Removal of phenol from aqueous solutions using persulfate-assisted, photocatalytic-activated aluminum oxide nanoparticles

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ABSTRACT
The combination process of UV/ S2O82-/Al2O3 leads to the production of radicals and radical hydroxyls, which could decompose and remove various pollutants, such as phenol. The present study aimed to investigate the photocatalytic efficiency of aluminum oxide nanoparticles and persulfate complicative processes in the removal of phenol. This experimental study was conducted in a discontinuous reaction chamber with a useful volume of one liter. In this process, we assessed the effects of the initial pH parameters (3, 5, 7, and 9), initial concentration of phenol (10, 20, 30, 50, and 100 mg/l), concentration of persulfate anions (20, 30, 40, 50, and 60 mg/l), reaction time (5 and 120 minutes), and dose of Al2O3 nanoparticles (10, 20, 30, and 40 mg/l). The applied pilot was composed of a low-pressure mercury lamp (55 Watt), which was inside the steel chamber. The obtained data were fitted to the pseudo-first- and pseudo-second-order reaction kinetics. According to the findings, the process had high efficiency in the removal of phenol. In optimal conditions (pH:5, persulfate concentration: 50 mg/l, nanoparticle dose: 40 mg/l, reaction time: 60 minutes), the efficiency of the process was determined to be 95% at the initial phenol concentration of 10 mg/l, which was fitted with first-rate kinetics (R²=0.98). Furthermore, the highest efficiency was observed in the photocatalytic process of aluminum oxide nanoparticles and persulfates in the optimal conditions of exploitation. Therefore, persulfate could be used as an appropriate oxidizer with aluminum oxide nanoparticles for the removal of phenol.

Keywords: Photocatalytic process, Aluminum oxide, Persulfateoxidation, Phenol, Aqueous solution

Introduction
Within the past decades, the production and application of artificial chemicals in industries has led to the entry of numerous compounds into the environment, including air, water, and soil. Phenols are a group of aromatic chemical compounds with high resistance to environmental degradation due to their halogen-carbon bond. Phenolic compounds in the presence of chlorine form complexes with objectionable taste and odor in the water. Chlorine substitution does not only increase the taste and smell, but it also exerts toxic effects on the environment. Nevertheless, the growing use of this substance in several industries and lack of proper wastewater treatment have led to the contamination of environmental resources, including groundwater and surface water.

One of the main consequences of phenols in water resources is the formation of chlorophenols, which are hazardous and carcinogenic compounds with adverse effects on biological processes. In addition, phenols could cause acute and chronic diseases and various symptoms in humans, including headaches, vomiting, tissue damage, liver and kidney damage, pancreatic damage, protein loss, disruption of the central nervous system, and fainting. Due to the mutagenicity, teratogenicity, and carcinogenicity of phenols, the United States Environmental Protection Agency (USEPA) has identified these...
compounds as priority pollutants, so that among 129 priority pollutants, phenols have been ranked 11th. Accordingly, the World Health Organization (WHO) has determined the permissible phenol limit in drinking water to be 0.001 mg/l, while the USEPA has reported the permissible phenol limit to be less than 1 mg/l and 1 ppb in industrial wastewater before discharge into the environment and in surface water, respectively.

Several mechanisms have been developed to remove phenolic compounds from aqueous solutions, such as biological treatment, degradation by soundwaves, membrane filtration, electrochemical oxidation, and adsorption, each of which has specific advantages and disadvantages. For instance, biological processes have high removal capability, while some of their limitations include the slow decomposition process and need for relatively prolonged retention. Another example in this regard is electrochemical processes, some of the main limitations of which are the high consumption of electrical energy and electrodes.

One of the key advantages of adsorption is its rapid process and simplicity, while this method is considered to be significantly costly due to the high cost of commercial carbon. In addition, adsorption requires substantial time to produce activated carbon. Another common method in this regard is photocatalytic degradation technology, which plays a key role in the treatment of wastewater, especially wastewater containing low levels of the organic matters that are resistant to chemical and biological decomposition.

