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Dechlorination of chlorophenols by zero valent iron impregnated silica

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Abstract

Laboratory studies were conducted to find out the efficacy of uniquely prepared zero valent iron impregnated silica in transforming xenobiotic chlorophenols namely 4-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol. Continuous mode column experiments were performed to investigate the transformation of chlorophenols by varying pH, column height, flow rate and initial chlorophenol concentration. Reusability study of the zero valent iron impregnated silica was studied as well as the morphological changes and the chemical composition of the catalyst medium were also investigated. Dechlorination kinetic studies were conducted and the order of dechlorination of chlorophenols was found to be 2,4,6-trichlorophenol > 2,4-dichlorophenol > 4-chlorophenol. The optimum pH, column height and flow rate were found to be 7, 20 cm and 0.75 L/hr respectively for all chlorophenols in the reaction duration of 4 hr. Intermediates formed during dechlorination study were identified by gas chromatography-mass spectroscopy analysis. This method was applied to real pulp and paper wastewater and was found satisfactory.

Key words: zero valent iron; silica; chlorophenols; dechlorination

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Introduction

Chlorophenols are used as disinfectants, biocides, preservatives and pesticides (Canadian Council of Resources and Environment Ministries, 1987; National Research Council of Canada, 1982). The International Agency for Research in Cancer (1986) has classified chlorophenols as possible human carcinogens. The acute toxicity (96 hr LC₅₀) of 4-chlorophenol (CP), 2,4-dichlorophenol (DCP) and 2,4,6-trichlorophenol (TCP) has been reported to be 3.8, 2.0 and 0.3 mg/L to bluegill sunfish (US Environment Protection Agency, 1986). The acute toxicity values show that with increase in the chlorine content of the benzene ring, the toxicity also increases. Hence, it is necessary to dechlorinate chlorophenols (CPs) from the industrial effluent.

Zero valent iron (Fe⁰-ZVI) is a mild reducing agent with reduction potential of -0.440 V. Treatment of recalcitrant chemicals using ZVI has been a main focus of research. It has been widely used for the degradation of pesticides (Ghauch, 2001), nitro aromatic compounds (Agrawals and Tratnyek, 1996), nitrates (Huang et al., 1998), chlorinated solvents (Ghillham and O'Hannesin, 1994), azo dyes (Cao et al., 1999) and chloro organic pollutants (Ishai et al., 2005). Recently, ZVI in form of nano particles have gained much attention due to its higher efficiency than the normal iron metal in the transformation of pollutants (Kim et al., 2008; Li et al., 2006, 2007). The potential risk of using nano ZVI (nZVI) is that it can agglomerate and

accumulate in the effluent as well as due to its nano nature it can get through the skin of the aquatic organisms. The different methods available for the preparation of ZVI are sonochemical (Suslick et al., 1996), chemical vapour condensation (Lee et al., 2005), thermal decomposition (Peng et al., 2006) and chemical reduction (Margeat et al., 2005). In the above mentioned methods the source of iron used was Fe(AOT)₂, Fe(CO)₅, FeCl₃ and FeCl₂. The main drawback for using ZVI was its accumulation in the effluent after the treatment.

In this article, an attempt has been made to prepare ZVI immobilized in silica with the help of sonication for better impregnation and to find its dechlorination efficiency for chlorophenols in continuous column mode. The ZVI immobilized silica can be reused and also the potential risk caused due to nZVI to the environment can be avoided. Hence, it is more environmental friendly than nZVI.

1 Materials and methods

1.1 Chemicals

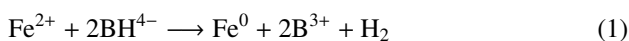
4-Chlorophenol, DCP, TCP (≥ 99% purity), ferrous sulphate hepta hydrate (FeSO₄·2H₂O, 99%–100% purity), sodium borohydride (NaBH₄ > 98% purity), concentrated sulphuric acid (H₂SO₄, 98% purity) and coarse silica (3–5 mm) used as dessicant were purchased from Merck, India. Sodium hydroxide was supplied by Chemical Drug House, India. All the chemicals were of analytical grade and were used without any further purification. All the reagents were

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prepared with distilled water.

1.2 Preparation of ZVI impregnated silica

The preparation was carried out by simple liquid-phase reduction. About 1 g of silica was first washed with water and then soaked in saturated $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution (6.5 g in 25 mL with 2 drops of concentrated H_2SO_4) for half an hour. After that, the soaked silica along with the saturated $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution was sonicated in an ultrasonic bath (Bandeline, Sonorex RK 52 H) for another half an hour. During sonication, the silica gets broken down to small pieces (1–3 mm). After sonication, the silica was washed thoroughly with distilled water. To the washed silica, 0.1 mol/L NaBH_4 was added slowly at ambient temperature, pressure and atmosphere. The ferrous ion impregnated into the silica was reduced to ZVI as per the following Reaction (1).



When the evolution of hydrogen gas ceased, the water was decanted and the silica was washed again quadruple time with distilled water to remove residual ferrous and unattached ZVI. The boron particles formed during the preparation of ZVI has to be taken care of separately as it is toxic in nature (Nikolay et al., 2009; Xuyang et al., 2009). The silica was dried and stored in a container without any preservative or controlled atmosphere.

