Degradation of chlorophenols by ferrous immobilized in alginate beads – heterogeneous Fenton method

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Abstract

Fenton's process has been one of the widely used methods for degradation of organic pollutants. But on the other hand secondary pollutant i.e. ferric arising as a byproduct after the treatment of pollutants, have been the main concern due to its mobilization into the environment and subsequent problems. To avoid this, it was investigated to immobilize ferrous in a support (alginate). EDS-HRSEM analysis revealed that almost 37% of freshly prepared ferrous alginate beads were made up of iron. The heterogeneous Fenton's method was used to degrade 4-chlorophenol (CP), 2,4-dichlorophenol (DCP) and 2,4,6-trichlorophenol (TCP), which were taken as model compounds. All the relevant parameters such as pH, H_2O_2 concentration and ferrous alginate dose were optimized. The effect of initial chlorophenol concentration, reactant volume and reusability studies were also carried out. Kinetic studies revealed that all the three chlorophenols followed pseudo first order and the order of ease of degradation was CP > DCP > TCP. This method was applied to real pulp and paper industrial effluent and was found to be efficient in reducing the phenols as well as COD in the effluent.

Keywords: Chlorophenols; Heterogeneous Fenton; Ferrous; Alginate; Paper and pulp industrial effluent

Introduction

Chlorophenols are group of chemicals containing chlorine atoms attached to hydroxy benzene rings and are mainly used in the manufacture of disinfectants, biocides, preservatives, pesticides as well as other chlorinated organic chemicals (CCREM 1987, NRCC 1982). Hence, the main industrial sources of chlorophenols are wood – processing plants, pesticide manufacturing and formulating plants and kraft pulp mills (NRCC 1982). Toxicity of chlorophenols increases with increase in the chlorine content on the benzene ring. The International Agency for Research in Cancer has classified chlorophenols as possible human carcinogens (IARC 1986). The acute toxicity (96 h LC_{50}) 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 (USEPA 1980).

The methods for removal or destruction of chlorophenols can be classified as biological, physical and chemical methods. The former method is not successful due to the toxicity of chlorophenols to biological systems, and the inability of the biological system to withstand shock load as well as longer retention time. The physical method like adsorption merely transfers the pollutants from one phase to the other and does not decrease the toxicity of the pollutant. The most widely known form of simple chemical methods for the destruction of organic compounds are chlorination, ozonation (David et al., 1995), Fenton's process (Barbeni et al., 1987).

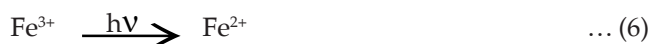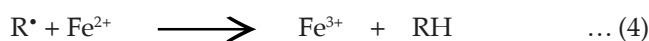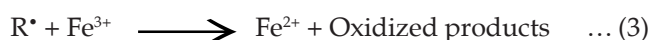Fenton (1894) reported that H_2O_2 could be activated by Fe (II) salts to oxidize tartaric acid. It was proposed that the active oxidant generated by the Fenton reaction is the hydroxyl radical ($^\bullet OH$), one of the most powerful oxidant Hydroxyl radicals produced during Fenton's reaction in acidic condition is the major reactant in degrading the chlorophenols. Equation 1 shows the Fenton's reaction (Walling, 1975).
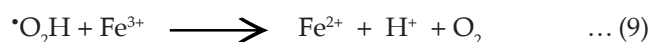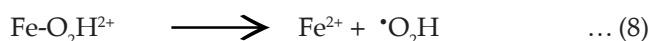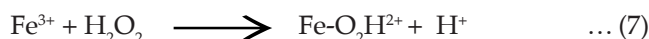
$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + {}^\bullet OH + OH^- \quad \dots (1)$$
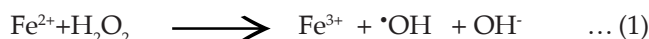
The hydroxyl radical generated further reacts with organic pollutants to form reactive organic radicals (equation 2).

$$^\bullet OH + RH \longrightarrow H_2O + R^\bullet \quad \dots (2)$$

The organo radicals formed react with Fe^{3+} and O_2 and gets oxidized.

