

Phenol Sulfonic Acid Oxidation in aqueous solution by UV, UV/H₂O₂ and Photo-Fenton Processes

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Abstract— In this study, advanced oxidation processes (UV, UV/H₂O₂, UV/H₂O₂/Fe(II) and UV/H₂O₂/Fe(III)) were investigated in lab-scale experiments for degradation of phenol sulfonic acid (PSA) in aqueous solution. The study showed that the UV/H₂O₂ process has removal percentage 90.9, 93.0 and 94.4 for neutral, basic and acidic conditions in 20 minutes respectively.

The experimental results showed that the optimum conditions were obtained at a pH value of 3, with 4 mmol/l H₂O₂, and 0.25 mmol/l Fe(II) for the UV/H₂O₂/Fe(II) system and 6 mmol/l H₂O₂ and, 0.4 mmol/l Fe(III) for the UV/H₂O₂/Fe(III) system.

The reaction was influenced by the pH, the input concentration of H₂O₂ and the amount of the iron catalyst and the type of iron salt. As for the UV processes, UV/H₂O₂ showed the highest degradation rate under acidic conditions.

Keywords— Photochemical Oxidation; phenol sulfonic acid; Photo-Fenton; UV radiation; Hydrogen peroxide; Degradation.

I. INTRODUCTION

Many industrial processes, such as oil refineries, petrochemical industries (olefin plants), Steel factories, plastic plants, paper plants, synthetic chemicals, pesticides, coal conversion generate flow streams that contain small concentrations of phenols and phenolic compounds. The removal of these pollutants from wastewater is one of the most critical topics in environmental research and is required prior to discharge or reuse of the waste flow.

Phenolic compounds are one of the major classes of organic pollutants generated through various industrial activities. For example, more than 97,000 tonnes of phenolic wastes were generated by the industries in the United States in 2000 [1].

Electrolytic tin plating on steel substrate has been widely used in food and beverage industries

due to its non-toxic nature [2]. Recently, it also has been applied in the semiconductor industry because of its strong resistance to corrosion and tarnishing of component leads, solderability and ductility. Phenol Sulfonic Acid (PSA) and its isomers work as electrolytes in electroplating baths for tin-plating applications also as a catalyst in the production of phenolic floral foam and in paint, textile and carpeting industries, tanneries, pharmaceuticals, glue production and etc. The acute toxicological effects of phenol and its derivatives are largely on the central nervous system. Acute poisoning can lead to severe gastrointestinal disturbances, kidney malfunction, circulatory system failure, lung edema and convulsions. Fatal doses can be absorbed through the skin. Key organs damaged by chronic phenol exposure include the spleen, pancreas and kidneys.

The toxic effect of phenol sulfonic acid (PSA) resembles those of phenol [3]. Various treatment technologies are available for the reduction of all levels of initial phenol concentration in phenolic wastes. These are classified as solvent extraction for high levels of phenols (above 500 ppm), physico-chemical and biological treatments for intermediate levels of phenols (5-500 ppm), ozonation and carbon adsorption for low levels of phenols [4].

The Photo-Fenton process, the combination of homogeneous systems of UV/H₂O₂/Fe compounds, produced the highest photochemical elimination rate for phenol (up to 100 ppm) [5, 6].

In this study, removal of PSA using advanced oxidation processes (UV, UV/H₂O₂, UV/H₂O₂/Fe(II) and UV/H₂O₂/Fe(III)) has been studied and its removal efficiency is compared.

II. MATERIALS AND METHODS

Phenol sulfonic acid (4-hydroxybenzenesulfonic acid), 65% solution in stable form was provided from Mreck. For PSA concentration measurement, calorimetric method with spectrophotometer was used. In this stage, solutions with concentrations of 0.1, 0.5, 1, 5, 10, 50, 100 and 400 mg/lit were prepared and their light absorption in UV mode and in two light wavelength of 235 and 259 nm were tested. Results showed that 235 nanometer wavelengths are sensitive to concentrations less than 10 mg/lit PSA and 259 nanometer wavelengths are sensitive to concentrations more than 10 mg/lit of PSA. Using these data, standard curves for the solutions were prepared and used for subsequent measurements.

Ferrous ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and ferric [$\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$] 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 was double distilled quality.

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 sulfonic acid were determined by a spectrophotometer (CARY 100 Scan, VARIAN) according to the standard methods [7]. The initial and treated solutions of phenol sulfonic acid were determined by the standard methods procedure [7]. The pH measurements were carried out with a Metrohm model 691 pH meter, calibrated with two buffer solutions of 3 and 7.

A. Experimental setup

All experiments were performed in a batch reactor with a cooling jacket. The schematic diagram of the experimental set-up used in the study is shown in Fig. 1.

