Degradation of Parachlorophenol by Electro-Fenton and Photo-Fenton Process Using Batch Recirculation Reactor

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Abstract

Chlorophenols are a group of special interest due to their high toxicity and low bio degradability. Advanced oxidation process constitutes a promising technology for the treatment of wastewaters containing non-easily removable organic compounds. Several electro chemical processes are based on mediated electro chemical oxidation. The present study envisages the utility of electro-fenton and photo-fenton process for the degradation of parachlorophenol from aqueous solution by the electro oxidation under acidic condition. Experiments were carried out under batch recirculation conditions with stainless steel as cathodes and RuO2 coated titanium expanded mesh as anodes. Electrolysis was carried out with various current densities and flow rate using mediated electro chemical oxidation process with fenton mediator (Fe^{2+} / Fe^{3+} + H_2O_2). Extent of dehydration and reduction in COD was studied as a function of applied current, electrolysis time and concentration of ferrous ion. The electrolysis was carried at optimised conditions to achieve efficiencies higher than 80%.

Keywords: chlorophenols, electrolysis, Fenton mediator, degradation, wastewater.

Introduction

Human activities have contributed to the introduction of wide variety of synthetic organic compounds into the environment, and many are causing significant pollution of ground and surface waters; of all the organic pollutant causing problems around the world, the most harmful are aromatic hydrocarbons, chlorinated hydrocarbons and pesticides [1].
Although pesticides have been detected in water since the 1950's, in the last 15 years their use has risen dramatically all over the world and has nearly doubled every 5 years since 1975. On this way, chloro phenols(CPs) constitute a particular group of priority toxic pollutant listed by USEPA (environmental

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protection agency) in the clean water act [2-7] and by the European decision 2455/2001/EC [1,8-12], because most of them are toxic and hardly biodegradable and difficult to remove from environment. Various contaminations such as azo dyes, organo chlorine and dramatic hydrocarbons have been ducted, and a number of the chemical components are suspected of being endocrine disrupting chemicals (EDCs). Chlorophenols are introduced in the environment as a result of several man-made activities. Because of their broad-spectrum antimicrobial properties, CPs have been used as preservative agents for wood, paints, vegetable fibres and leather and as disinfectants [28-32]. In addition, they have been widely employed in many industrial processes as synthesis intermediates or as raw materials in the manufacture of herbicides, fungicides, pesticides, insecticides, pharmaceuticals and dyes. CPs may also be generated as by products during waste incineration and dechlorination of drinking water.

The presence of chlorophenols has been detected in both surface and ground waters as by products generation during waste incineration, the bleaching of pulp with chlorine, in the dechlorination of drinking water and as pesticides [27]. The electro-Fenton process can be recommended for the degradation of p-chlorophenol, when it is present in the medium at low concentrations.

The present work aims to study the degradation of P-chlorophenol (150 ppm) by first type of electro-Fenton process, which uses Fe^{2+} and H_2O_2, photo-assisted electro Fenton process, which uses Fenton's reagent and mercury lamp. The degradation of p-chlorophenol was studied by the following parameters [13-18]:

- to estimate the applicability of electro-Fenton and photo Fenton for degradation of p-chlorophenol using batch recirculation reactor;
- to estimate the degradation of p-chlorophenol on different medium (sodium sulphate, sodium chloride, Fenton medium);
- to estimate the cod of the treated effluent at different time intervals and current densities;
- to estimate the variation in percentage absorption of chloride using spectroquant novac-60;
- to study the effect of flow rate on the removal of chloride ion and COD;
- to study the effect of current density on degradation of p-chlorophenol;
- to compare the degradation of p-chlorophenol by electro-Fenton and photo-Fenton method.

