Ultraviolet Radiation/persulphate/hydrogen Peroxide Treatment System for Acid Blue 80 Dye Degradation of Batch Flow Chemical Reactor: Effects of Operational Parameters, Mineralisation, Energy Consumption, and Kinetic Studies

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**Ultraviolet radiation/persulphate/hydrogen peroxide treatment system for acid blue 80
dye degradation of batch flow chemical reactor: Effects of operational parameters,
mineralisation, energy consumption, and kinetic studies**

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Abstract

This study offers a comprehensive investigation into the efficiency of degradation of acid blue 80 (AB80) dye using a system using ultraviolet (UV) radiation combined with hydrogen peroxide (H_2O_2) and persulphate (PS) oxidants (UV/PS/ H_2O_2). The degradation reactions were performed under different values of PS and H_2O_2 concentrations, initial AB80 dye concentration, pH, UV intensity, and contact time. The results revealed that the UV/ H_2O_2 provided the best performance at pH of 5, while the best performance for the UV/PS and UV/PS/ H_2O_2 systems was obtained at pH of 7. Besides, 15 mmol was found to be the optimum concentration for both oxidants. The efficiency of the combined process of the UV/PS/ H_2O_2 was higher than that of the other two processes i.e., UV/PS and UV/ H_2O_2 , which was 98.2 % for a dye concentration of 25 mg/L. Further, the BOD_5/COD ratios at the beginning and end of the UV/PS/ H_2O_2 process were 0.19 and 0.52, respectively, indicative of the conversion of the non-biodegradable dye molecules to biodegradable compounds. The toxicity test was performed using the bioassay method with *Daphnia magna*, and 90% reduction in toxicity was observed in the effluent. The lethal concentration 50 (LC_{50}) indicator was found to be 4.7 mg/L for the dye solution. The results also revealed that the degradation data followed the pseudo-first-order kinetics, and the reaction rate constant was higher for the UV/PS/ H_2O_2 system than for the other systems. The rate of mineralisation by this process was 0.92. Scavenging studies also showed that both the sulphate ($\text{SO}_4^{\circ-}$) and hydroxyl (OH°) radicals play an important role in the degradation process. Energy consumption in the UV/ H_2O_2 , UV/PS, and UV/PS/ H_2O_2 processes was 61, 47.8, and 20.8 kWh/m³, respectively. On conclusion, the UV/PS/ H_2O_2 is an effective and applicable process for the treatment of dye in wastewater, particularly when the medium is neutral.

Keywords: UV/PS/ H_2O_2 ; Acid blue 80 dye; Mineralisation; Radicals; Toxicity

1. Introduction

Industrial effluents are usually one of the major environment-polluting wastes (Adeniyi et al., 2019). Coloured wastewater is released from several industries namely, the textile and dyeing industries, pharmaceutical and food industries, and paper and leather industries, as well as in the production of cosmetics (Adeogun et al., 2017). The textile industry is one of the principal and basic industries in any country (Ali et al., 2018). In spite of the fundamental importance of the textile industry, the environmental impact it exerts is of great concern (Balarak et al., 2018). Normally, colour is the main characteristic of such effluents from these types of industries, caused by the use of coloured materials during the processes (Balarak et al., 2016). The generation of large quantities of wastewater having different qualities has been addressed as one of the main environmental issues related to this industry (Al-Musawi et al., 2021). In the dyeing processes, about 15% of the total dye produced, mixes with the wastewater thus forming coloured wastewater (Bulut et al., 2007). Most often the dyes used in these industries are synthetic ones. Synthetic dyes are normally distinguishable as acidic, reactive, direct, and base dyes, besides other groups (Dotto et al., 2011). The pigments are chiefly composed of one or more benzene rings which, due to their toxicity and slow decomposition, can irreparably damage the environment, if they are released into nature without treatment (Goshadrou et al., 2011; Gupta et al., 2013). Therefore, such effluents must be treated with appropriate methods prior to being discharged into the environment. Treating textile wastewater has been evaluated with many methods. Biological processes are the commonest methods employed in the treatment of wastewater containing dye solutions because they are inexpensive and environmentally friendly (Sillanpää et al., 2021). Nevertheless, the limitations in the degradation of biodegradable compounds have been identified for these processes since the textile-industry generated wastewater contains some toxic compounds, which curb or limit the growth and activity of the microorganisms (Igwegbe et al., 2016; Iram et al., 2010). A few

other processes, e.g., coagulation and adsorption, which are physico-chemical processes, can effectually remove the pollutants from the wastewater (Jauris et al., 2016). However, they can participate only in the transfer of organic matter from the liquid medium to the solid medium, which results in the production of a thick sludge that requires further treatment (Machado et al., 2016). Another effective technology used in the separation of pollutants from wastewater is membrane technology. Nevertheless, because of the possibility for fouling the membrane modules, the operating costs are observed to escalate (Menkiti et al., 2018; Azarpira et al., 2016). Electrochemical processes for petrochemical wastewater have also been studied; however, its large-scale application is limited due to high electrical energy consumption (Balarak et al., 2021).

