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Investigation of Phenol Removal by Proxy-Electrocoagulation Process with Iron Electrodes from Aqueous Solutions

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ABSTRACT

Background: Phenol as an aromatic hydroxyl compound are considered as a priority pollutant. Because of their stability, solubility in water and high toxicity had health important.
Methods: In the present experimental study, electrocoagulation reactor by iron electrodes are used in the presence of hydrogen peroxide to phenol removing from aqueous solutions. Effects of variables including H_2O_2 dosage, reaction time, pH, current density and initial phenol concentration were evaluated to estimate the efficiency of the process.
Results: The results showed that pH and H_2O_2 have the most important role in the removal of phenol. Increasing of H_2O_2 concentrations from 0.0125 to 0.025 M increased removal efficiency from 74% to 100%. Maximum removal was achieved at pH=3. However, increasing the pH to 9 lead to reducing removal efficiency to 9.8%. Also, by increasing of current density removal efficiency was increased. But with increasing initial concentration of phenol removal efficiency was reduced.
Conclusion: Proxy-electrocoagulation process as an effective and robust process can be used for handling of phenol containing wastewater.

Keywords:
Proxy-Electrocoagulation
Phenol
Hydrogen Peroxide
Water Solution

1. Introduction

Phenol and its derivate classified as aromatic compounds utilized in metal, artificial texture industry, resin and plastic production as catalyst, paint industry, automobile, pesticides, pharmaceutical industries and cosmetics and petrochemical industry [1].

Such hydroxyl Aromatics compounds considered as priority pollutants, since they are harmful in lower density and toxic in higher density [2].

However, they are considered as possible cancer/tumor causing factors. Phenol enters body through breathing, eating, and eye touch and manifested via skin and eye burning. In one hand, consumption of 1g causes instant death [3].

Particulars of the material include lower environmental decomposition, environmental sustainability, water dissolvable, higher toxicity and causing health problems [4]. American environmental protection agency determined 1

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mg/l for receiving water resource [5]. Iranian environmental protection standard, determined 1 mg/l as max density in surface water, agricultural uses and irritation [6].

The most common way to remove phenol and its compounds include: biological treatment, activated carbon adsorption, chemical oxidation, electrochemical method, chemical precipitation, ion exchange, membrane process, reverse osmosis, which bear problems such as higher costs, lower efficiency, and production of related toxic by-products [7]. Advanced oxidation process (AOP) is one of chemical oxidation methods used to transform complex and resistant molecules into simple molecules. This process is based on free hydroxyl radicals and utilizes peroxide, ozone and atmosphere as an oxidizer [6]. The common advanced oxidation process is called Fenton process. Fenton process is based on electron transition between H_2O_2 and catalyst metal Fe^{2+} [8]. Electro-Fenton process is mixture of Fenton and electrocoagulation process, which is carried to promote the process [3, 9]. Such chemical processes are based on unstable and reactive hydroxyl radical that accelerate non selectively oxidation of a vast range of dissolved organic pollutants [10]. Strategically, the process classified into four groups: first group ion Fe^{2+}, H_2O_2 electrically produced on sacrificed electrode and cathode electrode surfaces [3]. Considering second group, H_2O_2 added to reactor manually, while an iron electrode is used as electrical source. Considering third group, Fe^{2+} added to reactor manually and H_2O_2 produced via oxygen distribution on cathode electrode`s surface and fourth group Fenton reagent is used to produce hydroxyl radical [8]. General principles of advanced oxidation process by Fenton reagents are as following. First, oxygen reduction reaction is carried in cathode through which H_2O_2 is produced, by adding ferro-ions to the sample, ferric ions are produced as well. In this way, by H_2O_2 reaction with Fe^{2+} hydroxyl free radicals are produced and chemical oxidation is initiated [11, 12].