Compared to the conventional Fenton process, the electro-Fenton process has the advantage of allowing better control of the process and avoiding the storing and transport of the H_2O_2. Moreover, electricity as a clean energy source is used in the process, so the overall process does not create secondary pollutants. The utilization of photo-oxidative methods for the treatment of wastewaters offers several advantages, particularly the feasibility of total elimination of the organic pollutants. In spite of the proven efficiency of biological processes for the treatment of many types of wastewaters, they do exhibit limitations with respect to the range of concentration and toxicity of the pollutants. Photo-Fenton reaction can be driven with low energy photons in visible spectrum. Therefore, photo-

Fenton process is a potential low cost treatment that can be run under solar light irradiation [20-27].

Materials and methods
Experimental setup
Electro-Fenton process

Experiments were carried out under galvanostatic condition at current density $1A/dm^2$, $2A/dm^2$ and $3A/dm^2$ using RuO_2 coated titanium expanded mesh anodes and stainless steel as cathodes. Synthetic effluent containing parachlorophenol (150 ppm) is subjected to electrolysis in a batch recirculation reactor at fixed current density. Sodium sulphate solution (0.05 M) was used as an electrolyte solution. The fluid flow circuit consists of a reservoir, a magnetically driven self-priming centrifugal pump and an electrolytic cell. The electric circuit consists of a regulated DC power supply, ammeter and the cell with a voltmeter connected to the parallel to the reactor. The electrolyte was continuously stirred during the electrolysis using a magnetic stirrer. In order to generate the Fenton's reagent, the concentration of the mediator has been maintained at 0.25g/L and for the purpose of $OH^°$ free radical, H_2O_2 was added at the rate of 1.5 mL/h. These experiments were carried out again in batch recirculation at different flow rates, namely 5,10,15,20 and 25 mL/min (Tables 1-5).

Table 1. Current density: $1A/dm^2$; time: 6 h; current: 0.51 A; mediator: NaCl; reactor volume: 500 mL.

Sl. No.	Flow rate (mL/min)	C.V. (Volts)	COD (ppm)		% COD reduction
			Initial	Final	
1	5	3.9-4.3	980	530	45.91
2	10	3.6-4.2	960	470	51.04
3	15	4.1-4.4	860	430	50.02
4	20	3.9-4.4	920	560	39.13
5	25	3.4-3.9	880	620	29.54

Mechanism of degradation

The degradation of parachlorophenol involves its dehydration and hydroxylation reactions with $OH^°$. Hydroxyl radicals have strong oxidation capability and are responsible for oxidising various organic compounds. The attack of $OH^°$ on Parachlorophenol could occur at ortho or meta or para positions which could produce 6-chloro-1,2 dihydroxy benzene or 6-chloro-1,3 dihydroxy benzene or 6-chloro-1,4 dihydroxy benzene by the addition of $OH^°$ in the respective position of parachlorophenol and abstraction of hydrogen atom from the corresponding position. These compounds upon further oxidation with loss of Cl^- might yield a variety of intermediates. Stages of mechanisms include initial reaction, propagation, termination and parachlorophenol degradation.
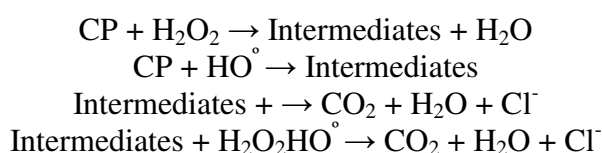
$$CP + H_2O_2 \rightarrow Intermediates + H_2O$$
$$CP + HO^° \rightarrow Intermediates$$
$$Intermediates + \rightarrow CO_2 + H_2O + Cl^-$$
$$Intermediates + H_2O_2HO^° \rightarrow CO_2 + H_2O + Cl^-$$

Table 2. Current density: $1A/dm^2$; time: 6 h; current: 0.51 A; mediator: Na_2SO_4; reactor volume: 500 mL.

Sl. No.	Flow rate (mL/min)	C.V. (Volts)	COD (ppm)		% COD reduction
			Initial	Final	
1	5	4.4-4.6	970	490	49.48
2	10	4.2-4.3	940	370	60.63
3	15	4.3-4.5	920	310	66.04
4	20	4.4-4.7	980	440	55.10
5	25	4.3-4.4	890	460	48.31

Table 3. Current density: $1A/dm^2$; Time: 6 h; current: 0.51 A; mediator: $FeSO_4 + H_2O_2$; reactor volume: 500 mL.

