Effects of solvent, pH, salts and resin fatty acids on the dechlorination of pentachlorophenol using magnesium–silver and magnesium–palladium bimetallic systems

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Abstract

The effects of pH, organic co-solvent, salts such as sodium chloride, sodium sulfate, and co-pollutants, resin and fatty acids (RFAs) on the dechlorination of pentachlorophenol (PCP) by magnesium/silver (Mg/Ag) and magnesium/palladium (Mg/Pd) systems were examined in the present investigations. Such studies provide relevant information about the applicability of bimetallic systems for remediation of raw wastewaters (such as pulp bleaching effluents) or groundwater. Removal efficiencies of $10\,mg\,L^{-1}$ PCP by Mg/Pd and Mg/Ag systems at the end of 1 h reaction were 93% and 78%, respectively, in the presence of acetone (1% v/v). On the other hand, the removal efficiencies were 86% and 70% for reactions conducted in alcoholic solvents (1% v/v) using Mg/Pd and Mg/Ag systems, respectively. The efficiencies of PCP removal by the two bimetallic systems could be correlated to the dipole moments of co-solvents used. The second order reaction rate constant for PCP removal by Mg/Ag system was highest ($0.03\,L\,mg^{-1}\,min^{-1}$) in the absence of any pH-control mechanism. Optimum pH for the dechlorination of PCP by Mg/Pd system was found to be ∼5.5 and >92% of the compound was removed within 15 min of reaction. Presence of chlorinated and non-chlorinated resin fatty acids (RFAs) resulted in substantial reduction in the rate and extent of PCP removal by Mg/Ag system whereas dechlorination by Mg/Pd remained unaffected. Presence of sodium sulfate or sodium chloride in the reaction phase reduced the rate and extent of PCP removal by Mg/Ag system. PCP dechlorination by Mg/Pd system was adversely impacted by the addition of sodium chloride and unaffected by the presence of sodium sulfate.
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1. Introduction

Pentachlorophenol (PCP) is a potent biocide used as a preservative to protect wood from decay and insect attack. Pentachlorophenol can be found in the air, water, and soil. It enters the environment through evaporation from treated wood surfaces, industrial spills, and disposal at uncontrolled hazardous waste sites. Its mobility in soil increases with increase in the pH due to reduced adsorption. It has been reported that elevated blood levels of pentachlorophenol ($>25\,\mu g\,L^{-1}$) were responsible for histories of habitual abortion, unexplained infertility, menstrual disorders, or the onset of menopause in women [1].

PCP is also listed as a priority pollutant by USEPA [2]. The use and the uncontrolled incineration of technical grade PCP is one of the most important sources of PCDDs and PCDFs (polychlorinated dibenzo dioxins and furans, respectively) in the environment. Proposition 65 of the Office of Environmental Health Hazards, EPA, CA, identifies PCP as a carcinogen [3]. Harmful characteristics of PCP necessitate its removal from the environment.

A wide variety of advanced oxidation processes (AOPs) have been reported for the removal of pentachlorophenol which have been reviewed by Pera-Titus et al. [4]. Electrochemical reductive dechlorination and electrooxidation by *in situ* generated hydroxyl radicals are also reported [5–7]. Advanced oxidation processes (AOPs) can completely mineralize the target compounds but they are non-selective (attack both, chlorinated and non-chlorinated compounds) and especially expensive for small and medium scale units. On the other hand, electrochemical reductive dechlorination of PCP may result in the accumulation

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of partially/dechlorinated intermediates. Anaerobic and aerobic biodegradation have been shown to achieve high efficiency of removal of PCP and lower chlorinated phenols [8–12]. Anaerobic degradation of chlorophenols is known to occur under low reduction potential (methanogenic or sulfidogenic conditions) which may limit its application in the field. On the other hand, aerobic degradation of PCP involves ring cleavage prior to dechlorination and such ring-cleaved products may be toxic if accumulated in the environment [13]. Disposal of waste biosludge laden with adsorbed chlorinated phenols can contaminate groundwater due to leachate generation while incineration of such sludge can lead to formation of highly toxic chlorinated dioxins.

In the last decade, extensive research has been carried out on the application of bimetallic systems to dechlorinate chlorinated organic compounds [14–18]. Bimetallic systems make use of two metals, one in the zero-valent form (with a negative reduction potential like Mg^{+2}/Mg^0, Fe^{+2}/Fe^0, etc.) to produce nascent hydrogen by anodic corrosion, and the other metal with a relatively high (positive) reduction potential (such as Ag^{+1}/Ag^0, Pd^{+4}/Pd^0) as a catalyst. Nascent hydrogen produced, is intercalated by the catalyst to form a metal hydride (M-H), which reacts with the target substrate to reduce it [19]. The main advantage of bimetallic systems is the ability to conduct the reaction at room temperature and pressure without exclusion of atmospheric oxygen. However most of the studies on dechlorination by bimetallic or zero-valent metal systems have been carried out using pure solutions of chlorinated organic pollutants. Very sparse literature related to the effects of reaction phase pH [15,20–22], type of organic co-solvent [23–25] and impurities (co-pollutants) other than the target compound is available. Studies on the effect(s) of various environmental parameters as listed above are relevant for assessing the applicability of bimetallic systems for remediation of groundwater or raw industrial effluents containing chlorinated organic compounds.

In our recent publications we reported that the efficient dechlorination of PCP by Mg/Ag and Mg/Pd systems through nucleophilic substitution required the addition of acid [17,18]. However in these studies the required amount of acid was added in one step at the beginning of the reaction and thus pH of the reaction phase was not maintained during the course of reaction. It was observed that the corrosion of magnesium and hence the production of hydrogen was very rapid in the initial phase of reaction. Since the bimetallic systems involve intercalation of hydrogen on the catalytic metal (Ag^0 or Pd^0), it is reasonable to assume that a large fraction of hydrogen produced may not have been fruitfully utilized for the reductive dechlorination reaction. Thus regulation of pH during the course of reaction may be important to facilitate slow corrosion of magnesium granules in order to sustain the efficiency of dechlorination.