$$R^\bullet + Fe^{3+} \longrightarrow Fe^{2+} + \text{Oxidized products} \quad \dots (3)$$

$$R^\bullet + Fe^{2+} \longrightarrow Fe^{3+} + RH \quad \dots (4)$$

$$R^\bullet + O_2 \longrightarrow ROO^\bullet \longrightarrow HO_2^\bullet + \text{Oxidized products} \quad \dots (5)$$

$$Fe^{3+} \xrightarrow{h\nu} Fe^{2+} \quad \dots (6)$$

Apart from these reactions, the ferric formed (as per equations 1 and 4) reacts with hydrogen peroxide and forms a complex intermediate $Fe\text{-}O_2H^{2+}$ (equation 7). This intermediate can be cleaved in the presence of sonication as Fe^{2+} and $°O_2H$ as per equation 8 (Zhu et al., 1996). The peroxyl radicals formed reacts with ferric to produce ferrous (equation 9).

$$Fe^{3+} + H_2O_2 \longrightarrow Fe\text{-}O_2H^{2+} + H^+ \quad \dots (7)$$

$$Fe\text{-}O_2H^{2+} \longrightarrow Fe^{2+} + {}^\bullet O_2H \quad \dots (8)$$

$$^\bullet O_2H + Fe^{3+} \longrightarrow Fe^{2+} + H^+ + O_2 \quad \dots (9)$$

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The ferrous ions formed react with hydrogen peroxide as per the classical Fenton's reaction to generate powerful hydroxyl radicals (equation 1).

The main drawback of Fenton's method is the inability to retrieve back the ferrous ion used up for the reaction due to the homogeneous nature of the reaction. Thus, replacement of homogeneous catalyst with heterogeneous ferrous iron came into existence where the catalyst can be separated from the waste stream. Many different ways like Nafion iron membranes, binders, cation exchange resins, chelating agents, doped photocatalysts etc have been tried and tested to immobilize the iron.

In this work, ferrous alginate beads were prepared and used for degradation of chlorophenols (CP, DCP and TCP) by heterogeneous Fenton method. The relevant parameters like pH, ferrous alginate dose and hydrogen peroxide concentrations were optimized. The kinetics for the degradation of chlorophenols was investigated. Finally, this method was tested with real pulp and paper wastewater effluent to find its efficacy in degrading organic pollutants.

MATERIALS AND METHODS

Reagents

Ferrous sulphate hepta hydrate, sodium alginate, sulphuric acid, hydrogen peroxide (30% w/v), 4-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol were of analytical grade, purchased from Merck. Distilled water was used to make aqueous solutions.

Preparation of ferrous alginate beads

Instead of preparing iron impregnated calcium alginate beads (Rocher et al., 2010, Kim et al., 2010) which requires treatment with ethanol, in this study ferrous alginate beads itself was prepared by a very simple procedure. Saturated solution (10 mL) of ferrous sulphate was mixed thoroughly with sodium alginate (1 g) to make a semi solid paste. This paste was introduced drop wise with the help of a dropper into a beaker containing distilled water adjusted to pH 2 with concentrated sulphuric acid. Within 5 min, the drops of ferrous alginate in the presence of acidic medium solidified into tiny pear shaped light green solids. The size of the beads varied from 1-3 mm.

Experimental set up

A 600 mL beaker was used as a reactor vessel. The reactor volume was taken as 500 mL. A known quantity of hydrogen peroxide and ferrous alginate were added into the chlorophenol solution. At regular intervals, the samples were drawn out and the chlorophenol concentration was measured spectrophoto meterically.

Analytical method

The chlorophenol concentration was determined spectrophotometrically by 4- amino antipyrine method[21]. The absorbance was measured at 500 nm using Spectronic 20 Genesys spectrophotometer. The detectable limit was found to be 0.30 mg/L, 0.25 mg/L and 0.58 mg/L for CP, DCP and TCP respectively.

The strength of hydrogen peroxide was found by Iodometric titration using standardized thiosulfate (Furniss et al., 1996).

