe^0 was prepared from 40 mesh iron particles that was washed copiously with 1M HCl and rinsed with distilled water following the general procedure of Wu and Marshall, 2000 and. An amount of $AgNO_3$ aqueous solution sufficient to result in 2% (m/m) surface coverage on iron particles was added to the aqueous suspension of iron. The suspension was then mixed gently on a rotary evaporator for 12 hours. Finally, the mixture was washed with distilled water and dried at 110^oC for 6 hours. An appreciable surface oxidation was observed as evidenced by the color change of the iron particles from black to reddish-brown.

2.2.2 Instrument and Apparatus

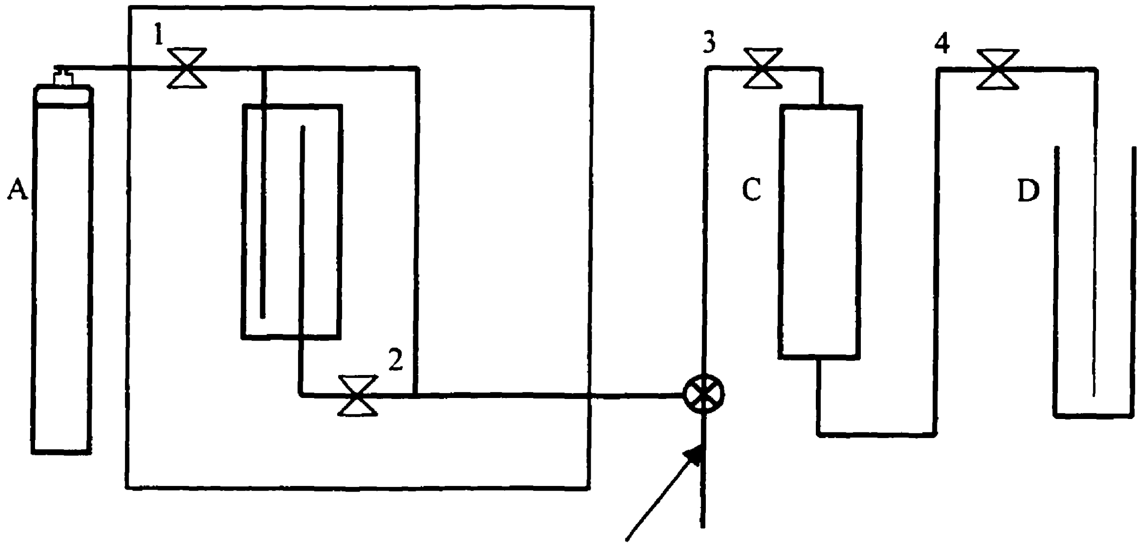
A PrepMaster, Suprex Corporation, Pittsburg, PA, U.S.A. was used as SFE unit to deliver the SC-CO_2 from the cylinder of compressed gas. A model 110A HPLC pump, Beckman, (capable of pumping 0.01 to 10.0 ml/min at pressures up to 6000 psi.) was used to deliver the OC feedstock solution to a low dead volume mixing tee. An HPLC column assembly (10 mm inner diameter), 12mm (outer diameter) x 25cm, Supelco, Oakville, ON, was filled with metal particles. Heating tapes (CRFC-7512/120 consisting of vacuum formed ceramic fiber radiant heaters 30.48 cm x 7.62 cm x 0.64 cm, OMEGA Technologies, Laval, QC) was energized by a variable heating regulator, POWERSTAT, Bristol, UK, to heat the HPLC column. Stainless steel capillary tubing (1/16 " I.D.) and other HPLC fittings were supplied by Supelco, Oakville, ON. Fused silica capillary tubing (0.05 mm I.D.) was supplied by Chromatographic Specialties, Brockville, ON. Agilent Technology, Montreal, QC supplied a HP model 5890 series II GC interfaced with mass detector model HP 5971. All glassware was of 'A' grade from either KIMAX or PYREX.

2.3 Methodology

2.3.1 Reactor system

The dechlorination reactor consisted of standard HPLC fittings and column assemblies that were rated to 6000 psi. The PrepMaster supplied SC-CO_2 after compressing CO_2 (1800 psi) received from a K-type cylinder. SC-CO_2 at 250 atm pressure was pumped through an automated valve to the column containing metal particles. The HPLC pump delivered the feedstock solution to the mobile phase SC-CO_2 via a mixing tee, (Figure 6).

The flow of SC-CO_2 was 0.2 to 0.65 L/min as decompressed gas. The sample solution was transported by the SC-CO_2 through the heated column (250 to 450^{O}C) and the reaction products were trapped in an appropriate solvent as they exited the capillary restrictor. Arbitrarily, each experiment consisted of collecting six successive traps, each trap corresponding to 10 minutes of cumulative trapping of reactor elute. Subsequent experiments were performed in which cumulative 30-minute traps were collected. The course of dechlorination and identification of trapped products were monitored by GC/MS, or by titration to measure levels of residual organically bound chlorine in each trap.



Feedstock from an HPLC pump

Figure 6: Reactor System for thedechlorination of OCs with a system consisting of an SFE unit

A, CO_2 cylinder, B, extraction vessel for saturation; C, HPLC Column; D, Trap; and 1 to 4 needle control valves

2.3.2 Gas Chromatography

GC interfaced with HP 5971 mass detector. The HP 5890 series II gas chromatograph was fitted with 30m by 0.250mm i.d HP1 capillary column that was eluted with helium at 0.500 ml/min. The course of reaction was monitored by periodically withdrawing 0.2μl of sample from a trial solution and injecting (in the splitless mode) on to the column inlet with an initial temperature of 40 ^{O}C that was held for 2.5 minutes. The temperature program consisted of injection at 25 ^{O}C/min up to 80 ^{O}C and held for 1 minute followed by ramping at 10^{O}C/min. up to a final temperature of 250 ^{O}C and held for 1 minute. The injection port temperature was 250 ^{O}C and the detector temperature was 280 ^{O}C. Eluting components were identified by the comparison of experimental mass spectra with NIST and Wiley 318 spectral libraries. The identification was also corroborated by co-chromatography with authentic standard.

2.3.3 Organically bound chlorine

Organically bound chlorine was determined following the general method of Ware et al, 1988 followed by the detection of the equivalence point with the Fajan's method. The procedure (for the test solution in an organic medium) consisted of two steps: digestion of organically bound chlorine to release chloride into the aqueous layer followed by argentometric titration of residual chlorides with standardized 0.01M $AgNO_3$ solution. Sodium dispersion (≈ 2ml) was added to a stirred 10ml sample of the trap solutions diluted in ether. If the trap solvent was methanol, the extra addition of MeOH was not required. After 5 minutes of vigorous stirring 15 ml of 2-propanol was added to complete the reaction followed by the addition of 70 ml of distilled water. After 1 minute of vigorous stirring, the aqueous phase was recovered and diluted to 100ml. A 20ml aliquot of the diluted aqueous phase was acidified with dilute HNO_3 and then neutralized with $NaHCO_3$ to a pH of 6.0 to 7.0. The change in color of potassium chromate from yellow to reddish brown signaled the equivalence point of the titration. $AgNO_3$, 1ml of 0.01M, is equivalent to 0.355 mg of chloride. To determine the levels of chloride in the initial aliquot of sample, a blank was performed in the absence of sodium dispersion.

Amount of chloride = W1 -W2 x 0.355 mg x 2.5 x 5;

Where W1 = volume required for the sample solution

and W2 = volume required for the blank solution

Chapter III

3.0 Introduction

The sources of OCs contamination and their toxic effects in the environment were discussed in previous chapters. For many of the OCs, the most frequently used method of destruction remains incineration at elevated temperature. Although incineration is a very efficient process for destroying OCs, it can be incomplete and can result in the formation of more acutely toxic products including PCDDs and PCDFs. To date, degradation of OCs by chemical, biological or catalytic methods has met with limited success because of the cost, lack of speed and efficiency. Scientists have been attempting to define or optimize more efficient methods to dechlorinate these toxic materials. The dechlorinations of OCs can be mediated by the reaction with zero-valent metal or bimetallic mixtures. An efficient, relatively rapid and continuous method is desirable for these purposes.

The dechlorinations of aliphatic and aromatic compounds by zero-valent metal and bimetallic mixtures have been reported by a number of researchers (Muftikian, et al, 1995; Chuang et al, 1995; Fernando et al,1995; Boronina et al, 1998; Wu and Marshal, 2000). They have described the dechlorination status and effectiveness of their respective procedures. Among them Grittini (1997) and Wu (2000) described the most active metal systems for the dechlorination of PCP, PCB, DDT and other OCs.

3.1 Dechlorination of Lindane

3.1.1 Experimental

Lindane contains some 74% of chlorine by weight. A number of lindane solutions in various solvents or solvent mixtures were assessed as feedstock for the dechlorination process. Zero valent zinc, iron and silver-coated iron were evaluated at various temperatures under a constant flow of SC-CO_2 and pressure.

Lindane solutions (10% w/v) were diluted to 25 ml in volumetric flask. The solvents were diethylene glycol diethyl ether (DGDE), cyclohexanol, acetic anhydride (AcA.) and mixtures of DGDE + AcA in different ratios. The trapping solvent was DGDE. The empty HPLC column assemblies (25 cm X 1 cm i.d) were filled with 100 mesh Zn particles or 40 mesh Fe particles or 40 mesh Ag/Fe particles. SC-CO_2 (1 ml/min) was passed through the column after mixing with a stream of the lindane solution (0.1 ml/min) added with an HPLC pump via a low volume tee fitting. The temperature for the reaction system was maintained at 100 or 110 ^{O}C for Zn whereas for Fe^0 the temperature was maintained at $300^{O}C$. The reactor eluate was collected during sixty minutes and the trapping solution was replaced with fresh solvent at 10-minute intervals. The trap solutions were then analyzed by gas chromatography (GC). Organically bound chlorine was determined by argentometric titration of the trap solution after digestion with metallic sodium (dispersed in oil). Prior to titration, the pH of the solution was adjusted to pH 6.0 to 7.0 with 1M HNO_3 and then neutralized with sodium bicarbonate. The efficiency of the reaction for lindane was evaluated by both the results from gas chromatography and the residual organically bound chlorine as determined by titration.

