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Removal of phenol at high concentrations using UV/Persulfate from saline wastewater

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ABSTRACT

This study investigated the degradation of phenol at high concentrations from saline wastewater using UV/Persulfate (UV/PS) in a bench scale reactor. The effect of operational variables such as PS concentration (50, 80, 100, 150, and 200 mM), solution pH (3, 7, and 10), initial phenol concentration (200, 450, 1,000, 1,500, and 2,000 mg/L), and NaCl concentration (30,000, 50,000, and 70,000 mg/L) were surveyed. The results revealed that maximum removal of phenol (91%) was obtained after 60 min of reaction at PS molar concentration of 150 mM. Also, changes in pH values had no significant effect on removal efficiency and had slightly greater removal at acidic pH, so pH 3 was selected as optimum. Phenol removal efficiency was increased from 91 to 93% with an increase in the NaCl concentration from 30,000 to 70,000 mg/L, respectively. In addition, phenol removal percentages decrease with an increase in the initial phenol concentration. Efficiency of PS and UV photolysis were 30 and 21%, respectively. The results showed that UV/PS process could be optimally used to remove phenol from saline wastewater and could be effective, economically and environmentally.

Keywords: UV/Persulfate; Saline wastewater; Phenol removal; Advanced oxidation process

1. Introduction

Phenol is an aromatic compound used in many industries including petrochemical, pharmaceutical, plastics, wood products, dye, and paper industries and it can be discharged to the environment through effluent of these industries. Since this pollutant is toxic, even at low concentrations, and since it is difficult to be treated biologically, there are strict standards for the discharge of phenol-containing materials into the environment [1]. Owing to the toxic nature of this

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compound, American Environmental Protection Agency has stated that the standard level of phenol in filtered water must be less than 1 μg/L. Phenol is quickly absorbed through the skin and causes skin and eye burns. Overexposure to phenol can lead to convulsions, cyanosis, coma, and death [2]. Moreover, phenol affects liver, kidneys, lungs, and vascular system. Several industries such as petroleum refineries, petrochemical plants, olive oil processing industries, and insecticide manufacturers produce saline wastewater which contains substantial amounts of phenol and its derivatives [3]. High concentrations of salt and difficult degradation of these materials are the major challenges during treatment of such wastewater. Therefore, treating saline wastewater containing phenol is one of environmental problems; many studies have been carried out to find effective processes for biological treatment of saline wastewater [4,5]. Saline wastewater from the industries generally contains high salinity as high as seawater. In saline wastewater, concentration of salt ions is usually greater than 20,000 mg/L and, in some cases, higher than 150,000 mg/L [5,6]. Saline wastewater treatment involves the removal of organic substances in biological processes and the reduction of salinity in the physical and chemical separation processes. If saline wastewater is discharged into the environment without any treatment, it results in contamination of soil, groundwater, and surface water [5–8]. Due to the adverse effect of salt on bacterial growth, plasmolysis of cells and reduction of microbial activity, biological treatment processes cannot be used as a cost-effective way for the treatment of saline wastewater [5,9]. Therefore, these wastewaters are conventionally treated through physico–chemical processes. Persulfate (PS) is a non-selective anion and its solution is relatively stable at ambient temperature and is the most powerful oxidant of peroxide family. It is widely used in oil industries to correct the hydraulic flow or to start the reaction in petrochemical industry [10]. Among strong oxidants, PS and its sulfate radical have special and unique properties such as high kinetics speed, more stability compared to the hydroxyl radical and less dependent on natural organic matters [11]. PS oxidation potential is 2.01 V which is stronger than hydrogen peroxide (1.8 V) and permanganate (1.7 V). Sulfate radical is a strong oxidant in aquatic environment with an oxidation potential of 2.6 V [12–14]. It should be noted that direct oxidation by PS has no substantial effect on organic pollutants under atmospheric conditions. However, if heat, light, or certain metal ions are used as catalysts, PS can produce sulfate radicals (Eqs. (1) and (2)) [15,16]. Therefore, in this study UV rays were used to activate and produce sulfate radicals:

$$S_2O_8^{2-} \xrightarrow{\text{heat}/h\upsilon} 2SO_4^{\cdot-} \tag{1}$$

$$S_2O_8^{2-} + M^{n+} \longrightarrow SO_4^{2-} + SO_4^{\cdot-} + M^{(n+1)+} \tag{2}$$