Today, advanced oxidation processes (ozone, ozone/hydrogen peroxide, ozone/ultraviolet, hydrogen peroxide/ultraviolet) are considered to be more appropriate for the decomposition of organic compounds compared to conventional methods. Advanced oxidation processes have remarkable advantages (e.g., lack of high levels of sludge production) compared to conventional treatment methods. These techniques are often based on the production of hydroxyl radicals, which involuntarily attack all organic and inorganic pollutants in wastewater. For instance, catalytic oxidation is an advanced technology through which organic contaminants are completely degraded and eliminated. In this method, an optical source (usually UV light) is used along with a semi-conductive body as a catalyzer. Semi-conductive compounds normally have proper bandgap energy between the conduction bands and their valence.

Persulfate is a nonselective anion, which is soluble and relatively stable at room temperature. It is considered to be the most potent oxidant of the peroxygen family. The oxidation-reduction potential of persulfate is 2.1 V. Persulfate and the resulting sulfate radical have unique properties, including high kinetic rate, greater stability compared to hydroxyl radical, and less dependence on natural organic compounds, which further enhance their effects on organic compounds. In atmospheric conditions, persulfate oxidation has no significant effects on organic contaminants. However, if heat, light or special metal ions are used as the catalyst, the persulfate reaction increases significantly.

Aluminum oxide (Al2O3) nanoparticles are potent reductive agents, which are able to reduce chlorate organic compounds and other organic compounds. Some of the main properties of the method involving the use of these nanoparticles include high frequency and easy access to zero-valent aluminum (ZVAl), no increase in environmentally hazardous chemicals used for the removal of phenol, and easy removal of the added aluminum to the system.

In this regard, the study by Olmez-Hanci et al., which was entitled “S2O82−/UV-C and H2O2/UV-C treatment of Bisphenol A “, indicated that in both processes, bisphenol A was completely removed within less than seven minutes. Moreover, 70-85% of mineralization was carried out during the process.

In another research, Cheng et al. investigated the removal of phenol using the acidic washing method and aluminum nanoparticles in the presence of hydrogen peroxide, and the obtained results indicated that with the AW-ZVAl of 6 g/l of aluminum nanoparticles, the concentration of phenols decreased significantly. Furthermore, the
addition of proper levels of hydrogen peroxide could improve the phenol removal reaction. It is also notable that at the pH of 2.5-3.5, Al$_2$O$_3$ nanoparticles exhibited the highest degradation capacity for the removal of phenol from wastewater.

To date, no studies have attempted to remove phenol through combining various methods and compared the three methods of UV, persulfate, and photocatalytic process of aluminum oxide nanoparticles and persulfate. The present study aimed to provide a novel and efficient method for the removal of phenol using photocatalytic aluminum oxide nanoparticles and persulfate compitative processes and assess the effects of the utilization parameters.

**Materials and Methods**

This experimental study was conducted in a photochemical chamber. The pilot was used as a photochemical reaction chamber in a cylindrical shape with the useful volume of one liter, which was composed of a low-pressure mercury lamp with (55 Watt). The process occurred in the space between the quartz membrane around the lamp and steel chamber. Samples were synthetic effluents manufactured in the laboratory with various concentrations of phenol.

Some of the main parameters that were investigated included the primary pH parameters of the medium (3, 5, 7, and 9), concentration of persulfate anions (20, 30, 40, 50, and 60 mg/l), dose of aluminum oxide nanoparticles (10, 20, 30, and 40 mg/l), concentration of phenol (10, 20, 30, 50, and 100 mg/l), and reaction time (5-120 minutes). By obtaining the optimal values for each parameter, the experiments continued until reaching the optimal values for all the variables. All experiments were performed in triplicate, and the obtained mean values were considered as the final results of the report.

