FENTON PROCESS FOR THE PURIFICATION OF POLLUTED WATERS

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Abstract

The Fenton Process is based on the production of the highly reactive hydroxyl radical ($OH^{\bullet}$), which is resulting from the reaction between hydrogen peroxide (H_2O_2) and ferrous ions Fe(II) under acidic conditions. The oxidation system, which relies on Fenton's reagent, can be employed to treat various types of waters and wastewaters containing a range of organic pollutants like phenols, polycyclic aromatic hydrocarbons, pesticides, formaldehyde, wood preservatives, plastic additives and rubber chemicals. The treatment of polluted waters using Fenton process results in reduction of toxicity, improvement in biodegradability, odour and colour removal. The Fenton process can also be employed as a post- or a pre-treatment step in the treatment of high strength polluted waters with extremely toxic and refractory nature. In the Fenton process, iron and hydrogen peroxide are the two major chemicals that determine not only the operation costs but also the treatment efficacy (Zhang et al., 2009). The objective of the present investigation was to examine the effectiveness of Fenton Process in treating polluted waters of different origins. The performance of Fenton oxidation employed in the treatment of soil washing solution, landfill leachate and phenolic water was investigated with an aim of determining their optimum reaction conditions. For this purpose, all experiments were performed in the batch system. The influence of H_2O_2, $FeSO_4$ concentrations and reaction time on the removal efficiency were investigated. The pH of reaction mixture was adjusted at the start of the reaction. Required amounts of $FeSO_4$ and H_2O_2 were added simultaneously into the solution and then the mixture was shaken using a mechanical shaker. The progress of reaction was followed by monitoring the disappearance of the contaminant and chemical oxygen demand (COD). The results indicated that the Fenton process was successful in the treatment of polluted waters. Organic pollutants (e.g. phenol, fluorene, etc) were efficiently removed by the Fenton process. Removal efficiency depended on the reaction time and Fe(II) and H_2O_2 concentrations. 83% of phenol was degraded and 60% of COD was removed at conditions of H_2O_2 500 mg/L, Fe^{2+} 30 mg/L, phenol 250 mg/L and pH 3.0. Similarly, in the treatment of soil washing solution 40% of COD was removed under optimum conditions, which were 2 hours reaction time, 2% H_2O_2 concentration and 1/50 Fe/H_2O_2 ratio. In the treatment of landfill leachate, a COD removal of 66% was obtained for 5000 mg/L hydrogen peroxide and 30 min reaction time.

Keywords: polluted waters, Fenton process, system optimisation

Introduction

The Fenton Process is based on the production of the highly reactive hydroxyl radical ($OH^{\bullet}$), which is resulting from the reaction between hydrogen peroxide (H_2O_2) and ferrous ions (Fe(II)) under acidic conditions. The oxidation system, which relies on Fenton's reagent, can be employed to treat various types of wastewaters containing a range of organic pollutants like phenols, polycyclic aromatic hydrocarbons, pesticides, formaldehyde, wood preservatives, plastic additives and rubber chemicals. The wastewater treatment using Fenton process results in reduction of toxicity, improvement in biodegradability, odour and colour removal (Bagal and Gogate, 2014). The efficiency of process depends on temperature, pH, reaction time, hydrogen peroxide and ferrous ion concentration (Benatti and Tavares, 2012).

Fenton oxidation process is a catalytic reaction of H_2O_2 with iron ions that predominantly produces OH• radicals as the highly reactive oxidizing species (Rahim Pouran et al, 2014) (1). The reaction of ferric ions (Fe(III)) with H_2O_2 generates other radicals with lower oxidation potentials (2) (Garrido-Ramírez et al., 2010; Gallard and De Laat, 2001; Walling, 1975).

