

Dechlorination of chlorophenols using magnesium–palladium bimetallic system

Upendra D. Patel, Sumathi Suresh*

Centre of Environmental Science and Engineering, Indian Institute of Technology-Bombay, Mumbai 400076, India

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Abstract

Ninety-four percent removal of 10 mg L^{-1} of pentachlorophenol (PCP) was achieved by treatment with 154.5 mM Mg^0 and $0.063 \text{ mM K}_2\text{PdCl}_6$ in the presence of 175 mM acetic acid in 1 h reaction time. Dechlorination of PCP was found to be sequential and phenol was identified as the end product along with accumulation of trace concentrations of tetra- and trichlorophenols. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) revealed that palladium in its metallic form (Pd^0) produced by reduction of Pd^{4+} , was spatially separated from magnesium granules when acid was included in the reaction. These colloidal palladium particles generated active reductive species of hydrogen and dechlorinated chlorophenols. In the absence of acid, the efficiency of dechlorination of PCP by Pd/Mg^0 system was very low and chief mechanism of removal of the compound was through sorption onto solid surfaces. Thus, it was important to include acid in the system to: (a) facilitate corrosion of Mg^0 and reduction of Pd^{4+} to Pd^0 , (b) provision of protons to produce H_2 , (c) retard formation of insoluble oxides and hydroxides that may deposit on the magnesium granules and sorb PCP and its partially dechlorinated products and. Application of $154.5 \text{ mM Mg}^0/0.063 \text{ mM K}_2\text{PdCl}_6$ on PCP, 2,4,5-trichlorophenol (TCP) and 2-chlorophenol (MCP) with organic chloride equivalence showed that the rate and extent of removal increased with decrease in number of chlorine atoms on phenol.

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1. Introduction

Chlorophenols (CPs) with two or more chlorine atoms are either used as pesticides or raw material to synthesize pesticides. Pentachlorophenol (PCP) is one of such compounds that has been widely used as wood preservative and pesticide [1]. Chlorophenols including PCP have been identified as potential carcinogens [2,3]. Ecotoxicity of chlorophenols especially PCP, necessitate the development of rapid and reliable remediation techniques.

Electrochemical reduction/oxidation [4–9] and advanced chemical oxidation [10] of chlorophenols have been profusely studied in the last decade. Reductive electrochemical dechlorination of chlorophenols may be either complete [9] or partial resulting in accumulation of lower chlorinated phenols and phe-

nol [5,6]. On the other hand, both electrochemical and chemical oxidations have been reported to yield near complete mineralization of chlorophenols [7,10].

Both aerobic and anaerobic biodegradation of chlorophenols have been studied in great depth [11–16]. While biodegradation may prove economical, requirements for specific environmental conditions (methanogenic or sulfate reducing) particularly in case of anaerobic degradation, and long acclimation and retention times in general, can restrict its field application.

Zero-valent metals and bimetallic systems have been successfully utilized to dechlorinate chlorinated organics [17–21]. Such reactions are much faster as compared to biodegradation. The main advantage of bimetallic systems is the ability to conduct reactions at room temperature and pressure without exclusion of atmospheric oxygen. Bimetallic systems make use of two metals, one in zero-valent form (with a negative reduction potential like, $\text{Mg}^0 \rightarrow \text{Mg}^{2+}$, $\text{Fe}^0 \rightarrow \text{Fe}^{2+}$, etc.) that produces molecular hydrogen when in contact with water by anodic corrosion, and the other metal with a relatively high (positive) reduction potential (such as $\text{Pd}^{4+} \rightarrow \text{Pd}^0$) as the reducing catalyst. Molecular

* Corresponding author. Tel.: +91 22 2576 7859; fax: +91 22 2572 3480.

E-mail addresses: upendra@iitb.ac.in (U.D. Patel), sumathis@iitb.ac.in (S. Suresh).

hydrogen is dissociatively absorbed onto reducing catalyst to form a metal hydride (M–H), which in turn dehalogenates the target substrate.

PCP dechlorination was studied earlier by Morales et al. [19] using Mg/Pd system. The concentration of PCP used was very high (2.48 mM, $\sim 660 \text{ mg L}^{-1}$) as compared to its solubility in plain water ($\sim 10 \text{ mg L}^{-1}$) and therefore solubilized in 1:1 water–2-propanol mixture (v/v). Thus the bimetal concentrations used by authors for dechlorination of 2.48 mM PCP may not be cost effective for practical application to water containing low PCP concentrations. Detection limit for PCP was reported to be 0.39 mM (104 mg L^{-1}) using GC-FID while a much more sensitive detection of PCP can be achieved using GC-ECD. It may also be noted that authors did not account for the sorption of PCP onto residual solid surfaces. This is especially important in view of the fact that reactions were conducted in the absence of acid. Dechlorination studies at low PCP concentration using low concentrations of bimetal may have their own intricate problems. Hence, we carried out all our studies using 10 mg L^{-1} of initial PCP concentration. The major objectives of our study were to: (a) evaluate Pd/Mg⁰ system for its ability to dechlorinate PCP and lower CPs in aqueous phase, (b) study the role of acid in the reductive dechlorination, (c) identify the concentration of K₂PdCl₆ required for dechlorination of PCP (10 mg L^{-1}) since palladium is an expensive catalyst and (d) elucidate the mechanism of dechlorination by Mg/Pd system in the presence of acid.

