Aniline Degradation Using Advanced Oxidation Process by UV/Peroxy Disulfate from Aqueous Solution

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PAPER INFO

Paper history:
Received 02 September 2016
Received in revised form 11 February 2017
Accepted 10 March 2017

Keywords:
Aniline Degradation
Peroxy Disulfate
Ultraviolet
Advanced Oxidation

ABSTRACT

This study is focused on removing toxic aniline from aqueous solutions using advanced oxidation process by UV/peroxy disulfate. In this study, the effect of various parameters including pH (3-9), the level of radiation (ultraviolet 30 watt lamp, number 2-5), peroxy disulfate dose (0.02 – 0.08 mol/l) and the initial concentration (20 – 100 mg/l) at different contact times (10 – 60 min) on the efficiency of aniline removal in a laboratory reactor with UV lamps and in a batch mode, was studied. The results of this study showed that the efficiency of removing aniline decreased by increasing and decreasing pH from 5 (maximum efficiency = 66.6%, at pH= 5) and also by increasing the concentration of pollutant. But by increasing the amount of radiation and peroxy disulfate dosage (0.02 to 0.08 mol/l, the process efficiencies will be 46 to 82.8% after 60 min, respectively), the efficiency increased. The efficiency of removing aniline in the combined process of UV/peroxy disulfate increased significantly by using peroxy disulfate and UV, individually (96%). In the process, the efficiency of removing aniline from aqueous solution was due to the production of UV effect on Peroxy disulfate and the production of strong oxidizing radicals. Therefore, due to the high performance and low cost raw materials, this process can be used for removing resistant compounds from industrial sewages.


1. INTRODUCTION

In recent years, the growth of industrial activities has tried to meet the needs of human communities. At the same time, focusing on reducing the production of wastewaters and also reducing water consumption produces more toxic and strong wastewaters [1]. Currently, about five million chemicals are used in the world and the CAS database lists thousands of new chemicals monthly [2]. Most of the chemical compounds are currently found in wastewaters of urban communities. New technologies should be used in production and refining wastewaters in order to reduce the level of pollutant emissions in various industries [3].

Aniline is one of the chemical compounds which is used for producing rubber accelerators, producing intermediate substances for pesticides and making Azo and plastic dyes, and this is why it is distributed widely in the environment [4, 5]. As a toxic substance, aniline can be solved in water to the maximum range of 36000 mg/l [6]. So, its solubility in water not only increases the risk of its presence in wastewaters but also in drinking water. Aniline is also a carcinogenic chemical compound that causes the risk of bladder cancer in human [6]. Hence, this pollutant should be prevented from entering into the environment or should be refined or removed before entering the environment [7, 8]. The common treatment methods are not able to completely remove these pollutants, so effective treatment methods need to be developed for removing these organic pollutants in order to reduce the toxic risks to the

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Researchers have tried to find appropriate methods for refining toxic and resistant pollutants [9, 10]. Some methods that have been used for removing aniline are absorption on solids, membrane processes, catalytic oxidation, biological treatment and advanced oxidation processes [11]. Common methods such as biological methods do not have high efficiency on removing aniline from wastewaters; on the other hand, for high capacities, the utilization and operating costs of these methods are very high, especially in developing countries [12]. Advanced oxidation processes (AOPs) which are based on producing strong oxidizing radicals are used for treating wastewaters containing toxic and biological irresolvable pollutants. These processes are very appealing, effective and useful [13]. One of the advanced oxidation processes is using sulfate compounds like peroxy disulfate \((\text{S}_2\text{O}_8^{2-})\) to produce sulfate radicals and then using them for the oxidation of organic compounds [12, 14]. In some studies, the researchers used sulfate radical for removing different pollutants, for example, Khataee et al. [13] used it for removing C. I. Basic Blue 3, Guo et al. [15] used it for removing tetra bromo bisphenol A from aqueous solutions, Mendez et al. [16] used it for the removal of sodium dodecyl benzene sulfonate (SDBS) from aqueous solution and Wang et al. [17] used it for the removal of tetra methyl ammonium hydroxide (TMAH) from aqueous solutions, and evidently, it had high efficiency in removing these types of pollutants. Peroxy disulfate (PDS) ion as a strong oxidizer with oxidation potential \(E^\circ = (2.07 \text{ v})\) is widely used in many industrial processes such as polymerization and oxidation of the surface of metal, for the treatment of hydraulic fluids in oil industry, or as an exciter of the reaction in petrochemical industry [18, 19]. In comparison with peroxy disulfate ions, sulfate radicals with oxidation power \(E^\circ = (2.6 \text{ v})\) decompose toxic compounds, biological and resistant non-biodegradable substances and they can convert them to safe substances such as carbon dioxide and water [9, 13]. As shown in Reactions (1 – 5), actuator factors like heat, ultraviolet light, intermediate metals ions (Fe, silver, and manganese) and ultrasonic waves can be used to accelerate the conversion reaction of peroxy disulfate ions to sulfate radicals [20].