Sl. No.	Flow rate (mL/min)	C.V. (Volts)	COD (ppm)		% COD reduction
			Initial	Final	
1	5	4.1-4.4	880	390	55.58
2	10	4.4-4.6	860	160	81.35
3	15	3.7-3.8	900	420	53.30
4	20	3.7-3.9	970	540	44.32
5	25	3.5-3.7	980	520	46.93

Photo-Fenton process

Synthetic effluent containing parachlorophenol (150 ppm) is subjected to electrolysis in a batch recirculation reactor at fixed current density $1A/dm^2$, $2A/dm^2$ and $3A/dm^2$ (Table 6). A continuous electrolysis was carried out at fixed current density in 0.05 M sodium sulphate solution containing H_2O_2 and ferrous sulphate (0.25 g/L). Similar to experimental conditions as electro-Fenton process, the photo-Fenton process requires low-pressure mercury vapour lamp for the generation of UV radiation supplied to parachlorophenol samples. Photo-Fenton process produces more hydroxyl radicals by the combination of H2O2 vapour lamp and UV radiation with Fe(II) or Fe(III) oxalate ion.

**Table 4.** Current density: $2A/dm^2$; time: 6 h; current: 0.98 A; mediator: $FeSO_4 + H_2O_2$; reactor volume: 500 mL.

Sl. No.	Flow rate (mL/min)	C.V. (Volts)	COD (ppm)		% COD reduction
			Initial	Final	
1	5	5.2-5.4	920	530	42.39
2	10	5.1-5.3	700	180	74.28
3	15	5.3-5.4	720	160	77.77
4	20	5.0-5.2	900	400	55.56
5	25	5.4-5.6	920	510	44.56

Table 5. Current density: $3A/dm^2$; time: 6 h; current: 1.47 A; mediator: $FeSO_4 + H_2O_2$; reactor volume: 500 mL.

Sl. No.	Flow rate (ml/min)	C.V. (Volts)	COD (ppm)		% COD reduction
			Initial	Final	
1	5	6.1-6.3	980	320	67.34
2	10	6.1-6.4	920	160	82.60
3	15	6.4-6.7	970	380	60.82
4	20	5.9-6.1	870	320	63.21
5	25	6.1-6.2	890	360	59.56

Mechanism of degradation

Advanced oxidation process is based on the formation of OH$^{°}$ radicals by means of the photolysis of the H_2O_2 and subsequent propagation of reaction. Degradation steps for parachlorophenol removal are the same as the ones exposed for reactions with Fenton's and UV/H_2O_2 reagents. Nevertheless, another step for initial reactions must be added, which does not take place in Fenton's reaction, because there is no radiation

$$H_2O_2 + Fe^{2+} + h\gamma \rightarrow Fe^{3+} + HO^{-} + OH^{°}$$
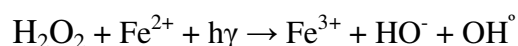
The absorptivity of H_2O_2 may be increased by using UV lamps with output at lower wavelengths. Due to the additional generation of hydroxyl radical in the degradation of parachlorophenol by the Photo-Fenton reaction, the degree of degradation is higher compared to direct photolysis. The final products of degradation should be CO_2, H_2O and Cl^- if complete mineralization is achieved.

Analysis of COD

COD of all samples were determined by the dichromate closed reflux method using a thermo reactor TR620-Merck. COD is generally considered as the oxygen equivalent to the amount of organic matter oxidizable by potassium dichromate. For COD analysis 1 mL of the sample was taken in COD tubes, and 2 mL of 0.25 N $K_2Cr_2O_7$ and 3 mL of sulfuric acid were added to the sample. These tubes were kept in the thermo reactor for 20 min. The organic matter of the sample was oxidized with a known excess of potassium dichromate in sulfuric acid solution. After 20 min, the COD tubes were cooled. The excess dichromate was titrated against a standard solution of 0.1 N ferrous ammonium sulfate (FAS). COD value can be calculated as follows:

$$COD, mgL^{-1} = \frac{(\text{Blank titre value - Sample titre value}) \times \text{Normality of FAS} \times 8 \times 1000}{\text{mL of sample taken for estimation}}$$

Table 6. Reactor volume: 500 mL; time: 6 h; mediator: $FeSO_4 + H_2O_2 + h\gamma$.