Dechlorination of chlorinated organic pollutants in a reaction mix containing large proportions (~20–60% v/v) of organic co-solvent has been reported using Fe/Pd system, Fe^0 and Pd/C [26–29]. Such studies are vital since remediation of soils/slurries contaminated with chlorinated organic pollutants usually involves washing with aqueous solutions containing organic solvents in different proportions [27]. The soil extracts

containing chloro-organic contaminants are then subjected to a suitable treatment for destruction/transformation of these compounds. On the other hand smaller proportions of organic polar solvents have been used in aqueous reaction phase for lab scale studies. For example, Liu et al. [30], Roy et al. [31], Kim and Carraway [16], Xu and Zhang [32], and Doong and Rai [33,34] used acetone and methanol in various proportions (1, 0.2, 0.5, 0.05% v/v) to prepare solutions of chlorinated compounds such as, chlorophenols, PCP, chlorobenzenes, and trichloroethylene (TCE). However, the fore-mentioned publications do not provide any justification for the selection of a co-solvent or its concentration. The presence of co-solvent can have profound influence on the rate of dechlorination reaction. First, co-solvent can improve the solubility of target chlorinated compounds thereby enhancing their mass transfer to the sites of dechlorination on the bimetallic systems. Secondly, co-solvent may directly participate in the reaction by acting as a hydrogen donor under suitable conditions. Therefore a study on the influence of smaller proportion (1% or lower v/v) of co-solvent on reductive dechlorination is very essential.

We studied dechlorination of PCP spiked in to pulp bleaching effluent using Mg/Ag and Mg/Pd systems (unpublished results). However, both the bimetallic systems failed to remove PCP to any appreciable level at the concentrations of bimetals used in previous investigations [17,18]. We therefore decided to study the effect of major constituents of pulp bleaching effluent such as salinity (sodium chloride and sodium sulfate) and co-pollutants such as chlorinated and non-chlorinated resin and fatty acids (RFAs) on PCP dechlorination by Mg/Pd and Mg/Ag systems.

In the light of ongoing discussion, objectives of present investigations were to study the dechlorination of PCP using Mg/Ag and Mg/Pd systems: (a) as a function of reaction phase pH (b) in the presence of small proportion of organic solvents (c) in the presence of sodium chloride, sodium sulfate, and co-pollutants such as chlorinated and non-chlorinated resin and fatty acids. This investigation is an effort to shed light on the influence of key environmental factors on the rate and extent of dechlorination of PCP by Mg/Ag and Mg/Pd systems.

2. Materials and methods

2.1. Sources of chemicals

Magnesium granules (~20 mesh), potassium hexachloropalladate (K_2PdCl_6), potassium carbonate, 2,4,6-trichlorophenol, 2,4,5-trichlorophenol, 2,3,6-trichlorophenol, 2,3,4-trichlorophenol, pentachlorophenol, 1,1-dichloro-2,2-bis (4,-chlorophenyl) ethylene (DDE) were purchased from Sigma–Aldrich Chemical Company. Cyclohexane, glacial acetic acid, 1-propanol, ethanol, and acetone were purchased from Merck India Ltd. Silver nitrate was procured from Qualigens. Methanol and acetic anhydride were purchased from S.D. FineChem Ltd. Dehydroabietic acid, chlorodehydroabietic acid, dichlorodehydroabietic acid, 9,10-dichlorostearic acid, 9,10,12,13-tetrachlorostearic acid were purchased from Helix Biotech corporation, Canada. Stearic acid and pentachlorophenol sodium salt (≥90%) were purchased from Fluka. All the

chemicals were of high purity and analytical grade. Potassium carbonate was baked in furnace at 400 °C, overnight, prior to use. No pretreatment was carried out with other chemicals. Deionized water (17 mΩ) obtained from Barnstead deionization system was used for making reagents.

2.2. Effect of co-solvents on PCP dechlorination using Mg/Ag and Mg/Pd systems

Experiments were carried out in test tubes by taking 4 mL of 10 mg L^{-1} aqueous PCP solution containing 1% (v/v) of chosen organic co-solvent. PCP was added from stock solutions (1000 mg L^{-1}) prepared in four different solvents, viz., methanol, ethanol, acetone, and 1-propanol. For Mg/Ag system, the reaction mixture contained 206 mM Mg^0, 1.46 mM AgNO$_3$, and 175 mM acetic acid. For Mg/Pd system, the reaction mixture contained 154 mM Mg^0, 0.063 mM K$_2$PdCl$_6$, and 175 mM acetic acid. Reaction samples were covered using punctured parafilms and incubated for 1 h. Two consecutive experiments were performed (each with triplicate test samples) at 30 °C in a temperature controlled oscillatory shaker set at 100 oscillations/min. To determine the concentrations of compounds sorbed on to residual solid surfaces, 175 mM acetic acid was added into the reaction mixture and incubated until all residual magnesium particles underwent corrosion and became silvery white. The solution was then analyzed to determine total residual concentration of parent compounds and products.

2.3. Effect of pH on PCP dechlorination using Mg/Ag and Mg/Pd systems

Kinetics of PCP dechlorination was studied in a completely mixed batch reactor (CMBR) of 1 L capacity. 500 mL of 10 mg L^{-1} PCP (prepared using 1000 mg L^{-1} PCP stock made in methanol) solution was taken in the reactor to which 0.063 mM K$_2$PdCl$_6$ and 154.4 mM of magnesium (for Mg/Pd system) or 1.46 mM AgNO$_3$ and 206 mM magnesium (for Mg/Ag system) were added. The pH of reaction phase was maintained at 4.5, 5, and 5.5 by careful addition of either 20% (v/v) acetic acid or glacial acetic acid using automatic pH controller (Cole-Parmar model A22025). Sorption of compounds on solid surfaces was determined as per the procedure outlined in the previous section. All the pH values mentioned above were maintained within ±0.2 pH unit of the set pH value. Total volume of acid required for all the experiments was <10% of the reaction volume and hence dilution effect was neglected. In the case of pH-uncontrolled experiments, the reaction was commenced by the direct addition of 175 mM acetic acid [17,18].

2.4. Effect of the presence of sodium chloride and sodium sulfate on PCP dechlorination by Mg/Pd and Mg/Ag systems

Experiments were conducted in a CMBR containing 150 mL of 10 mg L^{-1} PCP solution (prepared from methanol stock) and 50 mM sodium sulfate (anhydrous) or 50 mM sodium chloride. Concentrations of bimetals were as mentioned in Section 2.3. Acetic acid (175 mM) was included in each experiment. The sequence of addition of reactants was: PCP solution → Mg^0 → AgNO$_3$ (for Mg/Ag system) or K$_2$PdCl$_6$ (for Mg/Pd system) → sodium chloride or sodium sulfate → acetic acid. All the experiments were conducted in duplicate.

