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Photochemical Oxidation of Phenol in Olefins Plant Effluent by UV/H_2O_2 and Photo-Fenton Processes (Case Study)

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In this study, the application of advanced photochemiocal oxidation technologies (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 olefin plant effluent of Tabriz petrochemical company. 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 5-7 times the rate of the UV/ H_2O_2 process. The reaction was influenced by pH-value, the input concen-tration of H_2O_2 and the amount of the iron catalyst and the type of iron salt. Complete phenol removal was obtained by all applied processes. The experimental results show that the optimum conditions were obtained at a pH value of 3, with molar ratio [H_2O_2]/[phenol] equal 14.4 and molar ratio [iron]/[H_2O_2] is 0.057 and 0.043 for UV/ H_2O_2/Fe(II) and UV/H_2O_2/Fe(III), respectively. As for the UV processes, UV/ H_2O_2/Fe(III) showed the highest degradation rate.

Key Words: Phenol, Hydrogen peroxide, UV radiation, Photo-Fenton reaction, Advanced photochemiocal oxidation technologies, Wastewater.

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.

Phenols occupy a prominent place among the pollutants of ground waters[1]. A large part of that pollution is caused by industry. Due to the wide utilization in different industries, *e.g.*, chemical, petrochemical, paint, textile, pesticide plants, *etc.*, phenols have become the most abundant pollutants in industrial wastewater. They serve as intermediates in the industrial synthesis of products as diverse as adhesives and antiseptics[2]. Their presence contributes notably to the pollution of

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the effluents due to their high toxicity to aquatic life and may cause carcinogenic and mutagenic effects to humans[3]. Common commercial wastewater treatment methods utilize the combination of biological, physical and chemical treatment[4,5]. Biotreatment processes tend to be very large due to the slow rate of the biological reactions[5]. Furthermore, physical methods for wastewater treatment do not involve chemical transformations and generally transfer waste components from one phase to another. Chemical treatment of phenols, such as chlorination, can result with formation of chlorinated phenols and their by-products which are reported as toxic and non-biodegradable[6].

An attractive alternative for the treatment of toxic organic contaminants present in wastewater, including phenols, are so-called advanced oxidation processes (AOPs) which generate hydroxyl radicals in sufficient quantities for oxidizing the majority of the organics present in the effluent water[7-10]. Common AOPs involve Fenton and Fenton "like" processes, ozonization, photochemical and electrochemical oxidation, photolysis with H_2O_2 and O_3, high voltage electrical discharge (corona) process, TiO_2 photocatalysis, radiolysis, water solutions treatment by electronic beams or γ-beams and various combinations of these methods[8-10]. The mostly used AOPs are Fenton type processes. The primary benefits of Fenton type processes are their ability to convert a broad range of pollutants to harmless or biodegradable products and the fact that their relatively cheap reagents are safe to handle and are environmentally benign[11]. The degradation of organic pollutants by Fenton type processes could be significantly accelerated in the presence of UV light irradiation, resulting with complete mineralization of organic pollutants[12].

EXPERIMENTAL

Ferrous and ferric 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. Wastewater (phenoly water) used in the experiments was obtained from olefin plant effluent of Tabriz petrochemical company in the north-west of Iran. Characteristics of the wastewater are summarized in Table-1.

TABLE-1
MAIN CHARACTERISTICS OF THE OLEFIN PLANT WASTEWATER USED IN THE STUDY

Parameter	Value
COD (mg/L)	131-205
BOD (mg/L)	76-114
Phenol (mg/L)	35-50
Total Fe (mg/L)	0.1-0.15
Conductivity (micro S/cm^2)	109-186
pH	6.0-8.5

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, 240-250 nm, from ARDA Company in France) which was immersed in the glass tube.

The reactor was equipped with a cooling water jacket system. The reactor was filled with the reaction mixture. Mixing was accomplished by the use of a magnetic stirrer.

Photodegradation procedures: For each experiment, the laboratory unit was filled with 1.5 mL of the olefine plant wastewater. For runs using UV/H_2O_2 system, hydrogen peroxide at different amounts was injected in the reactor before the beginning of each run. Concerning knowledge from the literature which reports the usage of Fenton process for the treatment of phenol wastewater[12-16], at the beginning of all experiments pH was adjusted at 3 using 1 N sulfuric acid, which was followed by addition of Fenton reagent. 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 start up, then a given weight of iron salt was added. The iron salt was mixed very well with the wastewater 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 hydro-gen peroxide.

Analytical methods: Samples were taken at appropriate time intervals from the reaction vessel and pipetted into (3 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 (DR2500, HACH) according to the standard methods[17]. The initial and treated solutions of phenol were determined by the standard methods procedure[17]. The pH measurements were carried out with a Metrohm model 691 pH meter calibrated with two buffer solutions of 3 and 7.

