<u>*Araştırma Makalesi*</u>   <u>*Research Article*</u>

Removal of Phenol by Electro-Fenton Process

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Abstract

In this study, removal of phenol from wastewater using Electro-Fenton method was achieved. The effect of operational parameters such as current density, initial concentration of phenol, and hydrogen peroxide dosage on the removal of phenol were investigated. The removal efficiencies were determined using chemical oxygen demand (COD) concentrations. The results showed that, the removal of phenol was dependent on the concentrations of hydrogen peroxide and applied current. Increasing the applied current resulted in higher removal efficiency (RE) of phenol. On the other hand, the energy consumption also increased with the increasing the current density. Thus when the optimal current density and potential have been selected, either higher removal rate or lower energy consumption can be preferred. The phenol removal significantly increased by increasing H_2O_2 dosages from 1500 to 2500 mg L^{-1}. The phenol concentration of 300 mg L^{-1} was removed with the removal efficiency of 93% at the current density of 40 mA cm^{-2} with the using of 2500 mg L^{-1} H_2O_2. Increasing of initial phenol concentration resulted in decreasing of removal efficiency. Removal efficiency decreased from 75% to 62 % when the initial phenol concentration increased from 100 to 500 mg L^{-1} after 45 min of operating time. As a result of the study, it can be said that, the removal of phenol was successfully achieved using Electro-Fenton method.

Keywords: Phenol, Electro-Fenton, COD, Iron electrodes, Wastewater treatment.

Elektro-Fenton Prosesi ile Fenolün Giderilmesi

Öz

Bu çalışmada, Elektro-Fenton yöntemi kullanılarak atık sudan fenol giderimi gerçekleştirilmiştir. Fenolün uzaklaştırılmasında akım yoğunluğu, başlangıç fenol konsantrasyonu ve hidrojen peroksit dozu gibi işlem parametrelerinin etkisi araştırılmıştır. Giderim verimleri, kimyasal oksijen ihtiyacı (KOİ) konsantrasyonları kullanılarak belirlenmiştir. Sonuçlar, fenolün uzaklaştırılmasının hidrojen peroksit konsantrasyonlarına ve uygulanan akıma bağlı olduğunu göstermiştir. Uygulanan akımın artırılması, fenolün daha yüksek giderim verimliliği (RE) ile sonuçlanmıştır. Öte yandan akım yoğunluğunun artmasıyla birlikte enerji tüketimi de artmıştır. Böylece optimum akım yoğunluğu ve potansiyeli seçildiğinde, ya daha yüksek giderim oranı ya da daha düşük enerji tüketimi tercih edilebilir. Fenol giderimi, H_2O_2 dozunun 1500 mg L^{-1}'den 2500 mg L^{-1}'e yükseltilmesiyle önemli ölçüde artmıştır. 2500 mg L^{-1} H_2O_2 kullanılarak 40 mA cm^{-2} akım yoğunluğunda 300 mg L^{-1} fenol konsantrasyonu %93 verim ile giderilmiştir. Başlangıç fenol konsantrasyonunun artması, giderim veriminin düşmesine neden olmuştur. 45 dakikalık çalışma süresinden sonra ilk fenol konsantrasyonu 100 mg L^{-1}'den 500 mg L^{-1}'e yükseldiğinde giderim verimliliği % 75'ten % 62'ye düşmüştür. Çalışma sonucunda, Elektro-Fenton yöntemi kullanılarak fenol gideriminin başarılı bir şekilde sağlandığı söylenebilmektedir.

Anahtar Kelimeler: Fenol, Elektro-Fenton, KOİ, Demir elektrot, Atıksu arıtma.

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1. Introduction

Water is one of the most essential elements for life on Earth, and its significance is only growing as a result of population expansion, climate change, urbanization, and the spread of irrigated agriculture (Kılıç, 2020). The lack of access to clean water supplies, particularly in some nations and regions, hinders human activity and economic growth (Boretti & Rosa, 2019). Water scarcity was included as one of the top global threats in the World Economic Forum's 2019 and 2020 reports in terms of possible impact over the following ten years (March and McLennan, 2020). Because of this, it is crucial to treat and recycle wastewater that is produced after being used for human consumption and after industrial processes.