2. Materials and methods

2.1. Chemicals

Magnesium granules (~ 20 mesh), potassium carbonate, 3-chlorophenol, 2-chlorophenol, 4-chlorophenol, 3,4-dichlorophenol, 2,3-dichlorophenol, 2,5-dichlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol, 2,4,6-trichlorophenol, 2,4,5-trichlorophenol, 2,3,6-trichlorophenol, 2,3,4-trichlorophenol, 2,3,4,6-tetrachlorophenol, 2,3,5,6-tetrachlorophenol and pentachlorophenol were purchased from Sigma–Aldrich Chemical Company. Cyclohexane, phenol, 2-propanol and acetic acid were purchased from Merck India Ltd. Potassium hexachloropalladate was procured from Sigma–Aldrich Chemical Company. Methanol and acetic anhydride were purchased from S.D. FineChem Ltd., Mumbai, India. All the above listed chemicals were of high purity ($\geq 98\%$) and analytical grade. Potassium carbonate was baked in furnace at 400°C , overnight, prior to use. No pretreatment was carried out with other chemicals. Stock solutions (1000 mg L^{-1}) of all the chlorophenols were prepared in methanol and required concentrations of CPs were prepared by diluting the stock into deionized water.

2.2. Dechlorination experiment according to Morales et al.

Dechlorination experiment described by Morales et al. [19] was carried out by taking 1 g Mg^0 and $10 \text{ mg K}_2\text{PdCl}_6$ (concentrations equivalent to 2659 ppm) in a test tube followed by the addition of 5 mL of 2.48 mM PCP prepared in 1:1 (v/v) water:2-

propanol. After initial mixing on high speed vortex mixer, the test tubes were maintained on a translatory shaker for 48 h at 30°C . The method used for quantification of sorption of PCP and its reaction products on solid surfaces following completion of the reaction is described in Section 2.4.

2.3. Influence of acid on the kinetics and extent of dechlorination of PCP by Mg/Pd system using completely mixed batch reactor (CMBR)

Kinetics studies were carried out with 150 mL of sample volume in a 250 mL reagent bottle containing 10 mg L^{-1} of PCP in the absence or in the presence (175 mM) of acetic acid. The concentrations of $\text{Mg}^0/\text{K}_2\text{PdCl}_6$ were $154.5 \text{ mM}/0.063 \text{ mM}$. Sequence of addition of reaction mixture components for all the CMBR studies was: $\text{PCP} \rightarrow \text{Mg}^0 \rightarrow \text{K}_2\text{PdCl}_6 \rightarrow \text{acid}$ (when-ever present). Contents of the reactor were continuously mixed on magnetic stirrer at $26.5\text{--}27.5^\circ\text{C}$ through out the reaction period. Aliquots were withdrawn at various time points, derivatized and analyzed for residual PCP concentration by GC-ECD. Experiments were conducted in duplicate. Control experiments were performed under similar conditions as test experiments except that Mg^0 and K_2PdCl_6 were omitted from the reaction mixture.

2.4. Quantification of sorption of PCP and dechlorinated products

In order to quantify sorption of PCP and its reaction products on solid surfaces, supernatant was separated following reaction in a CMBR. Residual solids were washed with deionized water equivalent to three times of reaction volume. Subsequently, one reaction volume of deionized water and 175 mM acetic acid were added to dissolve the magnesium granules completely. This solution was analyzed to determine the concentration of sorbed compounds. The protocol described above was also used to quantify sorption of PCP and products following reactions conducted as per Morales et al. [19], except that concentrated HCl (1.5 mL for 5 mL reaction volume) was used to dissolve the magnesium granules completely.

2.5. Experiments using Mg^0 in combination with pre-reduced palladium (Pd^0)

A combination of Mg^0/Pd^0 granules were prepared by mixing 2 mL of water containing 2.06 M Mg^0 with $0.88 \text{ mM K}_2\text{PdCl}_6$ (Pd/Mg ratio $\sim 0.173\%$ w/w). The contents were mixed for 30 s and allowed to incubate for 5 min for the reduction of Pd^{4+} to Pd^0 . The change in the color of K_2PdCl_6 solution from orange to pale yellow was taken as an indication of completion of reduction process. Following reduction, the clear aqueous phase was discarded and Mg^0/Pd^0 particles were collected, washed using 2 mL water and dried in air at room temperature. Experiments were carried out by adding 15 mg of Mg^0/Pd^0 particles into 4 mL of solution containing 10 mg L^{-1} PCP and 175 mM acetic acid.

2.6. Effect of varying concentrations of K_2PdCl_6 and magnesium on PCP removal

Dechlorination of 10 mg L^{-1} of PCP was studied in CMBR by varying magnesium concentration (51.5, 103, 154.5, 205 and 308 mM) at a fixed concentration of 0.063 mM K_2PdCl_6 . Likewise, we also studied the effect of varying K_2PdCl_6 concentrations (0.032, 0.063 and 0.125 mM) with fixed Mg^0 concentration of 154.5 mM . Experiments were conducted in triplicates at 30°C in the presence of 175 mM acetic acid. The sequence of addition of components of reaction mixture to PCP solution was: $Mg^0 \rightarrow K_2PdCl_6 \rightarrow$ acetic acid.