RESULTS AND DISCUSSION

UV/H_2O_2 process: In this process hydroxyl radicals are formed according to eqn. 1[18]:

$$H_2O_2 \rightarrow 2OH^{\bullet} \qquad (1)$$

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. 1 illustrates the per cent degradation of phenol as a function of the irradiation time at different doses of hydrogen peroxide input. The photolysis of phenol in the absence of hydrogen peroxide gave rather moderate results and resulted in a slow degradation of phenol. By addition of hydrogen peroxide the degradation rate of phenol increased when hydrogen peroxide concentration increased. As can be seen from Fig. 1, the per cent degradation of phenol at 5 min was 11 in a direct photolysis experiment and was 90.8 at the same time when the photolysis was carried out in the presence of an initial hydrogen peroxide concentration of 7 mmol/L. 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[19]. When the concentration of hydrogen peroxide was higher than 15 mmol/L, its hydroxyl radical scavenging effect became important and the phenol degradation rate decreased.

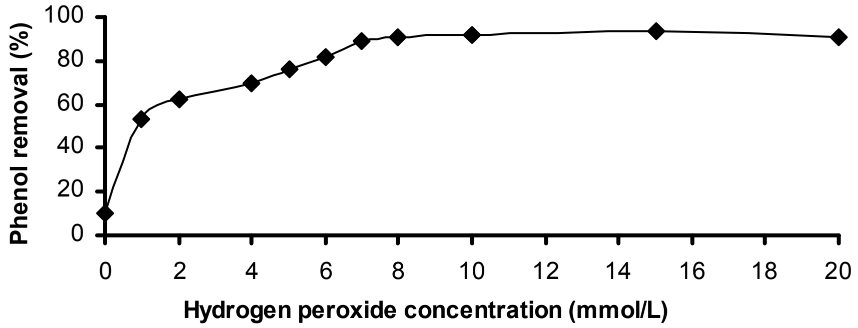

Fig. 1. Degradation of phenol with the UV/H_2O_2 process. The effect of hydrogen peroxide concentration (irradiation time = 5 min).

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[20]:

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + OH^\bullet \qquad (2)$$

Equation 2, already known as the Fenton reaction, possesses a high oxidation potential, but its revival in the application to wastewater treatment began only recently[21]. 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[22]. 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. 2 and 3 show the effect of the pH value during the use of the Photo-Fenton process. A maximum degradation of 97.2 % was obtained with the system UV/H_2O_2/Fe(III) at a pH = 3 and degradation of 95.8 % 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[20].

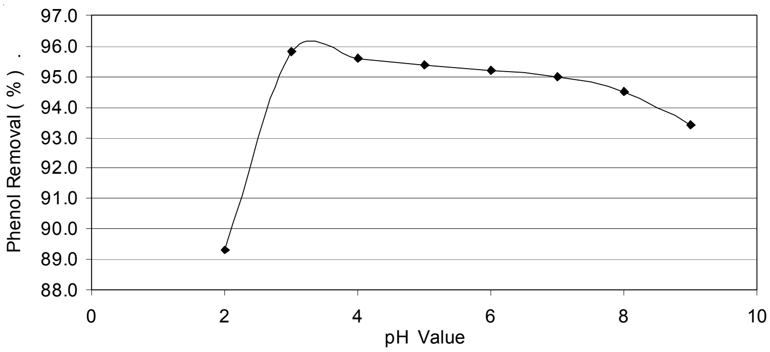

Fig. 2. Phenol degradation as a function of the pH value by using Photo-Fenton processes: $[Fe(II)]_0 = 0.4$ mmol/L, $(H_2O_2)_0 = 7$ mmol/L

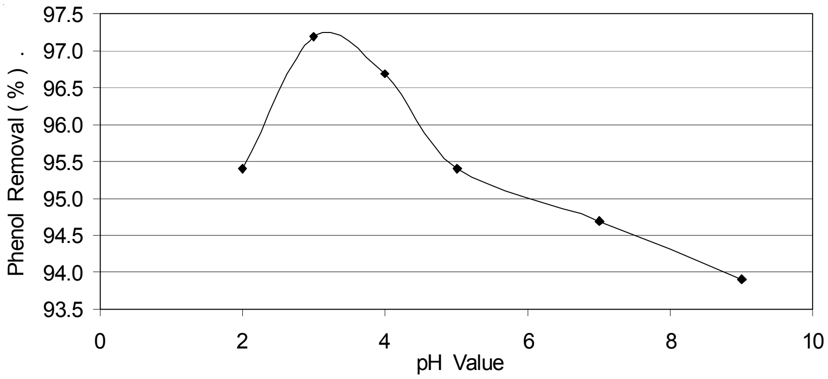

Fig. 3. Phenol degradation as a function of the pH value by using Photo-Fenton processes: $[Fe(III)]_0 = 0.3$ mmol/L, $(H_2O_2)_0 = 7$ mmol/L

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. 4 and 5 show the per cent 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.

