KINETICS APPROACH OF PHENOL OXIDATION PROMOTED BY CHELATED IRON

I. Sánchez1∗, L. Pramparo1, F. Stüber1, J. Font1, A. Fortuny2, A. Fabregat1, C. Bengoa1
1U. Rovira i Virgili, ETSEQ, DEQ, Av. Països Catalans 26, 43007 Tarragona, España
2U. Politècnica de Catalunya, EUPVG, DEQ, Av. Víctor Balaguer, s/n, 08800 Vilanova i la Geltrú, España

Abstract. The oxidation of phenol, in the presence of chelated iron and air was investigated. The reaction was carried out in a stirred tank reactor under extremely mild conditions, temperature of 20°C and atmospheric pressure, in the presence of 150 mg/l of the organic compound, zero valent iron particles (10 g), ethylenediaminetetraacetic acid (EDTA, 0.30 mM) and air. The efficiency of the process has been evaluated based on the degree of conversion, XPh (%). The experimental results of this study show that an 85% of phenol conversion can be achieved after 6 hours. Kinetic data were obtained and used to model the reaction kinetics for phenol disappearance. The operational variables have been studied in the following ranges: temperature from 20 to 50°C, initial phenol concentration from 150 to 1000 mg·l⁻¹, EDTA concentration from 0.15 to 0.45 mM, iron mass from 5 to 15 g. An inspection to the conversion evolution shows that phenol disappearance is not first order with respect to phenol and that the process could not be expressed with a power law model. Using the Langmuir-Hinshelwood approach for the heterogeneous reaction, the developed kinetic model describe well the removal of phenol over the entire range of the variables studied. The reaction orders are found to be approximately 1.27 and 0.98 with respect to EDTA and iron concentrations, respectively.

1. Introduction

Wastewater treatment has become a major social, technological and economical. In general, industrial processes and agricultural activities generate a large diversity of wastewater containing organic pollutants. Theses compounds are in small concentrations so their economic recovery is not feasible and, in many cases, their biological treatment is not feasible since they are poorly biodegradable or toxic, as for instance, aromatic compounds such as phenols and its derivatives [1,2]. Most phenolic compounds are used as raw materials, so that wastewaters originated from these plants and/or activities contain phenols and phenolic compounds [3-5].

Because of the high concentrations of toxic materials in industrial wastewater, it is necessary to apply specific processes for their separation, transformation, and further decomposition. A variety of biological, physical, and chemical processes and their combinations are available for these purposes, but each technique has its own limitations [1, 6]. Among a wide variety of pollutant treatments, many are devoted to chemically destroy the target contaminant. By proper choice of the catalyst, and/or the operation conditions, it is possible not only to control the degree of conversion of pollutants but also to select different reaction routes [2].

* Corresponding author, Phone: +34-977558619, Fax: +34-977559621, e-mail: irama.sanchez@urv.cat
In this sense, the use of chelated metals in oxidation process became in a promising technology. By definition, chelation requires the presence of two or more atoms on the same molecule capable of metal liganding. Oxygen, nitrogen, and sulphur atoms of molecules are most commonly the metal ligands. Chelators in which oxygen atoms serve as the ligand of iron tend to stabilize Fe(III), thus decreasing the reduction potential of the iron [7]. As reported [8], the autoxidation of some iron chelates produces a powerful oxidant, which is stronger than the hydroxyl radical. For instance, the oxidation of methanol using iron chelates does not directly depend on the hydrogen peroxide used, since it is believed that ferryl species are formed during oxidation. These species are able to oxidise high reduction potential compounds as methanol. Other authors suggest the possibility of formation of iron-oxo complexes during the process or an iron(III)-hydroperoxo complex [9]. Therefore, this simple method could be applied to the degradation of refractory organic compounds such as aromatic compounds, like phenol. In addition, it is possible to combine benefits of non-soluble catalysts with complexes combining metallic iron, which provide the iron ions, with ethylenediaminetetraacetic acid (EDTA) [10], which acts as chelating agent.