Anodic reaction

$$Fe^{3+} + e- \rightarrow Fe^{2+} \qquad (1)$$

Catodic reaction

$$O_2+2H^{+}+ 2e- \rightarrow H_2O_2 \qquad (2)$$

Over all reaction

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH° + OH^{-} \qquad (3)$$

$$OH° + H_2O_2 \rightarrow H_2O + HO_2 \qquad (4)$$

$$Fe^{3+}HO_2 \rightarrow Fe^{2+} +H^{+} + O_2 \qquad (5)$$

$$Fe^{2+}+HO_2 \rightarrow Fe^{3+}+HO_2- \qquad (6)$$

$$Fe^{3+}+OH^{-} \rightarrow Fe^{2+}+OH° \qquad (7)$$

$$RHX + OH° \rightarrow X^{-} + \text{Oxidation products } (CO_2 + H_2O) \qquad (8)$$

Finally, organic materials are faced OH°, they are decomposed to non-toxic compounds such as H_2O, CO_2 [6]. Advantages of phenol oxidation include higher efficiency without residual production, purification stability in wide range of materials without any special equipment, operation facility, utilizing in different scales and economical consideration, requiring less time, not production of secondary pollutions, small size of the equipment, lack of chemical materials, some problems of the purification include need for acid pH and more sludge production [10]. The goal of present study is evaluating electrocoagulation process using iron electrode to remove phenol from aqueous solutions. Also, the effect of parameters such as reaction time, H_2O_2 density, initial pH, and initial voltage and density of phenol is studied .

2. Materials and Methods

Phenol (purity 97.5%), hydrogen peroxide (30%, w/v), ferri cyanide potassium and 4-Amino anti-pirine reagents were purchased from Merck Co. Other chemicals were of analytical grade and were used without further purification. Deionized and doubly distilled water was used throughout this study to prepare standard solutions. The pH of solution was adjusted using NaOH and H_2SO_4, where needed.

2.1. Methods

This is an experimental study. A batch plexy glass reactor, nominal volume 1750 mL, and 1500 mL useful volume was used, including 4 iron electrodes (2 cathodes and 2 anodes) with dimensions of 1 ×70×105 mm and 25 mm distance from each other placed in the reactor vertically, magnetic mixture, connection wires which is attached to electrode in one side and on the other side to power supply. Reactor schematics presented in Fig. 1.

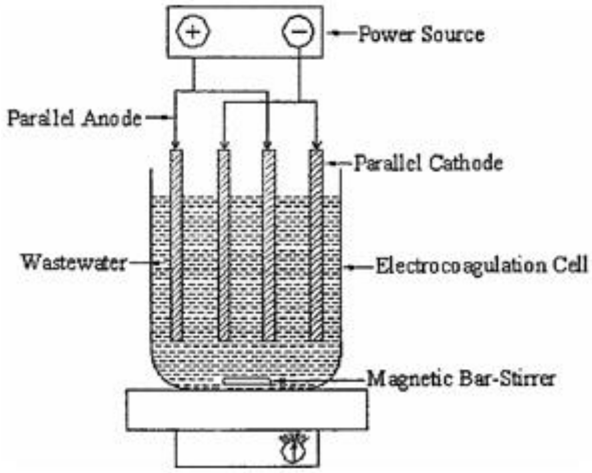

Fig. 1: Schematic of experimental set-up.

2.2. First Step

In order to determine initial density of H_2O_2, phenol 50 mg/L, peroxide hydrogen in 0.1- 0.0125 M range added to reactor in pH=4. Sulfuric acid was used in order to regulate pH. Then voltage adjusted on 10 V and 30 min delivered to remove phenol. A sample with above particulars without H_2O_2 considered as control. Urban water, because of suitable electrical convection, was used for the experiments. Second step, in order to investigate pH effect in 2-9 range, with optimum H_2O_2, and 50 mg/L phenol and 10 V voltage were used in electrocoagulation process. In the third step to determine the voltage, (5- 10- 20 V) levels in the reactor was used. Then 50-500 mg/L phenol used in order to get the effect of initial density in electro-Fenton process efficiency.

The samples were immediately analyzed to avoid further reaction. Before phenol analysis in order to remove particles intervention of reading, the samples were passed from 0.45 µ filter, then they were measured by direct standard colorometry via spectrophotometer based on amino anti-piprin method on 500 nm wavelength [13].

3. Results and Discussion

3.1. Initial H_2O_2 concentration effects

Initial H_2O_2 concentration plays an important role in oxidation process. It should be added at an optimal concentration to achieve the best degradation. Addition of H_2O_2 exceeding than optimal concentration did not improve the respective maximum degradation. This is clearly shown in Fig. 2.

