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SUMMARY

The study explores the utility of the electro-Fenton process for the degradation of o-chlorophenol (o-CP) from aqueous solution. The extent of degradation of o-CP is found to be a function of applied current, electrolysis time, concentration of o-CP and concentration of ferrous ions. Under optimized conditions it is possible to achieve efficiencies higher than 70%. Accelerating the regeneration of Fe²⁺ ions in the electrolyte determines the efficiency of the process. Addition of goethite as a catalyst in the medium did not significantly improve the process efficiency.

KEYWORDS: Fenton, Electro-Fenton, hydroxyl radical, degradation, o-chlorophenol, goethite.

INTRODUCTION

In recent years there is a great interest in the development of practical electrochemical methods for the destruction of toxic and biorefractory organic pollutants for wastewater treatment. Among these processes, the *in situ* generation of hydrogen peroxide received considerable attention since it can be coupled with ferrous ions to produce Fenton's reagent. This process is termed as "electro-Fenton process". Several authors have studied the removal of organic pollutants, such as formaldehyde [1], aniline [2, 3], phenol [4], 2,4-D [5], pesticides [6], pentachlorophenol [7] and atrazine [8] by electro-Fenton process. The present work aims to study the degradation of o-chlorophenol (o-CP) by electro-Fenton process, which uses ferrous ion and electro-generated H₂O₂. Chlorophenols have been detected during the manufacture of pesticides, bleaching of industrial wastewater, and chlorination of drinking water [9]. U.S. EPA has listed several of them among the 65 priority pollutants [10].

Chlorinated by-products, produced by chlorination of drinking water, have led to several health risks [11]. The conventional destructive technologies, such as biological treatment, incineration, adsorption, air stripping etc. [12], were associated with serious limitations. Besides, removal of these compounds becomes difficult and expensive when they are present at very low levels in the environment [13].

MATERIALS AND METHODS

Sodium sulphate (0.05 M) was used for the electrolyte solution and pH of the electrolyte was adjusted to 3.5 using H₂SO₄. For the electrolytic generation of hydrogen peroxide, oxygen gas was purged into the electrolyte at a constant flow rate of 3.75 l/min. A stainless steel plate served as the cathode, whereas a platinum gauze electrode served as the anode. In order to generate the Fenton's reagent, ferrous ions were added to the electrolyte solution. A D.C. power source was used to supply the required current for the electrogeneration of hydrogen peroxide. The concentration of o-CP was in the range of 40-160 ppm. The effect of applied current, electrolysis time, concentration of o-CP and concentration of ferrous ions on the extent of degradation was studied. The amount of chloride ions generated as a result of degradation of o-CP was analyzed by Volhard's method. Chemical oxygen demand (COD) was also determined to correlate the extent of degradation and the nature of intermediates formed. Goethite (α -FeOOH) was prepared by reacting 10 g of electrolytic grade iron powder (300 mesh) and 34 ml of conc. HNO₃ and increasing the pH of the resulting ferric nitrate solution to 13 with the addition of hot NaOH solution (70 °C). The ferric hydroxide precipitate was aged at 60 °C for two days. The effect of goethite addition on the extent of degradation of o-CP was also studied to evaluate whether it involves a radical or non-radical mechanism.

RESULTS AND DISCUSSION

Effect of applied current

The effect of applied current on the percentage degradation of o-CP and the percentage decrease in COD is shown in Table 1. It is evident that the extent of degradation of o-CP increases with increase in applied current in the range of 200 to 600 mA. The applied current is the driving force for the reduction of oxygen leading to the generation of hydrogen peroxide at the cathode. Higher applied current increases the quantum of hydrogen peroxide produced, thus increasing the number of hydroxyl radicals in the electrolyte medium, which are highly reactive and responsible for the degradation of o-CP. However, the increment in percentage degradation is decreased with increase in applied current from 200 to 600 mA. This could be attributed to the competing hydrogen evolution reaction, which decreases the efficiency of the process [14, 15].