3.1.2 Result

Zn°

In case of lindane, different solvents provided variable ranges of degradation with the different zero-valent metals or bimetallic mixtures. Table 10 presents the degradation mediated by Zn^0 at 110°C and a SFE pressure of 250 atm.

Table 10: Degradation of lindane [10% (w/v) solution in 2:8 (v/v) DGDE: AcA]

	1st trap	2nd trap	3rd trap	4th trap	5th trap	6th trap
% loss by GC	43.3	84.8	95.2	98.87	99.2	98.6
% dechlorination by titration.	42.9	82	93	95	96.5	97.2

Table 11 represents the degradation of 10% (w/v) lindane in DGDE by Fe^0, at 300°C and SC-CO_2 of 250 atm., during two consecutive runs of column operation with each run consisting of six traps collected sequentially.

Table 11: Degradation of 10% (w/v) lindane in DGDE by Fe^0.

	1st trap	2nd trap	3rd trap	4th trap	5th trap	6th trap
(GC)						
% loss (1st run)	21.9	74.3	98.3	97.1	100	100
% loss (2^{nd}run)	40	87.4	95.8	98.4	99	100
(Titration)						
% dechlorination (1st run)	51.4	76.3	79.2	81	81	81.5
% dechlorination (2^{nd} run)	67.6	77.5	79.2	81.5	82.7	82.1

Table 12: Degradation of 10% lindane in DGDE by Fe/Ag

	1st trap	2nd trap	3rd trap	4th trap	5th trap	6th trap
(GC)						
% loss (1st run)	42.3	82.3	100	100	100	100
% loss (2nd run)	33.3	84.7	98.5	100	100	100
% loss (3rd run)	53.4	93.3	99	100	100	100
(Titration)						
% dechlorination (1st run)	82	84.3	86	87.2	87.2	86.6
% dechlorination (2nd run)	78.9	80.1	80.7	82.5	82.5	83
% dechlorination (3rd run)	64.7	83	83.5	83.5	84.1	84.1

Table 12 summarizes the dechlorination of 10% (w/v) lindane by Fe/Ag during three consecutive runs of column operation with each run consisting of six traps collected sequentially.

The reactions were effected at different temperatures and subsequently, the temperature that yielded the most efficient degradation was used. Both GC peak-area and levels of organically bound chlorine were determined. The results were comparable but not identical to each other. The results obtained with different combinations of temperature and zero-valent metal are presented in Table 13. For Zn^0, the reaction was initiated by temperature as low as 80^OC however the maximum efficiency for this metal was observed at 110^OC. Because of the very low softening point of Zn (115^OC), the reaction temperature was not raised above 110^OC. Any further increase in reaction temperature caused the column to become blocked.

Table 13: Reduction of lindane solutions by zero-valent metals or bimetallic mixture.

.	Metal	% (w/v) lindane in feedstock	Feedstock solvent	Reactor temp.°C	% loss[a] of lindane)	% yield[b] of chloride
1	Zn	10	DGDE	100	23-48	23-48
2	"	"	DGDE:AcA(1:9)	100	54-67	41-63
3	"	"	DGDE:AcA(1:1)	100	50-72	
4	"	"	"	110	61-91	59-91
5	"	"	DGDE:AcA(2:8)	110	84-99	81-94
6	Fe	"	DGDE	300	74-100	76-81
7	"	"	"	300	87-100	67-82
8	Fe/Ag	"	"	300	82-100	82-87
9	"		"	300	84-100	79-83
10	"	"	"	300	93-100	83-84

[a] Percent loss of lindane in the reactor eluate (as determined by GC) relative to 1 ml (0.1 ml min^{-1} x 10 min) of the feedstock.

[b] One minus the ratio of organically bound chlorine in the trapping solution relative to the organically bound chlorine in an equivalent quantity of feedstock expressed as a percentage.

3.1.3 Discussion

It was observed that the identity of the solvent system influenced the reaction efficiency appreciably. In the case of Zn^0 particles, DGDE or DGDE/AcA solvent systems were used, but the 2:8 ratio of DGDE/AcA yielded the most efficient dechlorination among different solvent systems. This solvent provided 99% loss of peak area and 94% dechlorination as determined by titration for organically bound chlorine..

Similar dechlorination efficiencies were observed for both the Fe^0 and Fe^0/Ag^0 metallic systems. For these metals, the dechlorination efficiencies were 82% for Fe^0 and 84.5% by Fe^0/Ag^0. The most efficient reaction was observed at 300^0C in DGDE. Trials were performed with a DGDE/AcA mixed solvent, but the dechlorination efficiency was less than for reaction in DGDE alone.

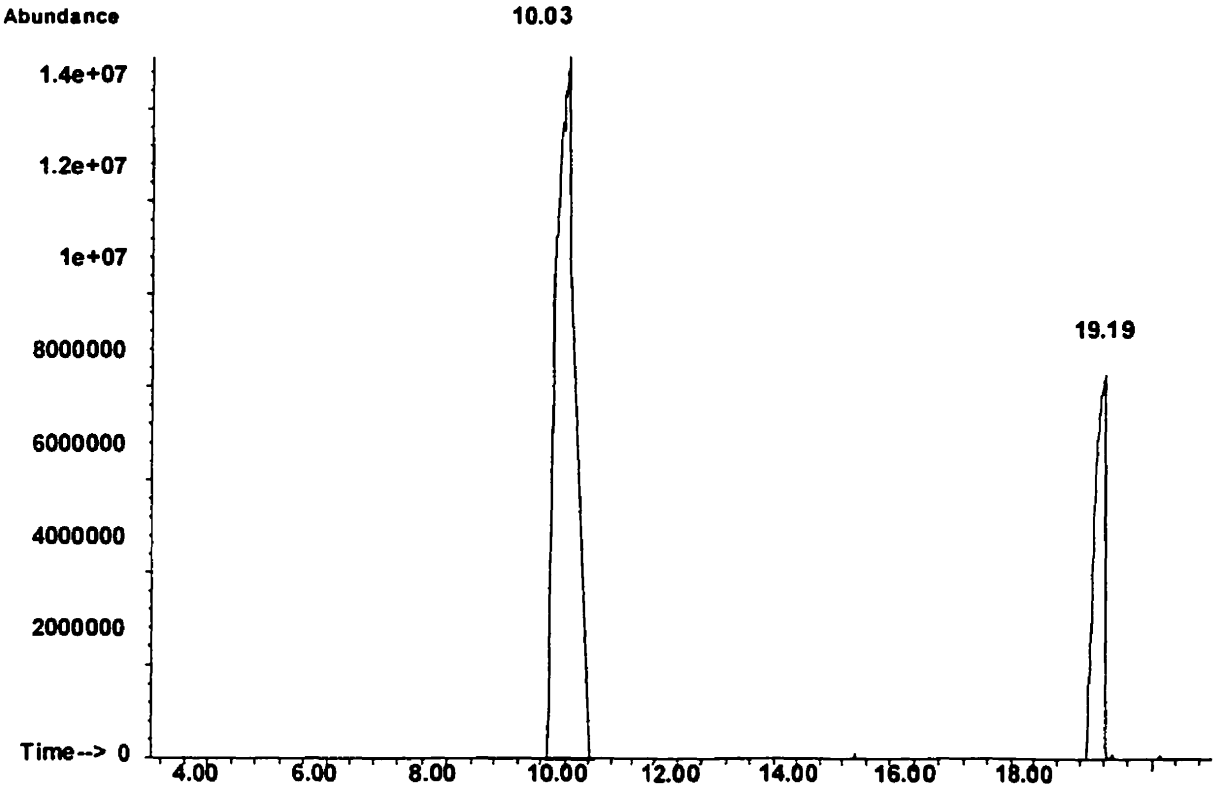


Figure 7: Chromatogram of 10% w/v lindane in DGDE before dechlorination by Fe/Ag.

The reaction efficiency as calculated by GC peak area indicated that virtually complete reaction was effected by both Fe^0 and Fe^0/Ag^0 particles. Titration, however, indicated the presence of 10-14% of organically bound chlorine.