Due to the depletion of water resources, industrial effluent must now be treated and recycled. Phenolic compounds constitute a group of pollutants particularly toxic to the aquatic fauna, flora and human (Org et al., 2012). Organic pollutants such as phenols, cresol and other substituted phenols are produced in high concentrations from different industries like pharmaceutical, oil refineries, pulp and paper mill, and food-processing (Liao et al., 2001). Phenols are highly corrosive, stable and nerve poisoning agents and recorded in USEPA list of priority pollutants (Liao et al., 2001). In industrial effluents, where phenol is present as an intermediary, phenolic compounds can be found in concentrations of 800-2000 mg/L. The release of phenol into the environment threatens human health and degrades the environment, necessitating the creation of cutting-edge techniques to get rid of phenol.

Such compounds are hard to remove by conventional biological treatment processes. Advanced oxidation processes (AOPs) are considered as possible alternative for the removal of persistent organic pollutants from wastewater (Liao et al., 2001). Among AOPs, the Electro–Fenton process which involves the concurrent use of Fe^{2+} ions and hydrogen peroxide is used to decompose and remove pollutants (Rahmani et al., 2016). No harmful and toxic substances are used in the Electro-Fenton (EF) process, it is an ecofriendly and low-cost method for the treatment of water and wastewater.

In EF, A nonselective powerful oxidant called hydroxyl radicals ($^\bullet$OH) are produced when the ferrous or ferric ions react with H_2O_2 (Xu & Wang, 2011):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^\bullet + OH^- \tag{1}$$
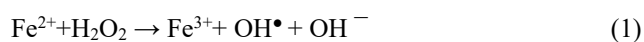
The pH, concentration, stirring speed, inter-electrode spacing, electrical conductivity, current density, and temperature are all factors that affect how well the EF process works (Brillas et al., 2009).

There are other EF oxidation processes that have been characterized, including EF-FeRe, EF-FeO$_x$, EF-H$_2$O$_2$-FeRe, and EF-H$_2$O$_2$-FeO$_x$ (Re denotes regeneration in the oxidation process). In EF-FeRe, Fe^{2+} is constantly produced at the cathode while H_2O_2 and Fe^{2+} are applied externally. In EF-FeO$_x$, H_2O_2 is delivered externally, and the source of Fe^{2+} is a sacrificial Fe anode. Moreover, depending on how the electrolytic cell is configured, Fe^{2+} may be continually created at the cathode. H_2O_2 and Fe^{2+} are simultaneously produced at the cathode in EF-H$_2$O$_2$-FeRe, with H_2O_2 creation taking precedence. H_2O_2 is produced at the cathode in EF-H$_2$O$_2$-FeO$_x$, whereas a sacrificial Fe anode provides Fe^{2+} (Tezcan Ün et al., 2009).

In this study, to further capitalize on the dissolved Fe ion present in the bulk phase, H_2O_2 was added externally to the electrolytic reactor whereas a sacrificial iron anode was used as the ferrous ion source (EF–FeO$_x$). The addition of hydrogen peroxide at the beginning of the experiments resulted in the rapid and efficient production of hydroxyl radicals.

The aim of this study was to investigate the efficiency of Electro-Fenton process using iron electrodes in oxidation of phenol. The effect of different parameters such as current density, operating time, concentrations of phenol and H_2O_2 were investigated.

