Efficiency comparison of advanced photochemical oxidation technologies in phenol removal from aqueous solution in Iran

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Abstract

In this study, advanced oxidation processes (UV, UV/H_2O_2, $UV/H_2O_2/Fe(II)$ and $UV/H_2O_2/Fe(III)$) were investigated in lab-scale experiments for degradation of phenol or benzene hydroxy in aqueous solution. The study showed that the photo-Fenton process, (a mixture of hydrogen peroxide and ferrous or ferric ion), was the most effective treatment process under acidic conditions and produced a higher rate of degradation of phenol at a very short radiation time. It accelerated the oxidation rate by 4-5 times the rate for the UV/H_2O_2 process. The reaction was influenced by the pH, the input concentration of H_2O_2 and the amount of the iron catalyst and the type of iron salt. The experimental results showed that the optimum conditions were obtained at a pH value of 3, with 6 mmol/1 H_2O_2, and 0.5 mmol/1 Fe(II) for the $UV/H_2O_2/Fe(II)$ system and 6 mmol/l H_2O_2 and, 0.4 mmol/1 Fe(III) for the $UV/H_2O_2/Fe(III)$ system. As for the UV processes, $UV/H_2O_2/Fe(III)$ showed the highest degradation rate.
Keywords: phenol, UV radiation, hydrogen peroxide (H_2O_2), advanced oxidation.

1 Introduction

Advanced oxidation processes (AOPs) have been defined broadly as those aqueous phase oxidation processes which are based primarily on the

intermediacy of the hydroxyl radical in the mechanism(s) resulting in the destruction of the target pollutant or xenobiotic or contaminant compound [1]. AOPs have been successful in degrading most of the organic compounds present in polluted water. The reason for the use of AOPs is due to the inability of biological processes to treat highly contaminated and toxic water. In AOP, the hydroxyl radicals (^0OH) are generated in solution and these are responsible for the oxidation and mineralization of the organic pollutants to water and carbon dioxide [1, 2]. A combination of H_2O_2 and UV radiation with Fe(II) or Fe(III), the so-called photo-Fenton process, where iron salts serve as photocatalysts and H_2O_2 as oxidizing agent. It represents an efficient and cheap method for wastewater treatment [3, 4] and produces more hydroxyl radicals in comparison with the systems $Fe(II)/H_2O_2$ or UV/H_2O_2, thus promoting the rate of degradation of various organic pollutants. The effect of the pH value, hydrogen peroxide and iron compounds on the photo-elimination of phenol solution was evaluated. Phenol is one of the most abundant pollutants in industrial wastewaters and its toxicity makes that compound dangerous for the aquatic life. Phenol is also a concern in the biological stage of wastewaters treatment, due to its bio-resistance and toxicity to microbial population [5, 6].

Fenton's reagent system consists in the generation of hydroxyl radicals by means of the reaction between hydrogen peroxide and iron (II) salts [7, 8]. The Formation of the hydroxyl radicals by using the Fenton process under application of Fe(II) occurs according to following Eq. (1):

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + {}^0OH + OH^- \qquad (1)$$
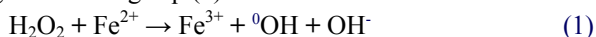
The mechanism for the ferric ion catalyzed decomposition of hydrogen peroxide in acid solution has been widely described by Walling and Goosen [9].

2 Materials and methods

2.1 Reagents

Phenol (C_6H_6O) in the purest form, is available from Merck Chemical Company. Ferrous ($FeSO_4.7H_2O$) and ferric [$Fe_2(SO_4)_3.7H_2O$] sulphate heptahydrate used as sources of Fe(II) and Fe(III), were all analytical grade and purchased from Merck. Hydrogen peroxide solution (30% w/w) in stable form was provided by Riedel-deHaen Company. All reagents employed were not subjected to any further treatment. Water was double distilled quality water.

