Organics deterioration from aqueous solutions by electro-Fenton process

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Abstract. A MnO₂-graphite electrode was used in the treatment of aqueous solution from phenolic compounds by an electro-Fenton process. The effect of operating conditions, i.e. current density and externally added Fe²⁺, on the efficiency of the electro-Fenton Process performance was investigated. The performance of the electro-Fenton process was estimated by the chemical oxygen demand (COD) removal percentage from the treated solution after 6 h elector-oxidation at 30 °C. Significantly, the removal increased with increasing the applied current density and Fe²⁺ added, while the maximum removal percentage was achieved when 1mM Fe²⁺ added and 8mA/cm² applied. Kinetic study of COD deterioration from the treated aqueous solution at the applied values of the operating parameters was carried out and the results were indicated that the COD decay over the MnO₂-graphite anode by electro-Fenton process followed zero order kinetics. Current efficiency and specific power consumption of the process were also predicted.

1. Introduction
Phenol is one of the most common organic pollutants that present in water. It is released into ecosystems due to natural phenomenon and anthropogenic processes[1]. Phenol concentration should not exceed 0.1 µg/L in drinking water and 1 mg/L in wastewater[2]. Therefore, technologies have been developed for phenol abatement from effluents before discharge into water bodies, for example, biological, physical-chemical, chemical, advanced oxidation processes (AOPs), and electrochemical advanced oxidation processes(EAOPs)[3]–[7].

Biological oxidation is certainly the cheapest process, however, the toxicity and bio-refractory of phenol may prevent this approach[8]. For this reason, physical-chemical methods and chemical oxidation are favorably applied[9]. Nevertheless, these techniques are insufficient because physical-chemical methods are not destructive [5], while in chemical oxidation processes, intermediates more toxic than mother pollutants may be produced in some cases, also chemical oxidation requires shipping and storage of toxic hazardous chemicals[10].

AOPs are an attractive alternative to traditional physical-chemical and chemical oxidation processes for phenol oxidation. AOPs depend on the formation of a strong oxidizing agent hydroxyl free radicals (•OH) using an individual oxidant (ozone (O₃)), multi-oxidants (ozone combined with hydrogen peroxide (O₃/H₂O₂)) or multi-oxidants with ultraviolet (UV) light (O₃/UV, H₂O₂/UV, O₃/H₂O₂/UV), and also from a combination of ferrous iron (Fe²⁺) with H₂O₂ (Fe²⁺/H₂O₂), which is called Fentons reagent. But the high cost of the oxidants or the cost of the source of UV light were considered drawbacks of the AOPs [8]. New methods of AOPs based on the electrochemical technology have been emerged. These processes are the so-called EAOPs used to remediate wastewater economically and effectively [10]. Among EAOPs, electro-Fenton technique have been
attracted great interest in water treatment from organic contaminants[11]. In electro-Fenton process, the powerful oxidizing species •OH employed in the oxidation of the organic contaminants and it is produced from the catalytic decomposition of H₂O₂ in the presence of iron catalyst (Fe²⁺) in an acidic solution[7]. H₂O₂ is electrochemically generated from oxygen (O₂) reduction reaction at a suitable carbon-base cathode such as graphite, carbon sponge, carbon felt, etc...[12]. Basic electro-Fenton reactions are described in Eqs. (1 and 2):

\begin{align*}
H_2O_2 + Fe^{2+} &\rightarrow OH^- + \bullet OH + Fe^{3+} \\
O_2 + 2H^+ + 2e^- &\rightarrow H_2O_2
\end{align*}

