Efficiency of Photo-Fenton Process in Degradation of 2-Chlorophenol

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Background & Aims of the Study: Phenolic compounds have been extensively used in industries for applications such as petrochemical, oil refineries, papers, plastics, steel, pharmaceuticals, textiles, coal conversion, and so on. Specified amounts of Phenolic compounds are lost in the process of their manufacturing and utilization and often cause environmental pollution problems. So, removal these compounds of industrial wastewaters are necessary. The aim of this paper, is the photo-degradation environmental pollutant 2-Chlorophenol (2-CP) using Fenton process which was used a photo reactor for photo-catalytic degradation of 2-CP in aqueous solution.

Materials & Methods: This is an experimental study on a laboratory scale. Fe2+ ions as a homogeneous catalyst applied for the degradation of 2-CP in aqueous solution. The study was performed on synthetic wastewaters that contain 2-CP pollutant. The effect of operational parameters such as: pH, initial concentration Fe2+, H2O2 concentration and temperature were studied. The effect of UV irradiation, UV/H2O2 and UV/Fe2+/H2O2 on photo-catalytic degradation of 2-CP were studied. The reaction kinetic was studied. In this paper, optimum conditions were determined for the photo-catalytic degradation of 2-CP using a factor at the time method.

Results: The optimal conditions for this reaction were obtained at pH of 6, initial concentration Fe2+ at 20 ppm, H2O2 concentration at 14 ppm and temperature at 45 °C. A first order reaction with rate constant (k=0.0375 min−1) was observed for the photo-catalytic degradation reaction. These experiments demonstrated that UV radiation, Fe2+ ions and H2O2 oxidation process were needed for the effective degradation of 2-CP.

Conclusion: The results showed that the photo-Fenton process can be suitable alternative to removal phenolic compounds from wastewaters.


Background

Phenolic compounds pollutants in aqueous solution such as 2-Chlorophenol (2-CP) have been listed as priority organic pollutants by the United State Environmental Protection Agency (USEPA) due to their toxic and carcinogenic (1-4). Phenolic compounds have been extensively used in industries for applications such as petrochemical, oil refineries, papers, plastics, steel, pharmaceuticals, textiles, coal conversion, and so on (5,6). Wastewater treatment plants in various industries are the best and most practical method and it is considered effective in this area. Degradation of the phenolic compounds is very essential since it is carcinogenic and has a hazardous effect on mankind and is a major concern of its impact on the environment (7). Among different techniques for the removal of organic compounds, the traditional ones, such as adsorption (8-10) coagulation–floculation (11,12) ozonation (13) Fenton, photo-Fenton process (14) H2O2 oxidation, photo-oxidation and combination of several techniques have
been applied (15-18). Advanced oxidation processes (AOPs) offer a highly reactive, non-specific oxidant namely hydroxyl radical (OH\(^\cdot\)), that oxidize a broad range of pollutants quickly and non-selective in water and wastewater. In the oxidation process a wide range of organic compounds into harmless compounds such as CO\(_2\), H\(_2\)O and inorganic acids. The Fenton’s reagent is one of the AOPs and it is an economic, simple and effective treatment to oxidize recalcitrant organic compounds. The photo-Fenton process consists of a combination of the Fenton reagent (Fe\(^{2+}/\text{H}_2\text{O}_2\)) and light energy. The mechanism of photo-Fenton reaction is usually described by the following (Eqs.1-5) (19-21):

\[
\begin{align*}
Fe^{2+} + \text{H}_2\text{O}_2 & \rightarrow Fe^{3+} + \text{OH}^- + \text{OH}^\cdot \\
Fe^{3+} + \text{H}_2\text{O}_2 & \rightarrow Fe^{2+} + \text{HO}^- + \text{H}^+ \\
Fe^{3+} + \text{H}_2\text{O} + \text{hv} & \rightarrow Fe^{2+} + \text{OH}^\cdot + \text{H}^+ \\
\text{H}_2\text{O}_2 + \text{hv} & \rightarrow 2\text{OH}^\cdot \\
\text{OH}^\cdot + \text{Organic compounds} & \rightarrow \text{Oxidized products}
\end{align*}
\]

(Eq. 5) 

In the presence of UV-light, the degradation rate of the photo-Fenton reaction was increased by the Fe\(^{3+}\) photo-reduction (Eq. (3)) that generates new hydroxyl radical and regenerates Fe\(^{2+}\) ions, and Fe\(^{2+}\) ions can further react with H\(_2\)O\(_2\) (21,22). As can be seen from Eq. (4), photolysis of H\(_2\)O\(_2\) can produce hydroxyl radical directly. So the catalytic activity for photo-Fenton can be enhanced by the synergistic effects.