2.5. Effect of the presence of chlorinated and non-chlorinated resin fatty acids on PCP dechlorination by Mg/Pd and Mg/Ag systems

Experiments were conducted in a CMBR containing 150 mL of 10 mg L^{-1} PCP solution in the presence of chlorinated or non-chlorinated resin fatty acids (RFAs). Concentrations of bimetals were as mentioned in Section 2.3. The total concentration of mixture of chlorinated RFAs was 1 mg L^{-1} constituting of 0.25 mg L^{-1} each of dichlorostearic acid, tetrachlorostearic acid, dichlorodehydroabietic acid, monochlorodehydroabietic acid while that of non-chlorinated RFAs was 1 mg L^{-1} constituting of 0.5 mg L^{-1} each of dehydroabietic acid and stearic acid. The stock solutions of PCP and RFAs were added from stock solutions prepared in methanol in such a way that the final concentration of methanol in the reaction medium was 1% (v/v).

2.6. Gas chromatography (GC) analyses

Samples were prepared for GC analyses as per the procedure described by NCASI 86.02 [35]. At designated time points during the kinetic studies, 0.3 mL of samples were withdrawn (from test tubes or CMBR), made up to final volume of 3 mL and derivatized by adding 78 μL of 4.35M potassium carbonate solution and 90 μL of acetic anhydride. Subsequently, the derivatized samples were extracted twice with 1.5 mL of cyclohexane on high-speed vortex mixer for 45 s and 0.2 μL of pooled extracts were injected for GC-ECD. GC analyses were carried out using an Agilent 6890N model equipped with μECD and FID. HP-5 or HP-1 column (30 m × 0.32 mm ID × 0.25 μM film thickness) was used. Temperature program used was: 1 min at 45 °C, temperature ramp 1: 45–100 °C @ 20 °C min^{-1}, hold time of 0.3 min, temperature ramp 2: 100–215 °C @ 4 °C min^{-1}, final hold time of 1 min. Injector and detector temperatures were set at 210 °C and 300 °C, respectively. Injections were performed in splitless mode using nitrogen as carrier gas (gas velocity 36 cm s^{-1}). Purge time and flow were set at 0.5 min @ 100 mL min^{-1}. Calibration plots for all chlorophenols were prepared in the concentration range of interest and were found to be linear with R^2 values >0.98. DDE (1,1-dichloro-2,2-bis [4-chlorophenyl] ethylene) was used as an internal standard for GC-ECD analyses.

3. Results and discussion

3.1. Effect of co-solvent on PCP dechlorination by Mg/Ag and Mg/Pd systems

Fig. 1 shows the effect of various co-solvents on the efficiency of PCP dechlorination by Mg/Ag system and the distribution of residual PCP between the aqueous and solid phases after 1 h
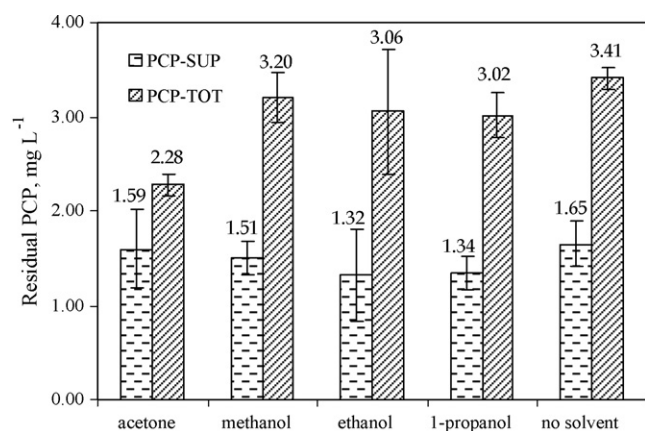
Fig. 1. Effect of co-solvent on the extent of PCP dechlorination by Mg/Ag system and relative distribution of residual PCP between aqueous and solid phases after 1 h of reaction. Reaction conditions: reaction volume, 4 mL; Mg^0, 206 mM; $AgNO_3$, 1.46 mM; acetic acid, 175 mM; solvent concentration, 1% (v/v); PCP, 10 mg L^{-1}. Data presented represent average values obtained from experiments conducted in triplicate. Legend: SUP is the concentration in aqueous phase, TOT the total concentration (sorbed + supernatant).

of reaction. Comparison amongst various solvents suggested that the maximum removal of PCP and minimum sorption was achieved in the presence of acetone. This effect may be attributed to improvement of mass transfer rate due to enhanced solubility of PCP by the acetone. While the aqueous phase concentrations of residual PCP were more or less similar for all the solvents, the concentrations of sorbed PCP were substantially higher for methanol, ethanol and 1-propanol.

Fig. 2 shows the effect of various co-solvents on the efficiency of PCP dechlorination by Mg/Pd system and the distribution of residual PCP between the aqueous and solid phases following 1 h of reaction. Here too, it can be seen that acetone achieved maximum removal of PCP while the extent of sorption of this
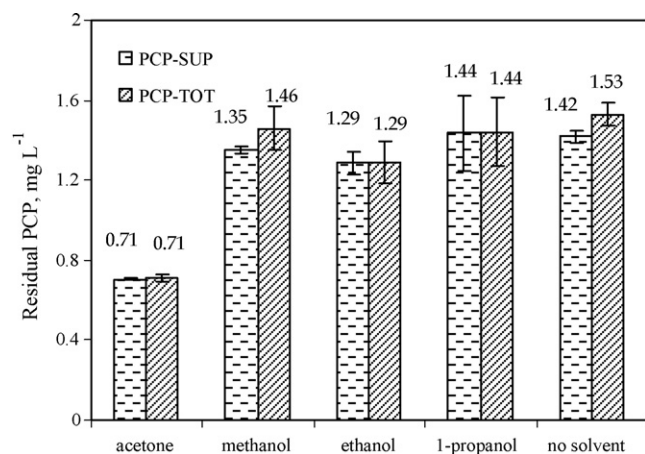

Fig. 2. Effect of co-solvent on the extent of PCP dechlorination by Mg/Pd system and relative distribution of residual PCP between aqueous and solid phases after 1 h of reaction. Reaction conditions: reaction volume, 4 mL; Mg^0, 154.5 mM; K_2PdCl_6, 0.063 mM; acetic acid, 175 mM; solvent concentration, 1% (v/v); PCP, 10 mg L^{-1}. Data presented represent average values obtained from experiments conducted in triplicate. Legend: SUP is the concentration in aqueous phase, TOT the total concentration (sorbed + supernatant).
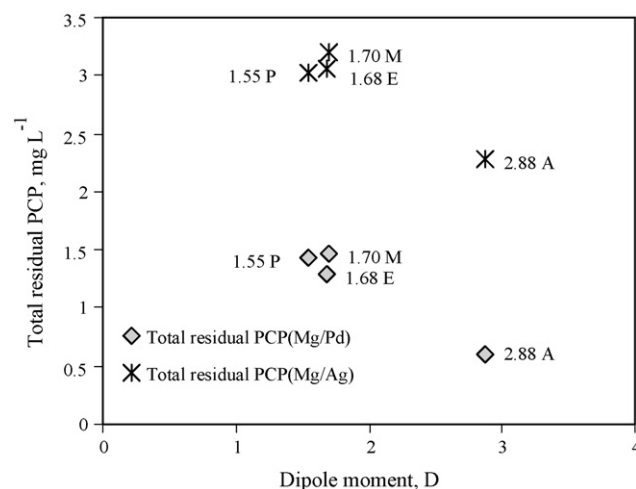