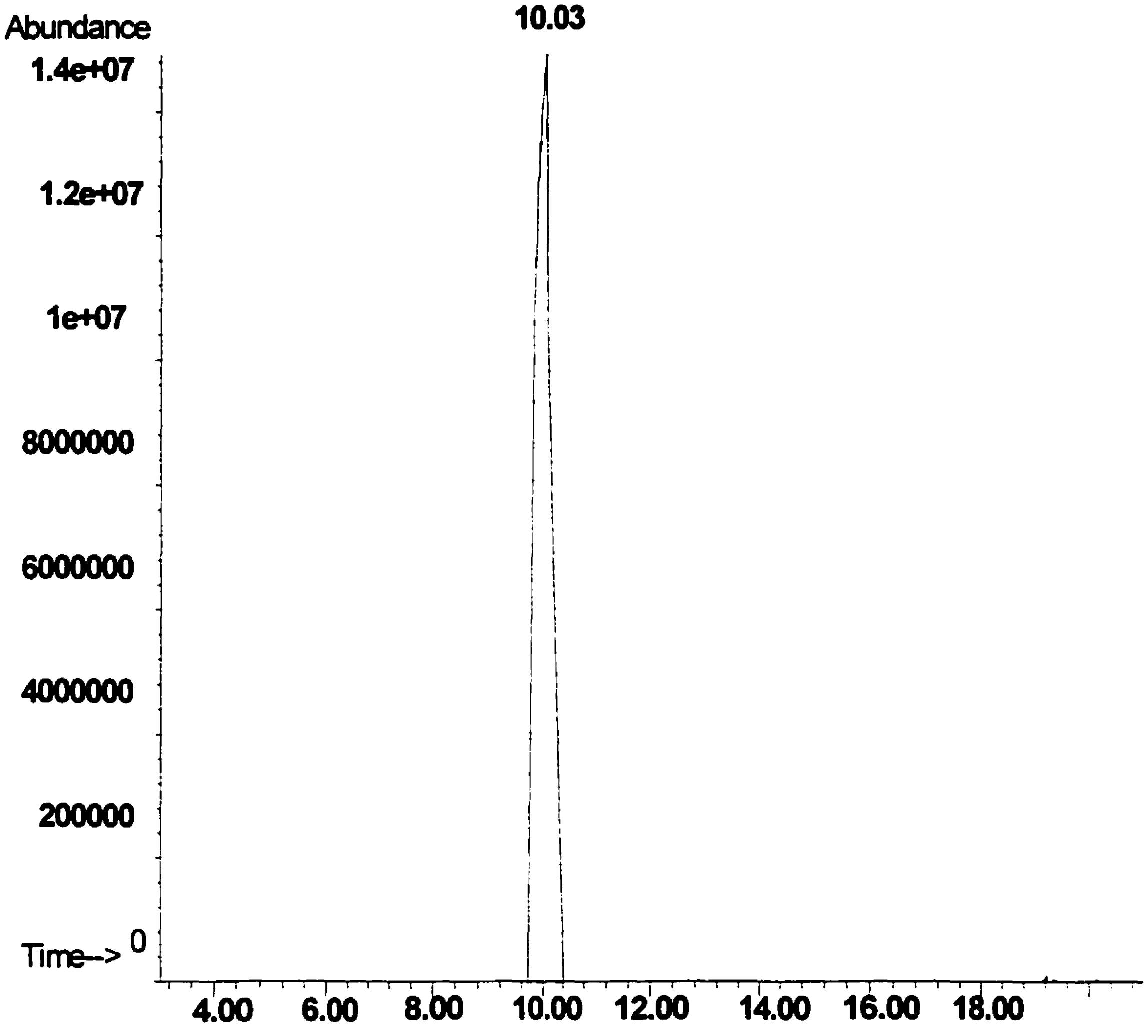


Figure 8: Chromatogram of 10% w/v lindane in DGDE after dechlorination by Fe/Ag

Gas chromatograms of reactor eluate summarize the dechlorination for lindane. The chromatogram of 10% (w/v) lindane solution in DGDE before and after the dechlorination illustrates the differences that indicate the virtually complete loss of lindane substrate in reaction mediated by the Fe/Ag bimetallic mixture (Figure 7 and Figure 8 respectively). A trace amount of monochloro benzene was identified and quantified but its concentration accounted for appreciably less than 0.5% of the substrate.

3.2 Dechlorination of Pentachlorophenol

3.2.1 Experimental

The procedures adopted to evaluate the dechlorination of pentachlorophenol (PCP) were identical to the procedures for lindane (section 3.1.1), except that different combinations of solvents were used. Due to the high solubility of the PCP substrate in alcohols; methanol, ethanol, iso-propyl alcohol and n-butanol were chosen. Particles of Fe^0/Ag^0 (2% w/v Ag^0) were used for the dechlorination of the substrate. The reaction was monitored at various temperatures as well as SC-CO_2 pressures and flow rates. Subsequently, the pressure of the SC-CO_2 was maintained at 250 atm and the column temperature at $450^{O}C$ with 250ml/min of CO_2 (as decompressed gas). The reactor effluent from a 20% w/v feedstock solution of PCP was collected in six consecutive traps of methanol. The eluents were analyzed by GC/MS and the residual organically bound chlorine was measured by titration. For corroboration of the identities of products by GC/MS several authentic standards were co-injected to demonstrate co-chromatography. A system comprising two reactor columns mounted in series was also evaluated.

The dechlorination effected by a single reactor column was evaluated for a 20% (w/v) solution of PCP. After continuous dechlorination during sixty minutes (6 traps), the column was washed with several column volumes of water to remove the chloride. The total quantity of chloride was determined by the titration with standardized $AgNO_3$ solution. Analyses by GC/MS were performed by injection 0.2 μLof the trap solution into the instrument. The injection port temperature was $250^{O}C$ and the detector temperature was $280^{O}C$. The temperature program consisted of an initial hold at $40^{O}C$ for

2.5 minutes followed by ramping to 100°C at 25°C/min. After 1 minute hold, the temperature was further ramped to 210°C at 10°C/min where it was held for 1 minute prior to cool down.

3.2.1 Result

Dechlorinations were carried out at different temperature and feedstock concentrations are described in Table 14.

Table 14: Percent loss of pentachlorophenol and dechlorination efficiency in a single reactor column of Fe^0/Ag^0.

Feedstock solvent[a]	% PCP in feedstock	Reactor temp.($^{\circ}$C)	% loss[b] of PCP	%yield[c] of Cl^-
MeOH	5	350	75-96	
MeOH		350	77-95	
MeOH		350	73-92	72-90
BuOH		400	96-100	84-93
DGDE		400	95-99	88-91
MeOH	10	400	95-100	89-95
AcA+DME(1+8)		400	97-100	76-81
IBMK		450	89-96	72-85
IBMK		450	88-98	71-87
MeOH	20	450	88-99	96-97
MeOH		450	100	91-94
MeOH		450	98-100	91-92
MeOH		450	100	93-95

[a] Feedstock solvents included methanol (MeOH), AcA+DME, BuOH etc.

[b] Percent loss of PCP in the reactor elute (as determined by GC)relative to 1 ml of the feedstock.

[c] One minus the ratio of organically bound chlorine in the trapping solution relative to the organically bound chlorine in an equivalent quantity of the feedstock expressed as a percentage.

Methanol, or other alcohol, yielded more efficient dechlorinations at higher operating temperatures. The dechlorination was also monitored at different flow rates of SC-CO_2. For these experiments, it was observed that more efficient dechlorinations were obtained at lower flow rates with the maximum dechlorination at 220 ml/minute of SC-CO_2 (as decompressed gas). Even with a flow of 600 ml/minute, the dechlorination efficiency varied between 87 and 91%, (Table 15).

Table 15:Influence of the SC-CO_2 flow rate at constant pressure on the percent reduction in the peak area of PCP for a single reactor column at 450^{O}C.

	Temperature (^{O}C)	Pressure (atm.)	Decompressed CO_2 Flow rate (ml min^{-1})	%loss[a] of PCP (Peak area by GC)
1	450	250	220	96.5 - 97.8
2	450	250	300	94.5 - 95.8
3	450	250	350	92.0 - 94.5
4	450	250	450	89.6 - 92.0
5	450	250	600	87.1 - 91.0

[a] Range observed among sequential traps of reactor eluate that each were collected for 10 min.

Table 16 presents the percent dechlorination observed with either two sequential Fe^0 reactor columns connected in series or a single reactor column for 20% w/v methanolic feedstock delivered at 0.1 ml/min to the reactor maintained at 450^{O}C under 250 atm of SC-CO_2.

Table 16: Observations with two siquential Fe^0 reactor colimns connected in series or a single reactor column for a continuous flow of 20% w/v methanolic feedstock, delivered at 0.1 ml min^{-1}, to the reactor maintained at 450^0C under 250 atm of $SC\text{-}CO_2$.

	1st trap	2nd trap	3rd trap	4rth trap	5th trap	6th trap
One column						
% PCP [a] loss	96.9	98.9	99.6	99.3	99.8	99.8
% loss [b] org Cl	92.9	94.3	94.8	95.3	95.3	95.3
Two columns						
% PCP [a] loss	100	100	100	100	100	100
% loss [b] org Cl	98	98	98.3	98.5	98.5	98.5

[a] percent reduction in the GC peak and [b] percent reduction in the quantity of organically bound chlorine.

Both the single and double column (in series) systems efficiently dechlorinated a 20% (w/v) PCP in ethanol. The % dechlorination of PCP with the two-column system was more efficient than with a single reactor column. Table 17 summarizes the dechlorination for both column systems as determined by the titration of organically bound chlorine.

Table 17: Dechlorination of 20% w/v PCP in ethanol mediated by Fe^0/Ag^0 as determined by titration.

	1st trap	2nd trap	3rd trap	4rth trap	5th trap	6th trap
Single column	94.6	95.5	96.5	97.0	97.0	97.0
Double column	98.3	98.3	98.5	99.0	99.0	99.0

Dechlorination with a single column system was carried out to determine the amount of chloride deposited on the surface of Fe^0/Ag^0 particles. Reduction was calculated by both

GC peak area and organically bound chlorine by titration with 0.1M $AgNO_3$ solution after digestion with metallic sodium (Table 18).

Table 18: Dechlorination of 20% (w/v) PCP in methanol (washed subsequently to recover deposited chloride.

	1st trap	2nd trap	3rd trap	4rth trap	5th trap	6th trap
% Red.(GC)	96.9	98.9	99.6	99.3	99.8	99.8
% Red.(Titr.)	92.9	94.3	94.8	95.3	95.3	95.3

From Table 18 it is observed that some 94.7% (average) of the organically bound chlorine was removed during passage over the metal particles. The reduction in the PCP peak area (GC) was calculated as 99% (average).

The 20% (w/v) solution of PCP contained 200 mg/ml of substrate. Collectively for the 6 traps, a total of 6ml (1200 mg) was reacted on the column. PCP also consists of 66.6% of chlorine by weight. A total of 799 mg chlorine was reacted and might have been deposited as chloride on the metal particles. The deposited chloride was determine by the titration of the cumulative column washes from elutions of column with 50 mL (each wash) of doubly distilled water (Table 19),

Table 19: Determination of chlorine from the washed solution.