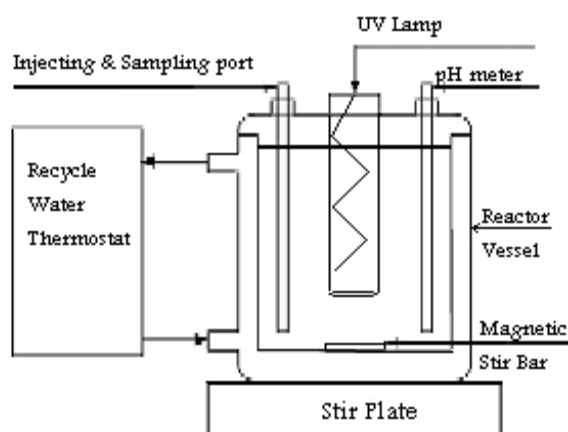


Fig. 1. Schematic diagram of photochemical oxidation system experimental set-up.

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.

C. Photodegradation procedures

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

III. RESULTS AND DISCUSSION

A. 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. 2 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 increased when hydrogen peroxide concentration increased. As can be seen from Fig. 2, the percent degradation of phenol sulfonic acid at 4 mmol/L hydrogen peroxide dosage was 67.5 and was 67.9 at 6 mmol/L 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 sulfonic acid degradation [8].

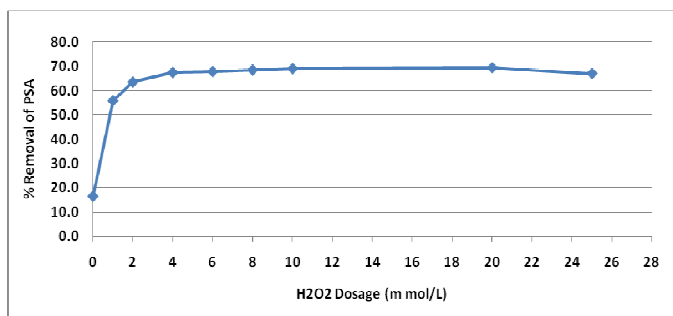
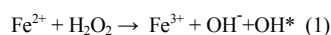


Fig. 2. Degradation of phenol sulfonic acid with the UV/H₂O₂ process. The effect of hydrogen peroxide concentration (irradiation time= 5 min.).

B. 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 Eq. (1) [9].



Reaction (1), already known as the Fenton reaction, possesses a high oxidation potential, but its revival in the application to wastewater treatment began only recently [10]. 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 [11]. The reaction time needed for the photo-Fenton reaction is extremely low and depends on the operating pH value and the concentrations of H₂O₂ and iron added. Within 5 mins above 80% destruction of phenol sulfonic acid could be observed using photo-Fenton processes.

C. 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 (a,b and c) show the effect of the pH value during the use of the photo-Fenton process. A maximum degradation of 94.4% was obtained with the system UV/H₂O₂ at a pH=3, degradation of 93.0% with the same system at a pH=8.5 and degradation of 90.9% at a pH=7.

D. The 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 H₂O₂ added. This can be explained by the effect of the additionally produced OH[•] radicals. Addition of H₂O₂ exceeding 20 m mol/L for UV/H₂O₂ system did not improve the respective maximum degradation; this may be due to auto-decomposition of H₂O₂ to oxygen and water and the recombination of OH[•] radicals. Since OH[•] radicals react with H₂O₂, H₂O₂ itself contributes to the OH scavenging capacity [8].