Data analysis was performed in the Excel software, and the sample size was determined using the one-factor- at-a-time method. In total, 23 samples were prepared. Figure 1 shows the reactor used in the process, and Table 1 shows the properties of the reactor.

In this study, the purity of the applied phenol was 99% (Merck, Germany), and the purity of the Al$_2$O$_3$ nanoparticles was 99.5% (TECNAN, Spain). The other required chemicals (e.g., sodium hydroxide and sulfuric acid) were purchased from Merck (Germany) and Sigma-Aldrich (USA). A pH-meter (model: Denial, HACH) and spectrometer (model: HACH, DR5000) were also used in the study. The sampling and testing procedures were carried out in accordance with standard guidelines.

![Fig. 1. Schematic view of experimental reactor](image)

**Table 1. UV Lamp properties**

<table>
<thead>
<tr>
<th>UV Lamp properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low-pressure vapor mercury lamp</td>
<td>55 W</td>
</tr>
<tr>
<td>Lamp lifetime (h)</td>
<td>5000</td>
</tr>
<tr>
<td>Maximum radiation area (nm)</td>
<td>253.7</td>
</tr>
<tr>
<td>Quartz Coating Diameter (cm)</td>
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</tr>
<tr>
<td>Lamp length (mM/L)</td>
<td>909</td>
</tr>
<tr>
<td>Lamp weight (mM/L)</td>
<td>26</td>
</tr>
<tr>
<td>Frequency (Hz)</td>
<td>50-60</td>
</tr>
<tr>
<td>Number of Lamps</td>
<td>1</td>
</tr>
</tbody>
</table>

**Measurement of phenol concentration**

Phenol concentration was measured using the colorimetric method described in the Standard Methods for the Examination of Water and Wastewater (20$^{th}$ edition; Section 5530D). Phenol concentration in the samples was determined based on the reaction of 4-aminoantipyrine in the presence of potassium ferricyanide as the color-producing substrate, and the absorbance of phenol was measured at the wavelength of 500 nanometers using a spectrophotometer. In addition, various concentrations of the phenol solution were prepared in order to prepare a standard concentration-absorbance curve, with each
containing specific concentrations of 4-aminoantipyrine reagent. Finally, the concentration-absorption curve was plotted for various concentrations of phenol.

**Effect of reaction time**

At this stage, the process efficiency was investigated within 5-120 minutes in cases where other parameters were optimal, and the optimal reaction time was determined for the process with the maximum efficiency.

**Effect of pH**

To determine the effect of the initial pH of the environment on the process efficiency, samples with the volume of 1,000 milliliters with the initial pH of 3, 5, 7, and 9 were added to the reaction chamber. At this stage, various other parameters were also considered, including the initial concentration of phenol (50 mg/l), concentration of persulfate anions (50 mg/l), concentration of nanoparticles (40 mg/l), and reaction time (60 minutes), and the process efficiency in phenol removal was investigated correspondingly. Finally, the effect of the initial pH of the environment on the process efficiency was determined, and environment pH was determined based on the maximum efficiency. It is also notable that 0.1 N NaOH and H$_2$SO$_4$ were used to adjust the pH.

**Effect of persulfate anion concentration**

In order to investigate the effect of persulfate anion on the process efficiency in phenol removal, samples with the volume of 1,000 milliliters and optimal pH, which were obtained in the previous stage, were added to the compartment, and the concentrations of 20, 30, 40, 50, and 60 mg/l were assessed. The considered parameters at this stage included the aluminum oxide nanoparticles dose (40 mg/l), reaction time (60 minutes), and initial phenol concentration (50 mg/l). After the designated time, sampling and measurement of the residual concentrations of phenol were carried out. Finally, the effect of persulfate concentration on the process efficiency was determined, and the optimal concentration was selected.