	1st wash	2nd wash	3rd wash	4rth wash	5th wash	Total
Chloride mg	633.85	61.57	28.25	13.04	0.18	736.89

Of the 799 mg that had been reacted, 736.89 mg of chloride was recovered in the washing solution (Table 19) indicated that ~92.22% of the organically bound chlorine

(799 mg) was deposited on the metal particles. This value is comparable to the mean reduction (94.7% = 757 mg Cl^- released) as calculated from the titration of organically bound chlorine residues in the eluate from the reactor column (average from Table 18).

The gas chromatogram of the solution before and after dechlorination with Fe^0/Ag^0 is presented in Figures 9 and 10 respectively. The products were identified by the co-chromatography with authentic standard.

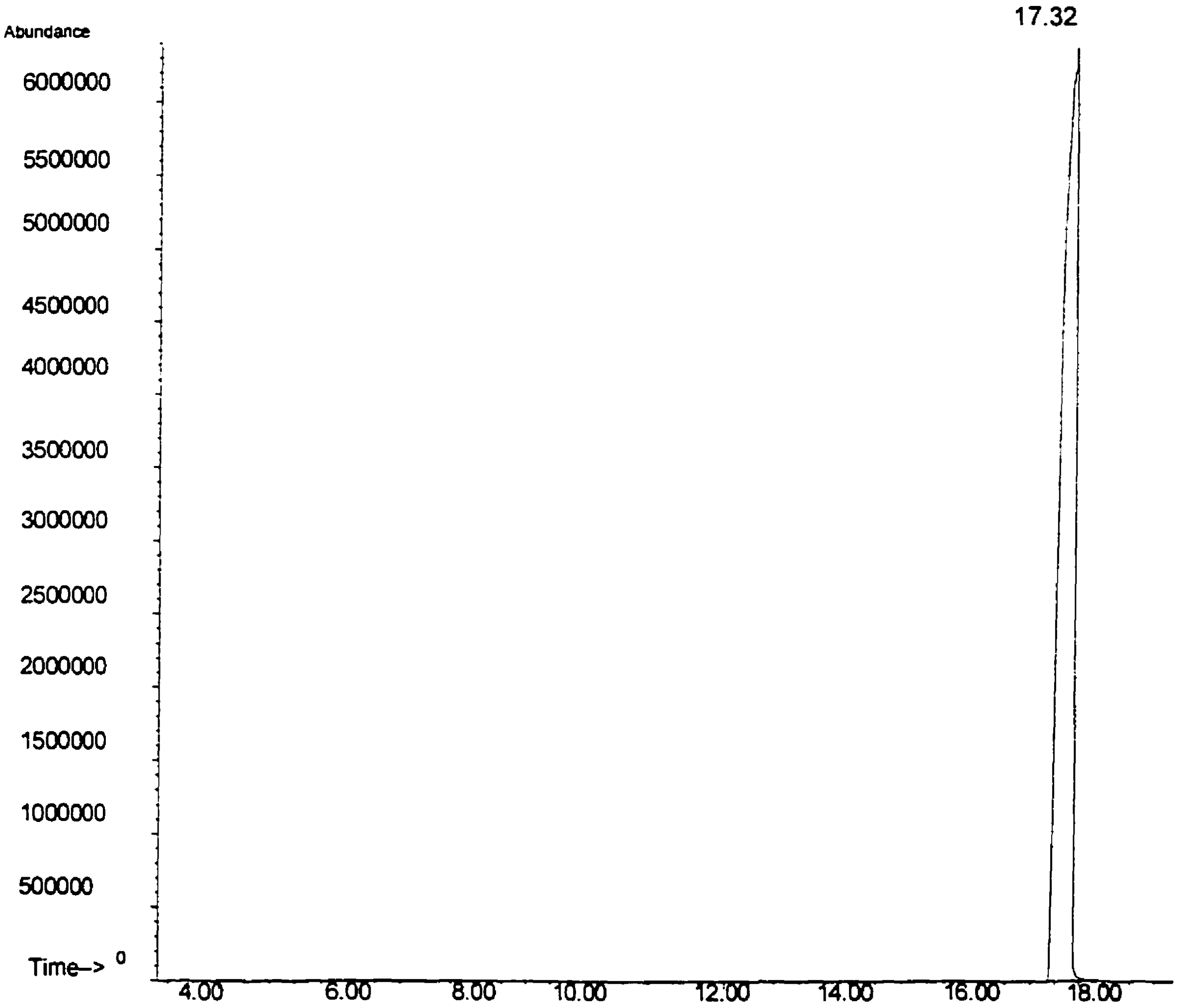


Figure 9: Gas Chromatogram of 20% w/v PCP in methanolic feedstock before dechlorination.

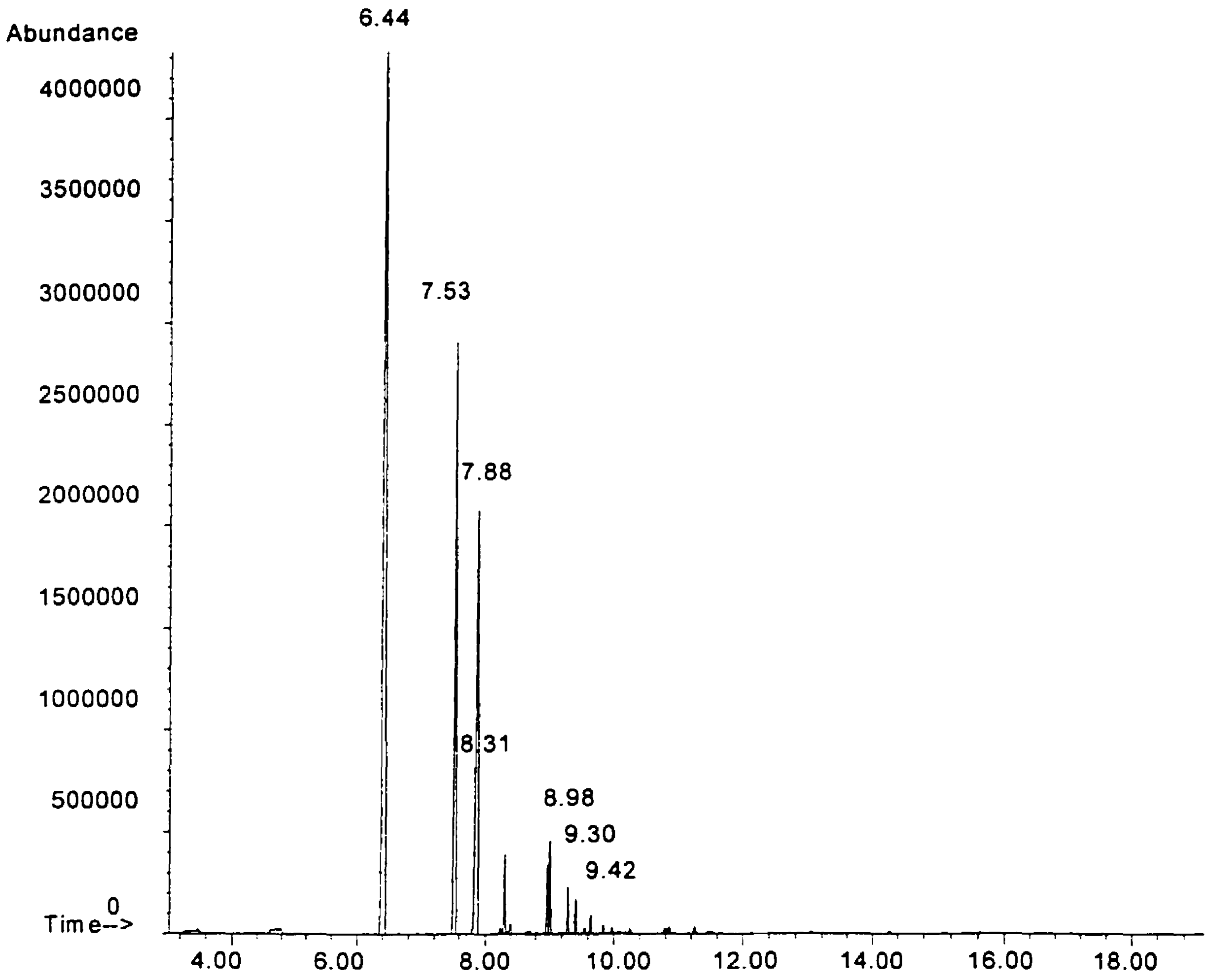


Figure 10. Gas chromatogram of the total ion current from 20% (w/v) PCP in the methanolic feedstock after dechlorination.

Seven prominent peaks characterized the gas chromatogram after dechlorination with retention time ranging from 6.44 to 10.8 minutes. The identities of each fraction were corroborated by their respective mass spectra. No product containing chlorine was observed.

The peak at 6.44 minutes in the chromatogram was identified as phenol (Figure 11). Other peaks were identified as *o*-cresol (7.53 min.), *m*-cresol (7.88 min.), 2,6-

dimethylphenol (8.31 min.), 2,4-dimethylphenol (8.98 min.), 3,5-dimethylphenol (9.30 min.) and 3,4-dimethylphenol (9.42 min.).