The aim of this study was to investigate the removal of phenol at high concentrations from saline wastewater using UV/PS process. In order to produce the persulfate radicals, UV ray has been used. The effect of operational parameters such as PS concentration, solution pH, initial phenol concentration, and NaCl concentration were surveyed on UV/PS process. Moreover, the effect of NaCl concentration as a common salt on the phenol removal was investigated in the present work.

2. Materials and methods

2.1. Materials and reagents

Phenol (purity > 99.5%) and PS were purchased from German Merck Company. Other chemicals and reagents used in this study were purchased in their purest forms (analytical grade). To prepare samples, double-distilled water was used. NaOH and HCl solutions (1 M) were used to adjust solution pH.

2.2. Experimental setup

In this empirical study, a UV reactor made of Shokufan Tosaeh Company (UV2M55 W) was used to provide UV radiation during experiments. The reactor used in this study was a circular cylinder with a capacity of 2.5 L and was made of very smooth stainless steel (in order to maximize light reflection inside the reactor). UV radiation used in this study was supplied by 55 W low-pressure mercury vapor lamp, which were made by Dutch Phillips Company

Table 1
Characteristics of UV lamp

Parameter	Unit	Amount
Low-pressure Hg lamps	W	55
Lifetime	h	5,000
Maximum wavelength radiation	nm	253.7
Quartz cover diameter	cm	3
Length	nm	909
Diameter	nm	26
Weight	gr	26
Frequency	Hz	50–60
Intensity of radiation	μws/cm	50,000
Number	–	1

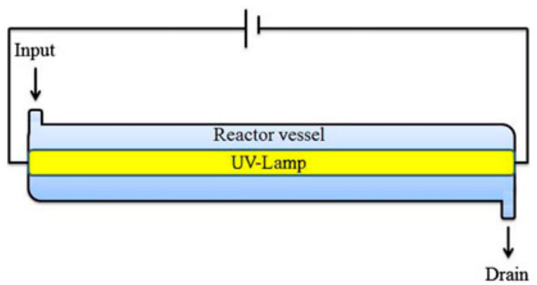

Fig. 1. Schematic of Experimental setup.

(253.7 nm). The lamp was placed into the hollow quartz located at the center of the reactor. Specifications of the UV lamp are presented in Table 1. Fig. 1 shows the schema of the photoreactor.

2.3. Experimental procedure

In the present study, the effects of some operational parameters such as PS concentration, pH, initial phenol concentration, and NaCl concentration were studied on UV/PS process. Experiments were carried out according to the Table 2.

To adjust the pH to its corresponding value, 1 M sulfuric acid and sodium hydroxide were used. The samples were taken with 10-min interval for 1 h by opening a valve installed at the outlet of the reactor.

In treated samples, phenol concentration was evaluated using a spectrophotometer with a UV/vis detector at a wavelength of 500 nm (DR 5000, HACH Co) according to the method (No. 5530) mentioned in the Standard Methods for the Examination of Water and Wastewater Book [17]. Moreover, COD was also examined by open reflux method in according to the method SM5220-B; it is one of the recommended methods in this field [17]. Phenol removal efficiency was calculated according to the following equation:

$$R\,(\%) = \left(\frac{C_0 - C_t}{C_0}\right) \times 100 \tag{3}$$

where C_0 is the initial concentration of the phenol (mg/L), C_t is the instant concentration of the phenol (mg/L), and R % is the percentage of phenol removal.