2. Material and Method

In this study, the wastewater sample was prepared using stock solution of phenol, 500 mg L^{-1}, which was prepared by adding 500 mg of phenol to 1 L of distilled water. The electrochemical system consists of a reactor, a mechanical stirrer, and a direct current (DC) power supply (GW Instek); its schematic representation is shown in Fig. 1. In the experiments, the iron anode and cathode was used. The iron cylindrical reactor that operated as cathode was of 6.6 cm height and had an internal diameter of 10.8 cm. The mechanical stirrer (Heidolph RZR 2102) consisted of blades and operated as the anode; it was dipped into the reactor containing wastewater. By vigorously swirling the liquid at 100 rpm, it was also utilized to maintain consistent composition and to facilitate the aggregation of flocs in the solution. The performance of the reactor was evaluated in the batch mode.

The EF process was carried out at pH 3, using different current densities (30, 40 and 50 mA cm^{-2}) and initial phenol concentrations (100, 300 and 500 mg L^{-1}). In each experiment, the 500 mL of wastewater poured into the cathode chamber and anode was dipped into the wastewater. The anode connected to the mechanical stirrer, and it was acted as anode and as stirrer. It consists of eight blades (each has 2 cm height and 1.5 cm wide) attached to a 4 cm diameter circle. The total surface area of anode was 73 cm^2. Before the EF experiments, 0.05 M of Na$_2$SO$_4$ was added to the wastewater as the supporting electrolyte to improve conductivity and the ionic strength. The iron electrodes were connected to a DC power supply. The determined H_2O_2 amount was also added to the wastewater at the beginning of the experiment. The degradation of phenol solution was determined by measuring chemical oxygen demand (COD) of effluent. The COD was measured by potassium dichromate titrimetric method as explained in Standard Methods (5220 CHEMICAL OXYGEN DEMAND (COD).

The calculation of removal efficiency (RE%) after EF and the electrical energy consumed per unit volume of treated wastewater (EEC) was calculated using the Eqs. (2), (3), respectively.

$$RE\% = (C_0 - C)/C_0 * 100 \tag{2}$$

where C_0 and C are the concentrations of COD before and after EF, respectively, in mg L^{-1} and

$$EEC = V*I*t/v \tag{3}$$

where EEC is the electrical energy consumption (kWh m^{-3}), V is the potential (V), I is the current (A), t is the time (h), and v is the volume of solution treated (m^3).

Different concentrations of H_2O_2 (1500, 2000 and 2500 mg L^{-1}) were also added to start the oxidative degradation of phenol.
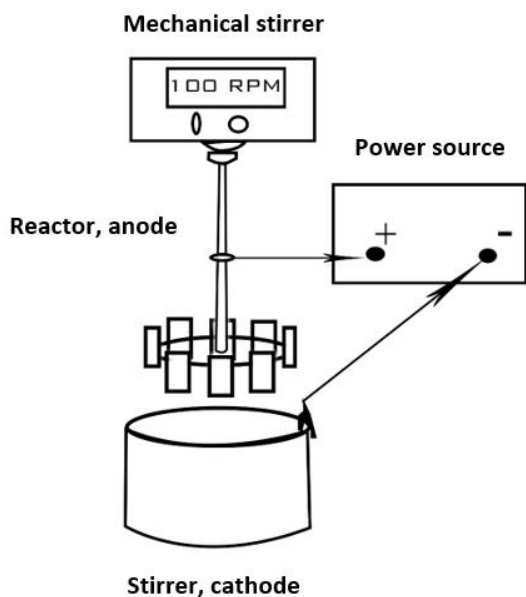
Figure 1. Experimental set-up.