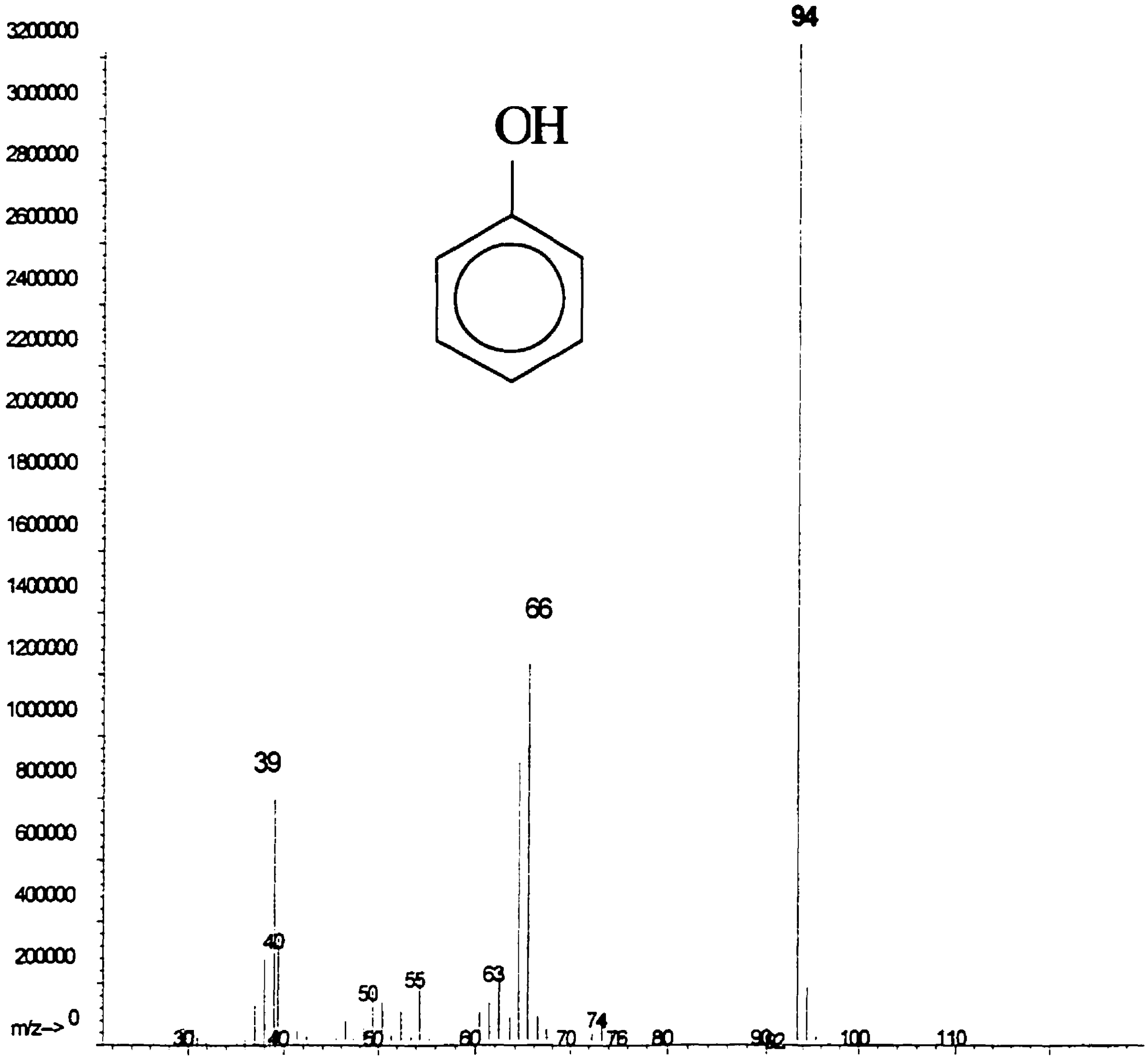


Figure 11: Mass spectrum of phenol (retention time, R_T, 6.44 min.))

Figures 12 and 13 present the mass spectra of the peaks in the chromatogram at 7.53 and 7.88 min for *o*-cresol and *m*-cresol respectively.

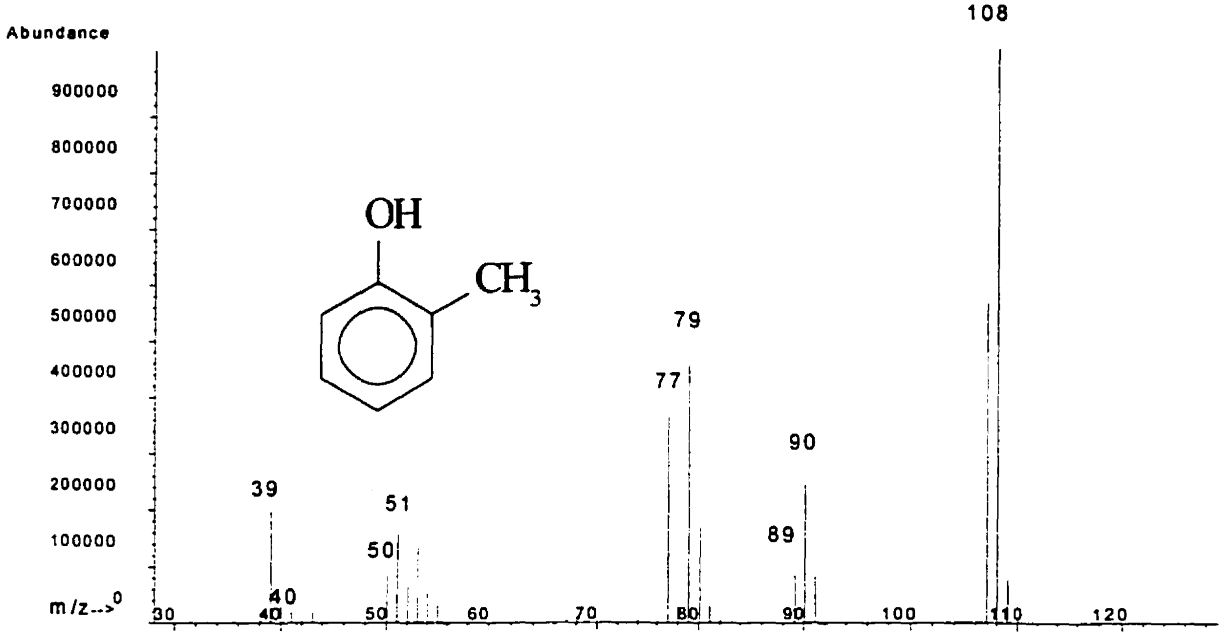


Figure 12: Mass spectrum of *o*-cresol, (retention time, R_T, 7.53 minutes)

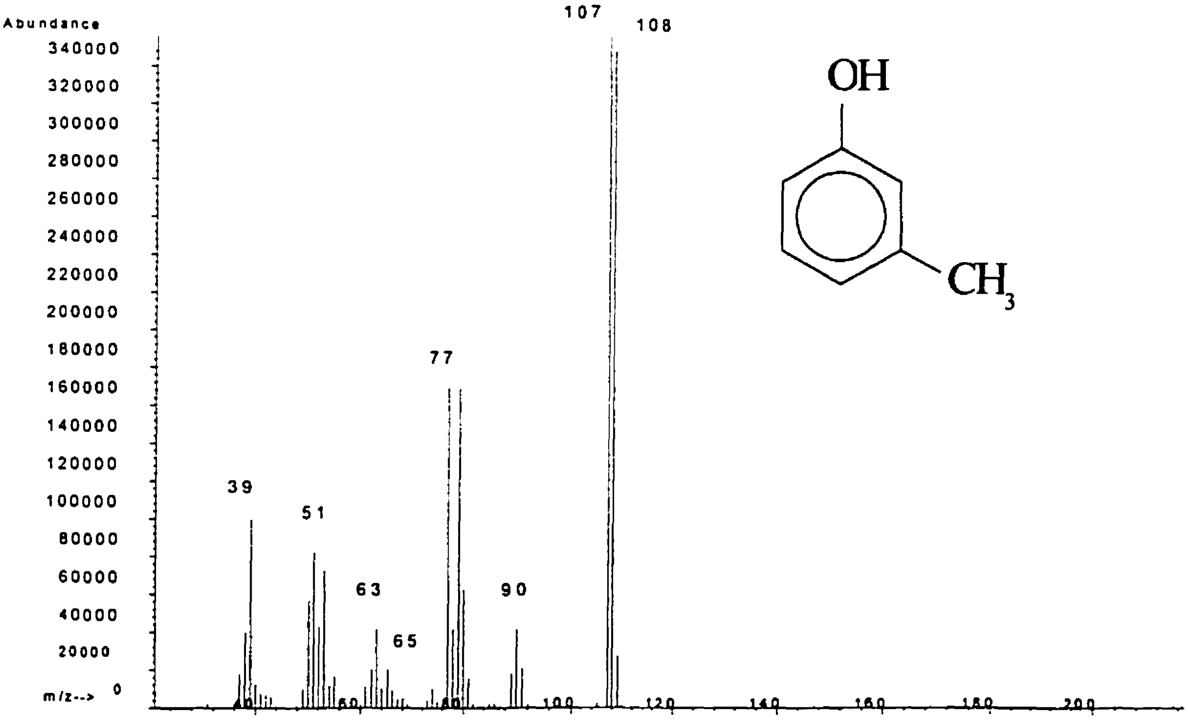


Figure 13: Mass spectrum of *m*-cresol (retention time, R_T, 7.88 min).

In a separate experiment, 10% w/v PCP solution in 2-propanol served as substrate for the dechlorination and was delivered at 0.1 ml/min, to a single reactor column of Fe^0/Ag^0 bimetallic mixture. For each of the six sequential traps, 375.5 µmole of PCP has passed through the reactor. The result, as determined by GC peak area indicated a total loss of the PCP peak whereas the reduction in the quantity of organically bound chlorine is ≥98% (Table 20). In terms of the mass balance approximately 88% of the PCP substrate was accounted for among the products (excluding trace quantities of ethyl and propyl phenols) after dechlorination.

Table 20: Dechlorination of 10% w/v PCP solution in 2-propanol by Fe^0/Ag^0.