3. Results and discussion

3.1. Effects of PS concentration

To investigate the effect of PS molar concentration on the process, the concentrations of 50, 80, 100, 150, and 200 mM of PS were prepared and examined in phenol initial concentration of 200 mg/L, NaCl concentration of 50,000 mg/L, pH of 7, contact time of 60 min, and UV radiation intensity of 50,000 μws/cm. The results are shown in Fig. 2. According to the results, phenol removal efficiency increased with the increase of PS concentration. The highest efficiency was observed at concentration of 150 mM. However, as concentration increased more than 150 mM, removal efficiency decreased, therefore, PS concentration of 150 mM was considered the optimal concentration in UV/PS process.

The PS is precursor of sulfate radical which is oxidizing agent in this process, so increasing concentration of PS will increase the production of sulfate radical, therefore reaction rate and efficiency will be increased.

The same studies have been reported that the removal efficiency of pollutants increased with increasing PS concentration. In contrast, as PS concentration increases more than a certain level, the removal efficiency decreased slowly, because of quenching of $SO_4^{-\bullet}$ in high concentration of PS (Eq. (4)) [18–22]:

$$SO^{\bullet-}_{4(aq)} + S_2O^{2-}_{8(aq)} \rightarrow SO^{2-}_{4(aq)} + S_2O^{\bullet-}_{8(aq)} \tag{4}$$

3.2. Effects of initial pH

The effect of pH on efficiency of the process was examined in the pH range of 3–10, initial phenol

Table 2
Experimental conditions

	Parameters	Unit	Range
1	PS concentration	mM	50, 80, 100, 150 and 200
2	pH	–	3, 7 and 10
3	Phenol concentration	mg/L	200, 450, 1,000, 1,500 and 2,000
4	Salinity	mg/L	30,000, 50,000 and 70,000

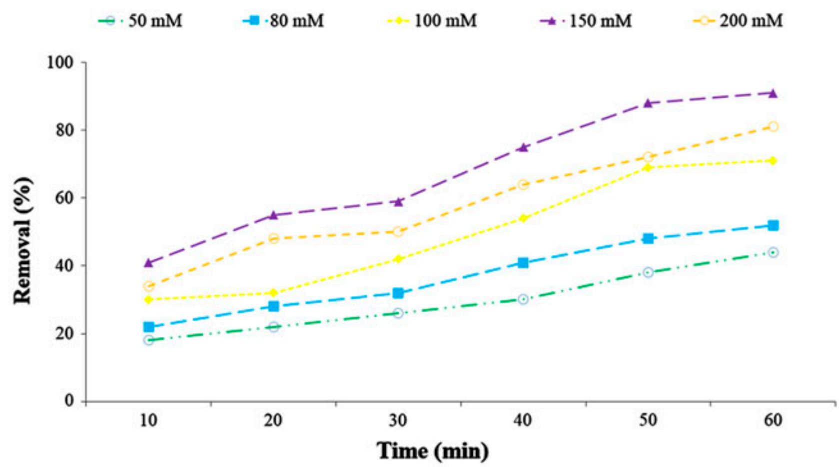

Fig. 2. Effect of PS molar changes in phenol removal from saline wastewater using UV/PS process (Experiment condition: UV = 50,000 μws/cm, Time = 60 min, pH 7, NaCl = 50,000 mg/L, Phenol = 200 mg/L, and PS = varied).