On the other hand, kinetic studies reported in the literature are often in disagreement. There are two main kinetic analyses, those describing the disappearance rate of phenol and those modeling the mineralization rate, or the rate of CO2 production. The difference arises from the fact that phenol does not oxidize directly to CO2 but rather oxidizes to several intermediate compounds [11].

For the catalytic oxidation of aqueous phenol or similar organic pollutants, the kinetic models proposed in the literature are in terms of either power laws or more complex equations based on adsorption-desorption mechanisms, i.e., Langmuir-Hinshelwood (LH) model [12].

Kinetic modeling of solid-catalyzed oxidation of pollutants in water is crucial to the design and scale-up of wastewater wet oxidation treatment. Due to their simplicity, the overall kinetics using power-law rates are often unable to capture the important features in such oxidation systems [13].

The reaction kinetics for catalytic air oxidation of phenol are shown in Eq. (2) [12,13]:

\[-r = \frac{k_o \cdot C_{ph}}{1 + K_1 \cdot C_{ph}}\]

(1)

where \(r\) is the global rate, \(C_{ph}\) is the phenol concentration, \(k_o\) and \(K_1\) are the rate constant and the adsorption equilibrium constant respectively.

When phenol concentration \(C_{ph}\) is low, the product of the phenol adsorption constant, \(K_1\), by the phenol concentration, \(C_{ph}\), will be fairly small compared to the 1 in the denominator, the denominator can be neglected and the eq (2) can be written as:

\[-r = k_o \cdot C_{ph}\]

(2)

Then, it is reasonable to state that the oxidation rate is approximately first-order with respect to phenol. On the other hand, when phenol concentration \(C_{ph}\) increases so that the value of \(K_1 \cdot C_{ph}\) becomes dominant in the denominator, the reaction of phenol oxidation will approach a zero-order reaction with respect to phenol, and the equation becomes:

\[-r = K\]

(3)

where

\[K = \frac{k_o}{K_1}\]

(4)
The rate constant \( k_o \) must be consistent with the Arrhenius law:

\[
\ln k_o = \ln A - \exp\left(\frac{E_a}{R.T}\right)
\]

were \( A \) and \( E_a \) should be positive [12,13].

In the same way, the adsorption equilibrium constant must be consistent with Van’t Hoff relationship: [12,13].

\[
\ln K_i = \frac{\Delta S}{R} - \exp\left(\frac{\Delta H}{R.T}\right)
\]

The aim of this work is to develop a kinetic model for the oxidation of phenol promoted by chelated iron.

2. Experimental

Materials

Phenol (Ph) was purchased from Panreac (ref. 144852, >99% purity), while o-cresol (98% purity, ref.C85719), 2-chlorophenol (98% purity, ref. 185779), aniline (99.5% purity, ref. 242284), p-nitrophenol (98% purity, ref. 425753) and nitrobenzene (98% purity, ref. N10950) were all purchased from Aldrich. Ethylene diamine tetra acetic acid disodium salt dihydrate (99% purity, ref. 14669) was provided from Panreac. Finally, metallic zero valent iron was purchased from Panreac (ref. 211934). Deionized water was used to prepare all the aqueous solutions.

Experimental Set-Up and Procedure

A 600 ml jacketed stirred reactor in batch operation was used for all oxidation reactions. Temperature was maintained by circulating water from a thermostatic bath through the jacket. A schematic diagram of the reactor is shown in figure 1.

![Schematic diagram of experimental apparatus](image)

Figure 1. Schematic diagram of experimental apparatus

The reactor was filled with 200 ml of solution and once the desired temperature was reached, the compressed air valve was open, and the air flow is set to 10 Nl·h\(^{-1}\) with a rotameter (KROHNE). A porous glass at the end of the air pipe allowed the formation of well
distribuied small air bubbles. Then, the stirrer was set to 700 rpm. Finally, metallic iron was added to start the reaction.