	Trap1	Trap2	Trap3	Trap4	Trap5	Trap6
%loss PCP (GC peak)	100	100	100	100	100	100
%loss org. chlorine (trtn.)	98	98.7	98.7	99.3	99.3	99.3
phenol (µmole)	162	160	168	170	168	167
1,2,4-trimethylbenzene (µmole)	118	120	120	122	120	121
o-cresol (µmole)	23	15	22	22	20	22
m-cresol (µmole)	17	9	10	14	14	17
2,4-dimethylphenol (µmole)	13	9	9	8	8	8
Total Mass (µmole)	333	313	335	332	330	332
% Mass Balance	88.7	83.3	89.2	88.4	87.8	88.4

Phenol and 1,2,4-trimethylbenzene were the main products, accounting for ≈75% of the recovered products, with 11-13% of *o*-cresol, *m*-cresol and 2,4-dimethylphenol. Among the trapping solutions traces of ethylphenol and propylphenol were also detected. No chlorine containing compounds were detected in any of the reaction traps by GC/MS. Figure 14 presents the chromatogram of 10% w/v of PCP in 2-propanol after dechlorination by Fe^0/Ag^0 at 450°C under 250 atm pressure of SC-CO_2. The chromatogram yielded no detectable peak at 17.32 minutes that indicating the complete reaction of PCP solution. There were about 8 peaks eluted between 6.42 to 10.68 minutes. Peaks at 6.42min, 7.51min, 7.84min and 8.41 min represent phenol, *o*-cresol, *m*-cresol and 2,6-dimethylphenol respectively; their mass spectra were identical to the spectra of the products produced by the dechlorination of PCP in methanol.

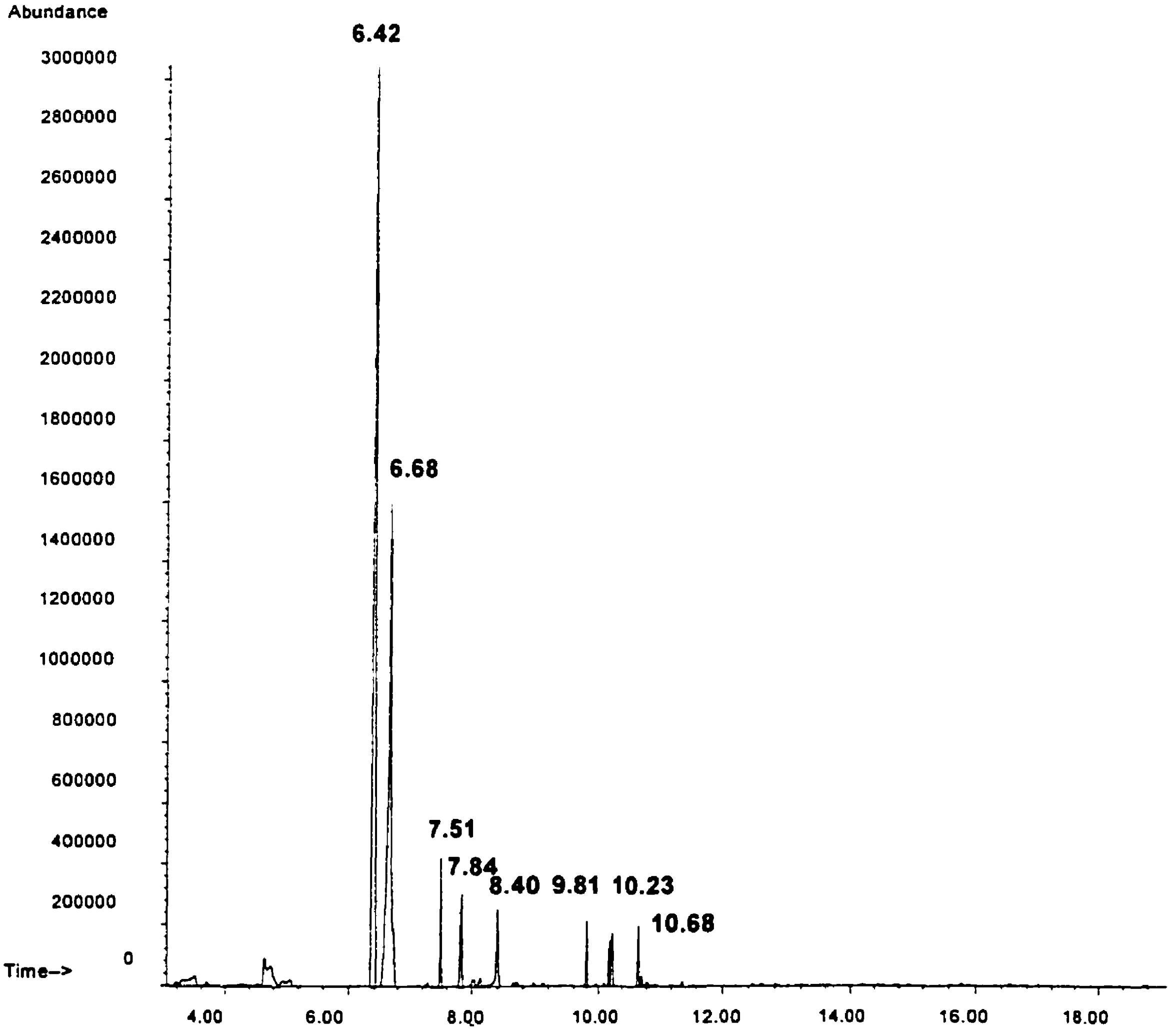


Figure 14: Gas chromatogram of 10% w/v PCP in 2-propanol after dechlorination.

There was a major product difference between the chromatograms of Figure 10 and Figure 14. The product, 1,2,4-trimethylbenzene was observed only in trace quantities in Figure 8. In addition, minor quantities of ethyl and propyl phenols were observed in the chromatogram at 9.81, 10.23 and 10.68 minutes respectively. Figure 15 presents the mass spectrum of 1,2,4-trimethylbenzene.

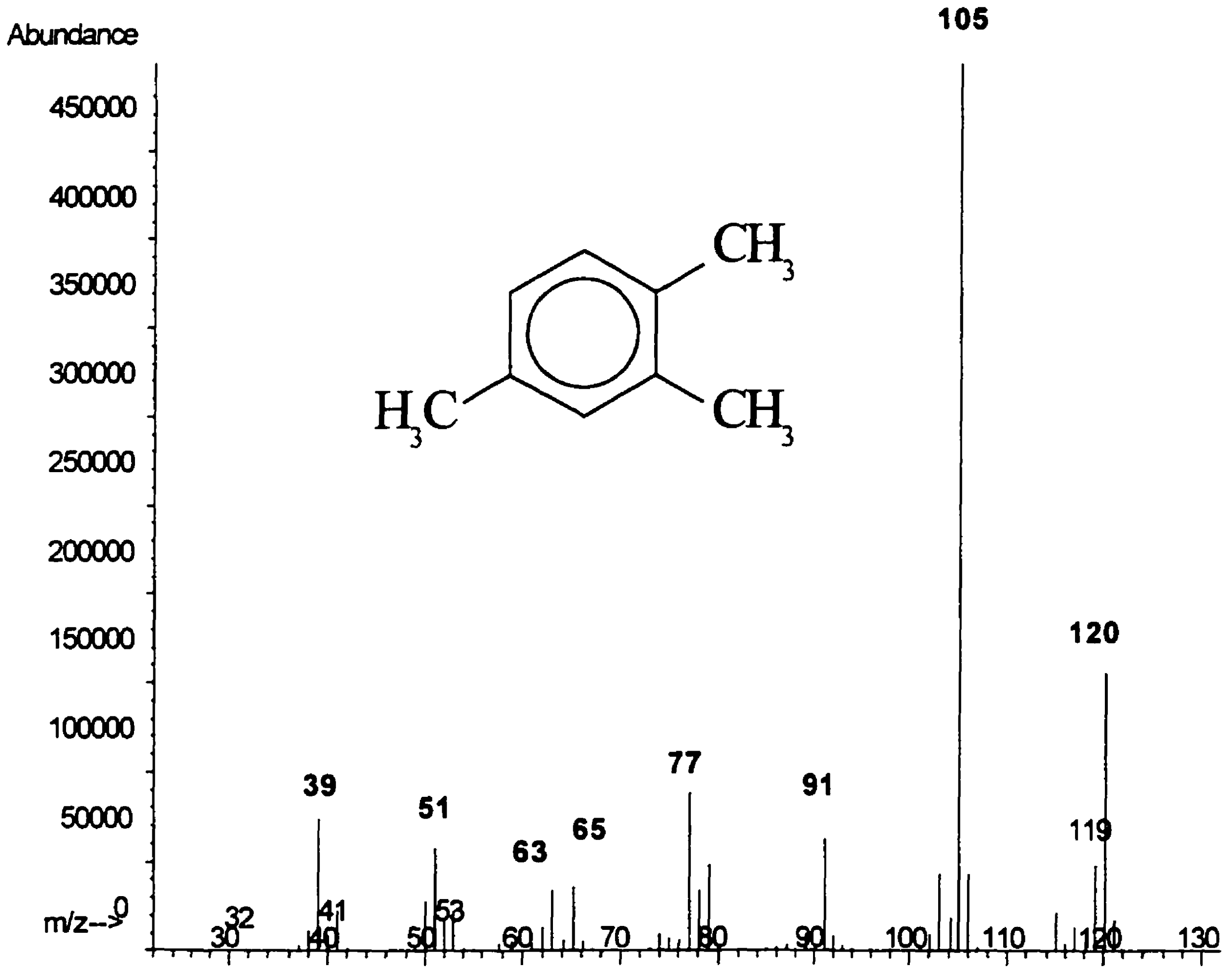


Figure 15: Mass spectrum of 1,2,4-trimethylbenzene (R_T, 6.68 min in Figure 13).