The degradation efficiency of the method was determined in terms of COD. An open reflux dichromate titrimetric method as per standard method procedure (APHA 1995) was employed for COD measurements. The mineralization efficiency was calculated by estimating the TOC using Micro C model 1997 (Analytik Jena, Germany) with auto sampler liquid injector ALS-C-104. Samples were pretreated by adjusting the pH to 2.0 with 10 % H_3PO_4 solution to remove any inorganic carbon formed during oxidation reaction.

The morphology and chemical analysis of the ferrous alginate beads were determined by Electron Dispersive Spectrophotometer (EDS) combined with High Resolution Scanning Electron Microscope (HR-SEM) from Hitachi (Model No. S- 3400 N). Gold coating was given with the help on 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).

RESULTS AND DISCUSSION

Characterization of ferrous alginate beads

Freshly prepared ferrous alginate beads were subjected to EDS-HRSEM analysis. The content of iron was found to be 37.01%. Figure 1 is the HRSEM image of ferrous alginate which shows the cross linked fibrous structure of ferrous alginate. The EDS spectrum is shown in Figure 2. From the HRSEM and EDS mapping data, it is confirmed that iron is immobilized inside the alginate. Presence of iron in the form of ferrous and not in the form of ferric was confirmed by simple chemical method. The addition of 1,10-phenanthroline solution lead to change of color of the bead from pale green to blood red color, which is a confirmatory test for ferrous ion. Whereas, the addition of ammonium thiocyanate solution, did not change the color of the beads. This confirms the absence of ferric in the ferrous alginate beads.

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Degradation of chlorophenols by heterogeneous Fenton method

Preliminary study

Blank run was carried to find the effect of time, pH and hydrogen peroxide concentration on the stability (disintegration) of ferrous alginate. It was assessed based on the TOC value obtained at regular intervals. As none other organic compound was present apart from alginate, the TOC value of the system was assumed to be due to the disintegration of ferrous alginate. It was found that TOC was d" 2 mg/L till 8 h at pH 2 even in the presence of hydrogen peroxide. But when the pH was varied from 2 to 7, there was a slight marginal increase in the TOC value till pH 4 from 1.3 to 7.1 mg/L. After pH 4 there was visible disintegration in the system. In near neutral pH solution, carboxylic acid moieties are deprotonated as the pKa values of guluronic and mannuronic monomers are 3.65, and 3.38, respectively. This increases polymer hydrophilicity and sets up an electrostatic repulsion, which subsequently expands the gel network, leading to a swollen gel state. Alternatively, at low pH, the pendant acids are protonated, resulting in uncharged polymer with limited solubility leading to rapid polymer rearrangement, expelling water out from the gel network and contracting to the original relaxed gel volume (Chan et al., 2009).

Effect of different operating parameters

Effect of pH

To find the effect of pH on heterogeneous Fenton using ferrous alginate beads, the initial pH of the solution was varied from 2 to 4 only, as above pH 4 there was visible disintegration of ferrous alginate beads took place. Both the Fenton's reaction and stability of the beads are highly dependent on the pH of the system. Hence pH is the foremost and crucial parameter to be studied taking chlorophenols as model compounds. Figure 3 represents the effect of pH on degradation of chlorophenols. As shown in the figure, the pH significantly affects the degradation of chlorophenols. Results revealed that as pH increased above 2 there was decrease in the efficiency of the system for all the three chlorophenols. This might be due to the increase in disintegration of the beads and also as pH increases, the oxidation potential of hydroxyl radical decreases. Bossmann et al. (1998) observed that at pH 0 the oxidation potential of hydroxyl radical was 2.59 whereas at pH 14 it was 1.64 V. This result was supported by the study reported by Kwon et al. (1999) in which Fenton's reaction worked best at pH 2 for the decomposition of CP.

Complete chlorophenol degradation was observed at 60, 75 and 90 min for CP, DCP and TCP respectively. The increase in degradation efficiency follows the sequence of TCP < DCP < CP. This is because, for chlorophenols, the hydroxyl group in the benzene is ortho and para directing with activation whereas chlorine substituent is ortho, para directing with deactivation (Morrison and Boyd, 2008). Hence as the number of chlorine atoms increase in the ring, the electron withdrawing property of chlorine group makes it less favorable to electrophilic hydroxyl attack leading to lesser degradation efficiency.