**Aims of the study:**

In this study, photo-catalytic degradation of 2-CP in aqueous solution using photo-Fenton process was employed to the degradation rate of 2-CP enhances. The reaction kinetic of 2-CP was studied. The effects of operational parameter such as pH, Fe\(^{2+}\) concentration, H\(_2\)O\(_2\) concentration and temperature on the process were studied and optimized using a factor at the time the experiment design. The results indicated that the UV/Fe\(^{2+}\)/H\(_2\)O\(_2\) could be used as an eco-friendly process to degrade 2-CP.

**Materials & Methods**

**Materials**

2-CP was obtained from Fluka Company (Germany). The structure and characteristics of 2-CP is shown in Table 1. The pH values were adjusted at desired level using dilute NaOH and H\(_2\)SO\(_4\). Ferrous sulphate heptahydrate (FeSO\(_4\).7H\(_2\)O) as the source of Fe\(^{2+}\), H\(_2\)O\(_2\) (30% w/w) were all Merck products (Germany). Double distilled water was used for preparation of requisite solutions.

**Apparatus**

Fig.1 shows the schematic diagram of photo reactor which was used for photo-catalytic decomposition of 2-CP. In this equipment, capacity 0.5 L with a mercury lamp Philips 15W (UV-C) was used in photo reactor. UV/Vis Spectrophotometer, Jenway (6505) was employed to measure the absorbance using glass cells of path length 1 Cm. For the chemical oxygen demand (COD) measurement, COD meter analyzer model AL250 AQUALYTIC was used. pH values were measured with Horiba M12 pH meter.

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Structure</th>
<th>(\lambda_{\text{max}}) (nm)</th>
<th>MW (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Chlorophenol (2-CP)</td>
<td>C(_6)H(_5)ClO</td>
<td><img src="image" alt="Structure of 2-CP" /></td>
<td>275</td>
<td>128.556</td>
</tr>
</tbody>
</table>
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Figure 1) Schematic diagram of photo reactor
1) tank (Pyrex), 2) pump, 3) temperature controller, 4) condenser, 5) UV lamp, 6) reaction flask.

Procedures
For the photo-degradation of 2-CP a solution containing known concentration of 2-CP (40 ppm) was prepared. The suspension pH values were adjusted at the desired level using dilute NaOH 0.1N and H₂SO₄ 0.1N. Then, the prepared suspension was transferred to reaction flask (Pyrex). The degradation reaction took place under the radiation of a mercury lamp while agitation was maintained to keep the suspension homogeneous. The concentration of the samples was determined (at 5 min intervals) using a Spectrophotometer (UV-Vis Spectrophotometer, Jenway (6505) at λ_{max}=275 nm. The degree of photo-degradation (X) as a function of time is given by (Eq.6)

$$X = \frac{C_0 - C}{C_0},$$ \hspace{1cm} (6)

where C₀ and C are the concentration of 2-CP at t = 0 and t, respectively.

Results

The effect of pH
pH is one of the main factors influencing the rate of degradation of organic compounds in the photo-catalytic process (23). The photo-Fenton reactions are strongly pH dependent. The pH value influences the generation of hydroxyl radicals and thus the oxidation efficiency. The effect of pH on degradation rate was studied from pH 2 to 10. The results pH using photo-Fenton process is shown in Fig. 2. It can be seen that the best results obtained in acidic solution, (pH=6, X=89.78%). The degradation rate in acidic condition is higher than that in alkaline condition. There is also the photo-catalytic degradation of 2-CP in acidic solutions, which is due to the formation hydroxyl radical as it can be inferred from H₂O₂ oxidation. In higher pH iron ions the sludge is exited from the reaction. At a pH above 6, the degradation rate decreased because Fe^{3+} starts to precipitate as Fe(OH)₃ and cause the decomposition of H₂O₂ into O₂ and H₂O and also complexes formation Fe^{2+} in higher pH reduced its concentration in the reaction and thus of reproduction Fe^{2+} is prevented according to the Eq.2 (24,25).