2.7. Comparison of kinetics of dechlorination of chlorophenols by Mg/Pd system using CMBR

The dose of Mg^0/K_2PdCl_6 ($154.5 \text{ mM}/0.063 \text{ mM}$) was further tested for its efficiency to dechlorinate 10, 12.5 and 25 mg L^{-1} of PCP, 2,4,5-TCP and 2-CP, respectively, wherein organic chlorine atom (6.63 mg L^{-1}) equivalence was maintained for each target compound. Control experiments were performed under similar conditions as test experiments except that Mg^0 and K_2PdCl_6 were omitted from the reaction mixture. One hundred seventy-five millimoles acetic acid was included in test and control experiments. Concentrations of parent compounds and dechlorinated intermediates/products were monitored at various time points (total reaction period = 1 h) using GC-ECD. Total residual organic chloride concentration was calculated based on the residual concentrations of chlorinated products and target parent compound at any time point, t .

2.8. Gas chromatography (GC) analysis

Samples were prepared for GC analyses as the procedure described by NCASI 86.02 [22] and Patel and Suresh [21]. GC analyses were carried out using Agilent 6890N model equipped with μECD and FID. DB-5 column ($30 \text{ m} \times 0.32 \text{ mm i.d.} \times 0.25 \mu\text{m}$ film thickness) was used. Temperature programme used was—1 min at 50°C , temperature ramp 1: $50\text{--}100^\circ\text{C}$ at $20^\circ\text{C min}^{-1}$, hold time of 0.3 min; temperature ramp 2: $100\text{--}215^\circ\text{C}$ at 4°C min^{-1} , final hold time of 1 min. Injector and detector temperatures were set at 210 and 300°C , respectively. Injections were performed in splitless mode using nitrogen as the carrier gas (gas velocity 36 cm/s). Purge time and flow were set at 0.5 min and 100 mL min^{-1} , respectively. Calibration plots for all chlorophenols were prepared in concentration range of interest and were found to be linear with R^2 values > 0.98 .

2.9. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) analyses

SEM and EDX analyses of settled and suspended solids were carried out using a Hitachi S3400N scanning electron microscope equipped with an EDX detector (Thermo NoranNSS200 instruments). The reaction mixture contained 10 mg L^{-1} of PCP and $154.5 \text{ mM}/0.063 \text{ mM}$ of Mg^0/K_2PdCl_6 . Dosing of acetic

acid (175 mM) was optional. Following the stipulated reaction time ($5\text{--}60 \text{ min}$), settled solids were separated from supernatant, dried and stored in air tight vials under nitrogen. Suspended particles were also collected from a number of experiments, separated from aqueous phase by centrifugation and dried overnight in an oven at 105°C .

3. Results and discussion

3.1. Dechlorination of PCP by Mg/Pd as per Morales et al.

We conducted dechlorination of 2.48 mM PCP in 2-propanol/water (1:1, v/v) using 10 mg/g of K_2PdCl_6/Mg^0 as described by Morales et al. [19] in the absence of acid. Experiments to quantify sorption revealed that three drops of concentrated HCl as mentioned by Morales et al. [19] could not even dissolve the surface deposits of residual solids. Much higher volume (1.5 mL) of HCl was required to achieve almost complete dissolution of residual solids. Based on this result a protocol for quantification of sorption of PCP onto residual solids was developed as described in Section 2.4. GC-ECD chromatography revealed that 20% of PCP remained unreacted in the supernatant of reaction mixture while 10% was sorbed onto residual solid surfaces at the end of reaction (Fig. 1). Thus, $\sim 30\%$ of PCP remained unreacted which was not accounted for by Morales et al. [19] due to the adoption of a detection technique (GC-FID) with lower sensitivity and ineffective procedure for quantification of sorption. Results obtained by us suggested that adsorption of parent compound due to precipitation of magnesium oxides and hydroxide on Mg^0 granules

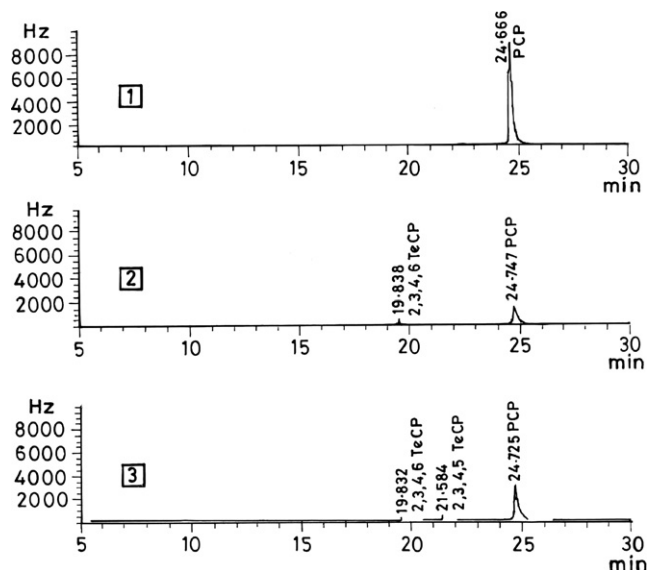


Fig. 1. Comparison of GC-ECD chromatograms showing PCP dechlorination by Mg/Pd system in the absence of acid (reaction conducted according to the protocol described by Morales et al.). (1) Unreacted 2.48 mM PCP (control), (2) supernatant of PCP containing reaction mixture following 48 h reaction with Mg/Pd and (3) 48 h reaction mixture supernatant that includes PCP and dechlorinated products desorbed from solids. Reaction conditions: volume = 5 mL ; $Mg^0 = 1 \text{ g}$; $K_2PdCl_6 = 10 \text{ mg}$; reaction time = 48 h; PCP concentration = 2.48 mM ; reaction phase = 1:1 water–2-propanol.

was inevitable when reactions were conducted in the absence of acid using Mg/Pd system. Several studies using zero-valent iron (ZVI) have demonstrated that dechlorination reaction occur at reactive sites on solid surfaces with simultaneous sorption at non-reactive sites [23,24]. Kung and McBride [25] reported that chlorophenols in phenolate form was sorbed onto metal oxide surfaces by inner-sphere coordination and desorption could not be accomplished by washing with water alone. Thus, on the basis of results presented in this section, experiments were conducted to study the effect of acid on extent and rate of removal of PCP.