The oxidized form of iron catalyst (Fe³⁺) then reduced chemically or electrochemically allowing the propagation of electro-Fenton process[13]. The efficiency of the electro-Fenton process depends on several parameters, such as pH of the solution to be treated, Fe²⁺ concentration, supporting electrolyte concentration, the material of the cathode electrode, applied current, and distance between anode and cathode electrodes[14]. The material of anode electrode plays an important role. Boron doped diamond (BDD) and platinum (Pt) are frequently used anodes in electro-Fenton process, but the high cost of BDD and Pt hinder their usages in industrial applications[13], [15]. So, economic alternative anode materials with good stability and good catalytic activity are required. Manganese dioxide electrode (MnO₂) is recently used as working electrode in different electrochemical processes and promising results were obtained[16]–[18]. Alaoui et al [16] studied the electrochemical oxidation of methylene blue (MB) in aqueous solution by direct oxidation technique using MnO₂ electrode as anode and more than 90% MB was removed. Abbar et al[17] verified the incineration of oxalic acid (OA) over a rotating MnO₂ anode by anodic oxidation process. They found that 97% of OA converted at the following operating conditions: 50 °C, 40 mA/cm², and 200 rpm in the presence of 1 g/L NaCl. Sotgiu et al[18] prepared three different types (A, B, and C) of MnO₂ electrodes and tested them in the oxidation of the azo dye Reactive Violet 5 and the best results obtained from using type-A MnO₂ electrode.

In the present study, the performance of MnO₂-graphite substrate electrode in COD electro-oxidation from phenol aqueous solution has been investigated by the electro-Fenton technique. Moreover, kinetic of COD deterioration over the MnO₂-graphite anode was predicted. The efficiency of each applied current value (current efficiency) on the COD reduction for the volume of the treated solution and the quantity of the energy consumed per kg COD removed (specific power consumption) were also discussed.

2. Experimental work
Experiments of COD deterioration from a synthetic phenolic aqueous solution (1320 ppm COD) by electro-Fenton process were carried out in an open undivided cell with a working volume of 0.5 L and equipped with two electrodes. The counter electrode was a hollow cylindrical graphite electrode (8 cm inside diameter, 10 cm outside diameter, and 15 cm length) while the working electrode was the MnO₂-graphite electrode (1.5 cm diameter and 6 cm length). The anode and cathode were fixed in concentric layout to achieve good potential and/or current distribution and the anode was rotated at 200 rpm. Prior to oxidation experiments began, oxygen bubbled into the aqueous solution to be treated for 20 min by applying a compressed air at a flow rate of 1 L/min using an electromagnetic air pump (ACO-001) to achieve O₂ saturation concentration in order to maximize H₂O₂ generation rate. The temperature of the solution kept at the desired value (30 °C) by using hot-plate magnetic stirrer (Stuart CB162). Moreover, the pH of the solution was adjusted to optimum value (3)[19] that makes electro-Fenton's reactions rate as great as possible (Eqs. (1 and 2)) by means of (Basic 20) pH meter. The experiments were performed with an applied current density ranging from 1 to 8 mA/cm² supplied by a DC power supply (UNI-TUTP3315TF-L) and an externally added 0.05, 0.2, 0.6, and 1 mM Fe²⁺ concentration and 0.5 M Na₂SO₃ to enhance electrical conductivity. The performance of the oxidation
process by the electro-Fenton technique examined by the percentage of COD removal which defined by the following equation (Eq. (3)):

\[
\text{Removal, } \% = \frac{COD_0 - COD_t}{COD_0} \times 100
\]  

(3)

Where COD₀ and CODₜ are the experimentally obtained COD concentrations in mg/L before and at t time of electrolysis, respectively.

In order to measure the COD before and at t time of electrolysis, samples were collected and only 2ml of each sample was digested with K₂Cr₂O₇ for 2 h at 150 °C in acidic media using COD digester (RD-125, Lovibond) and then analyzed by COD Lovibond Vario MD200 photometer to measure the amount of oxygen required to oxidize the organic matter in each sample.