Fig. 3. Co-relation between dipole moments of co-solvents and efficiencies of dechlorination of PCP by Mg/Ag and Mg/Pd systems. Values shown within figure are dipole moments of chosen co-solvents. Total residual PCP = PCP in supernatant + PCP sorbed at the end of reaction. M, methanol; A, acetone; E, ethanol; P, 1-propanol. 1 D (Debye) = 3.3356×10^{-30} coulomb-meter. Dipole moment values were noted from Lange's handbook of chemistry, 16th edition [40]. Concentration of co-solvent: 1% (v/v).

compound to solids was insignificant irrespective of the type of solvent used.

Effect of co-solvents on the extent of solubility, rates of mass transfer and dechlorination of PCP may be related to their thermodynamic and physical properties such as dielectric constants, dipole moments, viscosity and octanol–water partition coefficient, etc. In the present investigation, efficiencies of removal of PCP by Mg/Ag and Mg/Pd systems correlated well with the dipole moments of co-solvents (Fig. 3). It is evident from Fig. 3 that the maximum dechlorination of PCP was achieved by Mg/Pd system using 1% acetone as the co-solvent, which had the highest dipole moment. It may be noted that dipole moments for the alcoholic co-solvents were very close to each other (1.5–1.7) and so were the concentrations of residual PCP after 1 h of reaction. Another property of the solvent, which may influence the rate of dechlorination, is its tendency to solvate the attacking nucleophilic species. It is well known that reductive dechlorination reactions progress by nucleophilic substitution. In this context, acetone, a polar aprotic solvent, enhances nucleophilic substitution by leaving the anionic groups unsolvated [36]. Thus results of PCP dechlorination by Mg/Ag and Mg/Pd systems revealed that the type of organic co-solvents, although used in small proportions, had significant impact on the efficiency of dechlorination of PCP.

The rate of reaction and chemo-selectivity of the target compounds in the reductive catalytic hydrogenation/hydrodechlorination reactions using catalysts such as Pd/C [23,29], $PdCl_2$ [24], Raney-nickel [25] and Pd/Fe [27] have been shown to be influenced by the type of organic solvents used. These effects were attributed to thermodynamic interactions between the co-solvent and reactants which in turn improved the rate of mass transfer. However, the effects have been reported for very high proportions 18–60% v/v) of the co-solvent and thus direct comparison with the results of present investigation was

not possible. Clark et al. [26], reported decrease in the reaction rate constant values for the dechlorination of perchloroethylene (PCE) by ZVI with increase in ethanol fraction from 0 to 50% (v/v), and attributed this effect to the increased solubility and thus reduced sorption of PCE on ZVI surfaces. Korte et al. [27] employed ethanol:water and isopropanol:water (40:60 v/v) mixtures as reaction phases to study the dechlorination of polychlorinated biphenyls (PCBs). The authors attributed better removal efficiency in ethanol:water phase to higher dielectric constant of ethanol in comparison to that of isopropanol. Electrocatalytic dechlorination of 4-chlorobiphenyl (4-MCB) on Pd/Ni cathode was studied by Yang et al. in solvent:water (30:70) mixture using methanol, ethanol, isopropanol, and ethylene glycol as the co-solvents [37]. The authors ascribed higher efficiency of dechlorination of 4-MCB in methanol:water mixture to lower viscosity of methanol among the solvents employed. Based on the reported data and results obtained in the present study it is plausible that different thermodynamic properties of co-solvent may play dominant role depending upon on the type of reaction system. Nevertheless, one conclusion that can be drawn is that the organic co-solvents used in smaller or larger proportions, influence the rate and extent of dechlorination reactions.

3.2. Effect of pH on PCP dechlorination by Mg/Ag and Mg/Pd systems

3.2.1. Dechlorination of PCP by Mg/Ag system as a function of constant pH

Fig. 4(a)–(c) compares the time course profiles of PCP removal by Mg/Ag system, and emergence of tetrachlorophenols (TeCPs) and 2,4,5-TCP, respectively, at pH values of 4, 5, and 5.5, and that in the absence of a pH-control mechanism. Important observations to be noted from the Fig. 4 (a)–(c) are:

(i) The rate of PCP removal was highest in the absence of pH-control mechanism. The second order rate constant values for the removal of PCP by Mg/Ag system were $0.014 \, \mathrm{L \, mg^{-1} \, min^{-1}}$ and $0.016 \, \mathrm{L \, mg^{-1} \, min^{-1}}$ at fixed pH values of 4.0 and 5.5, respectively. In comparison, the rate constant value was twofold higher ($0.03 \, \mathrm{L \, mg^{-1} \, min^{-1}}$) for PCP dechlorination by Mg/Ag system in the absence of a pH-control mechanism.

(ii) The total concentrations of TeCPs and 2,4,5-trichlorophenol accumulated at the end of 1 h of reaction were the least in the absence of pH-control mechanism. The patterns of emergence of these dechlorinated intermediates were dissimilar for the pH-controlled and pH-uncontrolled experiments.

