The performance of MnO₂/graphite electrode for TOC removal from wastewater by indirect electrochemical oxidation process

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Abstract. Electrochemical oxidation in the presence of sodium chloride used for removal of phenol and any other organic by products formed during the electrolysis by using MnO₂/graphite electrode. The performance of the electrode was evaluated in terms fraction of phenol and the formed organic by products removed during the electrolysis process. The results showed that the electrochemical oxidation process was very effective in the removal of phenol and the other organics, where the removal percentage of phenol was 97.33%, and the final value of TOC was 6.985 ppm after 4 hours and by using a speed of rotation of the MnO₂ electrode equal to 200 rpm.

1. Introduction
Total organic carbon (TOC) is defined as any compound containing carbon atoms except CO₂ and associated matters such as carbonate, bicarbonate and the like[1].

Phenol is known as one of the most difficult organic molecules to be removed. A wide concern on the removal of phenol have brought due to the destructive effects of phenol like high toxicity and bad smell. Wastewater from several industries including petrochemical, plastics, dyes, and pharmaceutical contains phenol. Many handling technologies for phenol wastewater have been established, either by carbon adsorption, solvent extraction, biological and chemical or electrochemical oxidation[2, 3].

Electrochemical oxidation has drawn extensive research consideration due to its simplicity and robustness in structure and operation. Electrochemical oxidation can be used for handling of aqueous non-biodegradable recalcitrant organic contaminants of high toxicity through oxidation by mainly, but not solely, highly reactive hydroxyl radicals[4, 5]. Toxic organics can be well oxidized by electrochemical reaction and there is no need for chemicals to be added. In fact; only electrical energy is consumed for removing the organic pollutants and it has the potential to be developed as a cost-effective technology for the organic pollutants removal, particularly for low-volume applications. The effectiveness of the electrochemical oxidation of organics depends on many factors including the material of electrode, the current density, the presence in solution of species able to act as mediators, the flow dynamic regime, and the pH[6, 7].

Depending on the anode nature and pH conditions utilized, different pathways, intermediates, and side products have been recognized in the oxidation of phenol. Broad view of the degradation pathways for different organic pollutants has proved to be challenging despite of similarities. Thus, the kinetics of organics degradation by the anodic oxidation process should be examined[8].
Phenol degradation reaction sequence acquired by many workers, which consists of phenol decomposition, aromatic and aliphatic intermediates and \( \text{CO}_2 \) formation. Primarily, more toxic aromatic intermediates than phenol such as benzoquinone, catechol and hydroquinone, are generating depending on the experimental conditions. In alkaline media, there is no detection of hydroquinone and 1–4 benzoquinone in electrolysis (benzoquinone itself is unstable in alkaline solution). Still, in acidic media, hydroquinone and benzoquinone are the principle oxidation intermediates and the development of the anodic films is inhibited. In addition, oxidation of these toxic intermediates produces organic acids such as oxalic, maleic, fumaric acid, and/or harmless end-products (\( \text{H}_2\text{O} \) and \( \text{CO}_2 \)).

A better understanding of the processes taking place in electrochemical systems can be obtained by significant research effort. A number of models have been developed to describe the electrochemical treatment when wastewaters polluted with organic materials. Different methods of describing the physical processes taking place within the reactor had been represented by these models, besides their confirmation with experimental data offers support for the assumptions on which they are based.

Electrochemical oxidation of 2-chlorophenol was studied at Ti/PbO\(_2\) and Ti/SnO\(_2\) anodes by Polcaro et al. In order to better quantify the influence of different operating parameters on the electrochemical process, a simplified mathematical model was formulated. The overall oxidation process can be presented as: \( [R_1 \xrightarrow{k_1} R_2 \xrightarrow{k_2} 3R_3 \xrightarrow{k_3} \text{CO}_2] \), where \( R_1 \) is chlorophenol which would be oxidized electrochemically to quinonic compounds (\( R_2 \)), and aliphatic acids like oxalic acid (\( R_3 \)) would be formed by ring opening. Finally all these products would be converted to \( \text{CO}_2 \). The concentrations of chlorophenol and of its oxidation products were measured by HPLC. Steady state conditions was assumed for hydroxyl radicals production which would be consumed by organic oxidation and oxygen evolution and the reactions would be described by pseudo first order kinetics.