concentration of 200 mg/L, NaCl concentration of 50,000 mg/L, 150 mM of PS, contact time of 60 min, and UV radiation intensity of 50,000 μws/cm. The results of this part are shown in Fig. 3. According to the results, after 60 min of reaction, phenol removal efficiency at pH of 3, 7, and 10 was 91, 91, and 92%, respectively. Thus, it can be said that variation in pH values had no substantial effect on the removal efficiency. Based on previous studies, it was found that hydroxyl radical was dominant at alkaline pH, and that both sulfate and hydroxyl radicals were available at neutral pH. However, sulfate radical was dominant at acidic pH [23]. However, a slight increase was observed in phenol removal efficiency at acidic pH. It could be due to the role of sulfate radical which had more tendencies to react through electron-transferring mechanism. Moreover, sulfate radical was a dominant radical in acidic conditions in UV/PS process. Xsuming tang reported that pH had a substantial role in removing TOC such that as pH decreased, removal efficiency increased [24]. Also, the results are in agreement with the report of Wang and et al. on removal of tetramethylammonium hydroxide by UV/Persulfate process. They were shown that the process efficiency is strongly related to pH, such that removal efficiency was 100% at pH of 2 [22]. Also, it is should be noted that the final pH of the solutions was reached to about 2, because of the following reactions. (Eqs. (5) and (6)) [25]:

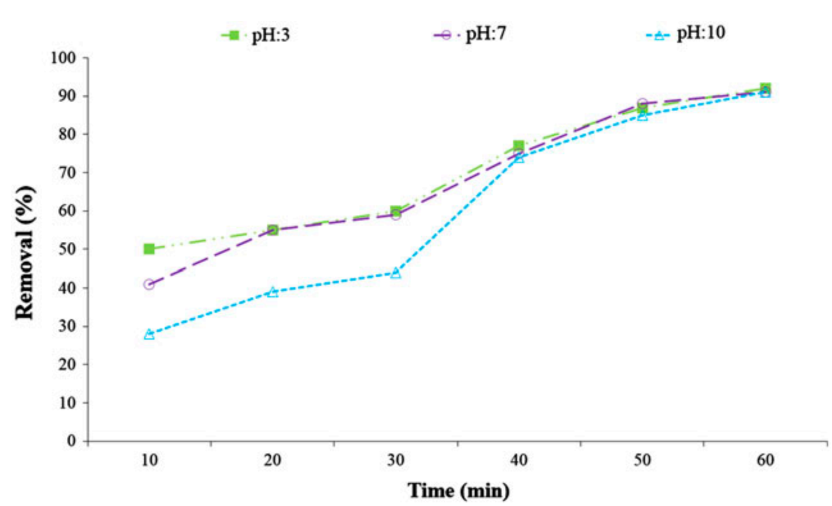

Fig. 3. Effect of reaction pH in phenol removal from saline wastewater using UV/PS process (Experiment condition: UV = 50,000 μws/cm, Time = 60 min, NaCl = 50,000 mg/L, Phenol = 200 mg/L, PS = 150 mM, and pH varied).

$$SO_4^{\cdot-} + H_2O \rightarrow SO_4^{2-} + OH^{\cdot} + H^+ \quad (5)$$

$$SO_4^{\cdot-} + OH^- \rightarrow SO_4^{2-} + OH^{\cdot} \quad (6)$$

3.3. Effect of phenol concentrations

To study the effect of different concentrations of phenol on the UV/PS efficiency, five phenol concentrations of 200, 450, 1,000, 1,500, and 2,000 mg/L were examined at optimum conditions determined in previous steps (PS concentration of 150 mg/L and pH of 3), contact time of 60 min, and UV radiation intensity of 50,000 μws/cm.

In this step of the experiment, to study the ability of UV/PS process, high concentrations of phenol were used. Results obtained from the experiments are shown in Fig. 4. As shown in the results, as concentration of pollutants increased, the UV/PS efficiency decreased such that the highest and lowest removal efficiency of 91 and 35% was obtained for initial phenol concentrations of 200 and 2,000 mg/L, respectively. According to literature, an increase in the initial concentration of pollutants requires greater oxidant, and thus, the process efficiency decreased with a constant amount of oxidant [26–28].