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^{-} + OH\bullet \qquad E_a = 39.5 \text{ kj mol}^{-1}\ k_1 = 76\ M^{-1}s^{-1} \qquad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2\bullet + H^{+} \qquad E_a = 126 \text{ kj mol}^{-1}\ k_2 = 0.001\text{-}0.01\ M^{-1}s^{-1} \qquad (2)$$

Various simultaneous reactions occur among the radicals and chemicals in the solute, that cause to the scavenging of radicals as well. Hydroxyl radicals also react with the organics in solute starting a chain reaction (Benatti and Tavares, 2012).

$$OH\bullet + RH \rightarrow H_2O + R\bullet,\ RH = \text{organic substrate} \qquad (3)$$

$$R\bullet + O_2 \rightarrow ROO\bullet \rightarrow \text{products of degradation} \qquad (4)$$

The treatment of high strength wastewaters with extremely toxic and refractory nature, is mostly an arduous process. The Fenton process can be employed as a post- or a pre-treatment step. In the Fenton process, iron and hydrogen peroxide are the two major chemicals that determine not only the operation costs but also the treatment efficacy (Zhang et al., 2009). The objective of the present investigation was to examine the effectiveness of Fenton Process in treating wastewaters of different origins. The performance of Fenton oxidation employed in the treatment of soil washing solution, landfill leachate and phenolic wastewater was investigated with an aim of determining their optimum reaction conditions.

Materials and Methods

Experiments were performed in the batch system. The influence of H_2O_2, $FeSO_4$ concentrations and reaction time on the removal efficiency were investigated. For the all experiments the pH of reaction mixture was adjusted at the start of the reaction. Required amounts of $FeSO_4$ and H_2O_2 were added simultaneously into the wastewater/soil washing solution/leachate and then the mixture was shaken using a mechanical shaker. The progress of reaction was followed by monitoring the disappearance of the contaminant and chemical oxygen demand (COD).

Results and Discussion

1. Treatment of Wastewater from Soil Washing Process

Each day more land on Earth is getting contaminated with different pollutants at different levels. However, it is known that to determine the extent of pollution on contaminated land and to eliminate pollution requires more time and major costs. Among the most important of these pollutants, polycyclic aromatic hydrocarbons were discussed. PAHs, petroleum and petroleum derivatives, are compounds which are released into environment by omissions, petrol spills and incomplete combustion of fossil fuels. In the present study, soil contaminated with fluorene which is one of the 16 PAH compounds was initially extracted with a non-ionic aliphatic surfactant. The soil washing solution was later on treated with the Fenton process. The influence of treatment time, H_2O_2 concentration and Fe(II)/H_2O_2 ratio on the removal efficiency was investigated.

In the kinetic study the H_2O_2 concentration and Fe(II)/H_2O_2 ratio was kept constant, which was 2% and 1/50, respectively. Results show that the COD removal from the washing solution increased with a decreasing trend and reached a maximum of 81% in 4 hours (Figure 1). The optimum treatment time was selected as 2 hours.

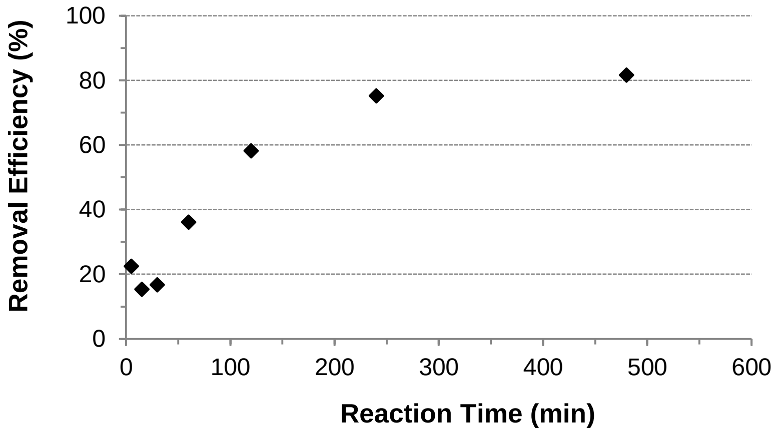

Figure 1a. Effect of reaction time on COD removal efficiency

The influence of H_2O_2 concentration on COD removal was investigated with 0.5-10% H_2O_2, a treatment time of 2 hours and a Fe(II)/H_2O_2 ratio of 1/50. Removal efficiencies were insignificant (>5%) for H_2O_2 concentrations below 1%. It was interesting to notice that the COD removal approached 45% with an increase to 2% H_2O_2. Almost all of the COD was removed with 10% H_2O_2 in 2 hours (Figure 1b).