**Effect of aluminum oxide nanoparticles dose**

In order to evaluate the effect of the nanoparticle dose on the process efficiency, we studied the samples with the volume of 1,000 milliliters, optimal pH, concentration of persulfate anions obtained in the previous stage, and initial phenol concentration of 50 mg/l. After the designated time, sampling and measurement of the residual concentration of phenol were carried out. Finally, the effect of the presence of various nanoparticles on the process efficiency and the optimal dose were determined.

**Reaction kinetics**

Kinetic evaluation is essential to the provision of data on the influential factors in reaction speed. Correspondingly, the chemical processes in the present study were designed based on the optimal pollutant elimination model using the Eq. 1 and 2:

First-order Pseudo-kinetics:

\[
C_t = C_0 e^{-k_1 t} \quad (1)
\]

Second-order Pseudo-kinetics:

\[
\frac{1}{C_t} = \frac{1}{C_0} + K_2 t \quad (2)
\]

Where $C$ is the phenol concentration, $K_1$ and $K_2$ represent the first- and second-order kinetic constants, $t$ shows the retention time, and $C_t$ denotes the concentration of phenol at time $t$.\cite{7,23}

**Results and Discussion**

**Specification of the Al$_2$O$_3$ nanoparticles**

Specification of the purchased Al$_2$O$_3$ nanoparticles was performed using X-ray diffraction (XRD) and scanning electron microscopy (SEM). Figures 2 and 3 show the XRD and SEM of the Al$_2$O$_3$ nanoparticles. The mean particle size, which was within the range of 45-50 nanometers (error at ±5 nm), was obtained using the XRD patterns of the nanoparticles. In addition, the SEM images demonstrated that the particles were scattered uniformly within a nanometer range with a spherical shape.
Fig. 2. XRD Image of Al₂O₃ nanoparticles

Fig. 3. SEM image of Al₂O₃ nanoparticles density compared to the other elements, respectively.

Effect of reaction time

At this stage, all the variables were adjusted to the optimal conditions with the retention time of 5-120 minutes, and the efficiency of the UV/S₂O₈²⁻/Al₂O₃ process in the removal of phenol was measured. As is depicted in Figure 4, the process efficiency within the reaction time of 60 minutes reached its maximum (95%), while in longer periods, the value remained constant. Therefore, the reaction time of 60 minutes was determined as the optimal reaction time.

Effect of pH

According to the results of the present study, the maximum removal efficiency of phenol was at the pH of 5 (55%). Furthermore, the process efficiency changed with the changing of the environment pH, so that the lowest efficiency could be observed with the initial pH of 9. Therefore, pH of 5 was determined as the optimal pH, which was applied to the remaining stages of the experiment. Figure 5 shows the findings regarding the effects of the changes in the initial environment pH on the efficiency of the UV/S₂O₈²⁻/Al₂O₃ process.

Fig. 4. Effect of reaction time on efficiency of UV/S₂O₈²⁻/Al₂O₃ process (persulfate concentration: 50 mg/l, pH=5, nanoparticle concentration: 40 mg/l, phenol concentration: 10 mg/l)

Fig. 5. Effects of changes in environment pH on phenol removal in process of UV/S₂O₈²⁻/Al₂O₃ (initial phenol concentration: 50 mg/l, reaction time: 60 min, nanoparticle concentration: 40 mg/l, persulfate concentration: 50 mg/l)

In advanced oxidation and photochemical processes and the processes that are composed of several processes, pH could be considered a major influential factor in conducting the process and determining its efficiency. Such examples are direct oxidation by ultraviolet radiation at wavelengths below 300 nanometers (254 nm) and the production of strong oxidizing radicals (e.g., radical sulfate), which could decompose, degrade, and remove contaminants due to their high oxidation and reduction number.