TABLE 1 - Effect of applied current on the % degradation of o-CP and % decrease in COD (concentration of o-CP: 80 ppm; concentration of ferrous ions: 0.5 ppm; electrolysis time: 60 min).

Applied current (mA)	% Degradation of o-CP	% Decrease in COD
200	28.44	16.40
400	48.02	35.03
600	59.12	47.45

Effect of electrolysis time

The percentage degradation of o-CP and the percentage decrease in COD as a function of electrolysis time is given in Table 2. Though the extent of degradation increases with increase in electrolysis time, a saturation level is reached after some time.

TABLE 2 - Effect of electrolysis time on the % degradation of o-CP and % decrease in COD (concentration of o-CP: 80 ppm; concentration of ferrous ions: 0.5 ppm; applied current: 600 mA).

Electrolysis time (min.)	% Degradation of o-CP	% Decrease in COD
30	21.85	16.52
45	35.47	25.60
60	59.12	47.45
90	63.57	51.62
105	64.20	53.40

It should be noted that during the entire duration of the experiment oxygen is continuously purged into the electrolyte solution, which implies a constant generation of hydrogen peroxide on a continuous basis. Moreover, the electro-Fenton process enables the generation of ferrous ions in the electrolyte solution by electrochemical reduction of ferric ions at the cathode. Hence the reason for saturation in extent of degradation of o-CP should be due to the decrease in availability of ferrous ions due to

some competing reactions. In fact, such an attribute is validated by the observation of a dark brown coloration of the electrolyte medium, which could be predicated to the formation of iron-organic complexes. Kwon et al. [16], using elemental analysis, atomic absorption spectroscopy and FTIR spectroscopy, have confirmed the unavailability of iron, due to complexation, for further reactions. The results of the present study support the hypothesis made by Kwon et al. [16] on the potential scavenging effect by the iron-organic complexes.

Effect of concentration of o-chlorophenol

Table 3 depicts the percentage degradation of o-CP along with the percentage decrease in COD for varying concentrations of o-CP in the range of 40-160 ppm. For a given set of experimental parameters it is obvious to expect a decrease in the extent of degradation of o-CP, when its concentration in the electrolyte solution is increased.

TABLE 3 - Effect of concentration of o-CP on its % degradation and % decrease in COD (applied current: 600 mA; concentration of ferrous ions: 0.5 ppm; electrolysis time: 1 hour).

Concentration of o-CP (ppm)	% Degradation of o-CP	% Decrease in COD
40	84.85	72.05
80	59.12	47.45
120	40.77	28.50
160	32.70	20.36

This implies the requirement of additional treatment time when the concentration of o-CP is higher in the electrolyte solution. When the treatment time is increased, obviously, being an electrolytic process, the increase in energy consumption significantly affects the economics of the process. Hence it is logical to recommend electro-Fenton process for the degradation of o-CP, when it is present in the medium at very low concentrations.

Effect of ferrous ions concentration

The effect of variation in ferrous ion concentration on the percentage degradation of o-CP along with the percentage decrease in COD is shown in Table 4. The extent of degradation increased with increase in concentration of ferrous ions. Since hydrogen peroxide is continuously electrogenerated at the cathode, increase in ferrous ion

TABLE 4 - Effect of variation in ferrous ion concentration on the % degradation of o-CP and % decrease in COD (applied current: 600 mA; concentration of o-CP: 80 ppm; electrolysis time: 1 hour).

Concentration of ferrous ion (ppm)	% Degradation of o-CP	% Decrease in COD
0.5	59.12	47.45
1.0	68.28	58.30
1.5	76.72	67.42
2.0	80.40	71.63

concentration is likely to increase the generation of hydroxyl radicals, which is the major reactive species for the degradation of o-CP. However, ferrous ions in the electrolyte solution, when present in excess, could consume the hydroxyl radicals and affect the extent of degradation. Besides, the ferrous/ferric ions readily form stable complexes with o-CP. Hence it is preferable to use a limited concentration of ferrous ions.