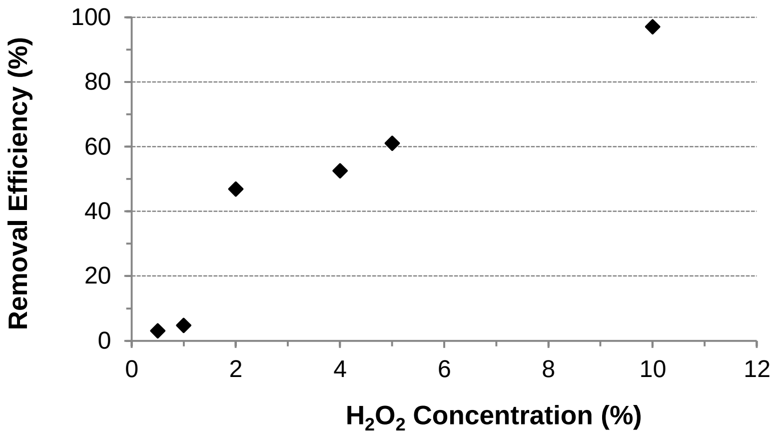

Figure 1b. Effect of different H_2O_2 concentrations on COD removal efficiency

The influence of Fe(II)/H_2O_2 ratio on COD removal was studied with Fe(II)/H_2O_2 ratios of 1/15, 1/30, 1/50, 1/100 and 1/200. Removal efficiency increased with higher ferrous iron dosages, which is reflected by greater ratios. About 69% COD removal was achieved within 2 hours with 2% H_2O_2 and a ratio of 1/15 (Figure 1c).

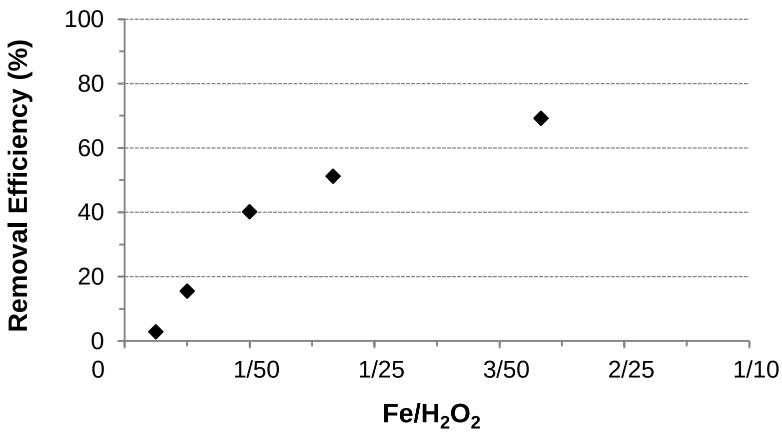

Figure 1c. Effect of different Fe/H_2O_2 ratios on COD removal efficiency

2. Treatment of Landfill Leachate

Recently, the applications of the electrochemical method in Fenton process, named electro-Fenton (E-Fenton) method, have been reported (Zhang, et al., 2006). These studies can be divided into various categories. In the first category, ferrous ion is externally applied, and both hydrogen peroxide and ferrous ion are concurrently generated at the cathode. In the second category, hydrogen peroxide is externally applied while a sacrificial iron anode is used as ferrous ion source (Lin and Chang, 2000). In the third, hydrogen peroxide is externally applied and ferrous ion is electrogenerated via the reduction of ferric ion or ferric hydroxide sludge (Chou et al., 1999). In the fourth category, both ferrous ion and hydrogen peroxide are electrogenerated at sacrificial anode and cathode via the two-electro reduction of sparged oxygen, respectively (Brillas and Casado, 2002).

In the remaining part of this article, the E-Fenton method is presented in which hydrogen peroxide is externally applied while a sacrificial iron anode is used as ferrous ion source. This method is used for the treatment of high COD strength landfill leachate. The effect of reaction time and added hydrogen peroxide dosage on the efficacy of COD removal from the landfill leachate is investigated.