There are two main types of electrodes, active and non-active. MnO\(_2\) can be considered as non-active electrode since it simply acts as electron sinks, and its components do not take part in the process. MnO\(_2\) is a metal oxide electrode which is very active for Cl\(_2\) evolution, so this agent is usually used in oxidation of organic components.

In the present work, a model describing the indirect electrochemical treatment of water containing phenol was applied to describe the processes taking place when wastewaters polluted with organic materials are treated in a batch reactor with non-active anode (MnO\(_2\)).

2. Experimental work
Phenol (LABO Chemie), NaCl (Thomas Baker), and H\(_2\)SO\(_4\) (Riedel-deHaën) were used. All these chemicals used in experiments were of the reagent grade and there was no need for further purification, and distilled water was used in the preparation of all aqueous solutions. The electrolytic solution of phenol removal experiments consisted of 1 L of distilled water, 150 ppm of phenol dissolved into it. Indirect oxidation was used in this study, so 0.017 M of NaCl and 0.1M of H\(_2\)SO\(_4\) as the supporting electrolyte were added to the solution. The final pH of solution was equal to 1.

The cathode electrode which was the hollow cylinder graphite (with outside diameter 100 mm and inside diameter 80 mm and 150 mm length) was dipped into the electrolytic solution. The anode electrode was a rod with 18 mm outside diameter and 80 mm length of MnO\(_2\)/graphite electrode which was fixed to the agitator and dipped into the electrolytic solution. The electrodes were connected to the DC power supply and a constant current density of 100 mA/cm\(^2\) was applied to the anode for a specified time of 4 hours and the rotation speed of the electrical stirrer was 200 rpm. The samples were collected during the electrolysis process, and the temperature of the electrolyte was maintained at about 25°C.

UV-Visible Spectrophotometer (Thermo Genesys 10 UV Electron Corporation Madison W153711 USA) was used for measuring the absorbency of samples at a wave length equal to 269 nm corresponding to the maximum absorbance for phenol. The absorbance was found to vary linearly with concentration, which was in agreement with the Lambert-Beer law.

The total organic carbon for the initial and electrolyzed samples during kinetic model experiment was determined using a TOC analyzer (Hach, IL 550 TOC-TN model, USA).
3. Results and discussion

A number of simplifying assumptions should be made. The main processes in terms of pollutant removal are irreversible reactions, and it can be assumed that only hydrogen evolution occurs in the cathodic zone.

Usually, during the process of electrochemical degradation of phenol and its derivatives, three irreversible steps are taking place[10]:

a) Oxidation of phenol \((R_1)\) and forming intermediates which are mainly cyclic organics.

b) A ring opening reactions of cyclic intermediates (like chlorophenol and others) to form organic acids (like oxalic acid that is considered as predominant, and it is the main product in the final step of reaction in all cases of electrochemical oxidation processes).

c) Mineralization of these organic acids to \(CO_2\).

There are many phenol derivatives during the process of electrochemical oxidation like chlorophenol, benzoquinone, hydroquinone, and oxalic acid. Analyzing these products was difficult since there is no exact definition for them so the intermediates \((R_n)\) that could not be defined can be measured by TOC analysis.

The model assumes that the electrochemical oxidation is mediated by \(Cl^-\) or \(HOCl\), besides steady state conditions can be assumed for \(Cl^-\) or \(HOCl\) that consumed by phenol and the other by product of electrochemical oxidation. Due to strong oxidizing effect towards most polluted compounds, \(Cl^-\) or \(HOCl\) radicals are able to eliminate both the phenol and its derivatives, so they do not accumulate in solution[10].

On the basis of assumptions revealed previously, the overall oxidation process can be indicated as follows:

\[
R_1 \xrightarrow{k_1} R_n \xrightarrow{k_2} CO_2
\]  

(1)

By making material balance on \(R_1\) (phenol):

\[
\ln = \text{out} + \text{Accumulation} \quad (2)
\]

\[
0 = k_1 \cdot C_{R_1} + \frac{dC_{R_1}}{dt} \quad (3)
\]

\[
\frac{dC_{R_1}}{C_{R_1}} = -k_1 \cdot t \quad (4)
\]

The boundary conditions of the above equation are, at \(t = 0; C_{R_1} = C_{R_0}\) integrating the above equation gives:

\[
C_{R_1} = C_{R_0} e^{-k_1 \cdot t} \quad (5)
\]