Effect of goethite addition

Addition of goethite (α -FeOOH) to the electrolyte solution is expected to increase the extent of degradation of o-CP, since goethite could act as a heterogeneous catalyst and also promote the homogeneous catalysis by supplementing the ferrous ion concentration following its reductive dissolution [17, 18]. The ability of goethite to act as a heterogeneous catalyst is determined by the adsorption of organic compounds on goethite surface. Lu et al. [19] suggest that the amount of o-CP adsorbed onto goethite surface was less than 8%. According to Ni and Chen [20], the maximum amount of adsorption of o-CP on alumina is only 2.2%. Hence it is clear that the contribution from adsorption towards the removal of o-CP from the electrolyte solution is minimal. The pH of the medium deter-

mines the mechanism of degradation of o-CP in presence of goethite whether it will be governed by OH^\bullet mediated pathway or by non- OH^\bullet radical pathway. Andreozzi et al. [21] observed that in the pH range 6.0-9.0 the degradation of 3,4-dihydroxybenzoic acid is directed by a non-radical oxidation mechanism. Teel et al. [22] suggested that at pH 3.0 in presence of goethite, 85-90% of degradation of trichloroethylene occurs by OH^\bullet mediated pathway while the remaining 10-15% may be due to non- OH^\bullet radical pathway. Based on the results of Lu [19], Andreozzi et al. [21] and Teel et al. [22], presence of goethite in the electrolyte medium in the present experimental conditions at pH 3.5 could generate additional ferrous ions, thus catalyzing the degradation of o-CP by homogenous pathway. Contrary to this expectation, the extent of degradation of o-CP in presence of goethite (2 g/l) did not increase significantly. Analysis of the iron content of the electrolyte solution as a function of electrolysis time reveals that the increase in iron content is very little to exhibit any significant change in the extent of degradation of o-CP. Increase in goethite loading and/or increase in treatment time could be beneficial. Further studies are required to optimize the conditions for achieving higher levels of degradation in presence of goethite.