Figure 2) Effect of pH on the degradation of 2-CP in photo-Fenton process (Fe^{2+} concentration=20 ppm, H₂O₂ concentration=14 ppm, T=45°C, irradiation time=50 min).

The effect of Fe^{2+} concentration
The concentration of Fe^{2+} is one of the main parameters to influence the photo-Fenton process. At this stage, the effect of different concentration of Fe^{2+} between 10 to 30 ppm for obtain optimum concentration was tested. The results are shown in Fig. 3. From results shown in Fig. 3 it can be seen that degradation rate of 2-CP increased with increasing the Fe^{2+} concentration to 20 ppm according to the Eq.1. Addition concentration of Fe^{2+} above 20 ppm in the process decreases the degradation rate. Because hydroxyl radical was consumed by the side reaction according to the Eq.7, degradation rate is decrease (26, 27).

$$OH^- + Fe^{2+} \rightarrow Fe^{3+} + OH^-$$ \hspace{1cm} (7)
The effect of H$_2$O$_2$ concentration

Fig. 4 shows the relationship between degradation rate of 2-CP and H$_2$O$_2$ concentration for photo-Fenton process. The effect of H$_2$O$_2$ concentration on the degradation of 2-CP was performed at a range of 8-20 ppm. The degradation rate increases with increase of H$_2$O$_2$ concentration until the 14 ppm. This can be explained by the effect of the additionally produced hydroxyl radicals. When the H$_2$O$_2$ concentration increased to 14 ppm, degradation after 50 min of irradiation could be achieved 93.39%. In higher concentrations than 14 ppm reduction in degradation efficiency is observed. This indicates that the excess amount of H$_2$O$_2$ is decomposed without promoting further degradation or maybe due to recombination of hydroxyl radicals and also reaction of hydroxyl radicals with H$_2$O$_2$, the concentration of hydroxyl radical and so degradation efficiency is decreased (Eqs. 8-10) (28, 29). So the optimum amount of H$_2$O$_2$ concentration was 14 ppm.

\[
OH^* + H_2O_2 \rightarrow HO_2^* + H_2O
\]  
\[
OH^* + HO_2^* \rightarrow O_2 + H_2O
\]  
\[
OH^* + OH^* \rightarrow H_2O_2
\]

The effect of temperature

Effect of temperature on the degradation process was tested in the range of 25-45 °C is shown in Fig. 5. The positive influence of the temperature can be observed. It can be seen that the best results obtained in (T=45°C, X=92.63%). An increase in the temperature of solution improves the formation hydroxyl radical. Thus, Increasing temperature of 25-45 °C indicated that the degradation rate of 2-CP increased with increasing temperature (30, 31). It is necessary to cause the temperature more than 45 °C was not selected was that at higher temperatures possible vaporization of the 2-CP solution increases and caused change the concentration of pollutant.

\[
\text{Figure 3) Effect of Fe}^{2+} \text{ concentration on the degradation of 2-CP in photo-Fenton process (pH}=6, \ H_2O_2 \text{ concentration}=14 \text{ ppm, } T=45^\circ C, \ \text{irradiation time}=50 \text{ min).}
\]

\[
\text{Figure 4) Effect of H}_2\text{O}_2 \text{ concentration on the degradation of 2-CP in photo-Fenton process (pH}=6, \ Fe^{2+} \text{ concentration}=20 \text{ ppm, } T=45^\circ C, \ \text{irradiation time}=50 \text{ min).}
\]

\[
\text{Figure 5) Effect of temperature on the degradation of 2-CP in photo-Fenton process (pH}=6, \ Fe^{2+} \text{ concentration}=20 \text{ ppm, } H_2O_2 \text{ concentration}=14 \text{ ppm, } \ \text{irradiation time}=50 \text{ min).}
\]
The effect of UV irradiation, UV/H₂O₂ and UV/Fe²⁺/H₂O₂ in photo-Fenton process of degradation 2-CP are shown in Fig.6. This figure indicates that in the presence of UV/Fe²⁺/H₂O₂ 93.8% of 2-CP was degraded at the irradiation time of 50 min while it was 66% for UV/H₂O₂. This was contrasted with 5.7% degradation for the same experiment performed under only UV irradiation. It is observed that the simultaneous use of UV irradiation, Fe²⁺ and H₂O₂ to a certain extent yielded a significant improvement of 2-CP oxidation compared to that use of UV irradiation and H₂O₂ oxidation (32).