3.2. Influence of acid on the kinetics and extent of dechlorination of PCP by Mg/Pd

3.2.1. Dechlorination in the presence of acid

pH profile of the reaction phase as a function of time and time course profile for PCP removal by $\text{Mg}^0/\text{K}_2\text{PdCl}_6$ (154.5 mM/0.063 mM) in the presence of 175 mM acetic acid in a CMBR are illustrated in Fig. 2. The above specified concentration of $\text{Mg}^0/\text{K}_2\text{PdCl}_6$ achieved ~80 and 95% removal of 10 mg L^{-1} of PCP after 5 min and 60 min of reaction, respectively. Since the reaction was rapid we were unable to determine the rate and order of PCP dechlorination reaction. The quantity of sorbed PCP and dechlorinated products following 1 h of reaction was negligible. Dechlorination of PCP was found to be sequential and phenol ($\sim 1.0 \text{ mg L}^{-1}$) was identified as the end product (Fig. 3) along with accumulation of trace concentrations ($\sim 0.1\text{--}0.25 \text{ mg L}^{-1}$) of tetrachlorophenols (Fig. 2) and trichlorophenols ($0.05\text{--}0.1 \text{ mg L}^{-1}$, profile not shown). We noted that the reduction of Pd^{4+} to Pd^0 occurred only after the addition of acid. An additional observation made by us was that the Pd^0 particles were spatially separated from the magnesium granules thereby implying that the dechlorination reaction did not necessarily occur on bimetallic interface of Pd^0/Mg^0 as proposed by Graham and Jovanovic [17]. Hydrodehalogenation by intercalation of molecular hydrogen on various Pd^0 catalysts has been reported extensively in literatures [26–28].

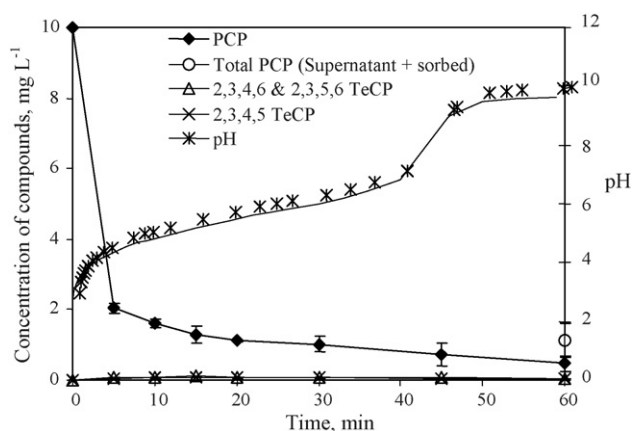


Fig. 2. Time course profiles showing change in the pH of reaction phase and removal of PCP by Mg/Pd system in the presence of acid. Also the appearance of trace concentrations of tetrachlorophenols is shown. Reaction conditions: initial concentration of PCP = 10 mg L^{-1} ; $\text{Mg}^0 = 154.5 \text{ mM}$; $\text{K}_2\text{PdCl}_6 = 0.063 \text{ mM}$; acetic acid = 175 mM. Results plotted are average of two experimental values.

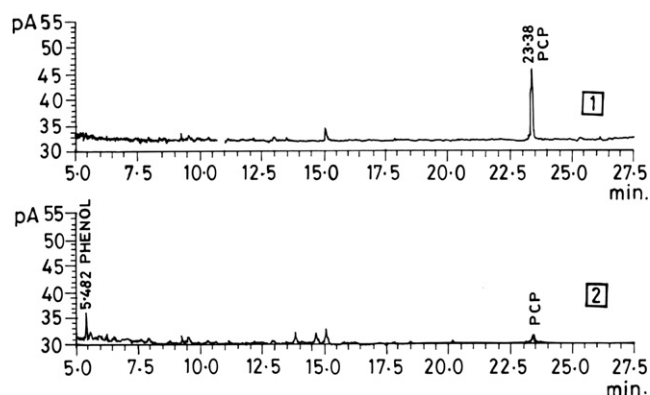


Fig. 3. GC-FID chromatograms showing removal of PCP and formation of phenol by Mg/Pd system. (1) Unreacted PCP (control) and (2) supernatant of PCP containing reaction mixture following treatment with Mg/Pd system. Reaction conditions: initial PCP concentration = 10 mg L^{-1} ; concentration of $\text{Mg}/\text{K}_2\text{PdCl}_6 = 154 \text{ mM}/0.063 \text{ mM}$; reaction time = 1 h; acetic acid dose = 175 mM.