Another experiment was carried out to impregnate ZVI on silica without sonication. The protocol mentioned above was followed as it is, except sonication. As soon as the hydrogen evolution ceased, the silica was washed with distilled water. Almost all the black patches covering the silica came off with wash water whereas in case of sonication the ZVI impregnation was firm. This kind of sonolytic enhancement in the impregnation of silica is due to acoustic cavitation bubble theory in which micro bubbles get formed and collapses creating localised area of high temperature and pressure. Due to this micro jets of solvents are formed which are reported to be perpendicular to the surface of the solid and with a speed of 100 m/sec hits the surface creating micro holes (Lacin et al., 2005). These micro holes become the active sites of adsorption of ferrous leading to better impregnation of iron onto silica.

1.3 Experimental procedure

Experiments were conducted out to transform chlorophenols in continuous column mode in which 500 mL of initial volume of CPs were recirculated using flow rate controllable peristaltic pump (PP10 EX, Miclins, India). The continuous column mode (recirculation) system increases the contact time between the reductant ZVI and the pollutant. This enhances the efficiency of the system. The total length of the column was 47 cm, outer diameter and inner diameter were 1.10 and 0.85 cm respectively. For the initial study, silica packed column height was taken as 10 cm. The pH of the solution was adjusted with concentrated sulphuric acid/sodium hydroxide (1 mol/L). The initial concentration of the chlorophenols was taken as 100 mg/L.

1.4 Analytical methods

The expected end product chloride ions were analysed by Ion Chromatograph, DX-120, Dionex, UK provided with Ion pack AS-4 Column, a pre guard column, auto suppression and a conductivity detector. The eluent used was 3.5 mmol/L Na_2CO_3 + 1.0 mmol/L NaHCO_3 at a flow rate of 1.0 mL/min. The samples were filtered through Gelman 0.2 μ acrodisc. The retention time for chloride was (4.20 \pm 0.50) min.

The morphology and chemical analysis of the ZVI impregnated silica were determined by electron dispersive spectrophotometer (EDS) combined with high resolution scanning electron microscope (HR-SEM) from Hitachi (Model No. S-3400N, Hitachi, USA). Gold coating was given with the help of Ion Sputter coater with gold target E1010. It has IRCC D camera for chamber viewing. The EDS detector system was LN2 free and peltier cooled (139 eV).

The amount of iron impregnated on the silica was cross checked with inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Thermo electron corporation, UK). The iron was leached out of the silica in sulphuric acid (0.5 mol/L) and then was analysed.

Intermediate product identification was carried out by Gas Chromatograph/Mass Spectrometer. Agilent 6890 N plus GC and Agilent 5973 N (Palo Alto, USA) mass spectrophotometer with a quadrupole analyser were used for identification of intermediate products. Fused capillary column used was DB 1701 with a length of 30 m, diameter of 0.25 mm and inner diameter of 0.25 μm and it was coated with chemically bonded 14% cyanopropyl-phenyl-methyl siloxane. The column temperature was programmed from 80°C held for 3 min to 300°C held for 7 min at a rate of 15°C/min. Carrier gas was helium (99.999%), the flow rate was 1.2 mL/min and the scan range was 50–600 amu. The samples were extracted twice with 50 mL ethylacetate. The extract was passed through a column packed with anhydrous sodium sulphate to remove trace water.

2 Results and discussion

2.1 Characterisation of ZVI immobilised silica

Figure 1a as well as Fig. 2a show the high resolution Scanning Electron Microscopic image, EDS spectrum of freshly prepared ZVI impregnated silica and its percentage chemical composition respectively. The SEM image shows a smoothened surface of silica with ZVI impregnation. The white patches are iron whereas the black patch is silica. The surface looks uniform because the micro holes formed during sonication has been filled with ZVI. The presence of iron in the chemical composition confirms the impregnation of ZVI. The ICP-AES analysis of the leached out iron, reconfirmed the percentage of iron to be around 8.5%. The EDS spectrum showed high percentage composition of silica and oxygen which are the main constituents of the silica. The energy spectrum indicates that the only reducing agent present in the silica is iron,

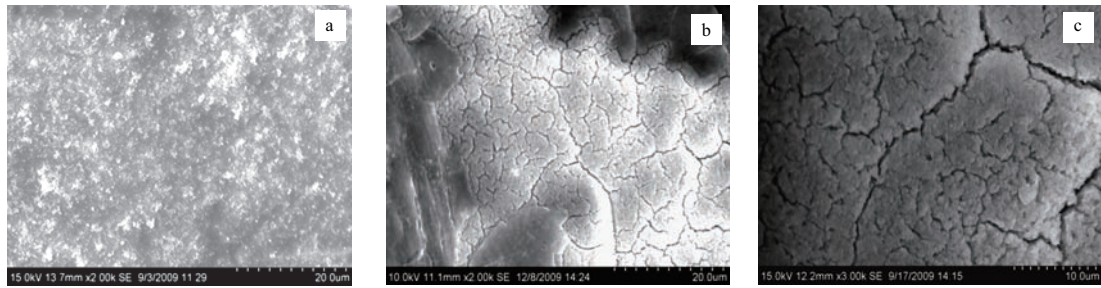


Fig. 1 HR SEM images of freshly prepared zero valent iron (ZVI) impregnated silica (a), after one trial run (b) and after five trial runs (c).