\[
\begin{align*}
\text{S}_2\text{O}_8^{2-} + \text{heat} & \rightarrow 2\text{SO}_4^{2-} \quad (1) \\
\text{S}_2\text{O}_8^{2-} + \text{UV} & \rightarrow 2\text{SO}_4^{2-} \quad (2) \\
\text{S}_2\text{O}_8^{2-} + \text{US} & \rightarrow 2\text{SO}_4^{2-} \quad (3) \\
\text{S}_2\text{O}_8^{2-} + \text{Fe}^{3+} & \rightarrow \text{SO}_4^{2-} + \text{SO}_4^{2-} + \text{Fe}^{3+} \quad (4) \\
\text{HSO}_5^- + \text{Fe}^{2+} & \rightarrow \text{SO}_4^{2-} + \text{Fe}^{3+} + \text{OH} \quad (5)
\end{align*}
\]

The final product of the process of advanced oxidation with UV/PDS is sulfate ions, which eventually increases the salt in wastewaters. These ions are neutral and if their concentration in drinking water is up to 250 mg/l, the environmental protection agency of America considers them to be in second water standards [19]. The major features of peroxy disulfate are high oxidation power, good stability, high solubility, non-selective reactivity, cheapness, easy to transport and above all the safety of the final products and by-products. These features are introduced as a hopeful oxidizer in AOPs [13, 18]. In previous studies, the effectiveness of AOP using UV/PDS in the decomposition of resistant organic combinations was demonstrated [17, 19, 21], but available sources indicated that this process has not been used for removing aniline. Therefore, the novelty of this work was use of UV/PDS for aniline degradation and aniline degradation using AOP by UV/peroxy disulfate from aqueous solution was investigated. The operating parameters such as initial pH, persulfate concentration, initial aniline concentration and UV intensity that may affect the efficiency of the aniline degradation process were studied.

2. MATERIALS AND METHODS

All the chemicals used which include aniline with purity of 99.5%, oxidizer ((NH)\(_2\)\(_2\)SO\(_4\)) sulfuric acid (H\(_2\)SO\(_4\)) and sodium hydroxide (NaOH) were purchased from Merck, Germany. In this study, 6 W Philips lamps were used for radiation. The research was conducted in laboratory scale and batch mode system (Figure 1). The used reactor was made up of Plexiglas and its volume was one liter. This reactor had two distinct parts which include wet and dry part, the wet part was for the solution containing pollutants and the dry part was considered as the cap of the reactor and 5 lamps were set-up on it. The UV lamps and their transformers were set-up on the caps at a distance of 1 cm from the reactor bed in a wooden case to prevent the propagation of ray into the environment. Each lamp was individually connected to a switching key.