Liquid samples were withdrawn at 0, 5, 15, 30, 60 min, and later every 60 min up to the end. After 6 hours of reaction, the cooling/heating jacket and the magnetic stirred were turned off and the air flowrate was cessed to stop the reaction. Table 1 list the whole range of experimental parameters inspected.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (atm)</td>
<td>1</td>
</tr>
<tr>
<td>Temperature (ºC)</td>
<td>20 – 50</td>
</tr>
<tr>
<td>Initial Phenol concentration (mg·l⁻¹)</td>
<td>150 – 1000</td>
</tr>
<tr>
<td>Zero Valent Iron mass (g)</td>
<td>5 – 15</td>
</tr>
<tr>
<td>EDTA concentration (mM)</td>
<td>0.15 – 0.45</td>
</tr>
<tr>
<td>Air Flow (NL·h⁻¹)</td>
<td>10</td>
</tr>
<tr>
<td>Stirred speed (rpm)</td>
<td>600</td>
</tr>
</tbody>
</table>

Analytical Procedures
For each measure, 1 ml of sample was taken from the reactor with a 5 ml disposable syringe. Then the sample was immediately filtered with a nylon filter of 0.2 µm (Teknokroma, ref. TR-200101) and placed in a glass vial for analysis. The concentrations of phenol were measured by High Performance Liquid Chromatograph (HPLC) (model 1100, Agilent Technologies) using a C18 reverse phase column (Hypersil ODS, Agilent Technologies). The analyses were performed with a mobile phase made of a mixture of methanol and ultrapure water (Milli-Q water, Millipore), with a proportion of 40:60 (v/v). The pH of the water was adjusted at 1.41 with sulfuric acid H₂SO₄. The detection was performed by UV absorbance at a wavelength 254 nm. Calibration curve was made using aqueous solutions of known composition.

3. Results And Discussion
Phenol Reaction Order
To study the order of the reaction kinetics four experiments were made at different initial phenol concentration. The conversion of organic compounds, X was defined as usual (eq. 7):

\[ X_{Ph} (%) = \frac{C_{Ph0} - C_{Ph}(t)}{C_{Ph0}} \times 100 \]  

(7)

where \( C_{Ph0} \) is the initial concentration and \( C_{Ph}(t) \) the concentration at a given time. As can be seen in figure 1, the experimental data show a shift in reaction kinetics due to feed concentration change. As the phenol concentration became high, the first-order dependence disappeared and the zero-order dependence was reached. This figure illustrate that an inverse proportionality relation is presented between the conversion and the initial phenol concentration.
Effect of temperature

The effect of reaction temperature on the phenol degradation was studied by altering the reaction temperature from 20 to 50°C. Figure 2 show results previously reported for this oxidation process [14].
As seen in Figure 2, an increase in the reaction temperature can significantly enhance the reaction rates. The $k_o$ values calculated at various temperatures were correlated by Eq. (8) and show in Fig. 3, which gives rise to an activation energy of 40.10 kJ/mol.

![Graph showing Arrhenius plot]

Figure 3. Determination of the Arrhenius parameters by equation (7).

The value of the activation energy obtained was within the range reported in the literature for phenol catalytic oxidation [15].

\[
\ln k_o = 11.94 - \frac{4.82}{T}
\]  

(8)

To calculate the adsorption equilibrium constant $K_1$, it is necessary to study the dependence of the initial phenol concentration with the temperature, this work is currently on progress.

The first approach to the reaction kinetics for this oxidation process is shown in Eq. (9):

\[
-r = \frac{k_o \cdot C_{ph}}{1 + K_1 \cdot C_{ph}}
\]  

(9)

The values obtained for the constants of the equations (5) and (8) are reported in table 2.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$ (min$^{-1}$)</td>
<td>15287</td>
</tr>
<tr>
<td>$E_a$ (kJ/mol)</td>
<td>40.10</td>
</tr>
<tr>
<td>$k_o$ (min$^{-1}$) at 20ºC</td>
<td>$1.1 \times 10^{-3}$</td>
</tr>
<tr>
<td>$K_1$ (l/mol)</td>
<td>1505</td>
</tr>
</tbody>
</table>

The profiles of concentrations for experimental and predicted data against time for different initial phenol concentration and different temperatures are shown in figures 4 and 5 respectively.
Figure 4. Experimental data (points) and predicted values (curves) of phenol concentrations in function of time for different initial concentration of phenol. \([\text{EDTA}_0] = 0.30 \text{ mM}, \text{mFe}_0 = 10 \text{ g} \text{ and } T = 20^\circ \text{C}.