The optimum pH was taken as 2, as it might favor the reusability of ferrous alginate beads for many cycles as well as Fenton's reaction takes place spontaneously at acidic pH only.

Effect of hydrogen peroxide concentration

Hydrogen peroxide acts as oxidant and is vital for the degradation of chlorophenols. The concentration of hydrogen peroxide was varied from 0.2 g/L to 1.4 g/L. The results are shown in Figure 4. The degradation efficiency increases with increasing hydrogen peroxide concentration due to additional hydroxyl radicals produced. The maximum efficiency of degradation was obtained at 0.6 g/L itself for all the chlorophenols. There are three ways in which hydrogen peroxide assists the degradation of chlorophenols. First, the ferrous ion combines with hydrogen peroxide as per classical Fenton's equation to produce powerful hydroxyl radicals. Secondly, the production of ferrous ion and peroxyl radicals as per equations 7 and 8 also adds on the efficiency of the system. Even though, peroxyl radicals are of lower potential compared to hydroxyl radicals, its reaction with the organic intermediates cannot be ignored. And last of all, being an oxidant, hydrogen peroxide itself will oxidize the organic compound. Above 0.6 till 1.2 g/L of hydrogen peroxide did not improve the efficiency of the system and the degradation of the chlorophenols were leveled off. This might be due to scavenging of the hydroxyl radicals by higher concentration of hydrogen peroxide. This kind of leveling off was also reported by Kwon et al.(1999) and El-Morsi et al.(2002).

Effect of ferrous alginate dosage

Ferrous ion has a catalytic role in the Fenton's process (Kavitha and Palanivelu 2003). In Fenton's process, ferrous reacts with H_2O_2 and •OH radical to produce ferric. This ferric is converted back to ferrous, when it reacts with the active organic radical (Equation 3). The behavior of ferrous alginate was explored in the range of 0.05 g/L to 0.20 g/L, towards the degradation efficiency of chlorophenols. The results are shown in Figure 5.

As the ferrous alginate dosage was increased from 0.05 to 0.10 g/L, the efficiency of the system increased. This might be due to higher production of hydroxyl radicals by Fenton's process. But further increase in the ferrous
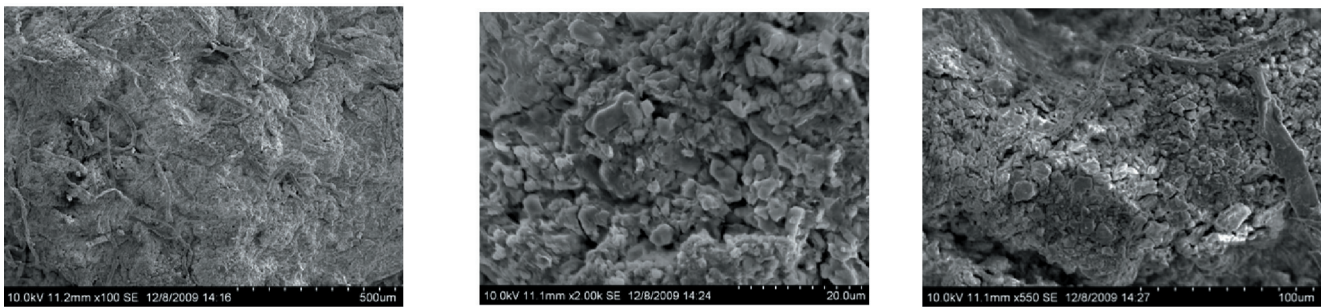
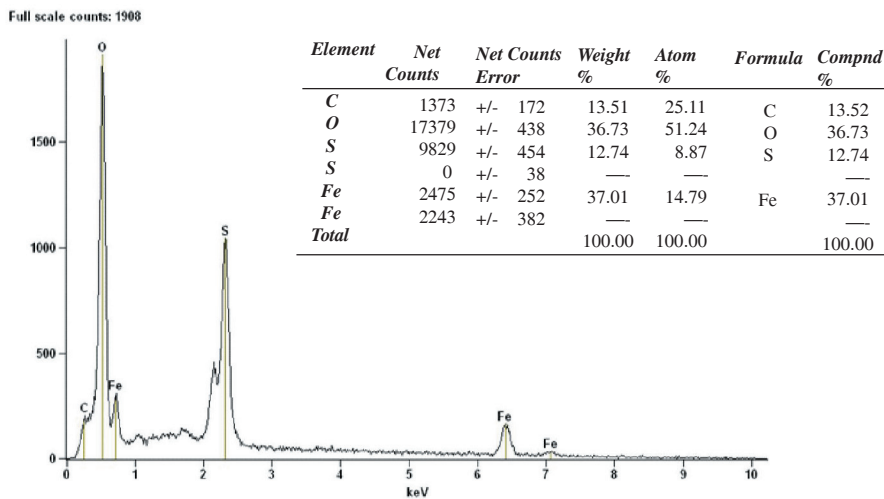**Figure 1 EDS-HRSEM images of ferrous alginate beads**