In each step, the required concentration of aniline was prepared using stock solution (40 mg/l) and distilled water that was distilled twice, and then it was poured into the reactor. After adjusting the desired pH with sulfuric acid and sodium hydroxide (0.1 N), peroxy disulfate solution was added to the reactor with different concentrations. Finally, number of desired UV lamps were “ON” at the top of the reactor, which contained the solutions. At all phases of the process, the sampling was done with the volume of 5 ml at specified intervals, and finally, the concentration of aniline was measured. The design of the experiments was based on one at a time and it was done in 4 distinct phases including determination of appropriate doses of pH, the amount of UV radiation (based on the number of lamps), the concentration of peroxy disulfate ammonium and the concentration of aniline at different times. In each phase, one parameter was variable and other parameters were fixed, and the appropriate value of the variable parameter was determined. According to the importance of pH in chemical reactions, at first, the proper value of pH in the range of 3 – 9 was determined in the first phase. Then, the optimal radiation intensity (2 – 5 lamps) was obtained with the suitable pH, and at the third phase, the optimal concentration of peroxy disulfate ammonium (0.2 – 0.8 mol) was determined by considering the pH values and intensity of radiation which were obtained from previous phases. Finally, the appropriate concentration of aniline at values of 20 – 100 mg/l was obtained by applying the optimal values of previous phases. The concentration of aniline was measured using PG Instrument limited model of spectrophotometer UV-Vis (Shimadzu) at the wavelength of 263 nm and HPLC (model CTO-10 A). In each phase, the efficiency of removing aniline was calculated using this formula:

\[ E = \frac{S_0 - S_t}{S_0} \times 100 \]  

(6)

where \( S_0 \) is the initial concentration of aniline and \( S_t \) is the concentration of aniline at different times. Finally, the excel software was used to analyze the results.

3. RESULTS AND DISCUSSION

3.1. pH Effect Figure 2 shows the effect of different pH values on the removal efficiency of aniline using UV/\( S_2O_8^{2-} \) process. According to the figure, by increasing and decreasing pH to and above 5, the removal efficiency decreased; the highest efficiency of aniline removal was 66.6\% in pH 5 and reaction time of 60 min. When pH=9, the highest removal efficiency was 28.8\% and in pH 3, the maximum removal efficiency was 38\%. By increasing the reaction time in all pHs, the efficiency of removing aniline increased, too. So, pH 5 was chosen as the optimum pH for the next pH research. According to the studies, the pH of a solution is one of the most effective environmental factors for removing pollutants in chemical processes. In AOPs, the value of pH has a direct effect on the production of hydroxyl and sulfate radicals in solution [22, 23]. The results of this study and similar studies show that the maximum efficiency for the processes of removing pollutants is in a neutral environment that is inclined to the acidic environment with pH of 4 to 6. In AOP process with the usage of UV, the pH values have an influence on the reactions of persulfate with the pollutants [22, 23]. This phenomenon may be due to further production of sulfate radicals in acidic conditions which are inclined to neutral conditions. In these conditions, because the concentration of sulfate ions in the environment is maximum, the sulfate radicals are produced with more energy [24, 25].

These results are similar to that of the studies of Cai et al. [26] and Gao et al. [24] on the removal of TCE and sulfumetazyn.

3.2. Radiation Rate Effect Figure 3 shows the effect of radiation rate (the number of lamps was 2, 3, 4 and 5) on the efficiency of aniline removal in UV/PDS process. As shown, increasing the radiation rate of UV lamps increased the aniline removal efficiency, too. Accordingly, the maximum removal efficiency was obtained in the maximum radiation with 5 lamps, while the reaction time was 60 min. The radiation rate of 5 UV lamps was chosen as the appropriate radiation rate for the next pH research. The results show that oxidation and the percent of aniline removal were affected by the rate of UV lamps radiation. This phenomenon is probably due to increasing the optical decomposition of peroxy disulfate ions by UV rays and production of sulfate and hydroxide radicals.

**Figure 2.** Effect of pH on aniline degradation rate (Experimental conditions: [Aniline]= 40 mg/l; [PDS] =0.06 mol/l; Temperature ~20 °C; UV lamps=4)
If radiation increases, the optical decomposition occurs more and faster [17, 22]. These results are similar to the findings of Khataee et al. [13] and Salari et al. [19] for the removal of C.I. Basic Yellow.