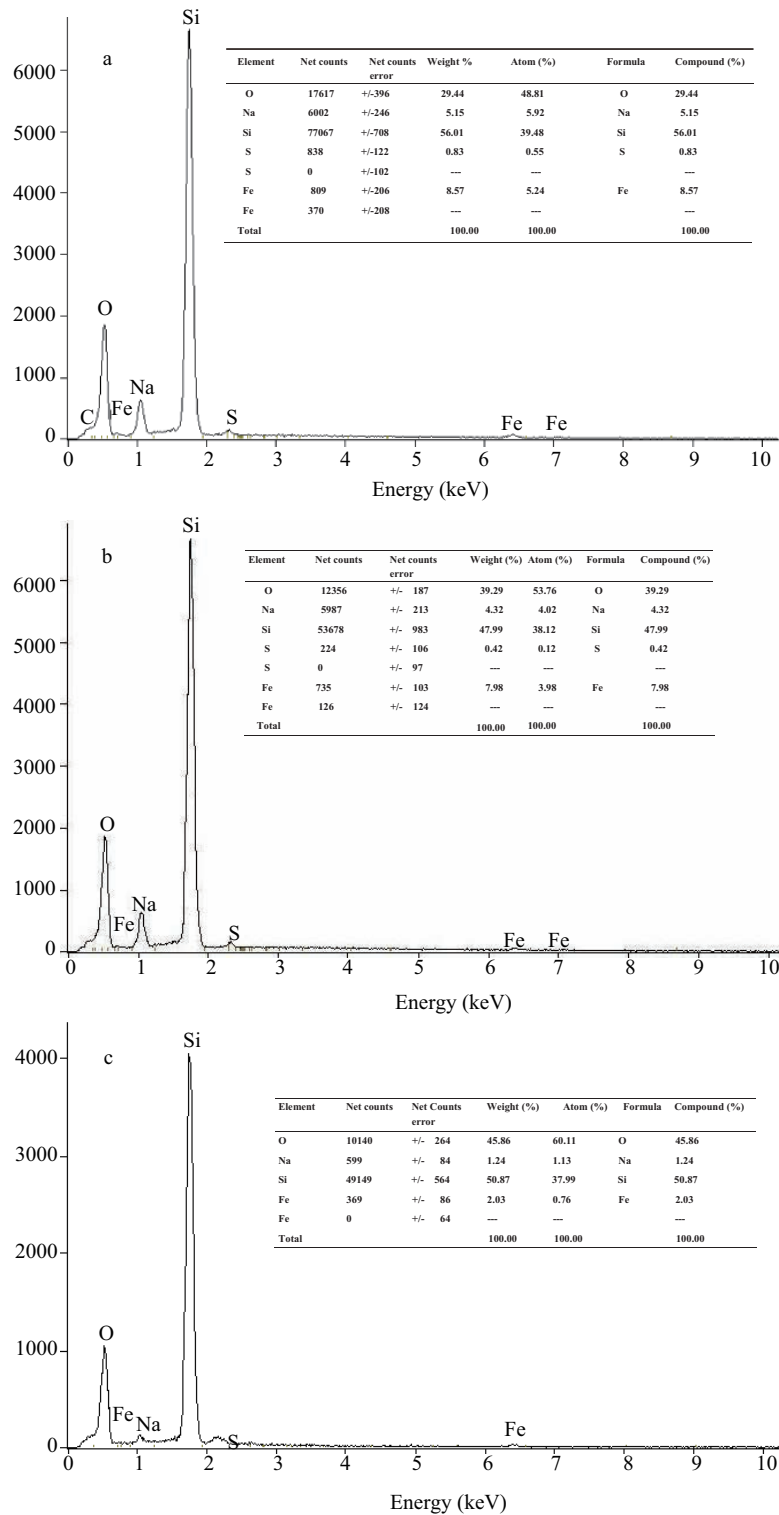


Fig. 2 EDX spectrum for freshly prepared ZVI impregnated silica (a), after one trial run (b) and after five trial runs (c).

which has the capability of dechlorinating CPs.

The ZVI impregnated silica was stored in a plastic container without any controlled atmospheric condition. After one week of storage, the ZVI impregnated silica was still black in colour. Figure 3a and b show the XRD spectrum of freshly prepared ZVI impregnated silica and after one week of storage respectively. The diffraction peak of iron corresponds to that of ZVI as per JCPDS No. 06-0696, the XRD obtained by other authors also supports the data (Li et al., 2010). It could be seen that even after one week of storage, ZVI is still present in the silica (2θ value 44°). Hence, the simple protocol proposed for the preparation of ZVI impregnated silica can also increase its shelf life also.

2.2 Transformation of chlorophenols

2.2.1 Iron leachability study

Experiments carried out in the pH range of (2 to 12), using distilled water (blank run) to find out the leachability of ZVI impregnated into silica, showed that the leaching of iron was higher and spontaneous in the case of highly acidic (pH 2) as well as alkaline (pH 12). This might be due to the immediate conversion of ZVI into soluble ferrous (acidic condition) and ferric (alkaline condition). At pH 4, 6, 7, 8 and 10, the amount of iron leached out was 29.5, 17.3, 10.1, 34.8 and 63.9 mg/L. pH 7 had minimum amount of iron leaching out when compared with other pHs. To facilitate maximum usage of ZVI impregnated silica further experiments were conducted in the pH range of 4 to 8 only.