2.2 Experimental set-up

All experiments were performed in a batch reactor with a cooling jacket. The reactor was cylindrical with 1.5 L volume and the internal part is made of quartz glass which was available for the transfer of the radiation and the outer part is made of Pyrex glass. Irradiation was achieved by using UV lamp (medium pressure mercury lamp UVOX 300 of 300 W, 245-265 nm, from ARDA Company in France) which was immersed in the glass tube. The reactor was equipped with a cooling water jacket system (with recycle water thermostat model OPTIMA 740,

Japan). The reactor was filled with the reaction mixture. Mixing was accomplished by the use of a magnetic stirrer.

2.3 Photodegradation procedures

For each experiment, synthetic aqueous solution of phenol was prepared in double distilled water as solvent For runs using UV/H_2O_2 system, hydrogen peroxide at different amounts was injected in the reactor before the beginning of each run. For runs, using the photo-Fenton process, the pH value of the solution was set at the desired value by the addition of a H_2SO_4 solution before startup, then a given weight of iron salt was added. The iron salt was mixed very well with the phenol before the addition of a given volume of hydrogen peroxide. The time at which the ultraviolet lamp was turned on was considered time zero or the beginning of the experiment which was taking place simultaneously with the addition of hydrogen peroxide.

2.4 Analytical methods

Samples were taken at appropriate time intervals from the reaction vessel and pipetted into (5 ml) glass vials. The vials were filled so as to leave no headspace and sealed with Teflon-lined silicon septa and screw caps. The samples were immediately analyzed to avoid further reaction. Concentration changes of phenol were determined by a spectrophotometer (DR 2500, HACH) according to the standard methods [10]. The initial and treated solutions of phenol were determined by the standard methods procedure [10]. The pH measurements were carried out with a Metrohm model 691 pHmeter, calibrated with two buffer solutions of 3 and 7.

3 Results and discussion

3.1 The effect of the amount of H_2O_2

Although hydrogen peroxide did not oxidize phenol at all, as observed in this work, when it combined with UV irradiation, the rate of phenol degradation increased significantly compared to that of direct photolysis. Fig. 1 illustrates the percent degradation of phenol as a function of the irradiation time at different doses of H_2O_2 input. The photolysis of phenol in the absence of H_2O_2 gave rather moderate results and resulted in a slow degradation of phenol. By addition of H_2O_2, the degradation rate of phenol first increased when hydrogen peroxide concentration increased however, the effect of peroxide is negative for hydrogen peroxide concentrations higher than 0.02 mol/1 for which the phenol degradation rate was even lower than that obtained from direct photolysis. As can be seen from Fig. 2, the percent degradation of phenol at 20 min was 70 in a direct photolysis experiment and was 60 at the same time when the photolysis was carried out in the presence of an initial hydrogen peroxide concentration of 0.05 mol/1. In this process, hydroxyl radicals generated from the direct photolysis of hydrogen peroxide were the main responsible species of phenol elimination.

However hydrogen peroxide also reacts with these radicals and hence acts as an inhibiting agent of phenol degradation [11]. As can be deduced from Fig. 1, when the concentration of hydrogen peroxide was higher than 0.02 mol/1, its hydroxyl radical scavenging effect became important and the phenol degradation rate decreased.
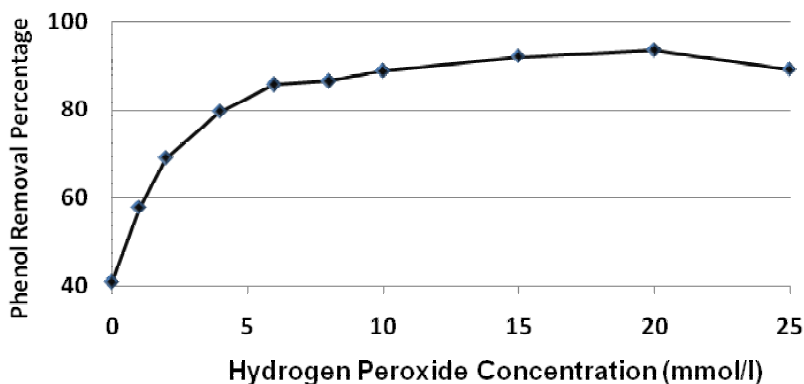

Figure 1:   Degradation of phenol with the photo-Fenton process (The effect of hydrogen peroxide concentration).