3. 3. PDS Dose Effect  

The effect of different doses of PDS on the efficiency of aniline removal in UV/PDS process is shown in Figure 4. According to the figure, if the dose of PDS, as the main factor in the production of sulfate radicals, increases, the removal efficiency increases significantly. So that when the concentrations are 0.02, 0.04, 0.06 and 0.08 mol/l, the efficiencies will be 46, 61, 16 and 82.8% after 60 min, respectively. According to the results, 0.08 mol of PDS was selected as an appropriate value for the next pH. Increasing the dose of peroxy disulfate increased the production of hydroxyl radicals and sulfate radicals (reactions 2 and 6) and subsequently increased the efficiency of aniline removal in aqueous solution [25].

Moreover, by increasing the value of PDS, sulfate radicals and hydroxyl will be increased and therefore the removal efficiency will be increased too.

3. 4. Initial Aniline Concentration Effect  

The effect of initial concentration of aniline on removal efficiency in the process of UV/PDS is shown in Figure 5. According to the figure, the efficiency of the process decreases with increase in the initial concentration of aniline. So that, when the concentration equals 100 mg/l and the reaction time is 60 min, only 33.8% of aniline is removed, whereas when the concentration equals 20 mg/l and the reaction time is 60 min, the efficiency is 94%. According to the operational point, the effect of initial concentration of pollutant on removal rate is one of the important factors. As shown in the results, increasing the concentration of pollutants decreases the removal efficiency.

On one hand, increasing the amount of peroxy disulfate to a certain concentration increases the production of radical sulfate and therefore increases the removal efficiency and according to Reaction 7, an inordinate increase of peroxy disulfate and use of sulfate radicals decreases the removal efficiency [25]. Since in this study, the range of the added dose of peroxy disulfate was lower than that expected to act as a radical abrasive, therefore, increasing the dose of peroxy disulfate increases the aniline removal efficiency.

\[
\text{SO}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}^+ + \text{SO}_4^{2-} \quad (7)
\]

\[
\text{S}_2\text{O}_8^{2-} + \text{SO}_4^{2-} \rightarrow \text{S}_2\text{O}_6^{4-} + \text{SO}_4^{2-} \quad (8)
\]

Liang et al. [27, 28] claimed that the cause of this phenomenon is increase of reactive radicals production in the solution. Panbehkar et al. [29] and Astereki et al. [30] showed that increasing free radicals of persulfate which is because of light radiation in the presence of water produces more hydroxyl radicals in the environment.

Figure 4. Effect of PDS dosage on aniline degradation rate (Experimental conditions: [Aniline]= 40 mg/l; Temperature ~20 °C; pH=5; UV lamps=4)

Figure 3. Effect of radiation rate (based on lamp number) on aniline degradation rate (Experimental conditions: [Aniline]= 40 mg/l; [PDS]=0.06 mol/l; Temperature ~20 °C; pH=5)

Figure 5. Effect of aniline concentration on aniline degradation rate (Experimental conditions: [PDS] =0.08 mol/l; Temperature~ 20 °C; pH=5; UV lamps=4)
The reason for this phenomenon is the proportion of aniline molecules to sulfate radicals and also the presence of intermediate substances that use free radicals [22, 24, 26], therefore, the removal efficiency will decrease at higher concentration. Guo et al. [15] and Wang et al. [17] presented similar results.

3.5. Time Effect

Figure 6 shows the effect of time on the efficiency of aniline removal in UV/PDS process using appropriate values for variables. As shown in Figure 5; the curve fitting of experimental data with Equation (9) was used to obtain rate constants. Changes in the initial concentration of aniline (40 and 60 mg/l) follows the kinetic model quasi – first class more than time does. Evaluation of the obtained experimental data over time shows that the reaction velocity follows kinetics quasi–first class. In addition, the reaction of aniline decomposition are shown in Equations (9)-(12):

\[ -r_{\text{Anilin}} = k_{\text{overall}}[\text{Anilin}] \]

\[ -\ln \left( \frac{C_t}{C_0} \right) = k_{\text{overall}} \cdot t \]

\[ -\ln \left( \frac{C_t}{C_0} \right) = -0.053 \cdot t + 2.652 \]

\[ -\ln \left( \frac{C_t}{C_0} \right) = -0.032 \cdot t + 1.572 \]

In the above equations, \( C_t \) is the concentration of aniline at time t in terms of mg/l, \( C_0 \) is the initial concentration of aniline in terms of mg/l and \( k_{\text{overall}} \) is the constant of velocity of the quasi-first class reaction in terms of 1/min, which is the slope of the diagram – \( -\ln \left( \frac{C_t}{C_0} \right) \) versus time. The obtained rate constants were 0.053 and 0.032 min\(^{-1}\) at aniline concentration of 20 and 40 mg/l, respectively.