3. Results and discussion

The effect of current density and Fe²⁺ concentration on the removal efficiency from the treated aqueous solution by the electro-Fenton process was investigated with an applied current density ranging from 1 to 8mA/cm² and an externally added Fe²⁺ ranging from 0.05 to 1 mM, and the results are shown in Figure 1. After 6 h electrolysis, the removal was increased with current density and Fe²⁺ concentration and the highest removal was attained at 8 mA/cm² when 1 mM Fe²⁺ added. This result could be attributed to an increase in the electrochemically generated H₂O₂ with the current density along with the beneficial effect of Fe²⁺ added which resulted in an increase of •OH radicals production, which react with the pollutants and improved the efficiency of COD abatement from the contaminated aqueous solution[20], [21].

![Figure 1](image-url)

**Figure 1.** The effect of current density on removal, T = 30°C, Na₂SO₃ = 0.5 M for 6 h electrolysis and different Fe²⁺ added.
The reaction of organic pollutants oxidation can be represented as:

\[ \text{Organic pollutants} + \bullet \text{OH} \rightarrow \text{Oxidation products} \]  

(4)

Because \( \bullet \text{OH} \) radicals are highly active and do not accumulate in the solution, its concentration reaches steady state during the remediation process. The oxidation rate of organic pollutants in term of COD deterioration can be expressed as in Eq. (5):

\[
- \frac{d[COD]}{dt} = k_{\text{abs}}[OH]^a[COD]^n
\]  

(5)

Where \( k_{\text{abs}} \) is the absolute degradation rate constant. Because \( \bullet \text{OH} \) concentration is constant at a steady state, \( k_{\text{abs}} [\bullet \text{OH}]^a \) corresponds to the apparent reaction rate, \( k_{\text{app}} \), and Eq.(6) can be rewritten as:

\[
- \frac{d[COD]}{dt} = k_{\text{app}}[COD]^n
\]  

(6)

The deterioration kinetics of 1320 ppm COD at 30 °C was investigated at different current densities and different Fe\(^{2+}\) concentrations. The hydroxylation reaction order and apparent rate constant over the \( \text{MnO}_2 \)-graphite anode were determined considering the \( n^{\text{th}} \)-order rate expression in Eq. (6), evaluated by nonlinear regression. COD deterioration over the \( \text{MnO}_2 \) anode followed a zero-order kinetics in current density and Fe\(^{2+}\) concentration (linear correlation between COD and time), and the calculated apparent rate constants increased with the applied current density and externally added Fe\(^{2+}\) concentrations as can be seen from Table 1. The zero-order kinetics indicates that the reaction was current and Fe\(^{2+}\) concentration controlled, and was attributed to the slower rate of \( \bullet \text{OH} \) radical generation compared to the pollutant diffusion rate to the electrode surface. Current control is an important feature in wastewater treatment as the remediation process does not slow down as the reaction proceeds [24].

Table 1. Rate constants (in 1/M.S) of COD deterioration at 30 °C for different Fe\(^{2+}\) concentrations and different current densities.

| Current density, mA/cm\(^2\) | Fe\(^{2+}\), mM | 0.05 | 0.2 | 0.6 | 1 |
|-----------------------------|----------------|------|-----|-----|---|
| 1                           | 177.173        | 181.463 | 192.896 | 204.328 |
| 2                           | 178.604        | 187.179 | 210.043 | 232.902 |
| 3                           | 180.033        | 192.896 | 227.188 | 261.472 |
| 4                           | 181.462        | 198.612 | 244.331 | 290.039 |
| 5                           | 182.892        | 204.326 | 261.472 | 318.602 |
| 6                           | 184.321        | 210.043 | 278.612 | 347.164 |
| 7                           | 185.750        | 215.758 | 295.751 | 375.725 |
| 8                           | 187.179        | 221.473 | 312.890 | 404.284 |

The efficiency of water remediation processes from the organic contaminants using the EAOPs is evaluated by COD decay from the treated solutions. COD data permit the estimation of the applied electro-Fenton efficiency concerning electrical charges used during the electrolysis. The average current efficiency (CE) and specific power consumption (SPC) evaluated 30 °C and 1 mM Fe\(^{2+}\) to assess the performance of the electro-Fenton process using \( \text{MnO}_2 \)-graphite base electrode at various current density. The CE at different time periods (in h) calculated from Eq.(7)[25].

\[
CE(\%) = \frac{\Delta COD F V_s}{B It} \times 100
\]  

(7)
Where: $\Delta$COD is the experimentally obtained COD in (g/l), $I$ is the applied current in (A), $V_s$ is the volume of the electrolytic solution in (L), and $F$ is the Faraday constant (96487 C mol$^{-1}$).