It was observed that the physical sloughing of metallic silver deposits from $\mathrm{Mg^0}$ granules was significantly delayed for experiments conducted at constant pH values of 4, and 5.5 as compared to that observed in pH uncontrolled experiments. Delayed sloughing of metallic silver from $\mathrm{Mg^0}$ granules during the initial reaction period may have resulted in reduced area of catalytic surface of silver thereby decreasing the rate of removal of PCP. On the other hand when the same reaction was conducted with one step addition of acid at the beginning of reaction there
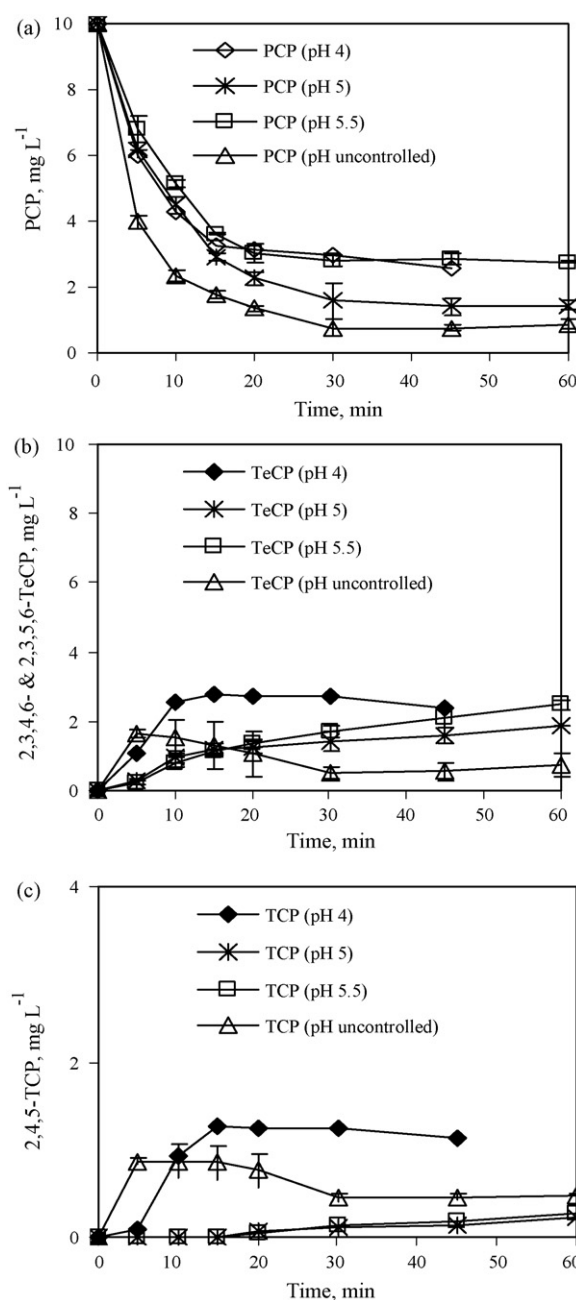

Fig. 4. Comparison of time course profiles of (a) PCP removal, (b) emergence of TeCP, and (c) emergence of 2,4,5-TCP at various pH values using Mg/Ag system. Reaction conditions: reaction volume, 500 mL; $\mathrm{Mg^0}$ concentration, 206 mM; $\mathrm{AgNO_3}$ concentration, 1.46 mM; initial concentration of PCP, $10 \, \mathrm{mg \, L^{-1}}$. Data presented represent average values obtained from experiments conducted in duplicate.

was almost instantaneous complete sloughing of silver deposits from the surface of $\mathrm{Mg^0}$ granules which in turn enhanced the initial rate of PCP dechlorination. It may be concluded from the ongoing discussion that pH-controlled experiments did not offer any specific advantage in terms of rate and extent of PCP removal by Mg/Ag system when compared to pH uncontrolled experiments. The result obtained by us is in contrast to that reported by Siantar et al. [38]. The authors demonstrated that the transformation of 1,2-dibromo-3-chloropropane (DBCP) in unbuffered
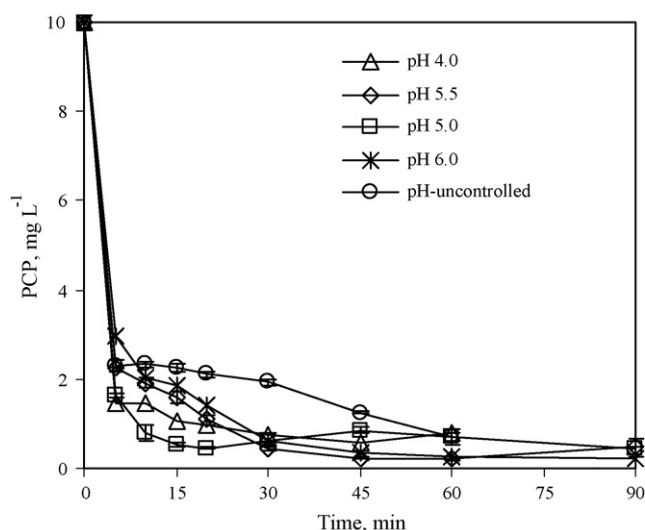
Fig. 5. Comparison of time course profiles of PCP removal by Mg/Pd system as a function of pH. Reaction conditions: reaction volume, 500 mL; Mg^0 concentration, 154.4 mM; K_2PdCl_6 concentration, 0.063 mM; initial concentration of PCP, 10 mg L^{-1}. Data presented represent average values obtained from experiments conducted in duplicate.

groundwater by zero-valent iron was 16–30 times slower as compared to that in HEPES buffer at pH 7. The authors proposed that the slower transformation rate resulted from the increase in pH from 8.0 to 9.0 during the course of reaction. However the reduction of pH to 7.0 by the dosing of acid into groundwater enhanced the rate of transformation by ∼25%.

3.2.2. Dechlorination of PCP by Mg/Pd system as a function of pH

The PCP disappearance profiles shown in Fig. 5 are the results of experiments conducted by maintaining pH at 4, 5, 5.5, 6.0, and that without any pH-control mechanism in the reactor using Mg/Pd system. Accumulation of partially dechlorinated products at any time point during the course of reaction was found to be less than 0.1 mg L^{-1} and hence their profiles are not shown in the figure. As depicted in Fig. 5, removal of PCP was very rapid within the first 5 min of reaction followed by a slow rate of reaction between 5 and 15 min at all pH values. We were unable to determine the order of reaction or rate constant values since the initial rate was very high. However the initial rates of reactions were estimated. Table 1 shows data related to initial rates of PCP removal by Mg/Pd system and concentrations of sorbed PCP as a function of pH. It may be seen from Table 1

Table 1
Effect of pH on PCP dechlorination by Mg/Pd system

pH	Initial reaction rate (dC_{PCP}/dt) (mg L^{-1} min^{-1})	Concentration of sorbed PCP (mg L^{-1})
4	1.71	–
5	1.67	Negligible
5.5	1.55	0.67
6.0	1.4	2.0
pH uncontrolled	1.53	∼0.9

that there was marginal increase in the estimated initial reaction rate (dC_{PCP}/dt) with the decrease in pH of the reaction medium. This result may be explained on the basis of increased corrosion of Mg^0 and reduced passivation of the metal at lower pH values [22]. It may be also noted from Table 1 that substantial sorption of PCP (∼2 mg L^{-1}) on the residual solid surfaces was observed for experiments conducted at pH value of 6.0 while almost complete dissolution of magnesium was observed at the end of 45 min of reaction conducted at pH 4.0. Linear increase in the reaction rate constant with decrease in reaction pH has been also reported for the dechlorination of carbon tetrachloride, atrazine, and trichloroethylene using Fe^0 by Matheson and Tratnyek [20], Dombek et al. [21], and Chen et al. [22], respectively. Based on the results presented in Table 1, the optimum pH for PCP dechlorination by Mg/Pd system may be considered to be ∼5.5 which required nominal dosing (70 mM) of acid. At this pH, PCP was removed efficiently with negligible sorption.

