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Degradation of Phenol in Aqueous Solution by Advanced Oxidation Process

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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 in aqueous solution. The study shows 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 accelerates the oxidation rate by 5-8 times the rate of the UV/H_2O_2 process. The reaction was influenced by pH, the input concentration of H_2O_2 and the amount of the iron catalyst and the type of iron salt. The experimental results show that the optimum conditions were obtained at a pH value of 3, with 6 mmol/L H_2O_2 and 0.5 mmol/L Fe(II) for the UV/H_2O_2/Fe(II) system and 6 mmol/L H_2O_2 and, 0.4 mmol/L 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.

Key Words: Advanced oxidation process, Degradation, Phenol, Ozone, UV, H_2O_2.

INTRODUCTION

Most organic compounds are resistant to conventional chemical and biological treatments. For this reason, other methods are being studied as an alternative to biological and classical physico-chemical processes. Of these, advanced oxidation processes (AOPs) will probably constitute the best option in the near future.

Advanced oxidation processes 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]. The AOPs studied here are pollutant treatment processes, which use ozone, UV, ozone in combination with UV (O_3/UV), ozone plus hydrogen peroxide (O_3/H_2O_2), hydrogen peroxide and ultraviolet light (UV/H_2O_2), Fenton's reagent and UV/O_2.

The main problem of AOPs lies in the high cost of reagents such as ozone, hydrogen peroxide or energy-light sources like ultraviolet light. However, the use of solar radiation as an energy source can reduce costs. Moreover, it should be pointed out that AOPs lead normally to the best yields in pollutant destruction when biological treatments are unfeasible. Advanced oxidation processes 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 ($^{\bullet}OH$) are generated in solution and these are responsible for the oxidation and mineralization of the organic pollutants to water and carbon dioxide. In recent years, various advanced oxidation processes, which produce hydroxyl radicals *i.e.* O_3/UV, O_3/H_2O_2, UV/H_2O_2, Fenton reagent [H_2O_2/Fe(II)], *etc.*, have been applied in wastewater treatment[1-5]. The photochemical advanced oxidation processes including photolysis and photocatalysis are attractive environmental remediation technologies and are gaining increasing importance for degradation of most of the organic pollutants[6].

The photolytic induced oxidation with ozone or hydrogen peroxide will result in expensive high energy requirements if the organic or inorganic pollutants of wastewater strongly absorb UV-radiation. The utilization of the metal salt Fe(II) as Fenton's reagent produces inorganic sludge that may cause a waste disposal problem[7].

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[8-10] 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 wastewater treatment, due to its bio-resistance and toxicity to microbial population.

EXPERIMENTAL

Phenol in the purest form is available from Merck Chemical Company. Ferrous ($FeSO_4 \cdot 7H_2O$) and ferric [$Fe_2(SO_4)_3 \cdot 7H_2O$] sulphate heptahydrate used as sources of Fe(II) and Fe(III), were all analytical grade and purchased from Merck. Hydrogen peroxide solution (35 % w/w) in stable form was provided by Riedel-deHaen Company. All reagents employed were not subjected to any further treatment. Water used was of double distilled quality.

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[11]. The initial and treated solutions of phenol were determined by the standard methods procedure[12]. The pH measurements were carried out with a Metrohm model 691 pHmeter, calibrated with two buffer solutions of pH 3 and 7.

All experiments were performed in a batch reactor with a cooling jacket (Fig. 1). 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.

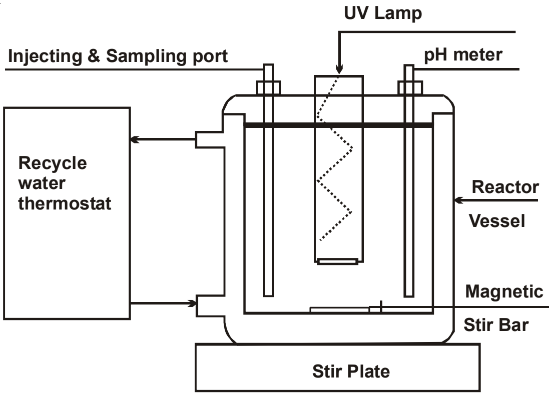

Fig. 1. Schematic diagram of photochemical oxidation system experimental set-up

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.

Photodegradation procedures: For each experiment, synthetic aqueous solution of phenol (to simulate a high loaded phenol containing industrial wastewater) was prepared in double distilled water as solvent. The laboratory unit was filled with 1.5 L of the phenol solution. 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 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.

RESULTS AND DISCUSSION

UV/H_2O_2 process: In this process hydroxyl radicals are formed[13] according to eqn. 1.

$$H_2O_2 \rightarrow 2OH^{\bullet} \tag{1}$$

The combination of UV and a little amount of H_2O_2 enhances strongly the efficiency of the degradation of phenol. Homogeneous photolysis methods, compared with photocatalysis, do not demand a separation procedure of solid catalyst after treatment. For effective treatment, photolysis requires short wavelength of strong energy UV light and other chemical oxidants such as hydrogen peroxide and ozone.