3.2.3 Discussion

The action of Fe^0/Ag^0 bimetallic mixture provides ample evidence of catalytic activity on PCP solutions in the reaction process. The role of different alcohols as solvent was not characterized by major differences in the products that were formed. The virtually quantitative recovery of chloride that had been deposited on the column corroborated that the dichlorination was very efficient and suggested that removal of this deposit might be crucial to prolonged operation. Removal of chlorine from the metal surface might reactivate the bimetal system and ensure the longer-term success of the process. The increased flow rate of SC-CO_2 limited the time that the substrate was in contact with the metal catalyst and limited the efficiency of the dechlorination (Table 12). The two columns in series provided a more efficient dechlorination than the single reactor column. The range of products from the reaction included phenol, methylated benzenes and methylated phenols as identified by their respective mass spectra. It was clear that methanol as a solvent enhanced the production of phenol as well as methylated phenols, whereas other alcohols including ethanol, 2-propanol and butanol yielded minor quantities of ethyl or propyl derivative of phenol. The mass balance did not account for 100% of the substrated PCP presumably because of products that were not detected when they were co-eluted with the solvent. These products might have included benzene and/or toluene

The reaction of 10% (w/v) PCP in DME was also carried out using sand instead of Fe^0/Ag^0 particles in the column to evaluate the magnitude of thermally induced dechlorination of this substrate. Six consecutive traps, each collected during 10 minutes, were analyzed by GC/MS. The resulting chromatogram indicated the loss of approximately 50% of PCP peak area and the formation of di-, tri- and tetra chlorinated phenols that comprised the remainder of the substrate. Only a trace of phenol was detected in the crude product mixture. These observations indicated that thermally induced dechlorination was inefficient relative to the action of the Fe^0/Ag^0 particles. Figure 16 presents the chromatogram that resulted from the thermally induced dechlorination of PCP solution.

The peaks were identified as 4-chlorophenol (R_T, 9.83 min), 2,3,5-trichlorophenol (R_T, 11.96 min), 3,5-dichlorophenol (R_T, 12.76 min), 2,3,4,5-tetrachlorophenol (R_T, 14.9 min), 3,4,5-trichlorophenol (R_T, 15.7 min) and pentachlorophenol (R_T, 17.32 min) from their respective mass spectra.

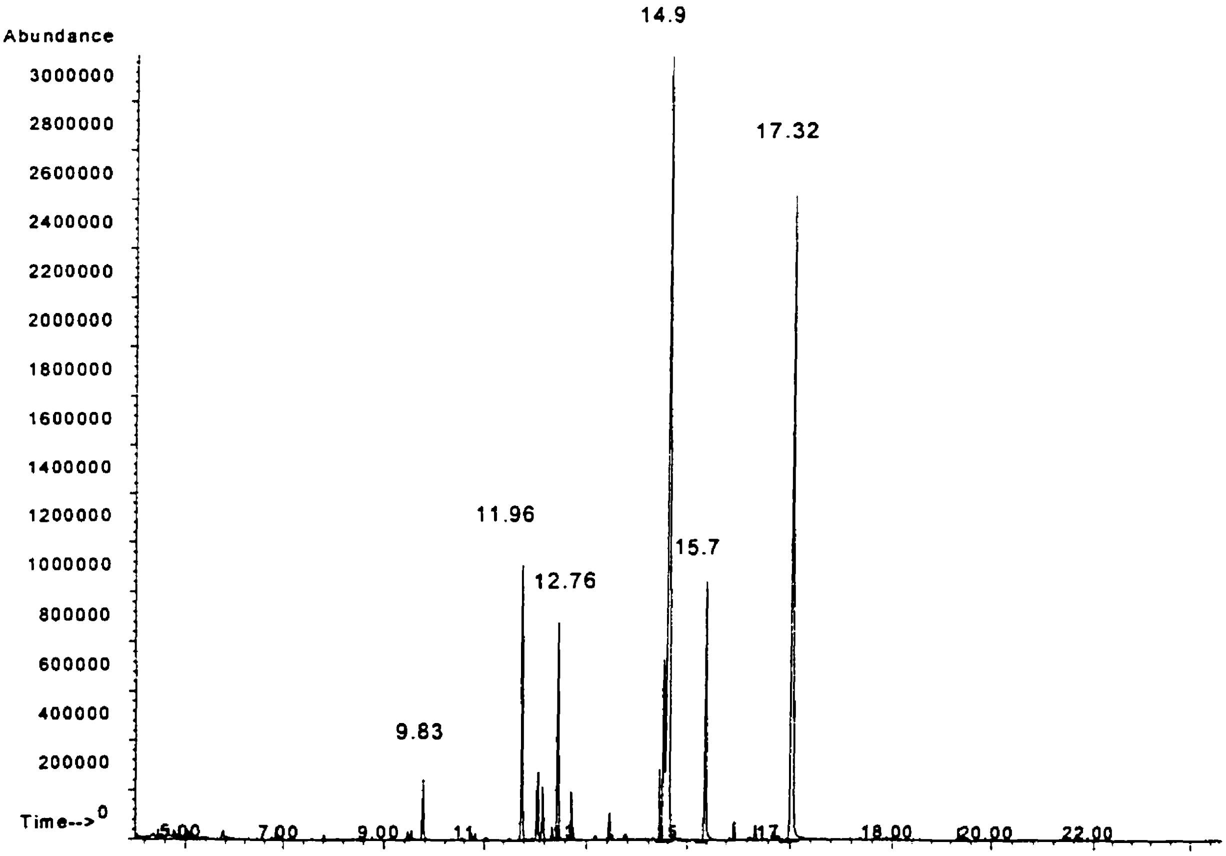


Figure 16: Gas chromatogram of 10% w/v PCP solution at 450°C by acid washed sand

In this research Fe^0/Ag^0 was selected as the catalyst due to its ease of production as compared to other bimetallic mixture such as Fe^0/Pd^0, Fe^0/Au^0, Al^0/Pd^0 or Zn^0/Pd^0. In addition, there was no evidence of any product formed by reduction of the aromatic ring to produce cyclohexanone and cyclohexanol as observed by Grittini (1997).

The source of the methyl group was presumed to be the SC-CO_2 and /or the solvents (methanol, ethanol, 2-propanol and butanol). Gilham et al (1996) described the formation of short hydrocarbon chains during the reaction of SC-CO_2 with zero-valent iron. From their results, approximately 92% of the product was methane. It might be possible that the ultimate source of the methyl groups in the products of our studies with the SC-CO_2. It was observed that the methanolic solution of PCP enhanced the production of methylated phenols than did in other alcohols.

The production of compounds by the loss of OH group is not considered to be preferred in the dechlorination process. The loss of OH group makes the products less polar, more lipophilic and more difficult to eliminate from fatty tissues. The less polar compounds are also more difficult to metabolize. So the methanolic feedstock of PCP appears to be the favorable reaction substrate for the dechlorination process due to the enhanced production of phenol and methylated phenols as main products.

Chapter IV

4.0 Continuous dechlorination of pentachlorophenol

4.1 Experimental

A number of successive traps of eluate were collected to evaluate the efficiency of the process when operated for extended periods of time for the dechlorination of 15% w/v PCP in methanolic feedstock. Successive traps were collected for 30 minutes (1689.75 μmole of PCP) from a single reactor column of silver-iron (2% w/w Ag^0/Fe^0) bimetallic mixture. A total of 28 traps were collected during 14 hours. The temperature of the column maintained at 450^OC and the pressure of $SC\text{-}CO_2$ was maintained at 250 atm. During the experiment, the column was washed four times with 30 ml of methanol-water (1+1) to remove accumulated chloride that had been deposited on the metal surfaces and was believed to be responsible for the reduced dechlorination efficiency. The eluate in trap 1 to 28 were analyzed by GC/MS

Analyses by GC/MS were performed by injecting 0.2 μL of the trap solution. The injection port temperature was 250^OC and the detector temperature was maintained at 280^OC. The recorded initial oven temperature program was 40^OC for 2.5 minutes then ramped at 25^OC/minute up to 100^OC and held for one minute, followed by 10^OC/minute to 210^OC and held for one minute. The total run time was 19.1 minutes. The peaks in the chromatograms were identified by comparison of experimental mass spectra with National Institute of Science and Technology (NIST) and Wiley 318 spectral libraries. The identifications were also corroborated by co-chromatography with authentic standards.

4.2 Result

Percent yields of products in successive 30 minutes traps collected at the exit of a single column of silver-iron (2% m/m Ag) bimetallic mixture from methanolic PCP (15% w/v) feedstock delivered to the reactor at 0.1 ml/min are presented in the following Tables.

Table 22: Percent Yields of products in 30 min cumulative fraction for first 17 traps.

Traps	Phenol	Methylated phenols	Methylated benzenes	Chlorophenols	Mass balance
1	31.96	35.35	3.31	-	70.6
2	35.27	35.90	3.91	-	75.1
3	36.81	36.93	3.61	0.36	77.7
4	35.51	36.06	3.91	0.59	76.1
5	35.74	33.83	3.36	0.68	73.6
6	33.61	34.86	1.81	-	70.3
7	37.4	35.80	2.14	-	75.3
8	37.88	36.83	2.60	-	77.3
9	37.99	36.63	2.96	-	77.6
10	38.7	35.80	3.22	-	77.7
11	38.23	35.27	2.65	-	76.2
12	37.88	31.60	2.67	-	72.2
13	42.61	30.12	2.53	-	75.3
14	43.91	27.26	2.33	-	73.5
15	43.68	26.64	2.34	-	72.7
16	43.56	26.98	1.92	0.71	73.2
17	43.14	27.21	2.08	1.26	73.7

The eluates in trap 1 to 28 were analyzed by GC/MS; no substrate could be detected in any of the chromatograms. The column was washed *off line* one time after trap 5 then *on-line* three times after collecting trap 11, trap 17 and trap 22 with 30 ml of methanol-water (1+1).