The effect of different hydrogen peroxide dosages on the COD removal efficiency is shown in Figure 2a. The COD removal efficiency was investigated at seven different values ranging between 250-10000 ppm at 20 mA/cm^2 current densities and 30 min electrocoagulation time. It was observed that the COD removal efficiency increased with increased hydrogen peroxide dosage. However, the removal efficiencies were approximately obtained at 5000 and 10000 ppm hydrogen peroxide dosage. The optimum COD removal efficiency of 66% was obtained at 5000 ppm hydrogen peroxide dosage. At this hydrogen peroxide dosage, the energy and electrode consumptions were 0.930 kWh/kg KOİ and 2.011 kg COD/kg Fe, respectively (Figure 2b and Figure 2c). For this reason, the optimum hydrogen peroxide dosage was determined as 5000 ppm and the electrocoagulation experiment was carried out at four different values ranging between 15-60 min at this hydrogen peroxide dosage. The effect of electrocoagulation time on COD removal efficiency at 5000 ppm hydrogen peroxide dosage is shown in Fig. 2d. It can be seen that COD removal efficiency of 56.25% was obtained at 15 min, which increased to 66%, 70%, 74.21% at 30, 45, 60 min, respectively. In this process, the organic compounds removed two steps with electrocoagulation and coagulation (Bidga,1995).