Comparison of time course profiles of PCP removal for pH-controlled experiments revealed that most of the PCP removal occurred within 10–15 min of reaction (Fig. 5). Since the amount of acid dosed within this period, was much less (approximately 20 and 70 mM for pH 6.0 and 5.5, respectively), a very low sustained rate of magnesium corrosion and evolution of hydrogen along with a uniformly distributed colloidal suspension of Pd^0 particles were observed [18]. The uniform suspension of colloidal Pd^0 particles provided very high surface area onto which hydrogen was efficiently intercalated. On the other hand, in pH uncontrolled experiments, where 175 mM acetic acid was provided in a single dose at the beginning of reaction, the corrosion of magnesium was very rapid resulting in rapid evolution of hydrogen gas, a large fraction of which was unutilized and escaped into the atmosphere. It was also observed that after 2–3 min of the addition of acetic acid, the colloidal suspension of Pd^0 particles agglomerated to form larger Pd^0 particles thereby reducing the effective catalytic surface area. Thus, reduced removal of PCP in pH-uncontrolled experiment (Fig. 5) may be attributed to lower efficiency of hydrogen intercalation.

3.3. Effect of the presence of inorganic salts and resin and fatty acids on PCP dechlorination by Mg/Ag and Mg/Pd systems

3.3.1. Impact of inorganic salts and resin and fatty acids on PCP dechlorination by Mg/Ag system

Data presented in Table 2 reveal that the second order rate constant values and the extent of PCP removal by Mg/Ag system were substantially reduced in the presence of chloride, sulfate, chlorinated and non-chlorinated RFAs. Maximum adverse impact on the dechlorination was observed in the presence of salts. Also the concentration of PCP sorbed on residual solid surfaces was higher (∼2.5 mg L^{-1}) in the presence of salts. It may be noted that the concentration of chlorinated RFAs included in the reaction mixture was much lower as compared to PCP and therefore the possibility of direct competition between PCP and chlorinated RFAs for dechlorination can be ruled out. This fact was further substantiated by the comparison of second order rate

Table 2
Effect of the presence of inorganic salts and RFAs on PCP dechlorination by Mg/Ag system

Impurity and its concentration	Second order reaction rate constant (L mg^{-1} min^{-1})	Net PCP removal at the end of 1 h reaction (%)	Concentration of sorbed PCP (mg L^{-1})
NaCl (50 mM)	0.006	56	2.4
Na$_2$SO$_4$ (50 mM)	0.009	51	2.8
Chlorinated RFAs (1 mg L^{-1})	0.018	68	0.9
Non-chlorinated RFAs (1 mg L^{-1})	0.014	70	1.2
None (control)	0.030	81	1.0

constant values for the dechlorination of PCP by Mg/Ag system which were 0.018 L mg^{-1} min^{-1} and 0.014 L mg^{-1} min^{-1} in the presence of chlorinated and non-chlorinated resin fatty acids, respectively. Doong and Lai [33], studied the effect of the presence of humic acid on tetrachloroethylene using ZVI. They reported that humic acid out-competed tetrachloroethylene for sorption on to reactive sites resulting in the reduction of reaction rate constant. Since RFAs are also long chain carboxylic acids similar to humic acid, their competition with PCP for sorption may be responsible for reduced reaction rate constant for PCP dechlorination by Mg/Ag system. To the best of our knowledge there are no reports on the effects of salts or RFAs on dechlorination by Mg/Ag system.

3.3.2. Impact of resin and fatty acids and inorganic salts on PCP dechlorination by Mg/Pd system

Fig. 6 shows the effect of the presence RFAs on PCP dechlorination by Mg/Pd system. Results indicated that Mg/Pd system was almost unaffected by the presence of RFAs and thus, palladium proved to be a better catalyst as compared to silver.

These results are consistent with that reported by Doong and Lai [34]. The authors studied the effect of the presence of 5–80 mg L^{-1} of humic acid on the dechlorination of 1 mg L^{-1} of tetrachloroethylene using Pd/Fe system and showed that the reaction rate constant was almost unaffected in the presence of 5 mg L^{-1} of humic acid as compared to that in the absence of humic acid. However, the rate constant value for the dechlorination of tetrachloroethylene decreased with further increase in humic acid concentrations. Since we have used a relatively smaller concentration of RFAs as compared to PCP, the effect of RFAs on PCP dechlorination by Mg/Pd system may be negligible.

Fig. 7 depicts the effects of the presence of inorganic salts on PCP dechlorination by Mg/Pd system. Results suggested that the profiles of PCP disappearance in the absence and presence of sodium sulfate were nearly superimposable. On the other hand the rate and extent of PCP removal were significantly reduced in the presence of sodium chloride. The concentration of PCP sorbed on the residual solid surfaces was also higher in the presence of sodium chloride ($\sim$1 mg L^{-1}) as compared to that in the presence of sodium sulfate ($\sim$0.5 mg L^{-1}). Addition of NaCl to Mg/Pd system may affect the rate of corrosion of magnesium, and/or catalytic activity of Pd. Further, the addition of
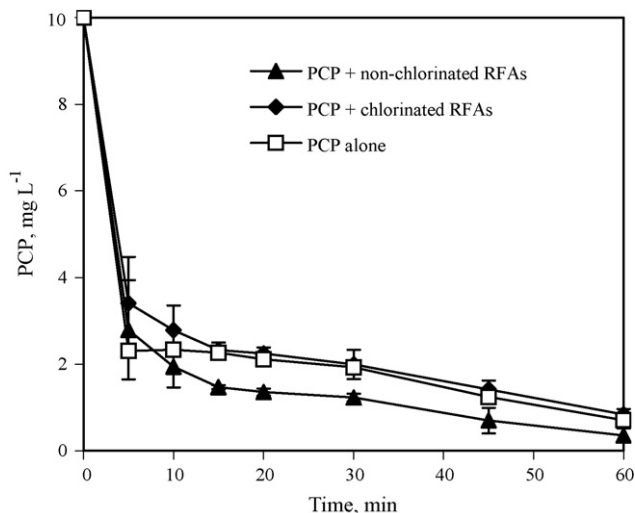