As can be seen in figure 4, the kinetic model fit well the experimental data; however, figure 5 exhibit a small deviation from the experimental data, due to the use of an unique value for the adsorption equilibrium constant calculated at 20°C.

Figure 5. Experimental data (points) and predicted values (curves) of phenol concentrations in function of time for different temperatures. \([\text{Ph}_0] = 150 \text{ mg l}^{-1}, \ [\text{EDTA}_0] = 0.30 \text{ mM}, \text{mFe}_0 = 10 \text{ g} \).
**Others Reaction Orders**

A higher initial rate of phenol destruction results from a higher EDTA concentration. Figure 6 illustrates the change in the phenol conversion for different initial EDTA concentration.

![Figure 6](image)

**Figure 6.** Phenol conversion evolution for different initial EDTA concentration. 
[Ph]₀ = 150 mg·l⁻¹, mFe₀ = 10 g and T = 20°C.

The time-dependent phenol degradation at different charges of ZVI mass is presented in figure 7.

![Figure 7](image)

**Figure 7.** Phenol conversion evolution for different mass of ZVI. 
[Ph]₀ = 150 mg·l⁻¹, [EDTA]₀ = 0.30 mM and T = 20°C.
This means that the EDTA concentration and the ZVI mass need to be considered in the kinetics expression. Because of this, the constant rate of the equation (2) must be expressed in this way:

$$k_o = k' \cdot C_{EDTAo}^\alpha \cdot m_{Feo}^\beta$$

(10)

The equation (7) became:

$$- r = \frac{k' \cdot C_{Ph} \cdot C_{EDTA}^\alpha \cdot m_{Fe}^\beta}{1 + k_1 \cdot C_{Ph}}$$

(11)

To calculate the values of $\alpha$ and $\beta$, one of the concentrations of the equation (11) was kept constant and the other one was varied. This leads to:

$$k_o = k_{EDTA} \cdot C_{EDTAo}^\alpha$$

(12)

or

$$k_o = k_{Fe} \cdot m_{Feo}^\beta$$

(13)

For $\alpha$, three EDTA concentrations were studied (0.15, 0.30 and 0.45 mM) for an initial concentration of phenol of 150 mg·l⁻¹, a ZVI mass of 10 g and 20°C of temperature. The equation (12) can be express as:

$$\ln(k_o) = \ln(k_{EDTAo}) + \alpha \cdot \ln(C_{EDTAo})$$

(14)

For $\beta$, three experiments with different zero-valent iron mass (5, 10 and 15 g) at 20°C with an initial concentration of 150 mg·l⁻¹ and a EDTA initial concentration of 0.30 mM were carried out. The equation (13) became:

$$\ln(k_o) = \ln(k_{Fe}) + \beta \cdot \ln(m_{Feo})$$

(15)

Figure 8 illustrate the relationship between the constant rate and the catalysts concentration for these experiments. The plots of $\ln(k_o)$ versus $\ln(C_{EDTAo})$ or $\ln(m_{Feo})$ represent a straight line for the studied samples. On this basis it may be assumed that the slope of them upon linear regression is equal to the order of reaction of the EDTA (Fig. 8a) and the ZVI (Fig. 8b).

$$k_o = k' \cdot m_{Feo}^{0.98} \cdot C_{EDTAo}^{1.27}$$

(16)
the new rate constant \( (k') \) must be consistent with the Arrhenius law:

\[
\ln k' = \ln A' - \exp\left(\frac{E_a}{R T}\right)
\]

As can be seen in figure 9, the value of the activation energy is the same in equations (7) and (17), the addition of the EDTA concentration and the ZVI mass to the equation (2) only affect the value of the pre-exponential factor \( A \).