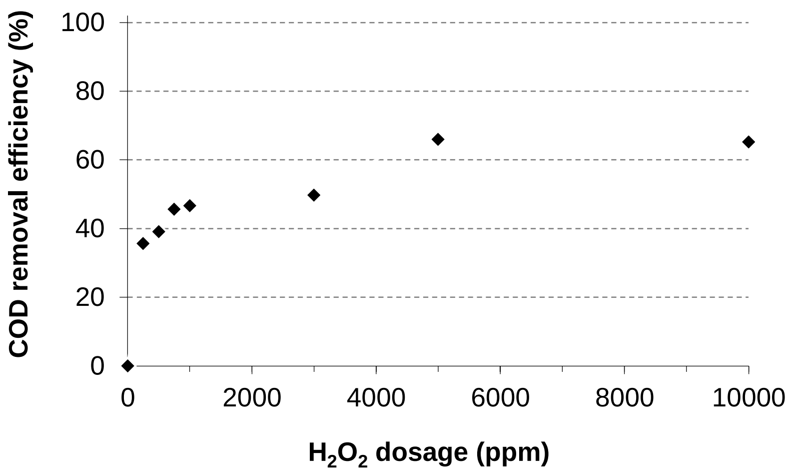

Figure 2a. Effect of different H_2O_2 dosages on COD removal efficiency

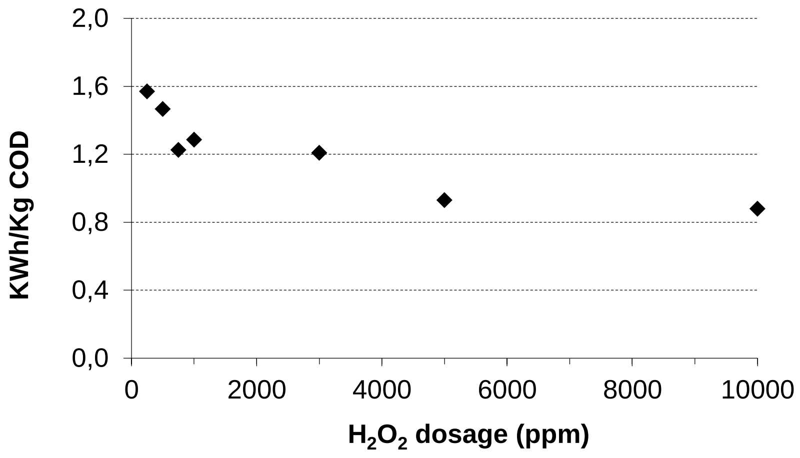

Figure 2b. Effect of different H_2O_2 dosages on energy consumption

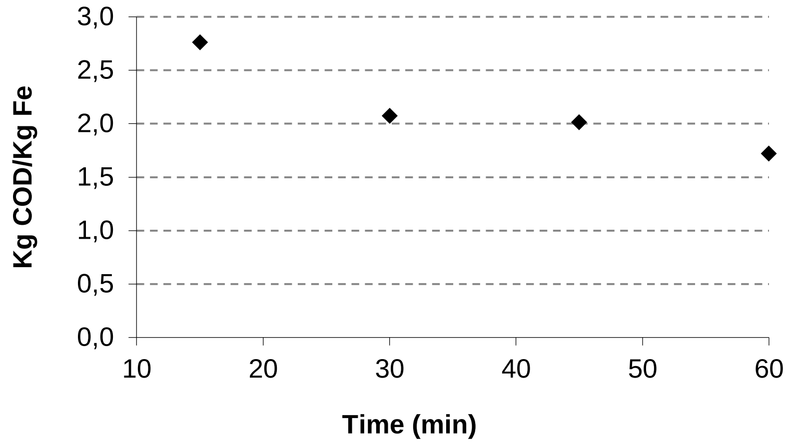

Figure 2c. Electrode consumption depending on operation time at H_2O_2 added

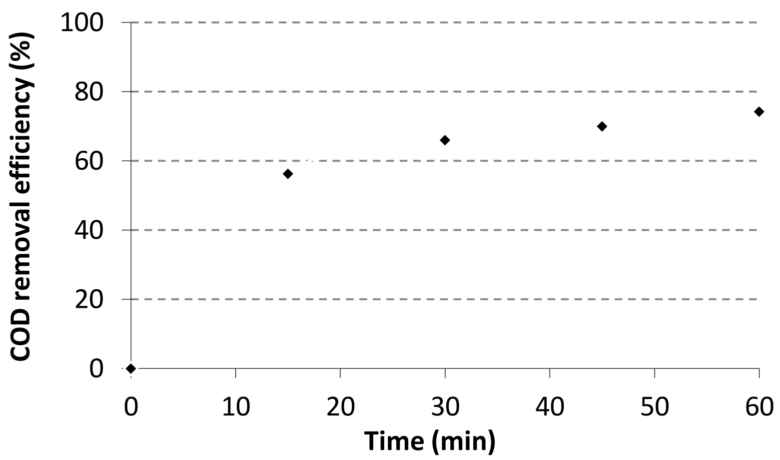

Figure 2d. The Effect of electrocoagulation time on COD removal efficiency

3. Treatment of Phenolic Wastewater

Industrial processes generate a variety of pollutants that may have negative impacts for ecosystems and humans (toxicity, carcinogenic and mutagenic properties). Phenol is one of the most common organic water pollutants, because it is toxic even at low concentrations, and also its presence in natural waters can lead further to the formation of substituted compounds during disinfection and oxidation processes (Busca et al., 2008).

In this study optimum reaction conditions of Fenton process for phenol removal were determined. The effect of Fe(II) concentration on phenol degradation and COD removal was investigated within the range of 15 and 60 mg/L at phenol concentration of 250 mg/L, H_2O_2 dosage of 500 mg/L, and pH 3.0. It was found that the removal rate increased with increasing initial Fe(II) concentration. It was obtained that phenol degradation efficiencies were 81.06%, 83.02%, 84.49% and 84.33% when Fe(II) concentration was 15, 30, 45 and 60 mg/L respectively. It was obtained that COD removal efficiencies were 58.75%, 60%, 63.75% and 64.38% respectively. It was also found that no further mineralization occurred after adding more than a 30 mg/L Fe(II) dosage. Therefore in the next experiments 30 mg/L constant amount of Fe(II) was used. Usually the rate of degradation increases with an increase in the concentration of ferrous ion. Also, an enormous increase in the ferrous ions will lead to an increase in the unutilized quantity of iron salts, which will contribute to an increase in the total dissolved solids content of the effluent stream and this is not permitted (Babuponnusami and Muthukumar, 2014).