3.2 The effect of the amount of iron salt

Iron in its ferrous and ferric form acts as photo-catalyst and requires a working pH below 4. To obtain the optimal Fe(II) or Fe(III) amounts, the investigation was carried out with various amounts of the iron salt. Fig. 2 shows the percent degradation of phenol as a function of the added Fe(II) and Fe(III). The figure shows that the addition of either Fe^{2+} or Fe^{3+} enhanced the efficiency of UV/H_2O_2 for phenol degradation. The degradation rate of phenol distinctly increased with increasing amounts of iron salt.

Addition of the iron salt above 0.5 mmol/1 Fe(II) or 0.4 mmol/1 Fe(III) did not affect the degradation, even when the concentration of the iron was doubled. A higher addition of iron salt resulted in brown turbidity that hindered the absorption of the UV light required for photolysis and caused the recombination of OH radicals. In this case, Fe^{2+} reacted with OH radicals as a scavenger [7].

It is desirable that the ratio of H_2O_2 to Fe(II) should be as small as possible, so that the recombination can be avoided and the sludge production from iron complex is also reduced.

3.3 The effect of the pH value

The pH value affects the oxidation of organic substances both directly and indirectly. The photo-Fenton reaction is strongly affected by the pH-dependence. The pH value influences the generation of OH radicals and thus the oxidation efficiency. Fig. 3 shows the effect of the pH value during the use of the photo-Fenton process. A maximum degradation of 97.4% was obtained with the system

UV/H_2O_2/Fe(III) at a pH=3 and degradation of 96.1%. with the system UV/H_2O_2/Fe(II) at the same pH value. For pH values above 4 the degradation strongly decreases because at higher pH values iron precipitates as hydroxide and that reduces the transmission of the radiation [7].
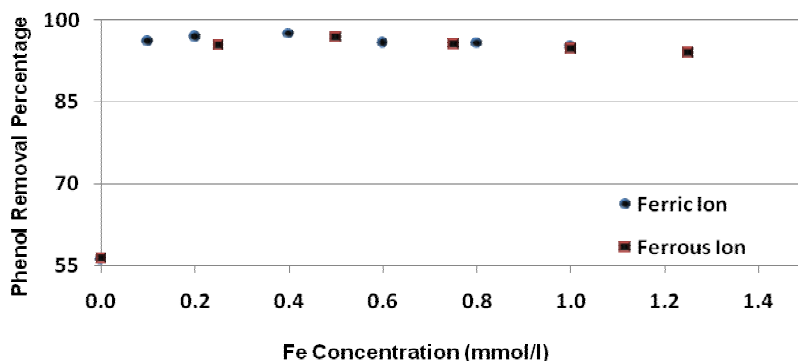

Figure 2:   Phenol degradation as a function of iron catalyst addition: $(H_2O_2)_0$ =6 mmol/1, pH=3.

4 Comparison between UV/H_2O_2 system and photo-Fenton process

4.1 Degradation rate

The photodegradation of phenol was investigated in both systems UV/H_2O_2 and photo-Fenton process [UV/H_2O_2/Fe(II) and UV/H_2O_2/Fe(III)]. The loss of phenol was observed as a function of irradiation time and data were fitted to a first-order rate model

$$Ln(C_1/C_0) = -K_0\, t \qquad\qquad (2)$$

where C_0 and C_1 are the concentration of phenol at irradiation times 0 and t, K_0 is a first-order rate constant (in min^{-1}) and t is the irradiation time (in min). The rate constants were determined using a first-order rate model [Eq. (2)]. The results are listed in Table 1.