Fig. 6. Comparison of PCP disappearance profiles using Mg/Pd system in the presence and absence of resin and fatty acids. Reaction conditions: reaction volume, 150 mL; Mg^0 concentration, 154.4 mM; K$_2$PdCl$_6$ concentration, 0.063 mM; acetic acid dosage, 175 mM; initial concentration of PCP, 10 mg L^{-1}; initial concentration of chlorinated RFAs (0.25 mg L^{-1} of each of monochlorodehydroabietic acid, dichlorodehydroabietic acid, 9,10-dichlorostearic acid, and 9,10,12,13-tetrachlorostearic acid) or non-chlorinated RFAs (0.5 mg L^{-1} of each of DHA and stearic acid), 1 mg L^{-1}. Data presented represent average values obtained from experiments conducted in duplicate and error bars represent ±1 S.D.
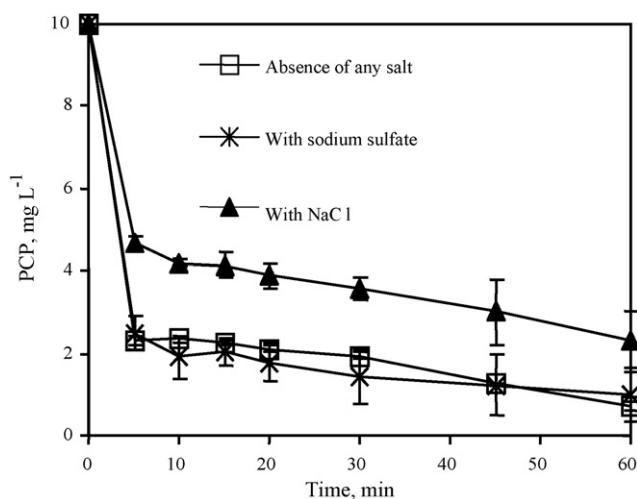

Fig. 7. Comparison of time course profiles for PCP disappearance using Mg/Pd system in the presence and absence of inorganic salts. Reaction conditions: reaction volume, 150 mL; Mg^0 concentration, 154.4 mM; K$_2$PdCl$_6$ concentration, 0.063 mM; sodium chloride or sodium sulfate, 50 mM; acetic acid dosage, 175 mM; initial concentration of PCP, 10 mg L^{-1}. Data presented represent average values obtained from experiments conducted in duplicate and error bars represent ±1 S.D.

chloride, a product of dehalogenation may reduce the rate of PCP dechlorination. Sianter et al. studied hydrodechlorination of 1,2-dibromo-3-chloropropane (DBCP) by zero-valent iron and hydrogen/palladium system in the presence of various anions in groundwater [38]. Dechlorination of DBCP by Fe^0 was inhibited by the presence of oxygen and nitrate/nitrite while sulfate and phosphate had little effect. In the same publication the authors reported that the rate of hydrodechlorination of DBCP by hydrogen/palladium system was reduced by ∼50% in the presence of sulfate, nitrate and chloride while sulfite caused 90% reduction in the rate. Schreier and Reinhard [39] reported that the rate of hydrodechlorination of perchloroethylene by 1% Pd-activated carbon powder in the presence of H_2 was reduced by 14% in the presence of 0.19 mM sulfate and almost unaffected in the presence of 10 mM sodium chloride. Complete deactivation of palladium was observed in the presence of 2 mM sodium bisulfide. Direct comparison of these results with ours may not be possible since the salt concentrations used in our study were much higher.

4. Conclusions

Following salient conclusions can be drawn from our study:

(i) Co-solvents, although present in small proportions (1% v/v) can significantly affect the rate and extent of PCP dechlorination by bimetallic systems such as Mg/Ag and Mg/Pd systems. Thus it is important to choose a right solvent for washing of contaminated soil or preparation of stock solutions. Amongst the four solvents used (ethanol, methanol, 1-propanol and acetone) maximum removal and minimum sorption of PCP and dechlorinated intermediates was achieved in the presence of acetone probably due to its higher dipole moment in comparison to alcoholic solvents.

(ii) pH of the reaction medium influenced the rate and extent of PCP removal by Mg/Pd and Mg/Ag systems. A pH of ∼5.5 was optimal for PCP dechlorination by Mg/Pd system while maximal dechlorination efficiency was noted using unbuffered medium with Mg/Ag system.

(iii) The presence of chlorinated and non-chlorinated RFAs significantly reduced the rate and extent of PCP dechlorination by Mg/Ag system probably due to structural properties of RFAs. However, the presence of RFAs did not affect PCP dechlorination by Mg/Pd system.

(iv) The presence of chloride had an adverse impact on the rate and extent of PCP dechlorination by Mg/Ag and Mg/Pd systems. PCP dechlorination by Mg/Pd system was unaffected by the presence of sodium sulfate while Mg/Ag system was adversely impacted by the salt.

Information related to the effect of environmental parameters such as pH, presence of co-solvents, salts and co-pollutants on the rates of dechlorination reactions is vital to assess the applicability of bimetals for the treatment of groundwater or raw industrial wastewaters such as pulp bleaching effluents.

References

[1] Agency for Toxic Substances and Disease Registry (ATSDR), Toxicological Profile for Pentachlorophenol, 2001.

[2] L.H. Kieth, W.A. Telliard, Priority pollutants. Part I. A perspective view, Environ. Sci. Technol. 13 (1979) 416–423.

[3] Proposition 65, Office of Environmental Health Hazard, EPA, State of California, USA, 2005.

[4] M. Pera-Titus, V. Garcia-Molina, M.A. Banos, J. Gimenez, S. Esplugas, Degradation of chlorophenols by means of advanced oxidation processes: a general review, Appl. Catal. B 47 (2004) 219–256.

[5] C. Cui, X. Quan, S. Chen, H. Zhao, Adsorption and electrocatalytic dechlorination of pentachlorophenol on palladium-loaded activated carbon fibers, Sep. Purif. Technol. 47 (2005) 73–79.

[6] C.-H. Lin, S.-K. Tseng, Electrochemically reductive dechlorination of pentachlorophenol using a high overpotential zinc cathode, Chemosphere 39 (1999) 2375–2389.

[7] M.A. Oturan, N. Oturan, C. Lahite, S. Trevin, Production of hydroxyl radicals by electrochemically assisted Fenton's reagent: application to the mineralization of an organic micropollutant, pentachlorophenol, J. Electroanal. Chem. 507 (2001) 96–102.

[8] A.P. Khodadoust, J.A. Wagner, M.T. Suidan, R.C. Brenner, Anaerobic treatment of PCP in fluidized-bed GAC bioreactors, Water Res. 31 (1997) 1776–1786.

[9] P.M. Armenante, D. Kafkewitz, G.A. Lewandowski, C.-J. Jou, Anaerobic–aerobic treatment of halogenated phenolic compounds, Water Res. 33 (1999) 681–692.