Full scale counts: 1908

Element	Net Counts	Net Counts Error	Weight %	Atom %	Formula	Compnd %
C	1373	+/- 172	13.51	25.11	C	13.52
O	17379	+/- 438	36.73	51.24	O	36.73
S	9829	+/- 454	12.74	8.87	S	12.74
S	0	+/- 38	—			—
Fe	2475	+/- 252	37.01	14.79	Fe	37.01
Fe	2243	+/- 382	—	—		—
Total			100.00	100.00		100.00

Figure 2 EDS spectrum for freshly prepared ferrous alginate beads

Table 1 Kinetic data for degradation of chlorophenol by heterogeneous Fenton method

Chloro phenol	Pseudo first order kinetic rate constant (k) (min^{-1})	R^2 value	$t_{1/2}$ (min)
CP	0.040	0.989	17.32
DCP	0.029	0.979	23.89
TCP	0.020	0.984	34.65

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

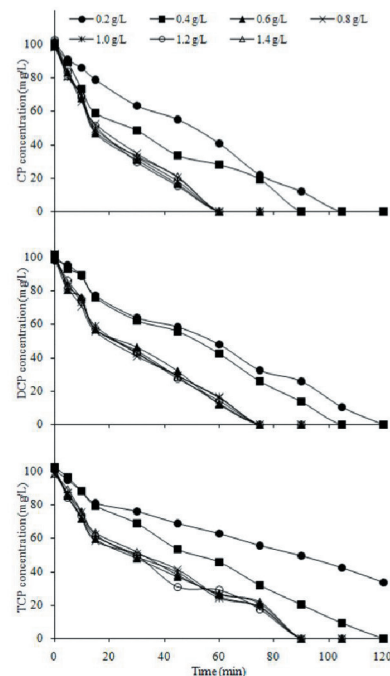| Parameters	Values before treatment	Values after treatment
pH	6.15	3.31
EC (µS/cm)	6530	7834
TDS (mg/L)	4178	4678
Chloride (mg/L)	124	287
Phenols (mg/L)	210	BDL
COD (mg/L)	512	129
TOC (mg/L)	189	83

Figure 4 Effect of hydrogen peroxide concentration on the degradation of chlorophenols by heterogeneous fenton method (Conditions: chlorophenol concentration-100 mg/L, pH - 2, Ferrous alginate-0.1 g/L)

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alginate dosage above 0.10 g/L, did not improve the efficiency of the system and was leveled off. This might be due to the scavenging effect of hydroxyl radicals by higher concentration of ferrous as shown in equation 10. For all the three chlorophenols, complete degradation took place in 60, 75 and 90 min for CP, DCP and TCP for 0.10 g/L of ferrous alginate.

$$Fe^{2+} + {}^{\bullet}OH \longrightarrow Fe^{3+} + OH^{-} \qquad \dots (10)$$

Further experiments were carried out at 0.10 g/L of ferrous alginate concentration.
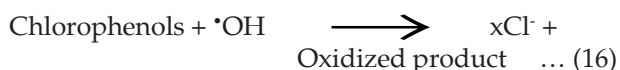
Effect of initial chlorophenol concentration