2.2.2 Effect of solution pH on dechlorination of chlorophenols

The initial concentrations of the chlorophenols were kept as 100 mg/L. The reactant volume, column height and flow rate were 500 mL, 10 cm and 1 L/hr respectively. Figure 4 illustrates the dechlorination profile for chlorophenols at different pH values. The experiments were carried out at pH 4, 6, 7, 8 and 10. The chloride release was monitored at different time intervals, which was then converted into the dechlorination of chlorophenol.

The general scheme of reaction for the dehalogenation

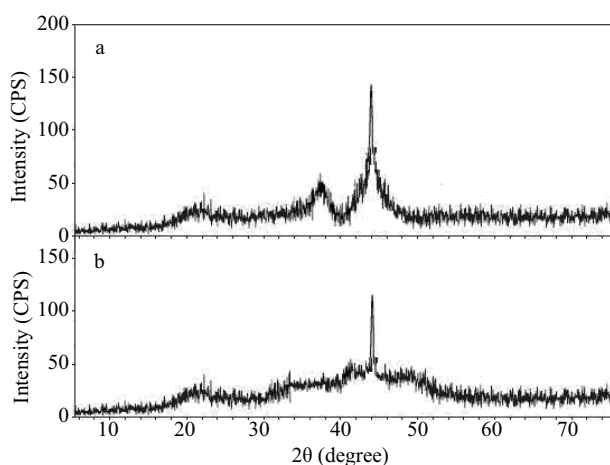


Fig. 3 XRD pattern of freshly prepared ZVI impregnated silica (a) and ZVI impregnated silica after one week of storage (b).

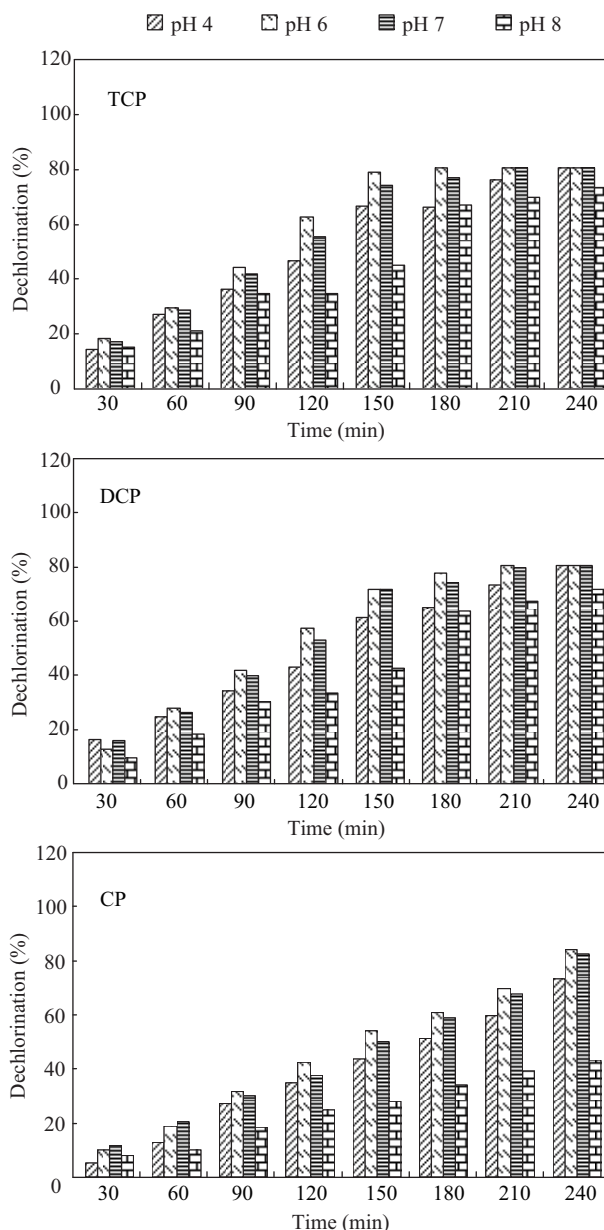
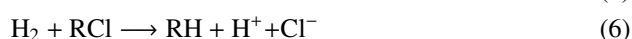
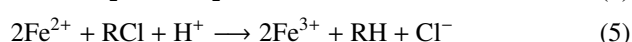
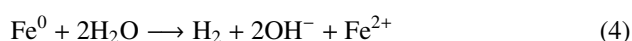
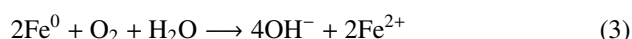


Fig. 4 Dechlorination profile of 2,4,6-trichlorophenol (TCP), 2,4-dichlorophenol (DCP) and 4-chlorophenol (CP) at different pH values.

of CPs is given below (Deng et al., 1999) in Reactions (2)–(7). From the Reactions (2)–(6), it could be inferred that theoretically not only the presence of protons but also presence of hydrogen, oxygen as well as water in the system, help in dechlorination of chlorophenols (Reactions (3) and (5)). The last Reaction (7) signifies the loss of ZVI from the system through formation of stable ferric hydroxide.



pH 6 and 7 had near about the same efficiency at the end

of 4 hr for all the three chlorophenols. Since, neutral pH is always better for treatment of wastewater, pH 7 was chosen as the optimal pH. The work reported by Gillham and O'Hannesin (1994) on dechlorination of TCE also supports the better efficiency of ZVI at neutral pH.