3. Results and Discussion

3.1. The Effect of Current Density

The amount of Fe^{2+} ions released from the anode and the amount of coagulant that results depend on the current supply to the EF system. The phenol concentration of 100 mgL^{-1} which corresponded to the COD concentration of 216 mg L^{-1} was used to determine the effect of current density. The effect of current density on phenol removal efficiency was increasing when applied current was increased. As seen from Fig. 2, the removal efficiencies were 25%, 62% and 63% at 30 mA cm^{-2}, 61%, 72% and 75 % at 40 mA cm^{-2} and 77%, 80.8% and 81% at 50 mA cm^{-2} for 15, 30 and 45 min, respectively.
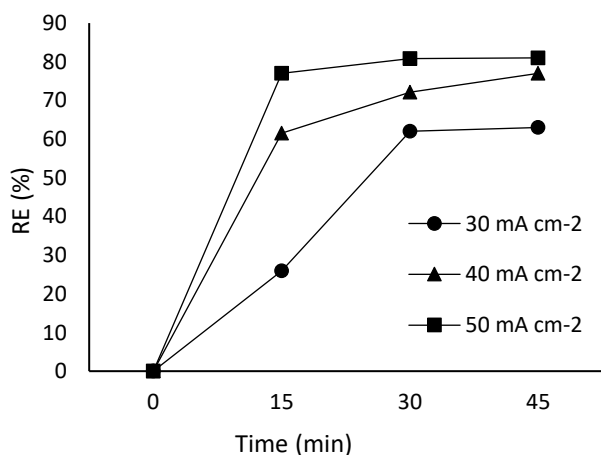

Figure 2. The removal efficiencies of phenol with different current densities (pH:3, C_{Na2SO4}:0.05 M, C_{Phenol}: 100 mg L^{-1} C_{H2O2}: 2000 mg L^{-1}).

Fig. 3 illustrates how the current density affects the EEC during the EC process. Electrical energy consumption increased more quickly as the current density increased. EEC increase as result of the applied potential rising due to an increase in current density. However, the potential and current grew linearly, EEC increased exponentially. Therefore, when the optimal current density and potential have been selected, either higher removal rate or lower energy consumption can be preferred.
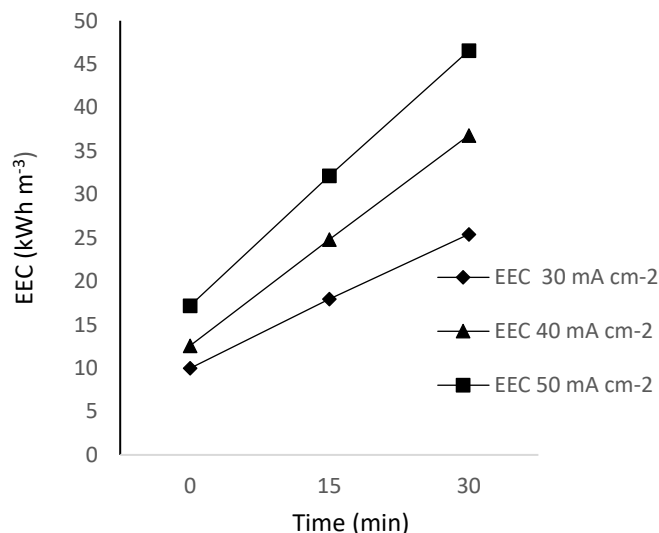

Figure 3. The effect of current density on EEC.

3.2. The Effect of Initial Phenol Concentration

The effect of initial phenol concentrations on EF process was examined in a range of 100, 300, 500 mg L^{-1} at pH 3 and 40 mA cm^{-2}. The initial COD concentrations of each solution were 216, 612 and 1196 mg L^{-1} for the phenol concentrations of 100, 300 and 500 mg L^{-1}, respectively. Increasing of phenol concentration from 100 to 500 mg L^{-1} resulted in a reduction in removal efficiency from 75% to 62% after 45 min EF (Figure 4). It was noticed that pH values were increased with increasing operation time.
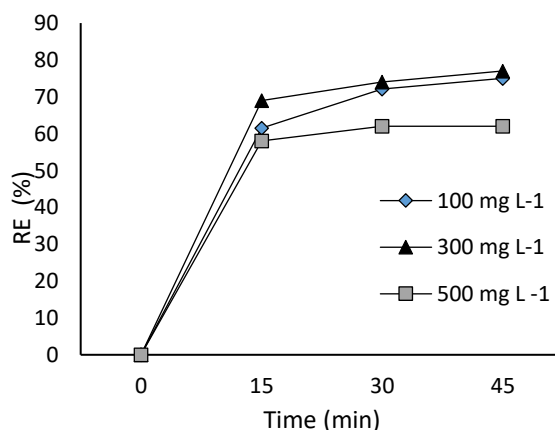

Figure 4. The removal efficiencies of phenol with different initial phenol concentrations (pH:3,C_{Na2SO4}:0.05 M, i: 40 mA cm^{-2}, C_{H2O2}: 2000 mg L^{-1}).