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. 2 illustrates the per cent 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 increased when hydrogen peroxide concentration increased. As can be seen from Fig. 2, the per cent degradation of phenol at 0.6 mL hydrogen peroxide dosage was 85.6 and was 86.4 at 0.8 mL hydrogen peroxide dosage. 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[14].

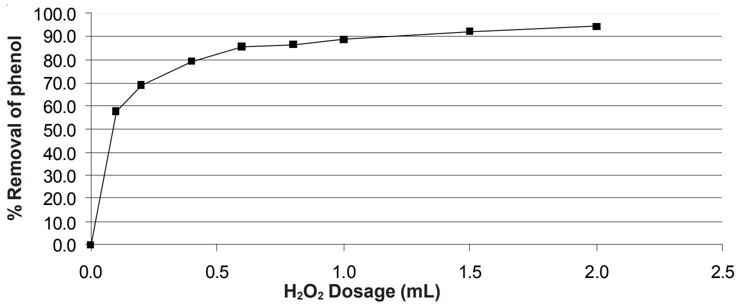

Fig. 2. Degradation of phenol with the UV/H_2O_2 process. The effect of hydrogen peroxide concentration (irradiation time = 5 min)

Photo-Fenton process: The formation of the hydroxyl radicals by using the Photo-Fenton process under application of Fe(II) occurs according to the following eqn. 2[15].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet \quad (2)$$

Reaction (2), already known as the Fenton reaction, possesses a high oxidation potential, but its revival in the application to wastewater treatment began only recently[16]. UV irradiation leads not only to the formation of additional hydroxyl radicals but also to a recycling of the ferrous catalyst by reduction of Fe(III). By this the concentration of Fe(II) increases and therefore the gross reaction is accelerated[17]. The reaction time needed for the Photo-Fenton reaction is extremely low and depends on the operating pH value and the concentrations of H_2O_2 and iron added. Within 5 min complete destruction of phenol could be observed using Photo-Fenton processes.

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. Figs. 3 and 4 show the effect of the pH value during the use of the photo-Fenton process. A

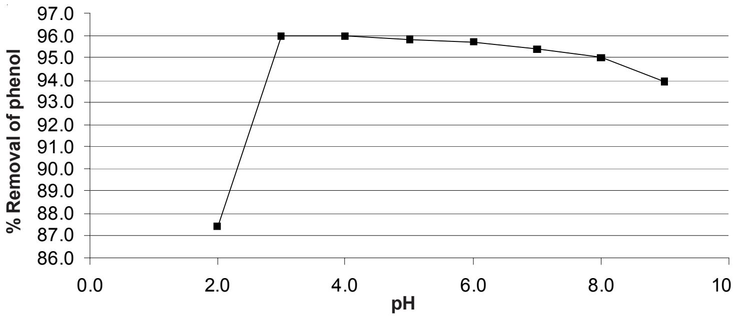

Fig. 3. Phenol degradation as a function of the pH value by using Photo-Fenton processes: $[Fe(II)]_0 = 0.5$ mmol/L, $(H_2O_2)_0 = 6$ mmol/L

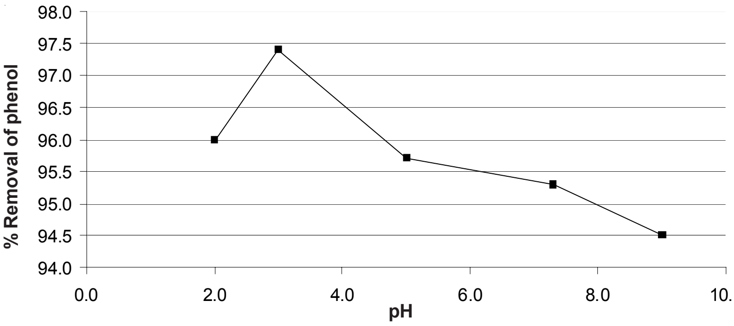

Fig. 4. Phenol degradation as a function of the pH value by using Photo-Fenton processes: $[Fe(III)]_0 = 0.4$ mmol/L, $(H_2O_2)_0 = 6$ mmol/L

maximum degradation of 99.85 % was obtained with the system UV/H_2O_2/Fe(III) at a pH = 3 and degradation of 96.5 % 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[15].

Influence of initial hydrogen peroxide concentration: Fig. 2 shows the effect of the initial hydrogen peroxide on the degradation of phenol with the use of Photo-Fenton processes. As expected, the degradation of phenol was increased by increasing the concentration of H_2O_2 added. This can be explained by the effect of the additionally produced $OH^•$ radicals. Addition of H_2O_2 exceeding 0.03 mol/L for UV/H_2O_2/Fe(II) system or 0.01 mol/L for UV/H_2O_2/Fe(III) system did not improve the respective maximum degradation. This may be due to auto-decomposition of H_2O_2 to oxygen and water and the recombination of $OH^•$ radicals. Since $OH^•$ radicals react with H_2O_2, H_2O_2 itself contributes to the OH scavenging capacity[14]. Therefore, H_2O_2 should be added at an optimal concentration to achieve the best degradation.