Kinetic of photo-catalytic degradation of 2-CP

Photo-catalytic degradation reaction kinetic of 2-CP completely correspond the kinetic of pseudo-first-order reaction model reaction (33,34). In the kinetic equation of pseudo-first-order relationship between COD and time (t) is in Eq.11:

$$\frac{-d[COD]}{dt} = k[COD],$$

(11)

the integral Eq.11 is in Eq.12:

$$\ln\left(\frac{[COD]_0}{[COD]}\right) = k.t$$

(12)

in which k is the apparent pseudo-first-order rate constant (that is affected by COD) and t the reaction time.

A plot of $\ln\left(\frac{[COD]_0}{[COD]}\right)$ versus t for optimum condition of photo-catalytic degradation of 2-CP is shown in Fig. 7. The linear plot suggests that the photo-degradation reaction approximately follows the pseudo-first-order kinetic with rate coefficient $k = 0.0375 \text{ min}^{-1}$.

**Discussion**

In this paper, for degradation of 2-CP as dangerous environmental pollutants used a photo reactor with capacity 0.5 L that shows the schematic diagram in Fig.1. The photo-Fenton process for degradation of phenolic compounds pollutants in aqueous solution were studied by many investigators (3,4,14,21). In this process the effect of operational parameters such as: pH, Fe²⁺ concentration, H₂O₂ concentration, temperature, UV irradiation, UV/H₂O₂, UV/Fe²⁺/H₂O₂ and reaction kinetic degradation of 2-CP was studied. pH is one of the main affecting factors and the optimum pH was obtained 6. The pH results in Fig. 2 shown that at a pH above 6, the degradation rate decreased. The result of several studies showed that with increasing pH, the degradation rate decreased (24,25). The concentration of Fe²⁺ is one of the main parameters to influence the photo-Fenton process. Addition concentration of Fe²⁺ in the process decreases the degradation rate. Because...
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hydroxyl radical was consumed by the side reaction according to the Eq.7, degradation rate is decrease. This effect is in agreement with the results of Hameed and Joseph (26,27). The optimum amount of H2O2 concentration was 14 ppm. Therefore photo-degradation rate of 2-CP decreased with an increase in higher H2O2 concentrations than 14 ppm according to the Eqs.8-10. The positive influence of the temperature is shown in Fig. 5. The best results obtained in T=45°C. According to studies by Sun et al. (2007) and Tunc et al. (2012) the degradation rate increased with increasing temperature (30,31). This Fig. 6 indicates that in the presence of Fenton reagent (UV/Fe2+/H2O2) 93.8% of 2-CP was degraded at the irradiation time of 50 min. The kinetics of photo-catalytic degradation of 2-CP is of the pseudo-first order with k= 0.0375 min⁻¹. In a experiments result indicated that the degradation rate of photo-catalytic oxidation of chlorophenol in photo-Fenton process fitted by the first order kinetic model (3).

Conclusion

Phenolic compounds and their derivatives have been extensively are used in various industries. Wastewater industries cause environmental pollution problems. So, wastewater treatment industries are necessary. In this study, photo-catalytic degradation of 2-CP pollutant was investigated by photo-Fenton process (UV/Fe2+/H2O2). The results demonstrated that the photo-Fenton process was powerful method for degradation of 2-CP. A photo reactor was used for degradation reaction. Various factors affecting in the degradation process such as: pH, initial concentration Fe2+, H2O2 concentration and temperature were analyzed and optimized. The results showed that pH=6, Fe2+ concentration at 20 ppm, H2O2 concentration at 14 ppm and temperature 45 °C was optimum conditions for this reaction. Also the results showed that simultaneous utilize of UV irradiation, Fe2+ ions and H2O2 oxidation process were needed for the effective degradation of 2-CP. The results showed that in the presence of UV/Fe2+/H2O2 93.8% of 2-CP was degraded at the irradiation time of 50 min. Kinetics of photo-catalytic decomposition reaction was determined. Pseudo-first-order model reaction with rate constant (k=0.0375 min⁻¹) corresponds to the experiment data of photo-catalytic degradation of 2-CP.

Footnotes

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Conflict of Interest:
The authors declared no conflict of interest.

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