3.3. The Effect of The H_2O_2 Dosage

In order to set the optimal dosage of H_2O_2, different concentrations of H_2O_2 such as 1500, 2000 and 2500 mg L^{-1} were added to each prepared sample. The pH was set to 3, and the experiment was performed. The addition of hydrogen peroxide at the beginning of the experiments resulted in the rapid and efficient production of hydroxyl radicals. The effect of different amounts of H_2O_2 on wastewater processing was investigated, and the results are shown in Fig. 5. The results show that increasing of H_2O_2 from 1500 to 2500 mg L^{-1} resulted in an increase in the phenol removal efficiency from 70 to 93%, respectively (Figure 5). The effects of hydroxyl radicals originated from H_2O_2 caused the rapid removal of COD at the beginning of the experiments. As the concentration of COD decrease with time, removal rate also decreased as expected as seen from Fig. 5.
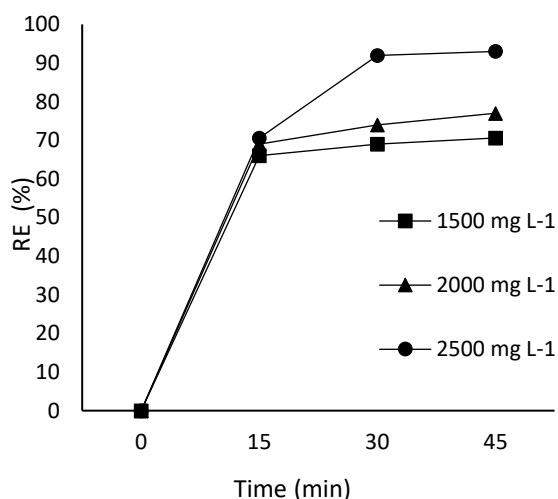

Fig. 5 The removal efficiencies of phenol with different H_2O_2 dosages (pH:3, C_{Na2SO4}:0.05 M, i: 40 mA cm^{-2}, C_{phenol}: 300 mg L^{-1}).

4. Conclusions and Recommendations

In this study, removal of phenol using the Electro-Fenton method was investigated. The effects of the different operational parameters on the removal of phenol were analyzed. The following conclusions can be drawn from the experimental results:

According to the results obtained from the above experiments, the removal efficiencies increased by increasing the current density. At higher current densitites, higher amount of iron ions were relased which results to produce more hydroxyl radicals in the system. Moreover, the energy consumption increased by increasing the current density. Thus when the optimal current density and potential have been selected, either higher removal rate or lower energy consumption can be preferred.

The effect of initial phenol concentration on the RE showed that the increase of the concentration of phenol from 100 to 500 mg L^{-1}, the removal efficiency values decreased from 75 to 62%, respectively. This is due to the fact that at a constant current density, the same amount of iron ions and hydroxyl radical passes

to the solution at different phenol concentrations (Org et al., 2012). Rahmani et al. (2016) found that increasing of phenol concentration decreased the RE. The high initial concentration of the pollutants required greater oxidation potential, and thus with a constant amount of oxidant, the efficiency of the process decreased (Khatri et al., 2018)

To investigate the effect of H_2O_2 concentration on EF performance, different amount of H_2O_2 concentrations were used. An increase in H_2O_2 concentrations, phenol removals also increased. The increase in phenol destruction can be assigned to the increase in generation of ●OH radicals at higher H_2O_2 dosage (Khatri et al., 2018)

As a result of the study, Electro-Fenton process using iron electrodes for phenol removal is a promising process in terms of environmental and low-cost features.

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