![Figure 9. Determination of the Arrhenius parameters by equation (17).](image)

The values obtained for this constant are summarized on table 3.

**Table 3. Apparent kinetics parameters.**

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A' ) ( (1^{1.27}.\text{mol}^{-1}.\text{g}^{-0.98}.\text{min}^{-1}) )</td>
<td>4.94x10^8</td>
</tr>
<tr>
<td>( k' ) ( (1^{1.27}.\text{mol}^{-1}.\text{g}^{-0.98}.\text{min}^{-1}) ) at 20ºC</td>
<td>2.2x10^{-4}</td>
</tr>
</tbody>
</table>

Finally, the reaction kinetics for this oxidation process can be expressed as:

\[
-r = \frac{k' \cdot C_{Ph} \cdot C_{EDTA}^{1.27} \cdot m_{Fe}^{0.98}}{1 + K_1 \cdot C_{Ph}}
\]

The effect of EDTA concentration and ZVI mass on the phenol degradation rate (predicted and experimental data) according to eq. (18) are shown in Figs.10 and 11 respectively. Figure 10 show that the model fit the experimental data in almost the whole range of values, deviation are noticed in the induction period (during the first hour of reaction).
Figure 10. Experimental data (points) and predicted values (curves) of phenol conversion versus time for different initial concentration of EDTA. 
$[\text{Ph}]_0 = 150 \text{ mg·l}^{-1}$, $m_{\text{Fe}}_0 = 10 \text{ g}$ and $T = 20^\circ\text{C}$.

In the same sense, the deviation presented for the model to adjust different mass of ZVI (figure 11) appear also in the induction period, meanwhile the rest of the experimental results are well fitted.

Figure 11. Experimental data (points) and predicted values (curves) of phenol conversion versus time for different mass of ZVI. $[\text{Ph}]_0 = 150 \text{ mg·l}^{-1}$, $[\text{EDTA}]_0 = 0.30 \text{ mM}$ and $T = 20^\circ\text{C}$. 
4. Conclusions
An inspection to the conversion evolution shows that phenol disappearance is not first order with respect to phenol. The reaction orders are found to be approximately 1.27 and 0.98 with respect to EDTA and iron concentrations, respectively. The reaction rate of the process can be expressed according to the L-H model:

\[ -r = k' \cdot C_{Ph} \cdot C_{EDTA}^{1.27} \cdot m_{Fe}^{0.98} \cdot \frac{1}{1 + K_1 \cdot C_{Ph}} \]

The activation energy is found to be 40.10 kJ/mol at the temperature range of 20 – 50°C.

5. Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Arrhenius pre-exponential factor (min⁻¹)</td>
</tr>
<tr>
<td>C</td>
<td>Concentration (mol·l⁻¹ or mg·l⁻¹)</td>
</tr>
<tr>
<td>Ea</td>
<td>Activation Energy (kJ/mol)</td>
</tr>
<tr>
<td>ko</td>
<td>Rate constant (min⁻¹)</td>
</tr>
<tr>
<td>K₁</td>
<td>Adsorption equilibrium constant (l/mol)</td>
</tr>
<tr>
<td>m</td>
<td>Mass (g)</td>
</tr>
<tr>
<td>r</td>
<td>Catalytic reaction rate</td>
</tr>
<tr>
<td>R</td>
<td>Universal gas constant (J/(mol.K))</td>
</tr>
<tr>
<td>T</td>
<td>Temperature (°C or K)</td>
</tr>
<tr>
<td>X_{Ph}</td>
<td>Conversion of phenol</td>
</tr>
<tr>
<td>ΔH</td>
<td>Adsorption Enthalpy (kJ/mol)</td>
</tr>
<tr>
<td>ΔS</td>
<td>Adsorption Entropy (kJ/(mol.K))</td>
</tr>
</tbody>
</table>

Abbreviations

- EDTA Ethylene diamine tetra acetic acid
- Fe Iron
- HPLC High Performance Liquid Chromatography
- LH Langmuir-Hinshelwood
- Ph Phenol
- ZVI Zero-valent Iron

6. Acknowledgments
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7. References