3.2.2. Dechlorination in the absence of acid

Fig. 4 illustrates the time course profile of PCP disappearance and pH change of the medium for reaction conducted using $\text{Mg}^0/\text{K}_2\text{PdCl}_6$ (154.5 mM/0.063 mM) in the absence of acid. Comparison of Figs. 2 and 4 clearly reveals that the rate and extent of PCP removal were significantly reduced in the absence of acid. Total concentration of PCP removed was 6 mg L^{-1} after 1 h of reaction which occurred through dechlorination and non-reactive sorption (contributions of 40 and 20%, respectively). Fig. 4 also reveals that pH of the reaction phase increased rapidly reaching close to 10 within the first 5 min of reaction due to the absence of acid in the reaction phase. In comparison, inclusion of acid facilitated maintenance of low pH (in the range of 4–5.5) for up to 40 min of the reaction (Fig. 2) which in turn sustained corrosion of Mg^0 . Similar observations were also reported by Boronina et al. [29] while studying the dechlorination of CCl_4 using Mg^0 in the absence of acid. The research group observed that the pH of the reaction medium was close to 10 and that

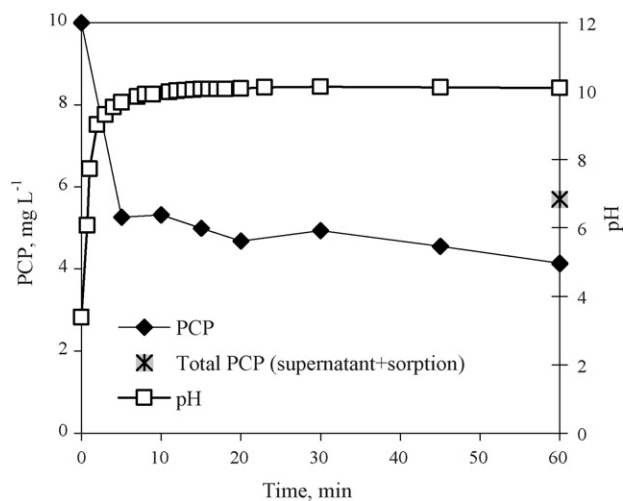


Fig. 4. Time course profiles showing change in pH of the reaction phase and removal of PCP by Mg/Pd system in the absence of acid. Reaction conditions: initial concentration of PCP = 10 mg L^{-1} ; $\text{Mg}^0 = 154.5 \text{ mM}$; $\text{K}_2\text{PdCl}_6 = 0.063 \text{ mM}$.

Table 1
PCP removal efficiencies of *in situ* and *ex situ* prepared Mg⁰/Pd⁰ granules

Mode of reduction of Pd ⁴⁺ to Pd ⁰	PCP removal mechanism(s)	Extent of PCP removal (%)	
		After 1 h of reaction	After 48 h of reaction
<i>In situ</i> (on-site reduction)	Dechlorination	85	93
	Dechlorination + adsorption	89	96
<i>Ex situ</i> (pre-reduced)	Dechlorination	38	51
	Dechlorination + adsorption	38.5	90

Reaction conditions—*In situ*: volume 4 mL, initial PCP concentration 10 mg L⁻¹, concentration of Mg⁰/K₂PdCl₆ 154.5/0.063 mM and acetic acid 175 mM. *Ex situ*: volume 4 mL, initial PCP concentration 10 mg L⁻¹, concentration of Mg⁰/Pd⁰ particles 15 mg and acetic acid 175 mM.

only small amount of CCl₄ was converted to CHCl₃ following 48 h of reaction. Our earlier study using magnesium–silver system established that sorption of PCP and dechlorinated products were much lower in the presence of acid as compared to that in the absence of acid [21]. Thus, addition of acid enhanced the rate of dechlorination of target compounds by: (a) facilitating corrosion of Mg⁰ and reduction of Pd⁴⁺ to Pd⁰, (b) providing protons to generate H₂ and (c) delaying the creation of alkaline conditions in the reaction phase and retardation of formation of insoluble oxides and hydroxides that may sorb PCP and its dechlorinated products. Considering the above listed advantages we conducted subsequent experiments in the presence of acid.

3.3. PCP removal efficiencies of *in situ* and *ex situ* prepared Mg⁰/Pd⁰ granules

Results presented in Table 1 clearly suggest that Mg⁰ in combination with *in situ* reduced palladium (Pd⁰) was more efficient in dechlorinating PCP as compared to *ex situ* prepared Mg⁰–Pd⁰ bimetallic granules. An explanation for this observation is that the surface properties of *ex situ* prepared Mg⁰/Pd⁰ deteriorated

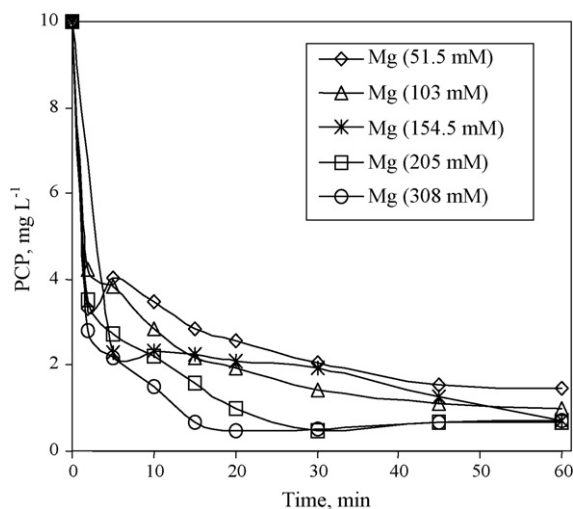


Fig. 5. Time course profiles for removal of PCP using varying concentrations of magnesium at a fixed concentration of K₂PdCl₆. All reactions were conducted in the presence of acid. Reaction conditions: initial concentration of PCP = 10 mg L⁻¹; Mg⁰ concentrations as indicated in the figure; K₂PdCl₆ = 0.063 mM; acetic acid = 175 mM.