According to the literature, the initial pH of the environment may extensively depending on the applied process and type of pollutant. This important factor in the process affects the formation of the active radicals of persulfate. According to the results of the present study, the process efficiency at acidic pH was higher compared to neutral and alkaline pH. In the
The process of UV/ $\text{S}_2\text{O}_8^{2-}$ at acidic pH (pH=5), the rate of radical sulfate production from anion persulfate was higher compared to the other pH values. As is shown in Figure 5, the process efficiency increased with the higher rate of the radical production of persulfates. In a study conducted by Sharma et al. regarding the treatment of bisphenol A using the UV/ $\text{S}_2\text{O}_8^{2-}$ and UV/ $\text{H}_2\text{O}_2$ processes, the optimal performance in both processes was obtained at acidic pH.27

**Effect of the Persulfate concentration**

At this stage, the process efficiency was investigated at the optimal pH of 5 and based on various other parameters, including the persulfate anion concentration (20, 30, 40, 50, and 60 mg/l), concentration of the aluminum oxide nanoparticles (40 mg/l), reaction time (60 minutes), and initial phenol concentration (50 mg/l). According to the findings, the highest removal efficiency of phenol was attained at the persulfate anion concentration of 50 mg/l, while the lowest process efficiency was observed at the concentration of 20 mg/l. Furthermore, phenol removal efficiency at the optimal persulfate anion concentration was determined to be 55% at the retention time of 60 minutes. Figure 6 depicts the findings regarding the effects of the changes in the concentration of persulfate on the removal efficiency of phenol in the UV/$\text{S}_2\text{O}_8^{2-}$/$\text{Al}_2\text{O}_3$ process.

According to the results of the present study, the UV/ $\text{S}_2\text{O}_8^{2-}$ efficiency was affected by the changes in the concentration of persulfate anions, so that the maximum removal rate of phenol could be attained at the concentration of 50 mg/l (55%) in this process.

Based on the decomposition formula of persulfate (Eq. 3 and 4), increasing the persulfate concentration resulted in the higher concentration of the H$^+$ ion, which in turn led to the highest removal efficiency of phenol. In a study by Zhou et al. entitled "Ferrous-activated Persulfate Oxidation of Arsenic (III) and Diuron in Aquatic Systems", it was reported that the removal efficiency increases by increasing the concentration of persulfate anions from 10 to 50 mg/l, while the process efficiency decreased at higher concentrations than 50 mg/l.28 This is consistent with the results of the present study.

\[
\text{S}_2\text{O}_8^{2-} + \text{H}^+ \rightarrow \text{HS}_2\text{O}_8^- \quad (3)
\]

\[
\text{HS}_2\text{O}_8^- \rightarrow 2\text{SO}_4^- + \text{H}^+ \quad (4)
\]

**Effect of the aluminum oxide nanoparticles concentration**

At this stage, the effects of various concentrations of the aluminum oxide nanoparticles (10, 20, 30, and 40 mg/l) on the efficiency of the UV/$\text{S}_2\text{O}_8^{2-}$/Al$_2$O$_3$ process were investigated (Figure 7). As is observed, changes in the concentration of the nanoparticles, as the activating agents of hydroxyl radical, had a significant effect on the removal efficiency of phenol; so that the maximum concentration of the nanoparticles (40 mg/l) was associated with the highest process efficiency. After 60 minutes, the process efficiency reached 55%. On the other hand, decreasing the concentration of the nanoparticles to 10 mg/l led to the reduction of the process efficiency to 29%.
According to the results of the present study, the efficiency of phenol removal increased at the higher concentrations of the nanoparticles. At the retention time of 60 minutes, the process efficiency at the highest concentration of the nanoparticles reached its maximum (93%). The increased efficiency of the UV/ S\textsubscript{2}O\textsubscript{8}²⁻/Al\textsubscript{2}O\textsubscript{3} process could be attributed to the increased degradation of persulfate anions by UV rays on the surface of aluminum oxide, which in turn increased the concentration of the active sulfate radicals on the surface and in the volume of the fluid.\textsuperscript{29,30} In this regard, Qi \textit{et al.} examined the effects of aluminum oxide superficial properties on 2, 4, 6-trichloroanisole (TCA) ozonation, reporting that increased concentration of the catalyst resulted in the higher density of surface-active groups, thereby accelerating the decomposition of TCA. In other words, the surface-active groups in the catalytic ozonation process are the main activity sites.\textsuperscript{31}