The results agree with other studies; Huang et al. [31] reported the quasi – first rate constants were in the range same of 0.026 -0.19 min\(^{-1}\) for acid blue 113 degradation.

3.6. Variables Synergism Effect

Figure 7 shows the synergic effect of variables on the efficiency of aniline removal in the process of UV/PDS. The effect of each variable was studied individually and also in combination with other variables with appropriate values and at different times. The separate processes of PDS and UV can only remove 10.5 and 7.5% of aniline from aqueous solution in 60 min. While the combined process UV+PDS was able to remove a maximum amount of aniline that was 96%. This implies the synergy of combining parameters in this process. The effect of different variables with appropriate values on removing aniline was studied individually and in combination. There was no significant change in aniline removal using UV and peroxy disulfate. Using UV singly had minimal removing efficiency, and it can only remove 7.5 % of aniline in 60 min. This low efficiency probably was due to the absence of oxidizing factors such as sulfate radicals or hydroxyl radicals [30]. Also, peroxy disulfate cannot remove a significant percentage of aniline alone; Zhao et al. and Chen et al. [21, 32] showed that it is related to the limited oxidation power of \( S_2O_5^2^- \) (E\(^0\)=2.01 V), which cannot be converted to free radicals in the solution. Combining the systems of \( S_2O_5^2^- \) and the radiation of UV lamps (the process of UV/PDS) in the reactor can increase the efficiency of aniline removal up to 93%, and this is because of the production of sulfate and hydroxide radicals. As shown in Reaction 2, the optical decomposition of proxy disulfate ions by activator factor of UV rays can produce these radicals [22, 32].

![Figure 6. Kinetic of aniline degradation (Experimental conditions: [PDS] =0.08 mol/l; Temperature ~20°C; pH=5; UV lamps=5)](image1)

![Figure 7. The effect of different variables and their interaction on the removal of aniline (Experimental conditions: [PDS] =0.08 mol/l Temperature~20°C; pH=5; UV lamps=5)](image2)
6. CONCLUSION

In the process of removing aniline using PDS/UV from aqueous solutions, the parameters for increasing the value of PDS and also the amount of radiation, increases sulfate radicals concentration and subsequently increases the removal efficiency and increasing the initial concentration of aniline, decreases the removal efficiency. In addition, when the pH is in the acidic range, the removal efficiency will have a maximum value. Combining the parameters, UV and PDS in the acidic pH increases production of oxidizing sulfate radicals and subsequently increases the removal efficiency. The optimum amount of parameters were PDS=0.08 mol, pH=5, UV= 30 W, aniline=20 mg/l and time= 60 min. So, using this process for removing different resistant pollutants, especially in industrial wastewaters, can be the best method and it is competitive with other methods.

7. ACKNOWLEDGEMENT

This study was supported by Lorestan University of Medical Sience. The authors are deeply grateful for their financial and spiritual supports.

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Aniline Degradation Using Advanced Oxidation Process by UV/Peroxy Disulfate from Aqueous Solution

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PAPER INFO

Paper history:
Received 02 September 2016
Received in revised form 11 February 2017
Accepted 10 March 2017

Keywords:
Aniline Degradation
Peroxy Disulfate
Ultraviolet
Advanced Oxidation

Doi: 10.5829/idosi.ije.2017.30.05b.08

In this work, the degradation of aniline from aqueous solution using UV/P2S5 was studied. The effect of various process parameters on the aniline degradation was investigated. The results showed that the UV/P2S5 process was effective in the degradation of aniline from aqueous solution. The degradation efficiency increased with decreasing pH, increasing UV dose, and increasing P2S5 concentration. The model results were in agreement with the experimental results. The proposed model was effective in predicting the degradation of aniline from aqueous solution using the UV/P2S5 process.