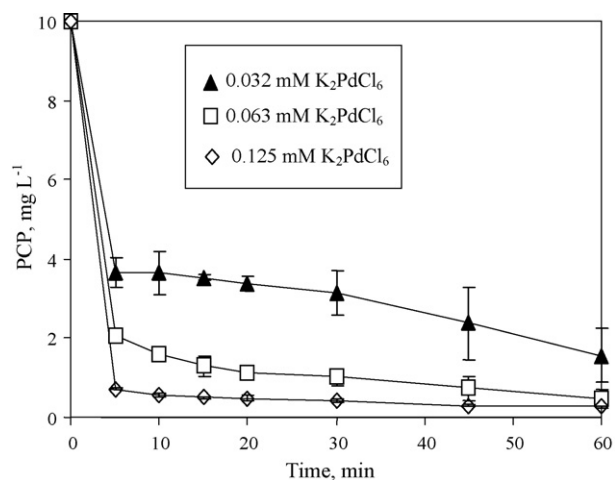


Fig. 6. Time course profiles for removal of PCP using varying concentrations of K₂PdCl₆ at a fixed concentration of magnesium. All reactions were conducted in the presence of acid. Reaction conditions: initial concentration of PCP = 10 mg L⁻¹; Mg⁰ = 154.5 mM; K₂PdCl₆ concentrations as indicated in the figure; acetic acid = 175 mM. Results plotted are average of two experimental values.

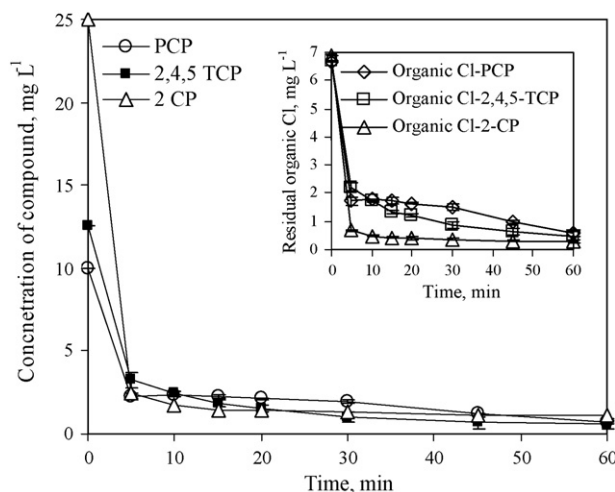


Fig. 7. Comparison of time course profiles for removal of PCP, 2,4,5-TCP, and 2-CP (with equivalent organic chlorine concentration) in a completely mixed batch reactor (CMBR) by Mg/Pd system in the presence of acid. The inset figure shows corresponding time dependent profiles for removal of organically bound chlorine. Reaction conditions: initial concentrations of: PCP = 10 mg L⁻¹; 2,4,5-TCP = 12.5 mg L⁻¹; 2-CP = 25 mg L⁻¹; Mg⁰ = 154.5 mM; K₂PdCl₆ = 0.063 mM; acetic acid = 175 mM. Results plotted are average of two experimental values. Error bars present ±1 standard deviation and symbols may appear bigger than the error bars at some points.

with time upon exposure to air, which in turn lowered the dechlorination efficiency. Kim and Carraway [18] reported that *ex situ* prepared Fe^0/Pd , Fe^0/Ni , Fe^0/Pt and Fe^0/Cu exhibited lower efficiencies in dechlorinating PCP as compared to Fe^0 (ZVI). It may be noted from Table 1 that sorption of PCP and dechlorinated products was almost negligible following 1 and 48 h reaction using *in situ* prepared Mg^0/Pd^0 . However, sorption of compounds was prominent subsequent to 48 h of reaction with *ex situ* prepared Mg^0/Pd^0 granules. Based on these results, all subsequent experiments were conducted using Mg^0 in combination with *in situ* produced Pd^0 .

3.4. Effect of varying concentrations of Mg^0 and K_2PdCl_6 on the extent of PCP removal

Fig. 5 compares time dependant profiles of PCP disappearance using varying concentrations of magnesium at a fixed K_2PdCl_6 concentration of 0.063 mM in the presence of 175 mM acetic acid. It is evident that except for the lowest magnesium concentration (51.5 mM), all other concentrations achieved ~90% removal of PCP at the end of 1 h of reaction with insignificant disparity in the initial rates of PCP removal. Similarly, Fig. 6 compares kinetics of PCP removal by varying concentra-