The evaluated CE as a function of the consumed electrical charge $Q$ (Ah/L) is presented in Figure 2. The highest CE value 48.31% was obtained when the lowest current density of 1 mA/cm$^2$ was applied at the beginning of electrolysis after consuming 0.03 Ah L$^{-1}$. At higher $Q$ values, the CE dropped strongly with time due to the formation of persistent intermediates[23]. The loss in the average efficiency with the higher applied electrical charges happened as a result of the promotion of the parasitic reactions that scavenging hydroxyl radicals generated. For example, $\text{H}_2\text{O}_2$ reduction at the cathode Eq.(8), disproportion of $\text{H}_2\text{O}_2$ in the bulk Eq.(9), oxidizing $\text{H}_2\text{O}_2$ at the anode Eqs.(10 and 11), and dimerization of hydroxyl radicals to hydrogen peroxide Eq.(12) are expected parasitic reactions that scavenging $\cdot$OH radicals.

\[
\begin{align*}
\text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^- & \rightarrow 2\text{H}_2\text{O} \quad (8) \\
2\text{H}_2\text{O}_2 & \rightarrow \text{O}_2(\text{g}) + 2\text{H}_2\text{O} \quad (9) \\
\text{H}_2\text{O}_2 & \rightarrow \text{HO}_2^- + 2\text{H}^+ + 2e^- \quad (10) \\
\text{HO}_2^- & \rightarrow \text{O}_2(\text{g}) + e^- + \text{H}^+ \quad (11) \\
2 \cdot \text{OH} & \rightarrow \text{H}_2\text{O}_2 \\
\end{align*}
\]

The SPC in (kW h/kg COD) is given by has been determined from Eq.(13)[24]

\[
SPC = \frac{VI}{3600\times\Delta\text{COD}V_s}
\quad (13)
\]
Where $V$ is potential of the cell in (volt), $I$ is the current density applied in (A), $t$ is the time of the electrolysis in (s), $\Delta$ COD is the experimentally obtained COD in (g/l), and $V_s$ is the volume of the treated solution in (L).

The general trend of the SPC (as shown in Figure 3) is linearly increased as the consumed charge increased with time. The highest SPC attained when 2.88 Ah L$^{-1}$ consumed after 6 hours, again the reason was the production of recalcitrant intermediates that require a longer time to be eliminated. Although higher applied current densities grow up the cell potential ($E_{cell}$), consequently, higher power will be consumed.

![Figure 3. The effect of consumed specific charges on the SPC at 1 mM Fe$^{2+}$, 30 C and different current densities for organics reduction efficiency from phenolic aqueous solution.](image)

4. Conclusion
The mechanism of COD reduction from phenol aqueous solution was based on the generation of OH radicals from the catalytic decomposition of the electrogenerated H$_2$O$_2$ in the presence of Fe$^{2+}$ (electro-Fenton process). The increase in the Fe$^{2+}$ concentration, and current density had a beneficial effect on the removal efficiency and the highest removal was attained when 1m M Fe$^{2+}$ added and 8mA/cm$^2$ applied. Predicted kinetic of COD deterioration from phenol aqueous solution showed that COD decay over the MnO$_2$-graphite substrate anode by electro-Fenton process followed zero-order kinetics, indicating that the reaction was under Fe$^{2+}$ concentration and current control. The performance of the electro-Fenton process for COD degradation using the MnO$_2$-graphite substrate anode was assessed by evaluating the CE and SPC values. The estimated CE and SPC values implied that in spite of higher removal percentages attained at higher applied currents, the process was highly efficient at the earlier time periods when low currents used.

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