In general, it can be inferred from Fig. 4 that the highly chlorinated phenols are degraded easily, i.e., the decreasing order of dechlorination is TCP < DCP < CP. The increasing reactivity with respect to increase in number of chlorine atoms might be due to two reasons (1) the decreasing C-Cl bond dissociation energy with increasing number of chlorine atoms and (2) the availability of chlorines in stabilizing radical intermediates (Kim and Carraway, 2003). TCP, DCP and CP were dechlorinated in 3.30 (100%), 4.00 (100%) and 4.00 hr (85.6%) respectively at pH 7.

No buffers were used during the reactions. An increase in the pH of the reaction mixture was noted. In the case of initial pH 7, the solution pH at the end of reaction in 4 hr was 9.21, 8.93 and 9.87 for TCP, DCP and CP. Since these pH values are above the pK_a values of the chlorophenols, the target compounds existed in the anionic form. This is an added advantage as anionic form of chlorophenol is available more easily for reduction than the neutral molecular form, as complete molecules of chlorophenols are less soluble in water and the solubility decreases as number of chlorine atoms increases. The increase in pH of the system is contributed by two factors: (1) the overall dechlorination reaction utilises proton; (2) as the parent compounds were converted to less chlorinated phenols, pH of the aqueous solution may gradually increase as the pK_a increases for chlorophenols as chlorine decreases (Kim and Carraway, 2003).

After running the experiment for one cycle at pH 7, SEM and EDS spectrum was taken to find the morphological and compositional change in the ZVI impregnated silica. Figure 1b and Fig. 2b show the HRSEM image, EDS spectrum and the composition of the ZVI impregnated silica after first cycle of dechlorination of CP. The image shows cracks on the surface of the iron impregnated silica which might be due to the weathering of silica by the force of aqueous solution passing through the column during continuous recirculation of the sample solution. The EDS spectra and the composition showed a decrease in iron content from 8.57% (freshly prepared ZVI impregnated silica) to 7.98% (after 1 run) which confirmed that there has been leaching out of iron from the ZVI impregnated silica.

2.2.3 Column height

The column height was varied from 5 to 25 cm to find its effect on the dechlorination of chlorophenols. Chlorophenol solutions were allowed to pass through the column at a rate of 1 L/hr and the results are illustrated in Fig. 5. As the column height and the amount of iron loaded had positive correlation, the percentage dechlorination increased with respect to increase in column height. When the column height was increased from 5 to 20 cm there was an increase in the dechlorination percentage. Above 20 cm, i.e., at 25

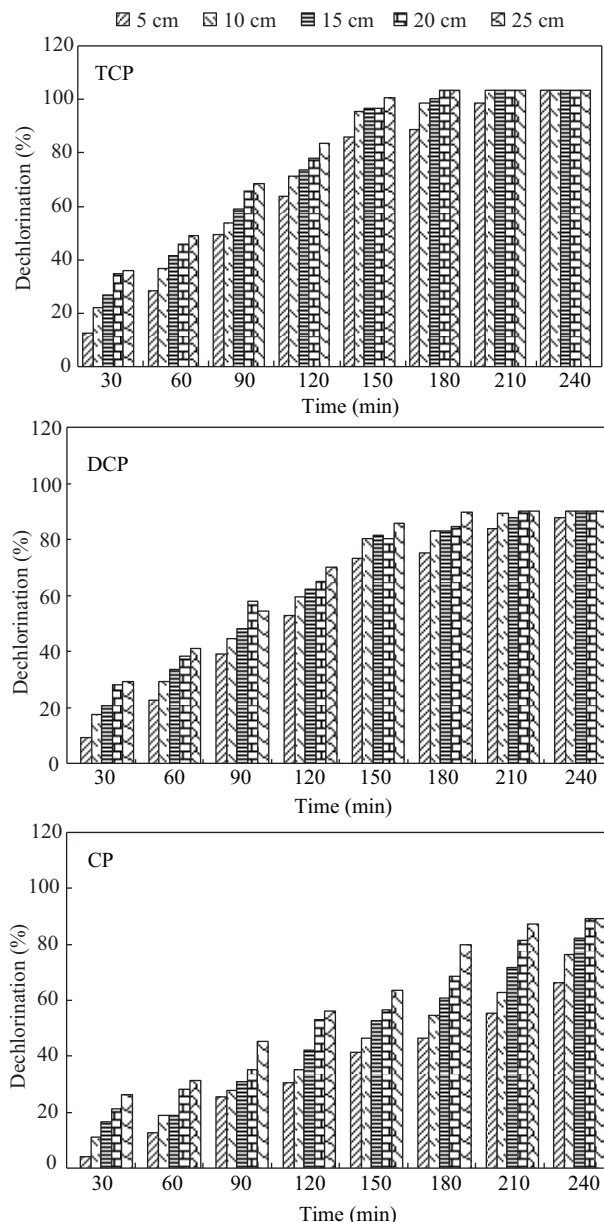


Fig. 5 Effect of column height on the dechlorination of TCP, DCP and CP.

cm the dechlorination efficiency was levelled off. Hence, further studies were carried out at 20 cm as the efficiency remained almost the same on increasing the column height.