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. Figs. 5 and 6 show the percent degradation of phenol as a function of the added Fe(II) and Fe(III). The figures show 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 1 mmol/L Fe(II) or 0.4 mmol/L 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[18,19].

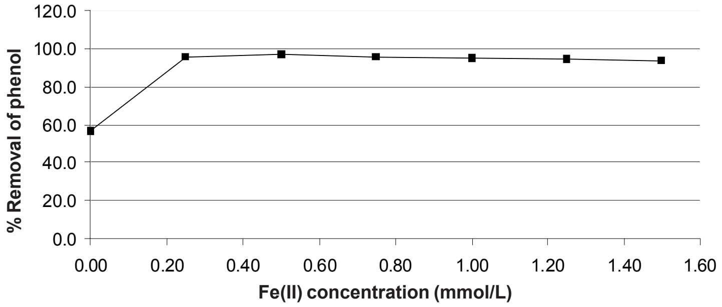

Fig. 5. Phenol degradation as a function of iron catalyst (Fe(II)) addition: $(H_2O_2)_0$ = 6 mmol/L, pH = 3

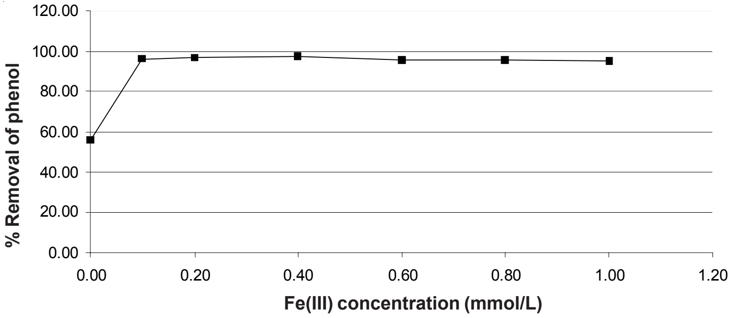

Fig. 6. Phenol degradation as a function of iron catalyst (Fe(III)) addition: $(H_2O_2)_0$ = 6 mmol/L, pH = 3

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.

Comparison between UV/H_2O_2 system and Photo-Fenton process

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.

$$\ln (C_1/C_0) = -K_0\, t \qquad (3)$$

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 (min^{-1}) and t is the irradiation time (min). The rate constants were determined using a first-order rate model (eqn. 3). The results are listed in Table-1.

TABLE-1
VALUES OF REACTION RATE CONSTANTS OF THE DEGRADATION OF PHENOL BY DIFFERENT TYPES OF ADVANCED OXIDATION PROCESS

Type of advanced oxidation process	K_0 (min^{-1})
UV	0.009
UV/H_2O_2	0.164
UV/H_2O_2/Fe(II)	0.641
UV/H_2O_2/Fe(III)	0.825

The experimental data in Fig. 7 show that Photo-Fenton processes had a significant accelerating effect on the rate of oxidation of phenol. The data in Table-1 show that addition of Fe(II) or Fe(III) to the UV/H_2O_2 system enhanced the rate of phenol oxidation by a maximum factor 5 and 9 for Fe(II) and Fe(III), respectively, over the UV/H_2O_2 system, depending on both H_2O_2 and Fe doses. This phenomenon of enhanced efficiency is also known from other investigations with Fe(II) and Fe(III)[20].

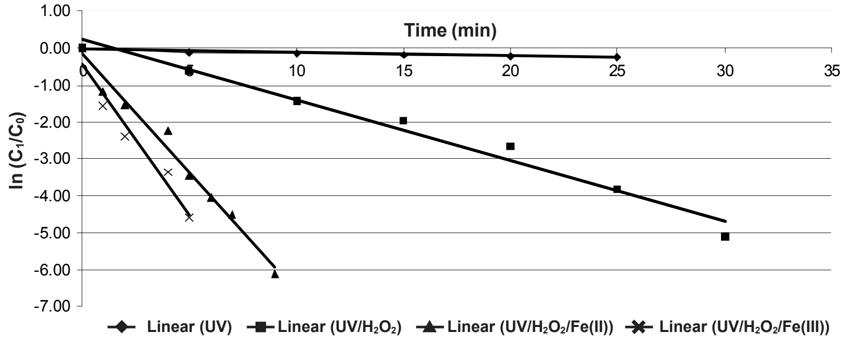

Fig. 7. First-order plot for degradation of phenol by UV, UV/H_2O_2 and Photo-Fenton processes

Conclusion

The results show that the degradation rate of phenol strongly accelerates by the photochemical oxidation processes. The Photo-Fenton process, the combination of homogeneous systems of UV/H_2O_2/Fe compounds, produced the highest photochemical elimination rate for phenol. 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 at pH = 3, a Fe(II) concentration of about 0.5 mmol/L and a H_2O_2 concentration of 6 mmol/L for UV/H_2O_2/Fe(II) system and a Fe(III) concentration of about 0.4 mmol/L and a H_2O_2 concentration of about 6 mmol/L 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 economical 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 advanced oxidation process with biological treatment is a promising alternative because one can take advantage of both methods and develop as a 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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