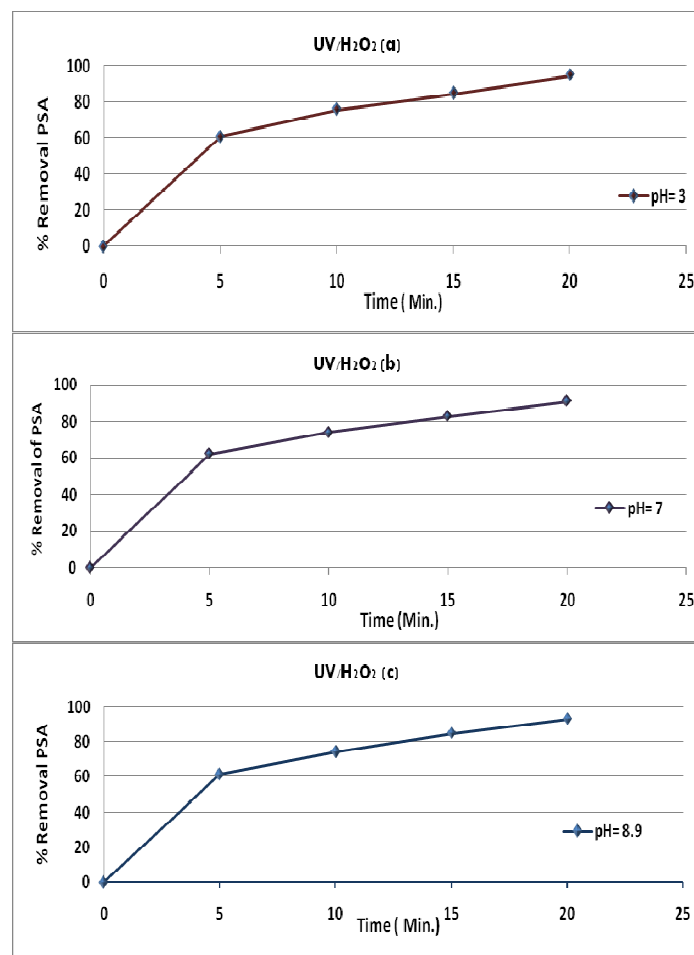


Fig. 3. Phenol sulfonic acid degradation as a function of the pH value by using UV/H₂O₂ process: (H₂O₂)₀ = 4 mmol/l [pH=3(a), pH=7(b) and pH=8.9(c)].

Therefore, H₂O₂ should be added at an optimal concentration to achieve the best degradation.

E. 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. 4 and Fig. 5 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 Fe²⁺ or Fe³⁺ enhanced the efficiency of UV/H₂O₂ for phenol degradation. The degradation rate of phenol sulfonic acid distinctly increased with increasing amounts of iron salt. Addition of the iron salt above 0.25 mmol/L Fe(II) or 0.40 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, Fe²⁺ reacted with OH radicals as a scavenger [12].

It is desirable that the ratio of H₂O₂ 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.

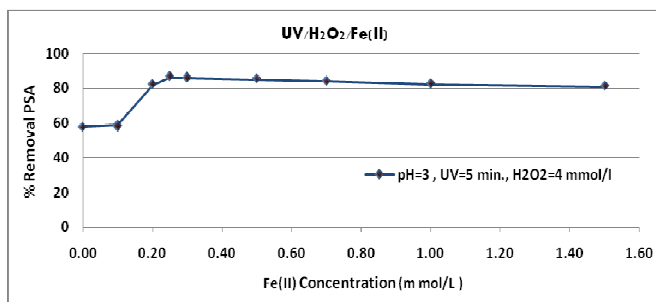


Fig. 4. Phenol sulfonic acid degradation as a function of iron catalyst (Fe(II)) addition: $(H_2O_2)_0 = 4$ mmol/l, pH=3.

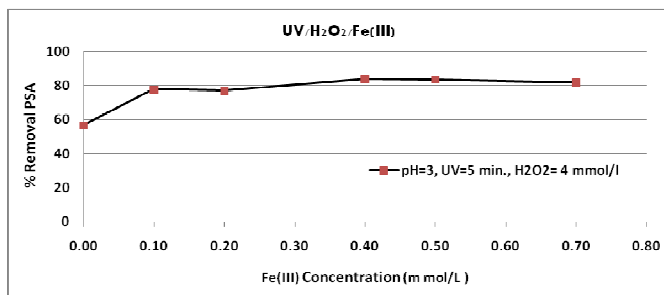


Fig. 5. Phenol sulfonic acid degradation as a function of iron catalyst (Fe(III)) addition: $(H_2O_2)_0 = 4$ mmol/l, pH=3.

IV. COMPARISON BETWEEN UV/H₂O₂ SYSTEM AND PHOTO-FENTON PROCESS

A. Degradation rate

The photodegradation of phenol was investigated in both systems UV/H₂O₂ and photo-Fenton process [UV/H₂O₂/Fe(II) and UV/H₂O₂/Fe(III)]. The loss of phenol sulfonic acid was observed as a function of irradiation time and data were fitted to a first-order rate model

$$\ln(C_1/C_0) = -K_0 t \quad (2)$$

Where C₀ and C₁ are the concentration of phenol sulfonic acid at irradiation times 0 and t, K₀ 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 Table 1 show that UV/H₂O₂ process had a significant accelerating effect on the rate of oxidation of phenol sulfonic acid. The data in Table 1 show that adding Fe(II) or Fe(III) to the UV/H₂O₂ system decreased the rate of phenol oxidation by a maximum factor 0.86 and 0.82 for Fe(II) and Fe(III), respectively, over the UV/H₂O₂ system, depending on both H₂O₂ and Fe doses.

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

Type of advanced oxidation process	K ₀ (min ⁻¹)
UV	0.379
UV/H ₂ O ₂	0.792
UV/H ₂ O ₂ /Fe(II)	0.684
UV/H ₂ O ₂ /Fe(III)	0.652

IV. CONCLUSIONS

The results show that the degradation rate of phenol sulfonic acid strongly accelerates by the photochemical oxidation processes. The UV/H₂O₂ process produced the highest photochemical elimination rate for phenol sulfonic acid. 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 and a H₂O₂ concentration of 4 mmol/l for UV/H₂O₂ system.

The advantages of the UV/H₂O₂ 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) is major problem 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 a result a potent wastewater purification method.

Considering the UV/H₂O₂ 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 reaction and then back to a neutral pH.

IV. ACKNOWLEDGMENT

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