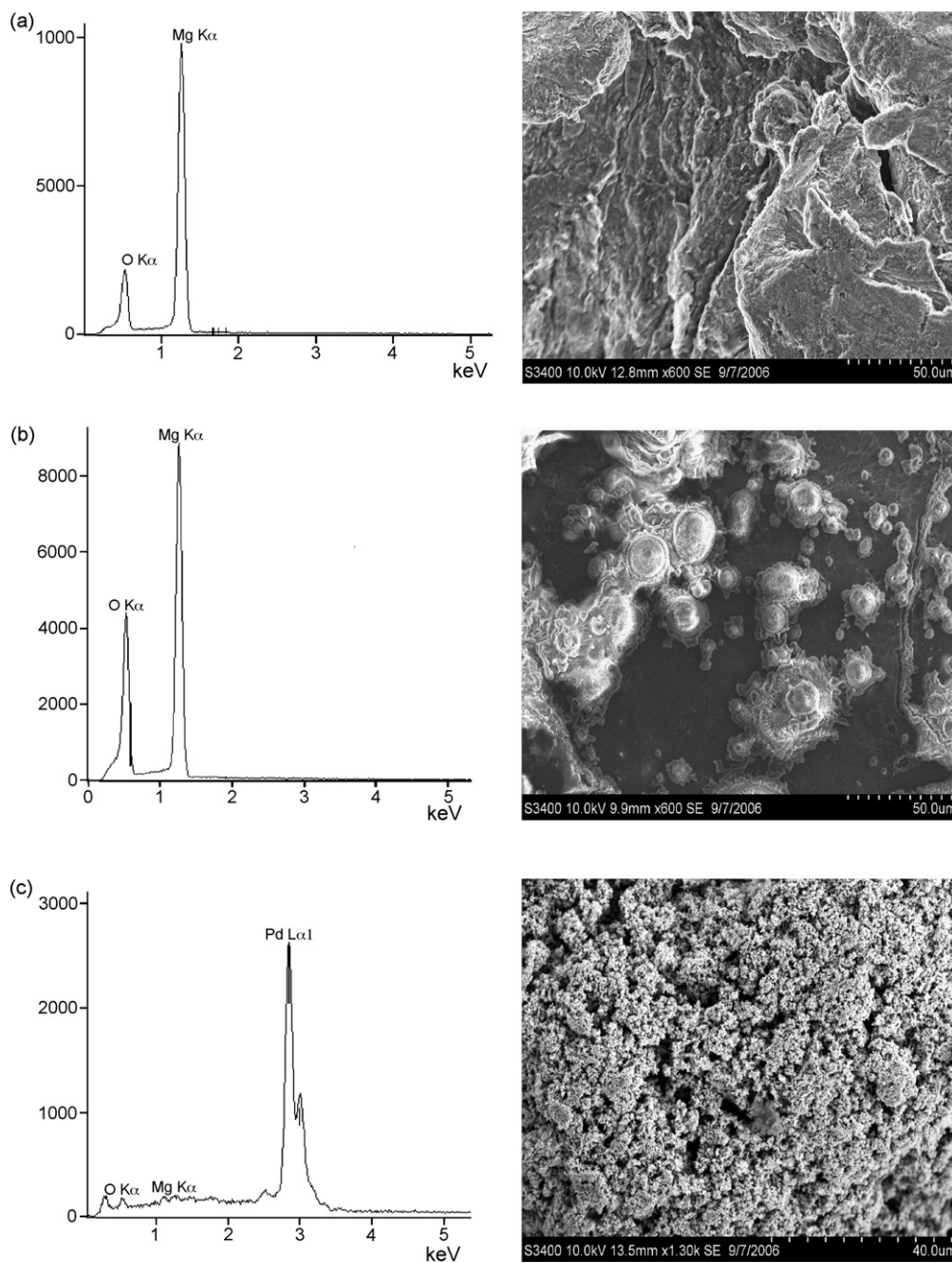


Fig. 8. SEM images and EDX profiles of (a) settled granule following reaction of Mg^0 with K_2PdCl_6 in 10 mg L^{-1} PCP solution for 5 min in the absence of acid, (b) settled granule following 1 h of reaction of Mg^0 with K_2PdCl_6 in the presence of 10 mg L^{-1} PCP and 175 mM acetic acid and (c) suspended black colloidal particles formed following 1 h of reaction of Mg^0 granules with K_2PdCl_6 in the presence of 10 mg L^{-1} PCP and 175 mM acetic acid.

tions of K_2PdCl_6 concentration at a fixed Mg^0 concentration of 154.5 mM in the presence of 175 mM acetic acid. Based on these results we considered Mg^0/K_2PdCl_6 concentration of 154.5 mM/0.063 mM for further experimentation. It may be noted that the ratio of Pd/Mg (0.173% w/w) determined by us was lower than that reported (0.266% w/w) by Morales et al. [19]. Further calculations revealed that the mass ratio (milligrams of Pd^0 used/milligrams of PCP treated) of 0.65 achieved almost complete removal of PCP as compared to the ratio of 0.81 as reported by Morales et al. [19].

3.5. Comparison of initial rates of dechlorination of chlorophenols in CMBR

It is expected that the energy required for disrupting equivalent number of C–Cl bonds in MCP would be lesser or greater than that of TCP or PCP. Therefore, experiments were conducted wherein the initial concentrations of PCP, 2,4,5-TCP and 2-CP in the reaction phase were adjusted to achieve organic chlorine equivalence (6.67 mg L^{-1}) and individually reacted with Mg^0/K_2PdCl_6 (154.5 mM/0.063 mM). The time dependent profiles for the removal of the above listed chlorophenols are compared in Fig. 7. The inset figure shows a comparison of time dependent profiles for the disappearance of organically bound chlorine for the three chlorophenols (calculated on the basis of residual concentration of all categories of chlorophenols as detected by GC-ECD at a particular time point). It may be noted that the rate and extent of organic chloride removal followed the order: 2-CP > 2,4,5-TCP > PCP. Similar results were also reported by Morales et al. [19]. Hoke et al. [30] studied dechlorination of chlorophenols using various reducing agents with Pd/C catalyst and reported reduction in rates with increasing number of chlorine atoms on the ring. The differences in the reaction rates may be explained on the basis of dechlorination mechanism that involves two steps. The first step is possibly the slow and direct heterolytic cleavage of C–Cl bond accompanied by the formation of a transient carbocation (electron deficient carbon) on the phenol ring. In the second step, the unstable carbocation combines rapidly with a nucleophile (presumably palladium hydride) to complete the octet of the positively charged carbon.