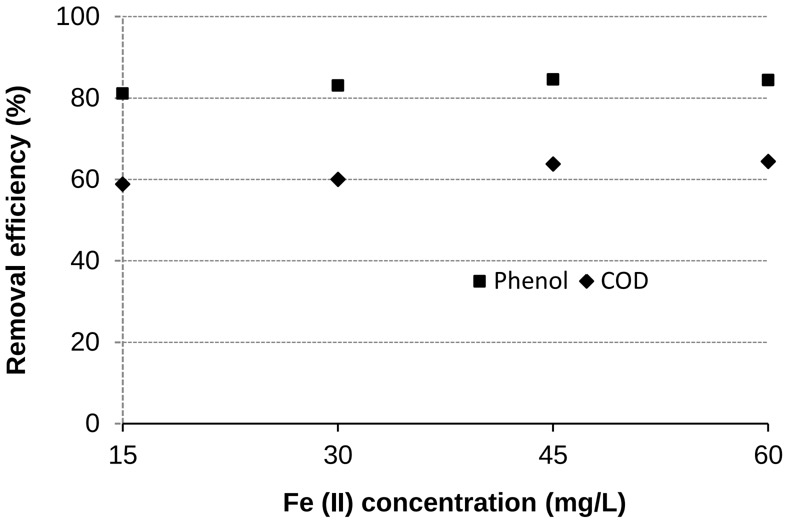

Figure 3a. Phenol and COD removal efficiency at different Fe(II) concentrations

The effect of H_2O_2 concentration on phenol degradation and COD removal was investigated at phenol concentration of 250 mg/L, Fe(II) dosage of 30 mg/L and pH 3. It was obtained that phenol degradation efficiencies were 74.35%, 83.02%, 83.92% and 88.74% when H_2O_2 concentration was 250, 500, 750 and 1000 mg/L respectively. It was obtained that COD removal efficiencies were 55%, 60%, 60.63% and 65.63% respectively. The increase in H_2O_2 concentration increased the phenol degradation and COD removal.

Several studies show that the degradation of the pollutants increases with an increase in the dosage of hydrogen peroxide. However, care should be taken while selecting the operating oxidant dosage. The unused portion of hydrogen peroxide during the Fenton process contributes to COD and hence excess amount is not recommended. Also, the presence of hydrogen peroxide is harmful to many of the organisms and will affect the overall degradation efficiency significantly, where Fenton oxidation is used as a pretreatment to biological oxidation. Another negative effect of hydrogen peroxide is the scavenging of generated hydroxyl radicals, which occurs at large quantities of hydrogen peroxide

(Babuponnusami and Muthukumar, 2014). Thus, the dosage of hydrogen peroxide should be optimised.

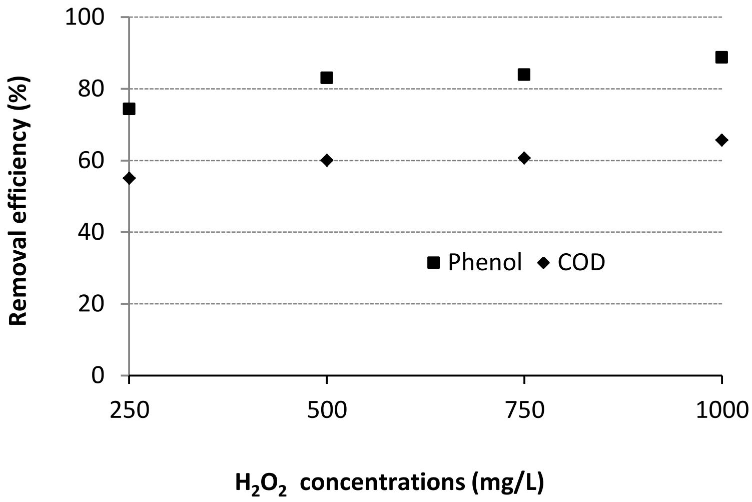

Figure 3b. Phenol and COD removal efficiency at different H_2O_2 concentrations

Conclusion

The results indicated that the Fenton process was successful in the treatment of different wastewaters. Organic pollutants (e.g. phenol, fluorene, etc) were efficiently removed by the Fenton process. Removal efficiency depended on the reaction time and Fe(II) and H_2O_2 concentrations. 83% of phenol was degraded and 60% of COD was removed at conditions of H_2O_2 500 mg/L, Fe^{2+} 30 mg/L, phenol 250 mg/L and pH 3.0. Similarly, in the treatment of soil washing solution 40% of COD was removed under optimum conditions, which were 2 hours reaction time, 2% H_2O_2 concentration and 1/50 Fe/H_2O_2 ratio. In the treatment of landfill leachate, a COD removal of 66% was obtained for 5000 mg/L hydrogen peroxide and 30 min reaction time.

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