The feasibility of heterogeneous Fenton method was investigated for higher concentrations of chlorophenol as it was found in literature that the chlorophenol concentration can be as high as 500 mg/L (as phenol) (Conway and Ross, 1980). Hence, Experiments were conducted at optimal conditions with different initial chlorophenols concentrations ranging from 100 to 500 mg/L. The concentration of chlorophenols was found to be BDL at the end of 60, 75 and 90 min for CP, DCP and TCP irrespective of the initial chlorophenol concentration (Result not shown). As the initial concentration was increased the degradation efficiency remained almost the same with less than 5% variation. This indicates that the efficiency was not altered by initial concentration provided optimal conditions are maintained. This kind of trend was also observed by other researchers (Li et al., 2009). Therefore it can be concluded that this method will work efficiently in aqueous samples having higher concentration of chlorophenols also.

Reuse of Catalyst

In the heterogeneous Fenton method, ferrous in ferrous alginate beads act as catalyst for hydroxyl radical generation. The viability of reusing the catalyst was studied after filtering out the ferrous alginate beads for all the three chlorophenols at optimal conditions. The reusability studies were carried out till there was decrease in the efficiency of the system. Chlorophenol was not detectable in the solution till 14th cycle for all the three compounds. After 14th cycle, chlorophenol was detected. This might be due to the disintegration of ferrous alginate beads after 14th cycle.

Kinetics of chlorophenol degradation by heterogeneous Fenton method

In heterogeneous Fenton method the hydroxyl radical generated by Fenton's process as well as by sonication plays a predominant role in the degradation of chlorophenols. The hydroxyl radical formed attacks the chlorophenols and degrades it as shown below

$$\text{Chlorophenols} + {}^{\bullet}OH \longrightarrow xCl^{-} + \text{Oxidized product} \quad \dots (16)$$

Thus the rate of degradation of Chlorophenols (CPs) can be expressed as follows

$$-\frac{d\,(CPs)}{dt} = k\,[{}^{\bullet}OH]\,[CPs]_0 \qquad \dots (17)$$

As the concentration of hydroxyl generated within the system will be very high, it is pertinent to find the order with respect to chlorophenol concentration. The operating variables namely H_2O_2, pH and ferrous alginate concentration were maintained at 0.6 g/L, 2 and 0.1 g/L. Table 1 furnishes the details about R^2 and kinetic rate constant (k) for all the three chlorophenols. The result revealed that the degradation under optimum condition obeyed the pseudo first order reaction kinetics. The results observed by Kwon et al. (2010) also support the fact that Fenton reaction follows pseudo first order kinetics. The study carried out by Dorathi et al (DCP) also proves that sono Fenton follows pseudo first order kinetics. From Table 1, it is clear that CP was degraded quickly when compared with other two chlorophenols whereas TCP was the slowest.

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. Therefore chlorophenol is present in major amount in the effluent. Wastewater contained phenol as its major composition. Details about wastewater characteristics are furnished in Table 2. The collected wastewater was treated by heterogeneous Fenton using ferrous alginate beads at optimum condition. The pH of the solution was adjusted to 2 with sulphuric acid. The method under study was found to efficiently degrade the phenols in the wastewater and also there was remarkable reduction in the COD and TOC values.

CONCLUSION

From the foregoing results, the following conclusion can be stated:

- Degradation of chlorophenols by heterogeneous Fenton using ferrous alginate was found to be feasible and the optimal pH, hydrogen peroxide concentration and ferrous alginate dosage was found to be 2, 0.6 g/L and 0.1 g/L.

- The degradation of chlorophenols by heterogeneous Fenton followed pseudo first order kinetics with $t_{1/2}$ values of 17.32, 23.89 and 34.65 min for CP, DCP and TCP respectively.