The efficiency increases by increasing H_2O_2 to an optimum level. By increasing H_2O_2 to 0.0125 M, removal rate increases to 74%. Complete removal was seen in 0.025 M H_2O_2. Such efficiency increasing is due to hydroxyl radical increase according to following reaction [3].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{-} + HO \qquad (9)$$

Considering 0.1 M H_2O_2 density, the removal decreases to 36%. Higher increase of H_2O_2 decreases efficiency of hydroxyl radicals via following reactions [11]:

$$OH^{0} + H_2O_2 \rightarrow OH_2^{0} + H_2O \qquad (10)$$

$$OH^{0} + OH^{0} \rightarrow 2OH_2 + O \qquad (11)$$

Maximum removal efficiency achieved in optimum density 0.025 and 0.05 M. However, considering time effect and lower density, H_2O_2 0.025 M, had more removal in 5 min in comparison to H_2O_2 0.05 M. This result confirms the finding of the other studies. The results of study on formaldehyde removal via electro-Fenton method indicates that adding peroxide hydrogen interrupted increases efficiency in comparison to adding hydrogen peroxide in one time [11].

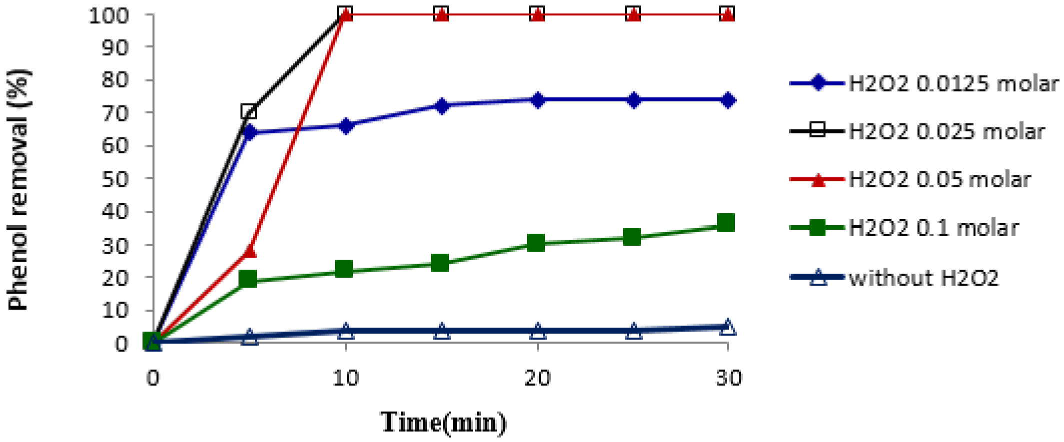

Fig. 2: The effect of H_2O_2 change and time on phenol removal (C_0= 50 mg/l, pH=4, Voltage= 10 V).

Degradability of olive oil sewage with Fenton Reagent showed that adding 0.2-0.5 M H_2O_2 significantly changes COD, however, no promotion observed above 0.5 M [14].

Similar results were repoted for dye removal from textile wastewater. Increasing peroxide hydrogen from 29 to 58 mM, decomposition increased, while reaching 73 mM led to decrease the removal efficiency [15]. Considering time effect, more removal of phenol obtained by passing time and in the highest density of selective H_2O_2, the effect of time passing in efficiency is obvious. In 0.0125 M, it seems that due to ending H2O2, time passing has not changed remaining phenol. However, in optimum density in 10 min, phenol removed totally and there is no need for extra time pass. Similarly, to remove COD and azitromaisen by proxy-electrophenton, by increasing time and consequently more production of hydroxyl radical for 60 min removal efficiency is increased and by passing time till 90 min efficiency is fixed [16]. Bagheri et al., studied aqueous solution containing high formaldehyde by electro-Fenton process, the efficacy increased during 1-10 min and reached maximum efficiency equal to 70 %, then efficacy decreased by temperature increase after 10 min and parasite reaction speed increased dissolution following 12, 13 reactions [11].

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad (12)$$

$$2H_2O_2 \rightarrow O_2\,(g) + 2H_2O \quad (13)$$

3.2. The effect of pH changes on phenol removal

PH has direct effect on peroxide hydrogen stability, hydroxyl radical production and determination Ferri statue in the solution [17]. As you can see in Fig. 3, pH changes are determined and removal rate in pH of 2,3,4,7, and 9 is 78%, 100%, 100%, 14%, and 9.8%, respectively. The most efficiency achieved in pH 3, phenol completely is removed during 10 min. The most removal obtained in acidic range (pH=3), with the increase of the pH value, the efficiency is decreased and only 9.8% phenol removed in pH=9 during 15 min.