The value of \(k_1\) can be obtained by plotting \(\ln(C_{R_0}/C_{R_1})\) vs. time as shown in Figure 1. It is obvious that \(k_1\) equal to 0.0151 min\(^{-1}\).
By making material balance on $R_n$ (phenol derivatives):

$$\text{In + generated} = \text{out} + \text{consumption} + \text{Accumulation}$$  \hspace{1cm} (6)

So Equation (6) would be reduced to:

$$\text{generated} = \text{consumed} + \text{accumulated}$$  \hspace{1cm} (7)

$$k_1C_{R_1} = k_2C_{R_n} + \frac{dC_{R_n}}{dt}$$  \hspace{1cm} (8)

$$\frac{dC_{R_n}}{dt} + k_2C_{R_n} = k_1C_{R_0}e^{-k_1t}$$  \hspace{1cm} (9)

To solve the 1st order differential equation above, integral factor method would be used[16].

$$R = e^{\int k_2t} = e^{k_2t}$$  \hspace{1cm} (10)

$$e^{k_2t}C_{R_n} = \int_0^t k_1C_{R_0}e^{-k_1t}.e^{k_2t} \ dt + C$$  \hspace{1cm} (11)

$$e^{k_2t}C_{R_n} = k_1C_{R_0}\frac{(k_2 - k_1)}{(k_2 - k_1)}\int_0^t e^{(k_2-k_1)t} \ dt + C$$  \hspace{1cm} (12)

$$C_{R_n} = \frac{k_1C_{R_n}}{(k_2 - k_1)}e^{-k_1t} + Ce^{-k_2t}$$  \hspace{1cm} (13)

To find the value of the constant, the following boundary condition would be applied: $t = 0$, $C_{R_n} = 0$
\[ C_{R_n} = \frac{k_1 \cdot C_{R_0}}{k_2 - k_1} [e^{-k_1 t} - e^{-k_2 t}] \] (14)

The concentration of phenol \( (C_{R_n}) \) has been measured by UV spectrophotometer for all the samples during the electrolysis process. The concentration of the intermediates has been measured by TOC analysis method \( (C_{R_n} = \text{TOC} - 6*C_{R_1}) \). The value of \( k_2 \) had been predicted by generalized reduced gradient nonlinear regression technique and it was found equal to 0.067 min\(^{-1}\).

By making material balance on CO\(_2\):

\[ \text{Generated} = \text{Accumulation} \] (15)

\[ k_2 \cdot C_{R_n} = \frac{dC_{CO_2}}{dt} \] (16)

\[ \frac{dC_{CO_2}}{dt} = \frac{k_2 k_1 C_{R_0}}{(k_2 - k_1)} [e^{-k_1 t} - e^{-k_2 t}] \] (17)

\[ C_{CO_2} = \frac{k_2 k_1 C_{R_0}}{(k_2 - k_1)} \int_0^t (e^{-k_1 t} - e^{-k_2 t}) dt \] (18)

\[ C_{CO_2} = \frac{k_1 C_{R_0}}{(k_2 - k_1)} e^{-k_2 t} - \frac{k_2 C_{R_0}}{(k_2 - k_1)} e^{-k_1 t} \] (19)

So the concentration of CO\(_2\) can be predicted by Equation 19. In Figure 2, concentration of phenol, intermediates, and CO\(_2\) are plotted versus time for electrochemical oxidation of phenol in the presence of 1 g/l of NaCl.

![Figure 2. Model prediction and experimental data from electrolysis of phenol and its derivatives at 100mA/cm\(^2\), and 200 rpm, with 150ppm of phenol.](image-url)
It can be seen obviously that the mathematical model can be successfully used to predict the system behavior.

4. Conclusion
Phenol and organics can be removed effectively up to 97.33% via the electrochemical indirect oxidation. The kinetics analysis prove that the electrochemical oxidation is mediated by Cl or HOCl, that consumed by phenol and the other byproduct of electrochemical oxidation. The kinetics study of the reactions in series of phenol to byproduct organics and then to CO$_2$, was done depending on the TOC results. The non-linear regression contributes reaction rate constants; $k_1$ equal to 0.0151 min$^{-1}$ and $k_2$ equal to 0.067 min$^{-1}$.

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