The experimental data in Fig. 4 show that photo-Fenton processes had a significant accelerating effect on the rate of oxidation of phenol. The data in Table 1 show that adding Fe(II) or Fe(III) to the UV/H_2O_2 system enhanced the rate of phenol oxidation by a maximum factor 4 and 5 for Fe(II) and Fe(III), respectively, over the UV/H_2O_2 system, depending on both H_2O_2 and Fe doses. This phenomena of enhanced efficiency is also known from other investigations with Fe (II) and Fe (III) [5].
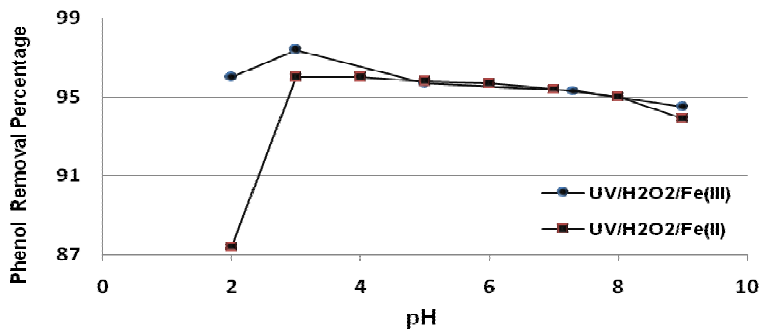
Figure 3: Phenol degradation as a function of the pH value by using photo-Fenton processes: $[Fe(II)]_0$= 0.5 mmol/1, $[Fe(III)]_0$= 0.4 mmol/1, $(H_2O_2)_0$ = 6 mmol/1.

Table 1: Values of reaction rate constants of the degradation of phenol by different types of AOP.

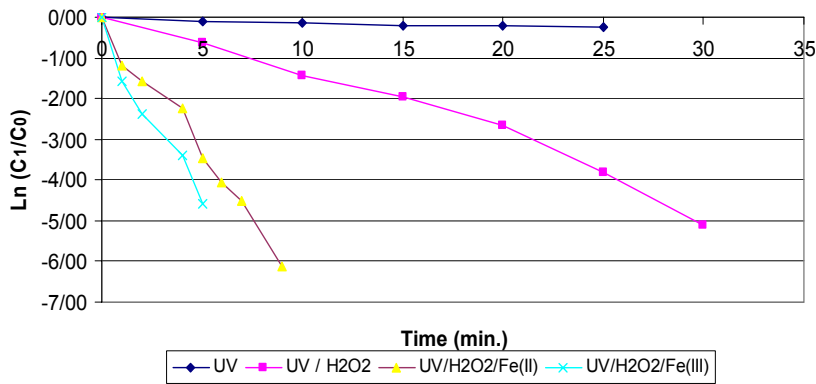| Type of advanced oxidation process	K_0 (min^{-1})
UV	0.01
UV/H_2O_2	0.16
UV/H_2O_2/Fe(II)	0.64
UV/H_2O_2/Fe(III)	0.83

Figure 4: First-order plot for degradation of phenol by UV, UV/H_2O_2 and photo-Fenton processes.

5 Conclusion

The results from this study showed that the oxidation rate was influenced by many factors, such as the pH value, the amount of hydrogen peroxide and iron salt and the type of iron added. The optimum conditions obtained for the best degradation were a pH =3, a Fe(II) concentration of about 0.5 mmol/1 and a H_2O_2 concentration of 6 mmol/1 for $UV/H_2O_2/Fe(II)$ system and a Fe(III) concentration of about 0.4 mmol/1, and a H_2O_2 concentration of about 6 mmol/1 for $UV/H_2O_2/Fe(III)$ system.

The advantages of the photo-Fenton process as an oxidative pre-treatment step over other photochemical oxidation processes are economics, efficiency especially if aromatic compounds are to be destroyed, easy handling of the method because no specific technical equipment is necessary, low investment, less energy demand and harmless process products. The acidic pH (<4) and the secondary treatment to remove the added iron are two major problems currently under examination. Combination of an AOP with biological treatment is a promising alternative because one can take advantage of both methods and develop as result a potent wastewater purification method. Considering the photo-Fenton method as a preliminary step prior to a biological wastewater treatment, one has to adjust pH twice, first to an acidic pH below 4 to perform the photo-Fenton method and then back to a neutral pH.

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