Sl. No.	Current Density (A/dm^2)	Current A	C.V. (Volts)	COD (ppm) Initial	COD (ppm) Final	% COD reduction
1	1	0.51	4.3-4.5	960	160	83.34
2	2	0.98	5.1-5.4	880	240	72.72
3	3	1.47	6.2-6.3	930	220	76.34

Analytical method

After sequential treatment, 20 mL of treated culture sample were subjected to various analytical methods. Biodegradation was analyzed by UV-Visible Spectrophotometer.

UV –Vis Spectrophotometer analysis

Samples were followed by monitoring changes in their absorption spectrum (λ 360-700 nm); they were carried out using a Varian UV-Vis-NIR-500 Double Beam Spectrometer and comparing the result with the respective controls. A

spectrophotometer was used together with a 1 cm optical path length to measure the UV spectra. A calibration graph was drawn by plotting absorbance against concentration (Tables 7 and 8).

Results and discussion

Effect of pH

At a pH above 4, the decomposition significantly decreases as pH increases, probably because the dissolved fraction of iron species decreases as colloidal ferric species appears. A second aspect of pH deals with its shift as the reaction progresses. The pH tends to decrease as ferrous ions as $FeSO_4$ are added, because it typically continues residual H_2SO_4. On the other hand, it also tends to decrease as hydrogen peroxide is added and continues gradually at a rate, which is largely dependent on Fe^{2+} concentration, because CPs fragmentizes into organic acids.

Table 7

Sl. No.	Current A	C.V. (Volts)	Time (hr)	Absorbance	Chloride (ppm)
1	0.51	3.9	1	0.706	42.12
2	0.51	4.0	2	0.762	63.97
3	0.51	4.1	3	0.769	77.23
4	0.51	4.2	4	0.813	83.86
5	0.51	4.3	5	0.847	97.12
6	0.51	4.3	6	0.852	99.07

Table 8

Sl. No.	Current A	C.V. (Volts)	Time (hr)	Absorbance	Chloride (ppm)
1	0.51	4.3	1	0.689	41.73
2	0.51	4.4	2	0.758	68.65
3	0.51	4.5	3	0.798	84.25
4	0.51	4.4	4	0.864	109.90
5	0.51	4.5	5	0.902	125.60
6	0.51	4.5	6	0.932	136.52

Effect of hydrogen peroxide concentration (H_2O_2)

The concentration of hydrogen peroxide has an important influence in the degradation of CPs in order to push the reaction to final extent, i.e., CO_2. The stoichiometric coefficient for the Fenton reaction has been found to be approximately 0.5 mol organic compound/mol H_2O_2. But for the purpose of generation of OH* (free radicals) H_2O_2 was added at the rate of 0.1 mL/h, which results in steady reduction in COD (or) removal of chloride by degradation of P-chlorophenol. The consumption of OH* (free radical) degrades p-chlorophenols.

Effect of catalytic ferrous ion concentration (Fe^{2+})

The extent of degradation also depends upon ferrous concentration, since increase in ferrous ion concentration likely increases the generation of hydroxyl radicals, which is the major reactive species for the degradation of p-chlorophenol. The excess concentration of ferrous ion results in consumption of

hydroxyl radicals according to the reaction and affects the extent of the degradation. Beside, the ferrous/ferric ions readily form stable complexes with p-chlorophenol as per reaction. Hence it is preferable to use a limited concentration of ferrous ion (0.25 g/L). Ferrous ions are utilized to degrade p-chlorophenol.