3.4. Effect of NaCl concentration changes

To study the effect of changes in the amount of salinity of wastewater on efficiency of UV/PS process, experiments were done at three different concentrations of NaCl (30,000, 50,000, and 70,000 mg/L), optimum conditions determined in previous steps (PS concentration of 150 mg/L, pH of 3, and initial phenol concentration of 200 mg/L), contact time of 60 min, and UV radiation intensity of 50,000 μws/cm. The results are shown in Fig. 5. As seen in Fig. 5, with the increasing NaCl concentration from 30,000 to 70,000 mg/L, the removal efficiency increased from 91 to 93%, which is insubstantial enhancement. Results obtained in this research were inconsistent with other studies which used advance oxidation process (AOP) to remove phenol from saline solutions [29,30]. In a study by Mousavi et al., catalytic ozonation process was used to remove phenol from saline solutions. Results of their study showed that phenol removal efficiency was 63% in the absence of NaCl, but as NaCl concentration increased to 500 mg/L, removal efficiency increased to 97.5%. As NaCl concentration increased to more than 50,000 mg/L, removal efficiency increased to 99%; their results were in line with the results of the present study [31]. In another study, photo-Fenton process was used to remove chlorophenol from saline wastewater, in which increasing chloride ion had no effect on removal efficiency [30]. Concerning various studies, it can be concluded that the effect of chloride ion on advanced oxidation processes depends on pollutant type and process type. Chloride ion mechanism was still unknown [31].

3.5. Degradation of phenol by UV photolysis alone and PS alone

In this step, the present study compared the efficiency of the combined UV/PS process with two processes of PS alone and UV alone under similar

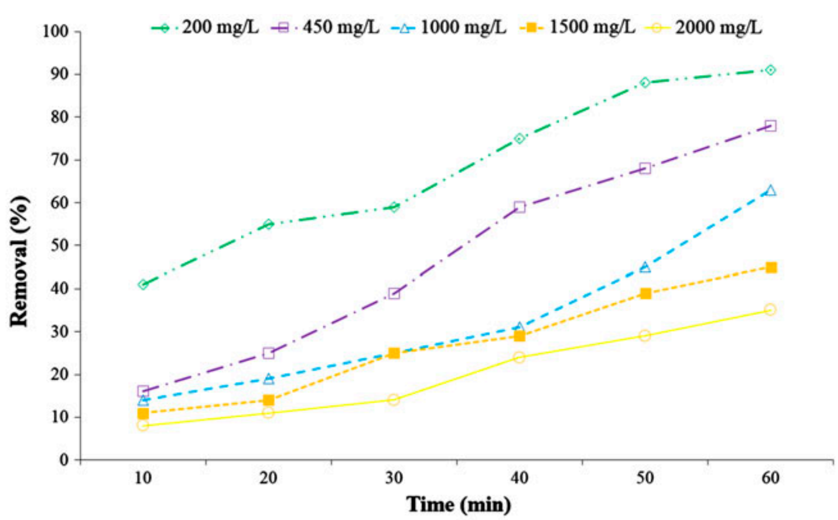

Fig. 4. Effect of initial phenol concentrations in phenol removal from saline wastewater using UV/PS process (Experiment condition: UV = 50,000 μws/cm, Time = 60 min, NaCl = 50,000 mg/L, pH 3, PS = 150 mM, and Phenol = varied).