2.2.4 Flow rate

Optimisation of flow rate for maximum dechlorination efficiency was conducted for all the chlorophenols. Constant column height of 20 cm was maintained throughout the study. The chlorophenol solution was allowed to flow through the catalyst by varying the flow rate from 2 to 0.5 L/hr. The results are presented in Fig. 6. When the flow rate was increased from 0.5 to 0.75 L/hr, there was a slight increase in the dechlorination efficiency of the system, whereas above 0.75 L/hr of flow rate, there was decrease in efficiency with increase in flow rate. Decrease in flow rate increases the contact time between the chlorophenol molecules and the active sites of the catalyst leading to increased efficiency. TCP, DCP and CP

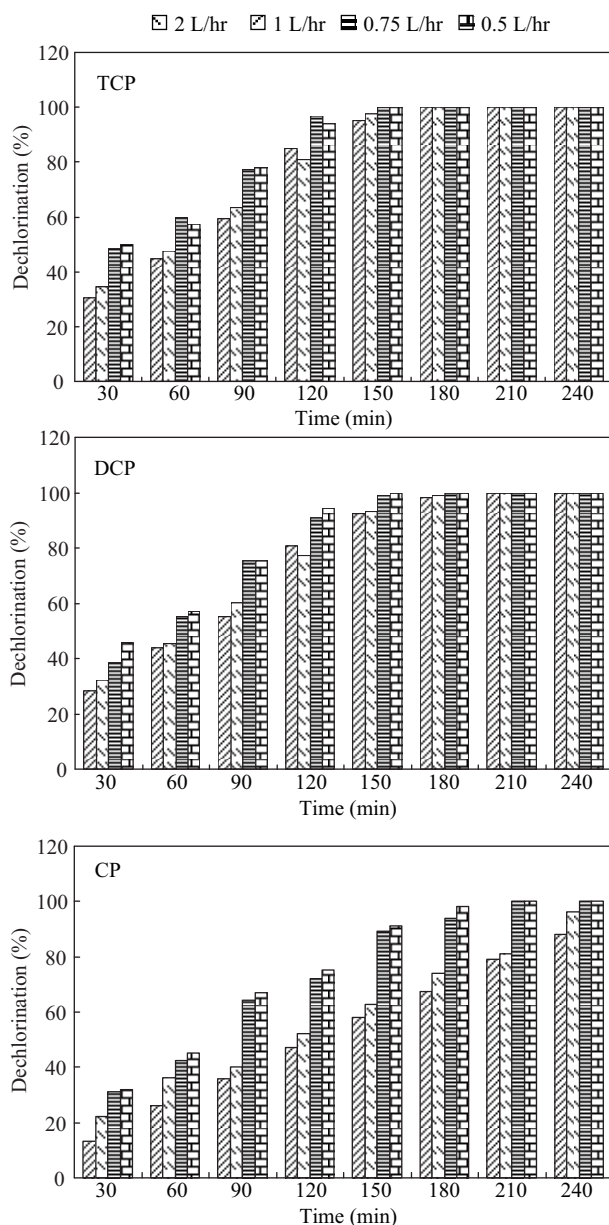


Fig. 6 Effect of flowrate on the dechlorination of TCP, DCP and CP.

were completely dechlorinated in 2.30, 3.00 and 3.30 hr respectively with flow rate of 0.75 L/hr. Hence, further studies were conducted at this flow rate only.

2.2.5 Initial Concentration

The investigation was carried out to find the dechlorination efficiency of the system with various initial concentrations of chlorophenols (100, 200, 300, 400 and 500 mg/L). The results are shown in Fig. 7. It could be seen that as the concentration of CPs increases the dechlorination efficiency of the system decreases, especially for concentration > 200 mg/L of CPs. But the difference between 100 and 200 mg/L was insignificant when compared with higher concentrations. This might be due to the insufficient sites for dechlorination purpose to accommodate higher concentration of CPs. This kind of difficulty in degrading higher concentration of CPs by ZVI has also been observed by other researchers (Johnson et al., 1996; Nam and Tratnyek, 2000).