[10] M.H. Kim, O.J. Hao, Cometabolic degradation of chlorophenols by *Acinatobacter* species, Water Res. 33 (1999) 562–574.

[11] M.D. Mikesell, S.A. Boyd, Complete reductive dechlorination and mineralization of pentachlorophenol by anaerobic microorganisms, Appl. Environ. Microb. 52 (1986) 861–865.

[12] C.M. Kao, C.T. Chai, J.K. Liu, T.Y. Yeh, K.F. Chen, S.C. Chen, Evaluation of natural and enhanced PCP biodegradation at a former pesticide manufacturing plant, Water Res. 38 (2004) 663–672.

[13] R.J. Irwin, M. VanMouwerik, L. Stevens, M.D. Seese, W. Basham, Environmental Contaminants Encyclopedia, National Park Service, Water Resources Division, Fort Collins, CO, 1997.

[14] J. Morales, R. Hutcheson, I.F. Cheng, Dechlorination of chlorinated phenols by catalyzed and uncatalyzed Fe(0) and Mg(0) particles, J. Hazard. Mater. B 90 (2002) 97–108.

[15] L.J. Graham, G. Jovanovic, Dechlorination of *p*-chlorophenol on a Pd/Fe catalyst in a magnetically stabilized fluidized bed: implications for sludge and liquid remediation, Chem. Eng. Sci. 54 (1999) 3085–3093.

[16] Y. Kim, R. Carraway, Dechlorination of pentachlorophenol by zero valent iron and modified zero valent irons, Environ. Sci. Technol. 34 (2000) 2014–2017.

[17] U.D. Patel, S. Suresh, Dechlorination of chlorophenols using magnesium–silver bimetallic system, J. Colloid Interface Sci. 299 (2006) 249–259.

[18] U.D. Patel, S. Suresh, Dechlorination of chlorophenols using magnesium–palladium bimetallic system, J. Hazard. Mater. 147 (2007) 431–438.

[19] P. Sabatier, The Method of Direct Hydrogenation by Catalysis, 1912. http://www.nobel.se/chemistry/laureates/1912/sabatier-lecture.html (website visited in May 2007).

[20] L.J. Matheson, P.G. Tratnyek, Reductive dehalogenation of chlorinated methanes by iron metal, Environ. Sci. Technol. 28 (1994) 2045–2053.

[21] T. Dombek, E. Dolan, J. Schultz, D. Klarup, Rapid reductive dechlorination of atrazine by zero-valent iron under acidic conditions, Environ. Pollut. 111 (2001) 21–27.

[22] J.-L. Chen, S.R. Al-Abed, J.A. Ryanb, Z. Li, Effects of pH on the dechlorination of trichloroethylene by zero-valent iron, J. Hazard. Mater. B 83 (2001) 243–254.

[23] R.A. Rajadhyaksha, S.L. Karwa, Solvent effects in catalytic hydrogenation, Chem. Eng. Sci. 41 (1986) 1765–1770.

[24] L. Lassova, H.K. Lee, T.S. Andy Hor, Catalytic dechlorination of chlorobenzenes: effect of solvent on efficiency and selectivity, J. Mol. Catal. A 144 (1999) 397–403.

[25] S.P. Bawane, S.B. Sawant, Hydrogenation of *p*-nitrophenol to metal using Raney nickel catalyst: reaction kinetics, Appl. Catal. A 293 (2005) 162–170.

[26] C.J. Clark, P.S.C. Rao, M.D. Annable, Degradation of perchloroethylene in cosolvent solutions by zero-valent iron, J. Hazard. Mater. B 96 (2003) 65–78.

[27] N.E. Korte, O.R. West, L. Liang, B. Gub, J.L. Zutman, Q. Fernando, The effect of solvent concentration on the use of palladized-iron for the step-wise dechlorination of polychlorinated biphenyls in soil extracts, Waste Manage. 22 (2002) 343–349.

[28] G.V. Lowry, K.M. Johnson, Congener-specific dechlorination of dissolved PCBs by microscale and nanoscale zerovalent iron in a water/methanol solution, Environ. Sci. Technol. 38 (2004) 5208–5216.

[29] N.C. Concibido, T. Okuda, Y. Nakano, W. Nishijima, M. Okada, Enhancement of the catalytic hydrodechlorination of tetrachloroethylene in methanol at mild conditions by water addition, Tetrahedron Lett. 46 (2005) 3613–3617.

[30] Y. Liu, F. Yang, P.L. Yue, G. Chen, Catalytic dechlorination of chlorophenols in water by palladium/iron, Water Res. 35 (2001) 1887–1890.

[31] H.M. Roy, C.M. Wai, T. Yuan, J.-K. Kim, W.D. Marshall, Catalytic hydrodechlorination of chlorophenols in aqueous solution under mild conditions, Appl. Catal. A 271 (2004) 137–143.

[32] Y. Xu, W.-X. Zhang, Subcolloidal Fe/Ag particles for reductive dehalogenation of chlorinated benzenes, Ind. Eng. Chem. Res. 39 (2000) 2238–2244.

[33] R.-A. Doong, Y.-J. Lai, Effect of metal ions and humic acid on the dechlorination of tetrachloroethylene by zerovalent iron, Chemosphere 64 (2006) 371–378.

[34] R.-A. Doong, Y.-J. Lai, Dechlorination of tetrachloroethylene by palladized iron in the presence of humic acid, Water Res. 39 (2005) 2309–2318.

[35] National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI), Methods Manual: Chlorinated Phenolics in Water by In-Situ Acetylation/GC/MS Determination (CP-86.02), 1997.

[36] R.T. Morrison, R.N. Boyd, Organic Chemistry, fifth ed., Prentice-Hall of India Private Limited, New Delhi, 1989.

[37] B. Yang, G. Yu, D. Shuai, Electrocatalytic hydrodechlorination of 4-chlorobiphenyl in aqueous solution using palladized nickel foam cathode, Chemosphere 67 (2007) 1361–1367.

[38] D.P. Siantar, C.G. Schreier, C.-S. Chou, M. Reinhard, Treatment of 1,2-dibromo-3-chloropropane and nitrate-contaminated water with zero-valent iron or hydrogen/palladium catalysts, Water Res. 30 (1996) 2315–2322.

[39] C.G. Schreier, M. Reinhard, Catalytic hydrodehalogenation of chlorinated ethylenes using palladium and hydrogen for the treatment of contaminated water, Chemosphere 31 (1995) 3475–3487.

[40] J.G. Speight, Lange's Handbook of Chemistry, 16th ed., McGraw-Hill, New York, USA, 2005.