Effect of flow rate on cell voltage

The characteristics of cell voltage vs. time at different current densities for degradation of p-chlorophenol in electro Fenton and photo Fenton processes are shown (Figs 1-4). The cell voltage variations with the inlet flow rate in all the current density are given in the tables. After continuous electrolysis, the optimum flow rate was found to be 10 mL/min.
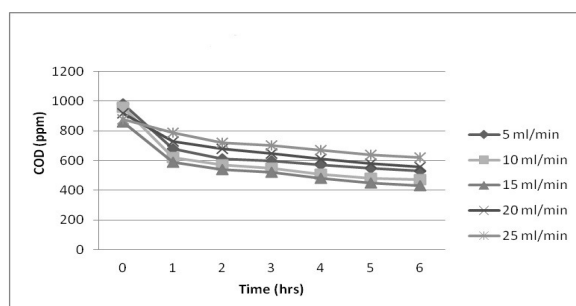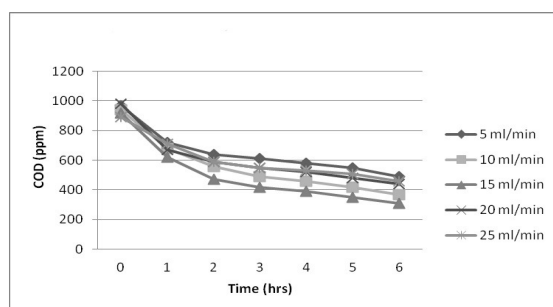

Figure 1. Electro oxidation with NaCl.

Figure 2. Electro oxidation with Na_2SO_4.

Effect of flow rate on the rate constants

The rate constant for the reaction of p-chlorophenols degradation for all the flow rate with various current densities are of the same order and are corresponding to the % reduction of COD. The rate constant for the flow rate of 0.6 L/h is the highest for the various current densities in electro-Fenton method as the % reduction of COD is the highest for that flow rate.
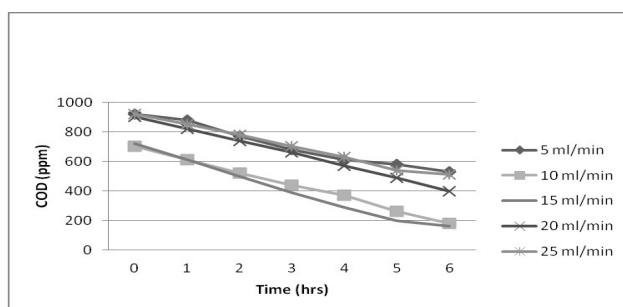

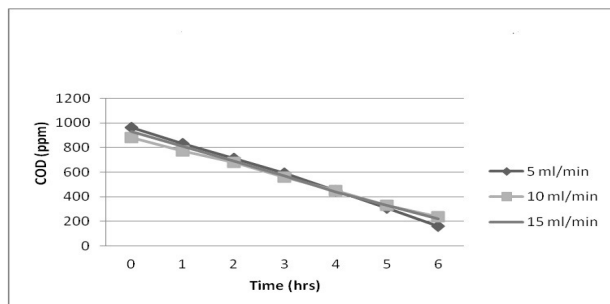**Figure 3**. Electro oxidation with Electro – Fenton's medium.

Figure 4. Electro oxidation with Photo – Fenton's medium.

Conclusion

From the study it can be concluded that electro-Fenton and photo-Fenton processes are highly useful in the degradation of p-chlorophenol from aqueous solution. It has been found that, the extent of degradation of p-chlorophenol is a function of the applied current, electrolysis time, concentration of p-chlorophenol and concentration of ferrous ion. The usage of electro-Fenton (or) photon-Fenton processes can be recommended for the degradation of p-chlorophenol at low concentrations, as the extent of degradation decreases when the concentration increases. The concentration of mediator was maintained at limited level in order to prevent the formation of stable complexes of ferrous ion with p-chlorophenol. Thus, from p-chlorophenol degradation result carboxylic acids as the major by-products, which finally are mineralized to CO_2.

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