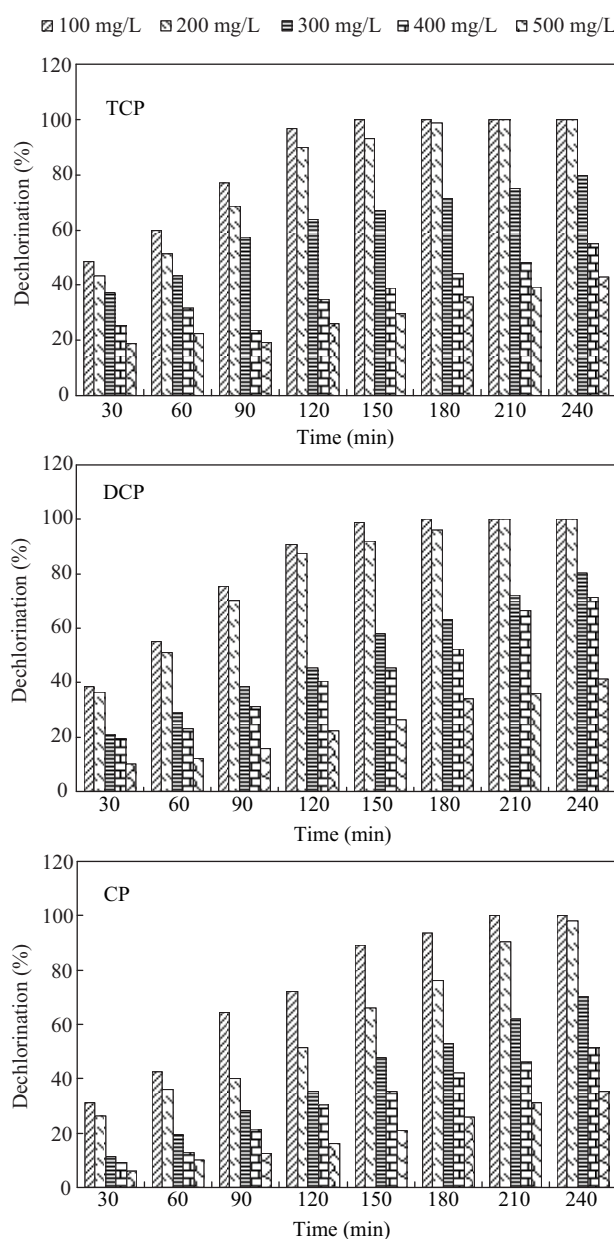


Fig. 7 Effect of initial chlorophenol concentration on the dechlorination of TCP, DCP and CP.

2.2.6 Reusability study

The main advantage of a heterogeneous system is the reusability of catalyst. The reusability study was carried out with TCP as model compound. There was a decrease in the dechlorination efficiency of the system from 100% dechlorination to 46% and 38% in 4th and 5th cycles respectively after time duration of 4 hr (Result not shown), which might be due to leaching out of the iron from the system. The iron content leached out from the system after each cycle was 3.3, 19.8, 27.9, 69.3 and 83.7 mg/L in the initial 5 min of the reaction. From the values, it can be inferred that as the number of cycles increased, the amount of iron leached out also increased. Reimpregnation of ferrous ions onto silica was also tried by soaking it in saturated ferrous sulphate solution. Sonication was not done, as it leads to breaking down of silica into fine particles and within 5 min of sonication, only powdered silica

was left behind in the solution. After soaking, the silica was treated with sodium borohydride, but only patches of ZVI (black colour) were adhered onto the silica, which was even lesser than that before reimpregnation. Hence, reimpregnation is not possible which might be due to its change in morphological structure and strength of silica after each cycle.

After the 1st and 5th cycles, the ZVI impregnated silica was again analysed by EDS, HRSEM analyser (Fig. 1b, 1c and Fig. 2b, 2c). There were lots of wide cracks on the surface of the silica and the composition analysis showed that there was a remarkable decrease in iron content (from 8.57% to 2.03%). These results account for the decrease in the efficiency of the system towards the fifth cycle.

2.2.7 Dechlorination pathway for chlorophenols

The chlorine group of the chlorophenols is highly electronegative and electron withdrawing group. Due to the negative potential of ZVI, it tends to lose electrons to become ferrous. Hence, it is highly attracted towards the chlorine group of chlorophenols, leading to the dechlorination of chlorophenols. The intermediates for all the three chlorophenols are identified with the help of GC/MS analysis. The chromatogram is given in Fig. 8 and the intermediates are listed in Table 1. The pathway is shown in Fig. 9. From the pathway, it is evident that the electron from ZVI is first transferred to the chlorine group nearer to the hydroxyl group leading to its liberation as chloride ion. This might be due to increase in electron deficiency in the proximity to chlorine group near the electron withdrawing hydroxyl group. Hence, only CP and phenol have formed during dechlorination of DCP, also TCP dechlorination lead to formation of DCP, CP and phenol.

2.2.8 Kinetics for dechlorination

Kinetics for dechlorination was studied at optimum condition with respect to generation of chloride ions. The dechlorination of CPs by ZVI is given in Reaction (2). The rate of reaction with respect to chloride generation can be written as follows:

$$d[\text{Cl}^-]/dt \longrightarrow k[\text{Cl}^-] \quad (8)$$

The order of reaction with respect to chloride generation was found to be first order. The slope obtained from $\ln C_0/C_t$ vs. time plot (Fig. 10) gives the rate constant of the reaction. The rate constant for TCP, DCP and CP was found to be 0.007, 0.005 and 0.003 min^{-1} .

Table 1 Identified intermediates of dechlorination of chlorophenols

	Retention time (min)	Compound	<i>m/z</i>
CP	5.05	Phenol	94
DCP	5.05	Phenol	94
	7.73	4-Chlorophenol	128.45
TCP	5.05	Phenol	94
	7.73	4-Chlorophenol	128.45
	8.35	2,4-Dichlorophenol	162.9