In the case of chlorophenols, the stability of transient carbocation and hence the overall rate of dechlorination is determined by the number of electron-withdrawing substituent groups such as chlorine atoms on the ring. More number of chlorine atoms on the ring (as in the case of PCP) tend to intensify the positive charge on the aromatic ring, destabilize the carbocation thereby reducing the overall rate of dechlorination reaction. The results obtained using Mg/Pd system were in contrast to earlier observations using Mg/Ag system wherein the rate and extent of removal of chlorophenols decreased substantially with the decrease in the number of chlorine atoms on the phenol ring [21]. Survey of literature in general, also revealed that dechlorination reactions mediated by zero-valent metals and bimetallic systems were increasingly difficult with decrease in the number of chlorine atoms on phenol ring [20,31].

3.6. Scanning electron microscope and energy dispersive X-ray spectroscopy analysis of Mg/Pd bimetal system at various stages of reaction

SEM images and corresponding EDX profiles are shown in Fig. 8. Fig. 8(a) shows the surface of a settled granule collected following reaction of Mg^0 with K_2PdCl_6 in PCP solution for 5 min in the absence of acid. The surface appeared similar to that of native, unreacted magnesium [21] while the adjoining EDX profile revealed the presence of a prominent peak of magnesium with no deposition of Pd^0 . Fig. 8(b) shows the surface of a settled granule collected following reaction of Mg^0 with K_2PdCl_6 in PCP solution for 1 h in the presence of acid. The presence of spherical deposits on the surface of granules were noted. The dominant peak corresponding to magnesium and increase in the height of oxygen peak in the adjacent EDX profile suggested that these deposits were corrosion products such as oxides and hydroxide of magnesium which were responsible for sorption of PCP and its reaction products. Absence of palladium peak suggested non-existence of Mg/Pd bimetallic interface. Fig. 8(c) shows SEM image of a suspended black particle collected following 1 h of reaction of Mg^0 with K_2PdCl_6 in PCP solution in the presence of acid. The presence of a dominant peak of palladium and relatively insignificant peak of magnesium in the

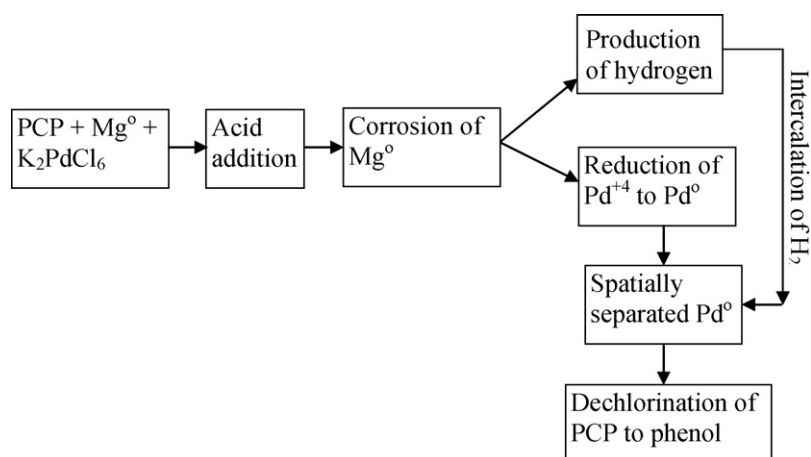


Fig. 9. Schematic representation of events occurring during dechlorination of pentachlorophenol (PCP) by Mg/Pd system.

adjacent EDX profile suggested that Pd⁰ particles were indeed spatially separated from magnesium granules. It may further be noted from Fig. 8(c) that Pd⁰ particles offered large surface area for intercalation of hydrogen and thus facilitated rapid dechlorination of PCP. On the basis of analyses of results presented in Fig. 8(a) sequence of events occurring during dechlorination reaction was proposed which is shown in Fig. 9.

4. Conclusions

Following salient points emerge from our study:

- (i) Pd⁰/Mg⁰ is an efficient system for complete dechlorination of PCP all the way to phenol.
- (ii) The rate and extent of organic chloride removal followed the order: 2-CP > 2,4,5-TCP > PCP.
- (iii) It is important to include acid in the system, to serve triple purposes of (a) corrosion of zero-valent metal and reduction of Pd⁴⁺ to Pd⁰, especially while treating low concentrations of PCP, (b) provision of protons to produce H₂ and (c) retardation of formation of insoluble oxides and hydroxides that may sorb PCP and its dechlorinated products.
- (iv) Mg⁰ in combination with *in situ* reduced palladium is more efficient in dechlorinating PCP as compared to Mg⁰ in combination with *ex situ* reduced palladium.
- (v) Pd⁰ produced by the reduction of Pd⁴⁺ was observed to be spatially separated from magnesium granules. These colloidal palladium particles intercalate hydrogen efficiently and mediate reductive dechlorination.

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