In more acidic condition, i.e pH below 3, peroxide hydrogen attracted one protein and oxonium ion ($H_3O^+{}_2$) forms which is more stable than H_2O_2 and its reaction decreases with Ferrous ions and production decrease of OH^0 obtained consequently causes efficacy decrease [18].

In the other hand, below pH 2.5 formation of Fe $(OH)^{2+}$ which reacts by H_2O_2 gradually, decreases OH0 radicals, as a result decreases the process efficiency [12]. Above pH 4, ferrous ions changed into ferric type and by increasing pH ions ferrous sediment as hydroxyl ferric $Fe(OH)_3$ and oxy hydroxyl ferric ($FeOO^{2+}$) and sludge production increases. In pH above 5, H_2O_2 decomposed into water due to unstable structure. However, oxidation power of hydroxyl radical decreases by reaching pH to 9, electro-Fenton process almost stops and replaced by electrical coagulation

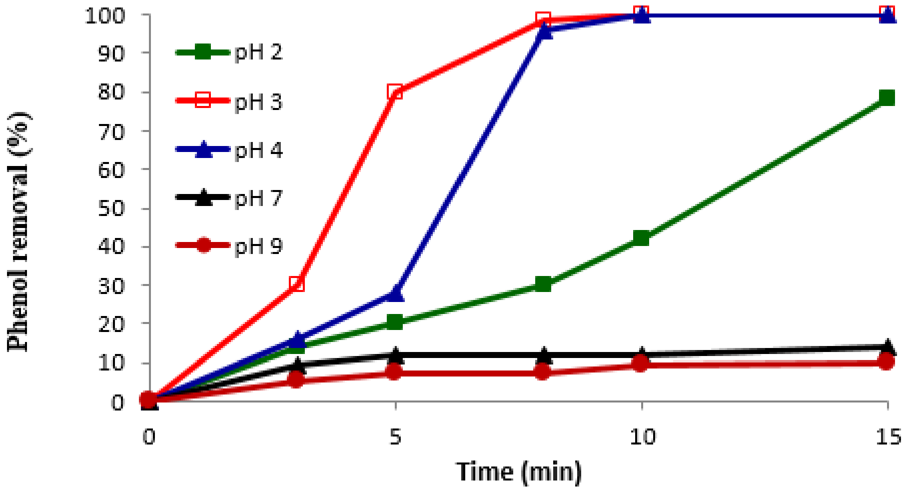

Fig. 3: The effect of pH changes on Phenol removal (H_2O_2= 0.025 M, Voltage= 10V, C_0 =50 mg/l).

Consequently, the efficacy will decrease significantly [17]. In a study to remove COD from olive oil wastewater, the optimum pH was obtained in the range of 2-4. However, recent studies indicate that pH range of Fenton oxidation process independent of sewage nature in 3-5 values [19]. In a study by Rahmani et al., optimized pH=3 obtained in phenol removal by electro Fenton system that firms this results [3].

3.3. The effect of voltage changes on Phenol removal

In electrochemical processes, current density is the most important factor to control reaction speed. According to Fig. 4, removal rate of phenol in the voltage levels 5, 10 and 20 V are ‹99.7%, 99.4% and 100%, respectively. In this study, current voltage 10 V determined as optimized voltage due to lack of significant difference in efficiency of phenol remove in comparison to 20 V current and releasing less iron. Malakootian et al., in a similar study, increased 10 V current to 20 V then 30 V, as a result dye removal via electro-Fenton turned from 85 to 98 and 100%, respectively [12].

Increasing current, due to producing more iron and hydrogen peroxide of oxygen loss on cathode surface, increases removal efficiency relatively. Consequently, it should be considered to determine optimum current [20]. It is defined by increasing voltage and time the faster chemical reaction takes place at the anode and cathode electrodes, resulting in more ions and hydroxides produced to get the pollutant. Moreover, bubble generation rate increases and their size decreases by increasing of cell voltage, resulting in a quicker removal of pollutant by H_2 floatation [21].

In a study by Esfandyari et al., using electrocoagulation proxy on olive sewage sample, increasing current density from 5 to 40 mA/cm^2 increased phenol removal efficiency of olive sewage from 60 to 89.9% [22].