Table 23: Percent Yields of products in 30 min cumulative fraction for trap 18 to 28.

Traps	Phenol	Methylated phenols	Methylated benzenes	Chlorophenols	Mass balance
18	31.96	28.95	2.79	-	63.7
19	39.06	32.34	2.57	-	74.0
20	40.36	30.76	2.85	0.61	74.6
21	39.53	30.25	2.66	0.76	73.2
22	36.69	29.01	2.25	0.75	68.7
23	40.24	28.77	2.12	-	71.1
24	41.66	30.91	1.65	-	74.2
25	42.85	29.61	1.42	-	73.9
26	43.32	29.76	1.34	-	74.4
27	43.08	28.58	1.30	-	73.0
28	41.31	27.55	1.32	-	70.2

The total reaction time was 14 hours for 28 traps and it was observed that the Fe^0/Ag^0 particles were sufficiently reactive to cause the virtually complete dechlorination of 15% (w/v) PCP in methanol. After each on-column wash with methanol-water, SC-CO_2 at 450^{O}C was passed for 30 minutes to elute any trace of water.

4.3 Discussion

In the previous section, (4.2), it was demonstrated that a continuous and virtually complete dechlorination of the 15% w/v PCP in a methanolic feedstock was feasible. The total time for this continuous process was 14 hours however there is no reason why it could not have been prolonged appreciably. The washes of the column were performed at 6, 11, 17, 22 traps due to the diminution in the dechlorination efficiency. Presumably, the efficiency of the dechlorination was reduced because of chloride that had been deposited on the metal surface and blocked access of the substrate to active sites on the catalyst surface.

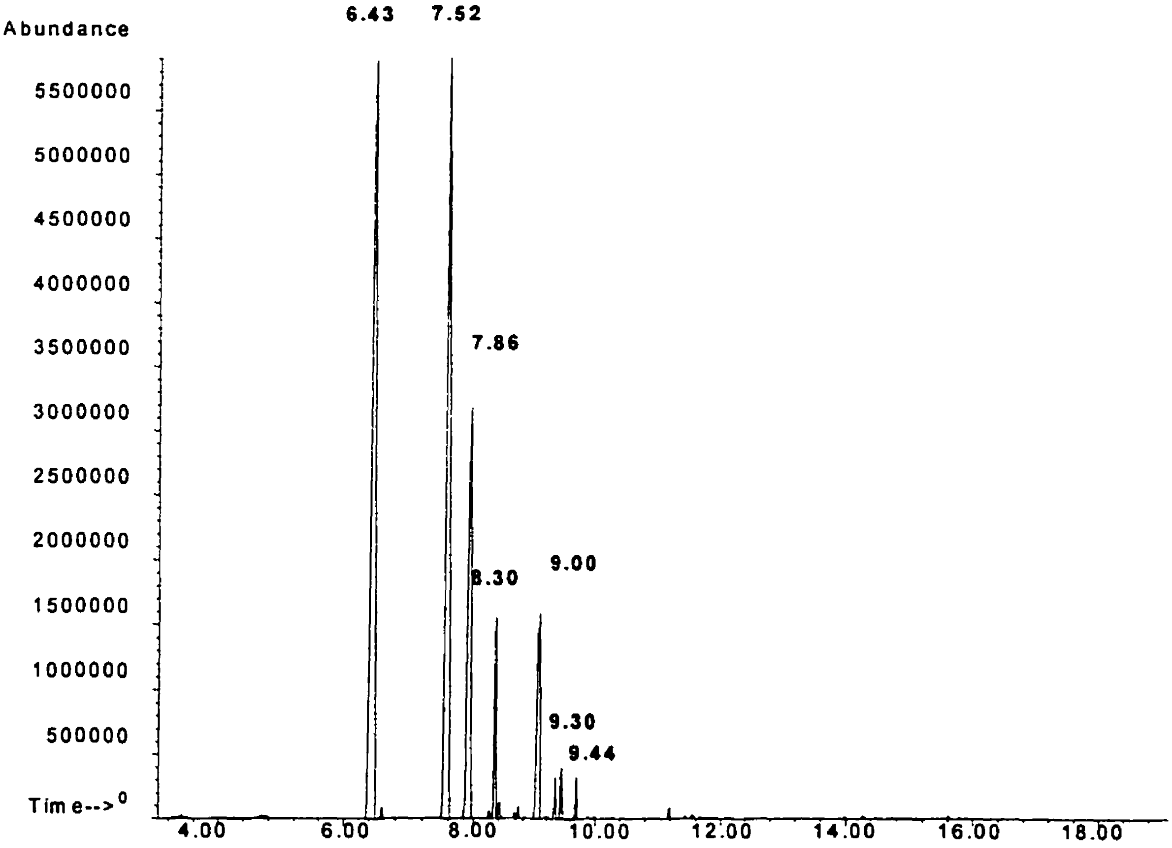


Figure17: Chromatogram of trap 6 from the continuous dechlorination of 15% w/v PCP.

Figure 17 presents one of the gas chromatograms of the continuous dechlorination (trap6). The identities of the components were corroborated by their respective mass spectra. The peak at R_T of 6.43 minutes in the chromatogram was identified as phenol. Other peaks were identified as *o*-cresol (R_T, 7.52 min.), *m*-cresol (R_T, 7.86 min.), 2,6-dimethylphenol (R_T, 8.30 min.), 2,4-dimethylphenol (R_T, 9.00 min.), 3,5-dimethylphenol (R_T, 9.30 min.) and 3,4-dimethylphenol (R_T, 9.42 min.).

The mass balance did not account for 100% of the PCP substrate presumably due to the formation of products that were co-eluted with the solvent. These products might have included benzene and toluene. The gas chromatogram and mass spectra of the trap solutions also provided no indication of chlorinated dibenzodioxins or dibenzofurans. In addition, neither cyclohexanol nor cyclohexanone was detected as had been reported previously by Grittini (1997).

Conclusion

Efficient dechlorination of lindane or pentachlorophenol was achieved by zero-valent metal or bimetallic mixture. The products of the dechlorination were monitored by GC/MS.

Silver-iron (2% w/w Ag) bimetallic mixture proved to be an efficient catalytic material for both lindane and pentachlorophenol. The dechlorination of pentachlorophenol not only yielded phenol but also methylated phenols and methylated benzenes (Figure 18) as well as traces of 4-chlorophenol and 2,4-dichlorophenol.

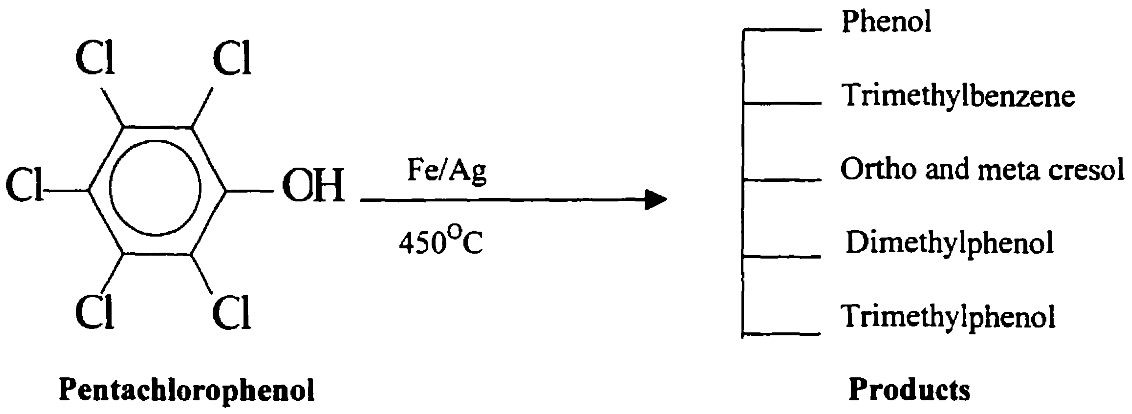


Figure 18: Reaction of pentachlorophenol with Fe^0/Ag^0 bimetallic mixture.

From the chromatograms and mass spectra of the product mixture there was no evidence of formation of any other chlorinated byproducts including chlorinated dibenzofurans or dibenzodioxins. The mass balance accounted for 70 to 76% of the starting material. There might have been other volatile products present, such as benzene or other hydrocarbons, those were not detected by GC/MS with our program parameters due their co-elution with the solvent.

The dechlorination technique that was optimized in these studies possessed several advantages that included:

- a simple reactor design fed with a stream of supercritical carbon dioxide.
- The reactor was capable of efficiently dechlorinating concentrated solution of substrate [10% w/v of lindane and 15-20% w/v of pentachlorophenol]
- Once optimized, the process was very efficient
- In terms of mass balance, some 70-76% of the influent substrate was accounted for by the products in the trap placed at the exit of the reactor.
- Although the efficiency of dechlorination gradually decreased with time, the reactor column could be restored to its original activity with a simple water-methanol wash so that extended operation was possible.

The capacity of the zero-valent column to dechlorinate organochlorine substrate is limited but the concentration of lindane in the feedstock could be increased above 15%w/v while reducing the flow rate of mobile phase to the column [0.07 ml/min rather than 0.1 ml/min. In the same way, the PCP concentration can be raised to 25% w/v with a mobile phase flow rate of 0.08 ml/min.

In future studies, the dechlorination technique could be applied to contaminated soil, water or other matrixes (containing chlorinated organic compounds like -HCH, PCP, PCBs). Prior to the application of this technique we will have to find an extraction procedure will have to be identified to extract these chlorinated compounds from the matrixes. For the identification of the products other coupling techniques like GC/MS/MS or GC/FTIR/MS could be applied.

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