**Effect of the initial phenol concentration**

Figure 8 depicts the effects of various concentrations of phenol (10, 20, 30, 50, and 100 mg/l) on the efficiency of the UV/ S\textsubscript{2}O\textsubscript{8}²⁻/Al\textsubscript{2}O\textsubscript{3} process. As is observed, the phenol removal efficiency increased with decreased phenol concentration. The maximum removal rate of phenol was observed at the concentration of 10 mg/l and retention time of 60 minutes (95%), while the minimum phenol removal rate was denoted at the concentration of 100 mg/l and retention time of 60 minutes (45%).

The findings of the current research indicated an inverse correlation between the input phenol concentration and removal efficiency in the studied system, so that the phenol removal efficiency reduced by increasing its initial concentration. This is in congruence with the results obtained by Shokoohi \textit{et al.}\textsuperscript{32} and Almasi \textit{et al.}\textsuperscript{33,34} In another study conducted by Almasi \textit{et al.}, phenol concentration was considered to be 100-400 mg/l, with the highest phenol removal rate observed with the concentration of 100 mg/l.\textsuperscript{35} Similarly, Shokoohi \textit{et al.} aimed to remove bisphenol A from aqueous solutions, reporting that the removal efficiency decreased with an increase in phenol concentration. Moreover, the highest system efficiency was obtained at the concentration of 10 mg/l, while the lowest system efficiency was denoted at the concentration of 100 mg/l.\textsuperscript{3} This is in line with the results of the present study which obtained the highest and lowest phenol removal rate at the phenol concentrations of 10 and 100 mg/l, respectively.

**Effects of separated processes on phenol removal in the optimal conditions**

Based on the optimal conditions, the efficiency of each process was determined separately for each intervener (figures 9 & 10).
Reaction kinetics

Our findings regarding the kinetics of phenol removal indicated that the pseudo-first-order kinetics had a higher regression coefficient ($R^2=0.9499$) compared to the pseudo-second-order model ($R^2=0.7924$) (Figure 11); as such, the phenol removal process was in accordance with the pseudo-first-order kinetic model. Therefore, it could be concluded that the phenol removal process complied with the pseudo-first-order model more than the pseudo-second-order model.

According to the absorption kinetic evaluations, the correlation coefficient ($R^2$) in the pseudo-first-order kinetic model was significantly higher than the pseudo-second-order kinetic model. Therefore, the kinetics of adsorption followed the pseudo-first-order model. In the pseudo-first-order kinetic model, the reaction rate was direct, and a linear correlation was also observed with the reactive substances (initial concentration of the pollutant). In most of the studied processes in the literature, it has been reported that the kinetics of the process follow the pseudo-first-order kinetic model. For instance, Gao et al., through the evaluation of removal of sulfamethazine from water by the UV/S$_2$O$_8^{2-}$ process, have concluded that the kinetics of the process followed the removal of the pollutant in pseudo-first-order kinetics. Another research by Lau et al. demonstrated that the efficiency of the UV/ S$_2$O$_8^{2-}$ process was followed by the removal of butylated hydroxyanisole (BHA) from pseudo-first-order kinetics.

Conclusion

Phenol is a resistant and highly biodegradable environmental pollutant, which could cause cancer through inhalation, threatening public health. Therefore, the monitoring of phenol-contaminated aquatic environments is of utmost importance. According to the results, the process of chemical photocatalytic oxidation and other advanced oxidation methods could be used as advanced treatments for the removal of contaminants such as phenol and other pollutants in industrial refineries.
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References