3.4. The effect of phenol initial concentration changes on removal efficiency

Fig. 5, shows the effect of initial phenol density on efficiency of electro-Fenton process. The experiment repeated with 100, 200 and 500 mg/L during 30 min and remaining phenol which is, zero, 0.7 and 41 mg/L, respectively. This indicates that efficiency decreases by phenol density increase. As in a study carried by Golbaz et al., phenol removal efficiency by oxidation fenton process decreased from 97 to 75% by increasing phenol density from 1.6 to 3.7 mol/l, in optimum condition 80% dye removal efficiency in 45 min may be achieved [23]. Malakootian et al., studied dye removal by electro-Fenton process, they found that required time for removing particular percent increases by increasing dye destiny, while in lower density or higher density same dye removal obtained at end of 60 min. While by increasing density, competitive hydroxyl radicals increased by intermediate products [12].

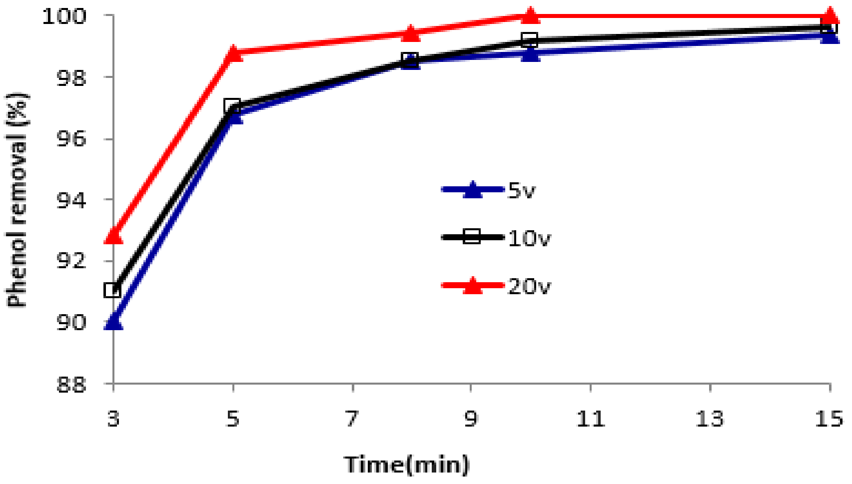

Fig. 4: The effect of voltage changes on phenol removal (H_2O_2= 0.025 M ،pH=3 ،C_0=200 mg/l).

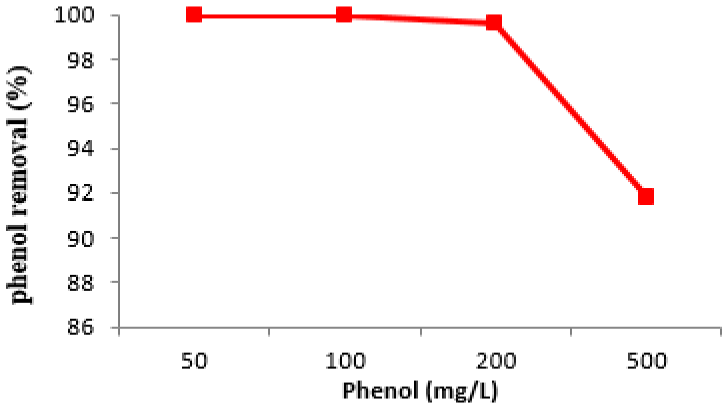

Fig. 5: The effect of initial phenol effect on phenol removal efficiency (H_2O_2= 0.025 M, pH =3, t = 15 min).

4. Conclusion

The results of this survey were shown that effectiveness of electrocoagulation process was sound suitable with 99.7% phenol removal in optimum condition. Current density, electrolysis time, initial pH, phenol concentration and conductivity were the central parameters of system. As the current density and electrolysis time increased the removal of color was also increased. It was found that the proper voltage and electrolysis time was 10 volts and 10 min. Phenol removal efficiency increased when the initial pH Decreased and conductivity value of the solution increased. Increasing in phenol concentration decrease in phenol removal efficiency. It is likewise known that, the growth on the current density and conductivity means the growth in energy use. As a result by achieving higher efficiency without extra cost, electrocoagulation process positively can be used in removing pollutants from aqueous phase.

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