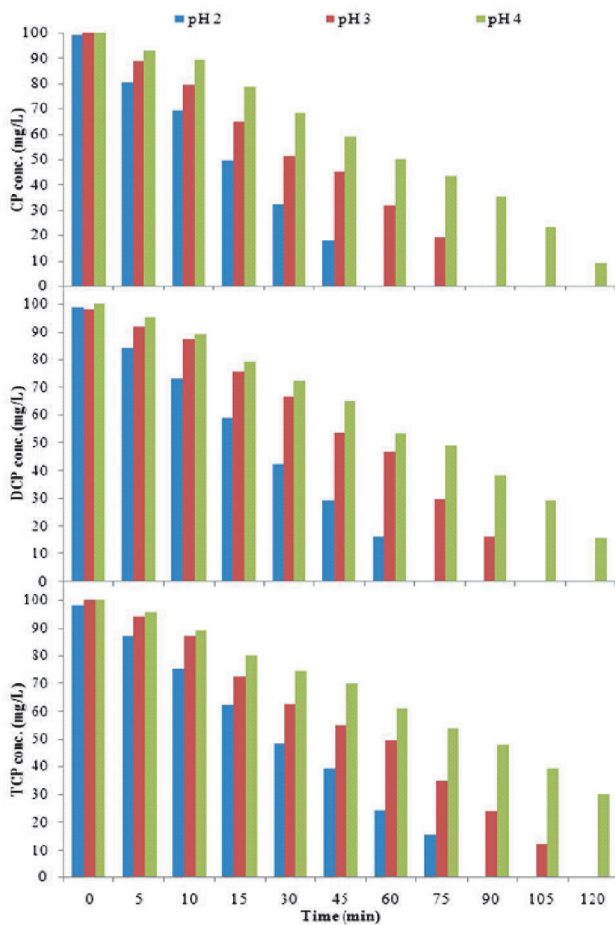- This method was found to be efficient for treating pulp and paper wastewater also.

Figure 3 Effect of pH on the degradation of chlorophenols by heterogeneous fenton method (Conditions: chlorophenol concentration-100 mg/L, H_2O_2-1.0 g/L, Ferrous alginate-0.1 g/L)
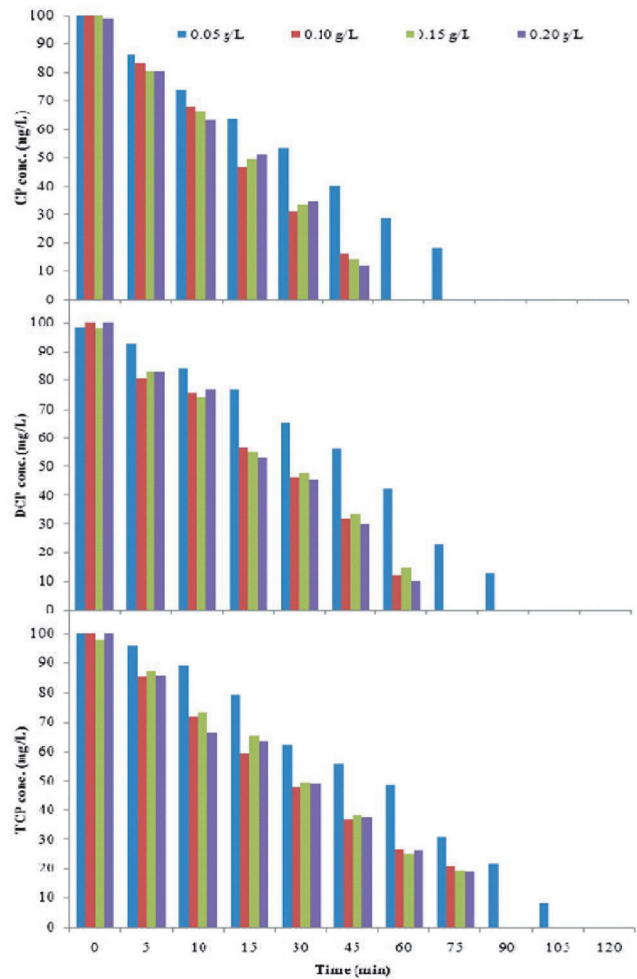
Figure 5 Effect of ferrous alginate concentration on the degradation of chlorophenols by heterogeneous fenton method (Conditions: chlorophenol concentration-100 mg/L, H_2O_2-0.6 g/L, pH - 2)

Acknowledgment

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