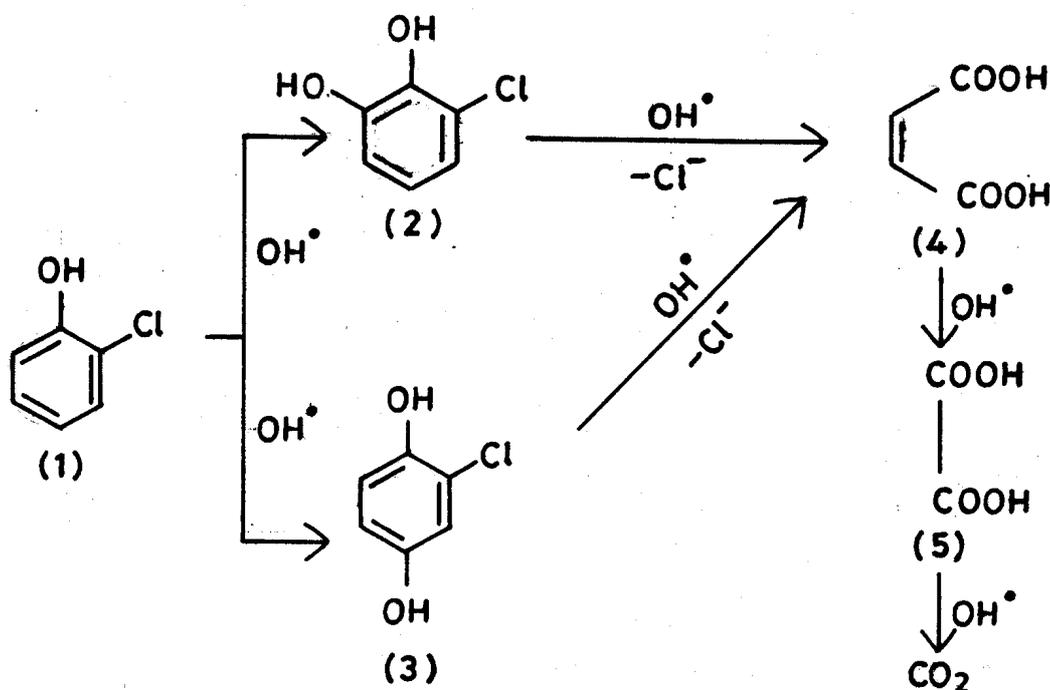


FIGURE 1

Mechanism of degradation of o-CP by electro-Fenton process.

[Key: (1) o-chlorophenol; (2) 6-chloro-1,2-dihydroxybenzene; (3) 6-chloro-1,4-dihydroxybenzene; (4) maleic acid; (5) oxalic acid]

Mechanism of degradation of o-chlorophenol

A general mechanism for the degradation of o-CP by electro-Fenton process is proposed in Fig. 1. The degradation process involves dehydrogenation and hydroxylation reactions of o-CP with OH[•]. The attack of OH[•] on o-CP could occur at *ortho*, *meta* or *para* positions, which could produce 6-chloro-1,2-dihydroxybenzene or 6-chloro-1,3-dihydroxybenzene or 6-chloro-1,4-dihydroxybenzene, by the addition of OH[•] in the respective positions and abstraction of a hydrogen atom from the corresponding position. Huang et al. [23] found that OH[•] reacts with phenol in the *ortho* and *para* positions. Ma and Lin [24], based on the formation of 2-chloro-p-benzoquinone as the major intermediate, suggest the preferential attack of OH[•] on *para* position during the decomposition of o-CP. Brillas et al. [25] and Sauleda and Brillas [26] proposed the attack of OH[•] on the *ortho* position during the degradation of p-chlorophenol. Based on the observations made in earlier studies, it is believed that the attack of OH[•] on o-CP is most likely to occur at *ortho* and/or *para* positions, respectively, yielding 6-chloro-1,2-dihydroxybenzene and/ or 6-chloro-1,4-dihydroxybenzene. These compounds upon further oxidation, with loss of Cl⁻, result in the formation of a variety of intermediates. Jung [27] proposed the formation of hydroxyhydroquinone, mucic acid, tartaric acid, oxalic acid, maleic acid, and hydroxymalonic acid as the intermediates during the degradation of o-CP by ozonation. Brillas et al. [25] and Sauleda and Brillas [26] have identified maleic acid, its trans-isomer, fumaric acid, and oxalic acid as intermediates of degradation of p-chlorophenol by electro-Fenton process. GC analysis of the degradation products of o-CP indicates the formation of several intermediates. The results of GC analysis corroborates well with the percentage decrease in COD, which is lesser than the percentage degradation of o-CP, for a given set of experimental conditions. Carboxylic acids, such as maleic acid, tartaric acid, etc. are the major by-products, which, in turn, are mineralized to CO₂ via oxalic acid.

CONCLUSIONS

From the study it can be concluded that electro-Fenton process is highly efficient for the degradation of o-CP. The extent of degradation is a function of applied current, electrolysis time, concentration of o-CP and concentration of ferrous ions. The non-availability of sufficient concentrations of ferrous ions with electrolysis time limits the efficiency of the process. Based on the extent of degradation obtained as a function of concentration of o-CP, it is logical to recommend the use of electro-Fenton process only when o-CP is present at low concentrations. Addition of goethite as a catalyst did not show any significant increase in the % degradation of o-CP, although a slight decrease in COD is noticed. A general mechanism for the degradation of o-CP by electro-Fenton process is

proposed. The degradation process involves dehydrogenation and hydroxylation reactions of o-CP with OH[•]. These compounds upon further oxidation, with loss of Cl⁻, result in the formation of a variety of intermediates. Carboxylic acids are the major by-products, which are finally mineralized to CO₂ via oxalic acid.

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