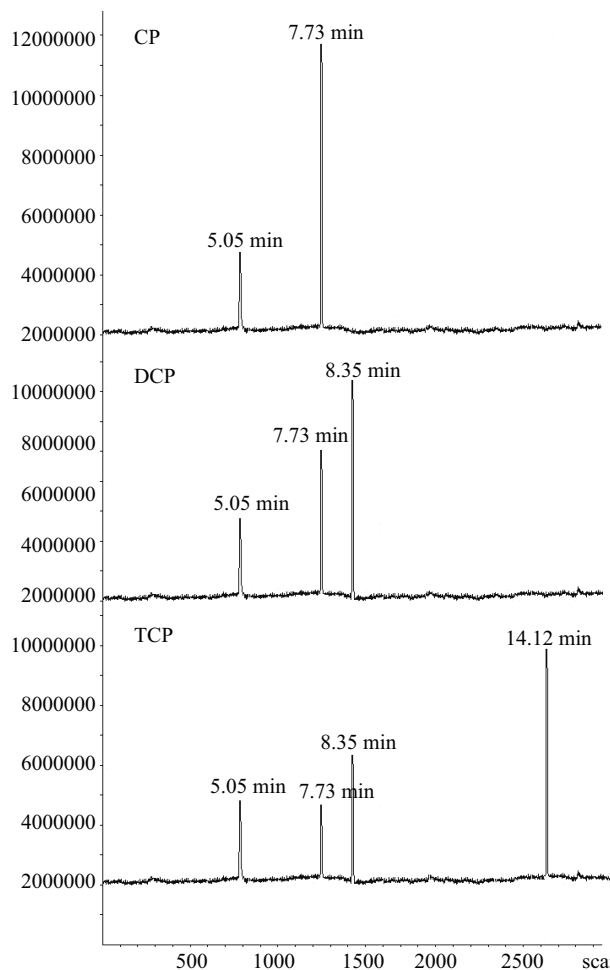


Fig. 8 Chromatograms for dechlorination intermediates of CP, DCP and TCP.

2.2.9 Characteristics of wastewater before and after treatment

The wastewater was collected from pulp and paper industry which is located in Tamil Nadu, India. The conventional pulp bleaching uses chlorine as bleaching agent. The advantage of using chlorine compounds is simply because of its low cost and high effectiveness in bleaching. As ZVI impregnated silica is able to dechlorinate only, the parameter Adsorbable Organic Halide was introduced in this section to know about the amount of organic halides dechlorinated. Details about wastewater characteristics are furnished in Table 2. Almost 93% of the organic halides were dechlorinated in the wastewater.

Table 2 Details about pulp and paper industrial wastewater before and after treatment

Parameter	Before treatment	After treatment
pH	8.12	7.42
EC ($\mu\text{S}/\text{cm}$)	5132	5815
TDS (mg/L)	2314	2419
Chloride (mg/L)	151	574
AOX (mg/L)	381	25.2

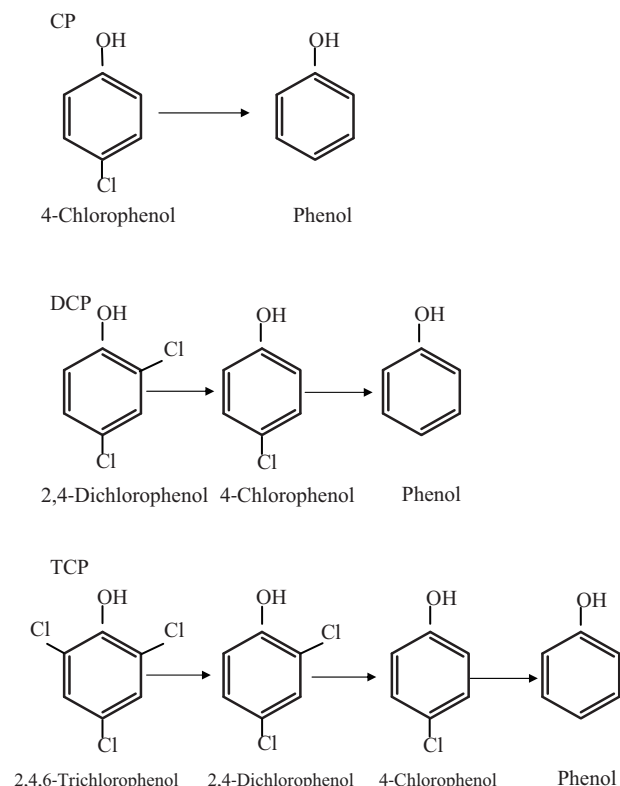


Fig. 9 Dechlorination pathways for CP, DCP and TCP by ZVI impregnated silica.

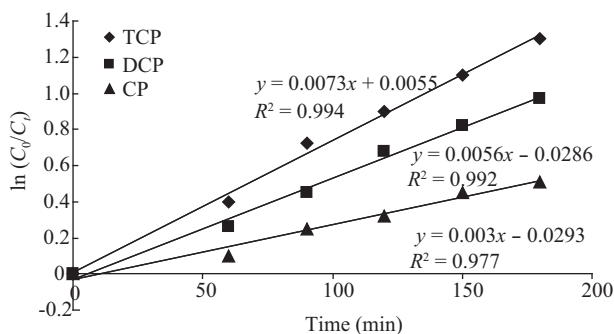


Fig. 10 Dechlorination kinetics for chlorophenols. Conditions: pH 7, column height 20 cm, flow rate 0.75 L/hr and chlorophenol concentration 100 mg/L.

3 Conclusions

The following conclusion can be stated from the present study. (1) ZVI impregnated silica can be used as a viable alternative, to homogeneous dechlorination of chlorinated phenols, which resulted in abatement of pollution due to release of iron after treatment into the environment. (2) The optimum pH of 7, column height and low flow rate increased the dechlorination of chlorophenols. (3) The rate of dechlorination with respect to chloride formation followed first order kinetics.

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