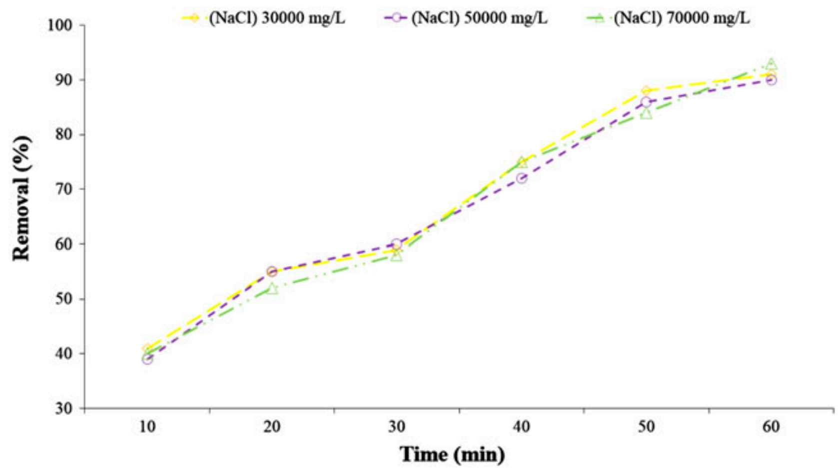

Fig. 5. Effect of NaCl concentration changes in phenol removal from saline wastewater using UV/PS process (Experiment condition: UV = 50,000 µws/cm, Time = 60 min, pH 3, PS = 150 mM, Phenol = 200 mg/L, and NaCl = varied).

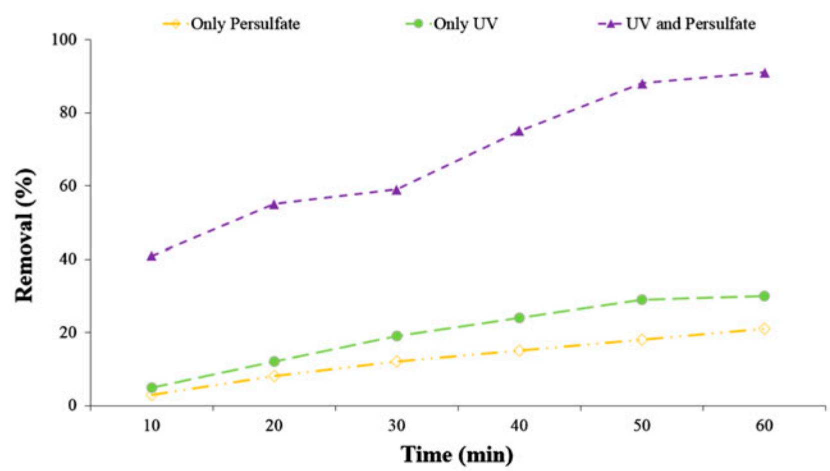

Fig. 6. Compare the efficiency of combined PS/UV with each processes alone (Experiment condition: Time = 60 min, pH 3, Phenol = 200 mg/L, and NaCl = 50,000 mg/L).

laboratory conditions that their results are shown in Fig. 6. All three processes were examined at pH of 3, initial phenol concentration of 200 mg/L and NaCl concentration of 50,000 mg/L. As shown in the figure, UV photolysis alone removed only 30% of phenol at radiation intensity of 50,000 µws/cm after 60 min. Moreover, PS alone had no substantial effect on removing phenol, and its removal efficiency was only 21%. The combined UV/PS efficiency was 91%. The results obtained from two processes of UV alone and PS alone were in line with results of literatures that showed these two processes decreased pollutants insubstantially [18,32]. For example, Gao et al. used UV/PS to remove sulfamethazine from aquatic solutions. In their study, UV photolysis alone, PS alone, and the combined UV/PS removed 22, 15.1, and 96.5% of sulfamethazine, respectively. Results of their study were, to huge extent, in line with the results of this study [21].

4. Conclusions

This study examined the capability of UV/Persulfate process to remove high concentrations of phenol from saline wastewater. The effect of several variables such as initial concentration of PS, initial solution pH, initial phenol concentration, and NaCl concentration was investigated, and the optimum condition of each variable was determined. The results showed that increased concentration of NaCl slightly increased the removal efficiency of the process. Moreover, the process efficiency reduced with an increase in the phenol concentration. According to the results, the final product of this process was the sulfate ion which was much less dangerous than phenol and was considered a secondary pollutant. Phenol removal efficiency was also suitable and acceptable; this process which is cost-effective can be easily used for removing phenol. Since the type of oxidant is different in AOPs and the oxidation mechanism will be different in the presence of different types of salt, the effect of different kinds of salt on AOP should be more closely studied using experiment design as a statistical method.

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