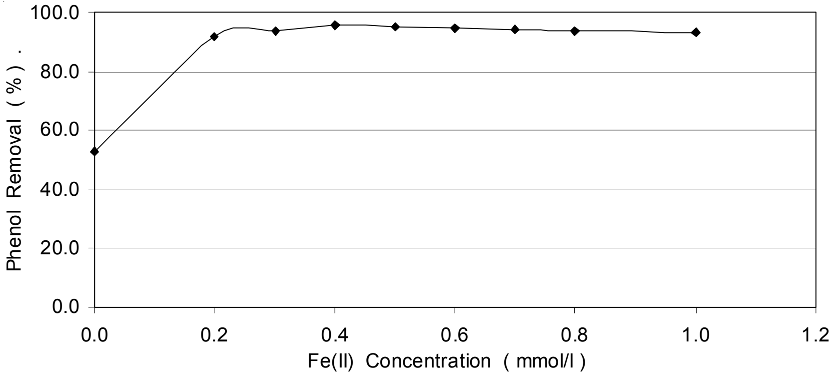

Fig. 4. Phenol degradation as a function of iron catalyst (Fe(II)) addition: $(H_2O_2)_0$ = 7 mmol/L, pH = 3

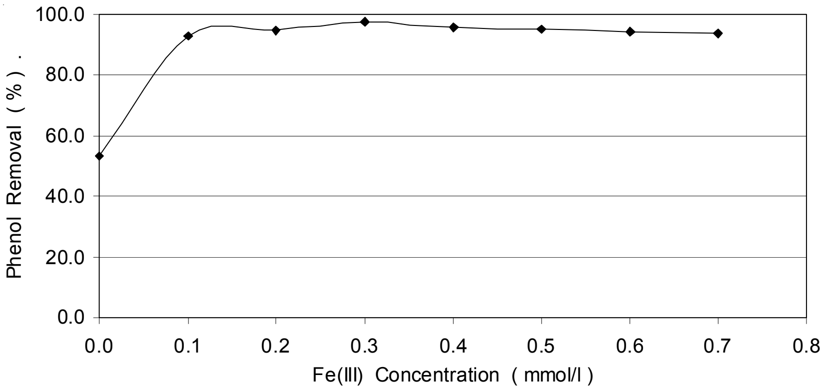

Fig. 5. Phenol degradation as a function of iron catalyst (Fe(III)) addition: $(H_2O_2)_0$ = 7 mmol/L, pH = 3

Addition of the iron salt above 0.4 mmol/L Fe(II) or 0.3 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[23,24].

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[24].

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:

$$\ln (C_1/C_0) = -K_0 t \tag{3}$$

where C_0 and C_1 are the concentration of phenol at irradiation times 0 and t, respectively 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 (eqn. 3). The results are listed in Table-2.

TABLE-2
VALUES OF REACTION RATE CONSTANTS OF THE DEGRADATION OF PHENOL BY DIFFERENT TYPES OF APOT

Type of advanced oxidation process	K_0 (min^{-1})
UV	0.01
UV/H_2O_2	0.11
UV/H_2O_2/Fe(II)	0.53
UV/H_2O_2/Fe(III)	0.74

The experimental data in Fig. 6 show that Photo-Fenton processes had a significant accelerating effect on the rate of oxidation of phenol. The data in Table-2 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 5 and 7 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[25] with Fe^{2+} and Fe^{3+}.

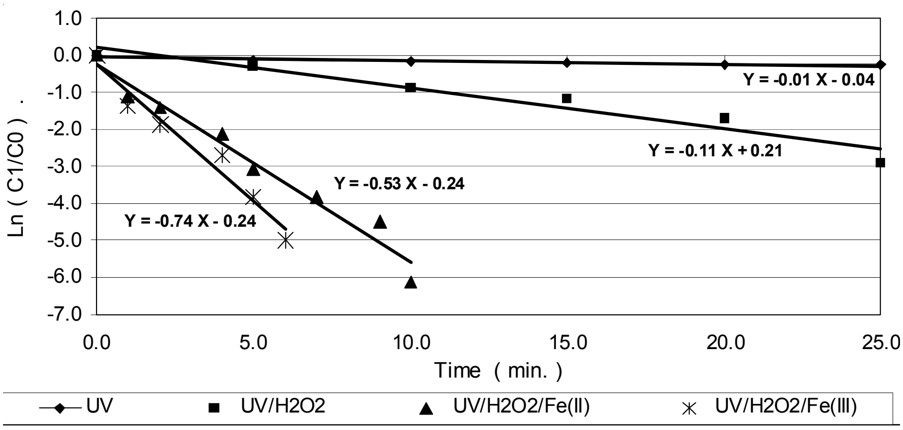

Fig. 6. First-order plot for degradation of phenol by UV, UV/H_2O_2 and Photo-Fenton processes

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 a pH = 3, with molar ratio [H_2O_2]/[phenol] equal 14.4 and molar ratio [iron]/[H_2O_2] is 0.057 and 0.043 for UV/H_2O_2/Fe(II) and UV/H_2O_2/Fe(III), respectively.

The advantages of the Photo-Fenton process as an oxidative pre-treatment step over other photochemical oxidation processes are economical, 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 APOT with biological treatment is a promising alternative because one can take advantage of both methods and develop as a result a potent waste-water 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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