Employing technologies such as advanced oxidation in water and wastewater treatment have many advantages. Fast vaporisation, less sludge production, a wide range of different types of pollutants in the aquatic environments, mineralisation of most organic compounds in these environments, besides others are some of the advantages offered by these technologies (Balarak et al., 2019). In the last decade UV-assisted photolysis has been used effectively in the elimination of organic compounds, exhibiting various kinetics and mechanisms, with by-products released as the degradation products of these compounds (Al-Musawi et al., 2021). The basis of the Advanced Oxidation Processes (AOPs) was found to be the production of free radicals; the radicals thus produced are powerful, possessing high reactivity for the effective degradation of the organic pollutants. These radicals can be produced in a variety of ways, the commonest being the use of a chemical oxidising agent, such as H_2O_2 (Baeza et al., 2011).

Recently, PS has been identified as a good alternative oxidant for the production of free radicals possessing the capacity to degrade various types of pollutants. In order to produce free radicals, these oxidants must be activated, either through the use of ultraviolet radiation (UV), transition

metals, and ultrasound; these can lead to the generation of $\text{OH}^\bullet$ or $\text{SO}_4^{\bullet-}$ radicals, in the presence of H_2O_2 and $\text{S}_2\text{O}_8^{2-}$, respectively (Canonica et al., 2011; Keen et al., 2008).

The $\text{OH}^\bullet$ and $\text{SO}_4^{\bullet-}$ radicals are strong oxidising agents with $E_0 = 2.7 \text{ V}$ and $E_0 = 2.6\text{-}3.1 \text{ V}$, respectively. The $\text{OH}^\bullet$ radical is a non-selective oxidant with a 20 ns lifetime (lifetime = 20 ns), while the $\text{SO}_4^{\bullet-}$ radical is a selective oxidant, having a longer lifespan (40 μs). Therefore, the $\text{SO}_4^{\bullet-}$ radical has greater opportunity of reacting with the organic compounds (Ahmed et al., 2012; Yang et al., 2016). The main purpose of this study is to compare the UV/PS and UV/PC and the combined process of UV/PS/ H_2O_2 in the removal of the AB80 dye from aqueous solutions. In this study, the quantity of mineralisation will be determined using the TOC and the degree of biodegradability will be calculated using the BOD_5/COD ratio. Also, the effect of various parameters such as contact time, oxidant concentration, pH and initial concentration of the AB80 dye were investigated. Further, to gain an economic perspective, the energy consumption was calculated for each system.

2. Materials and methods

2.1 Chemicals

The AB80 dye with the chemical formula of $\text{C}_{32}\text{H}_{28}\text{N}_2\text{Na}_2\text{O}_8\text{S}_2$, molecular weight of 678.6 g/mol, and CAS number of 4474-24-2 was purchased from the Sigma Aldrich Company. The stock solution of 1000 mg/L of dye was obtained by dissolving one gram of dye in 1 L of distilled water; the solutions necessary for this experiment were obtained by diluting the stock solution. The H_2O_2 (30% w/w), and sodium persulphate (99%) prepared using Merck pellets GR (99-100%) and the HCl solution prepared from 37% stock solution were all purchased from

Merck. All the aqueous solutions were prepared utilising double distilled water with less than 0.08 $\mu\text{S}/\text{cm}$ conductivity.

2.2 Experimental setup

The batch mode was considered for performing the photo-oxidation process at room temperature, with the use of a cylindrical quartz reactor (6 cm in diameter and 16 cm in height) containing 500 ml of coloured wastewater. The distance between the lamps and reactor was 3 cm. In fact, 1 to 4 UV-C lamps in number (8 W, Philips) were used, with the maximum emission at 254 nm. Safe operation conditions were ensured by placing the reactor and lamps in a wooden box, to prevent the penetration of excess UV light. Due to the heat generated by the lamps, the reaction chamber was placed in a bath equipped with a water inlet and an outlet pipe, to adjust the temperature. For the UV lamps to achieve a steady state a heating process was provided for 10 minutes, prior to photo-oxidation. The intensity of the lamps, in the centre of the reactor, was assessed as 7.25 mW/cm^2 . After pouring the samples into the reactor, the pH was adjusted using 0.1 N HCl or NaOH. Next, a specific quantity of the oxidant (H_2O_2 and PS) was added to the sample, while the solution was stirred with a magnetic stirrer. The initial pH values were in the 3 to 11 range, while the oxidant doses ranged from 2 to 20 mmol for H_2O_2 and PS, respectively. The quantities of the pH adjusting agent and oxidant dose, which were added, were negligible when compared with the total volume of treated wastewater. The samples were drawn at regular intervals for conducting the analyses including, COD, BOD_5 , TOC, and residual dye concentrations. Eq. 3 was used to calculate the degradation efficiency or efficiency (%) of the AB80.

$$\text{Efficiency (\%)} = \left[\frac{(C_0 - C_t)}{C_0} \right] \times 100 \quad (3)$$

By using the open reflux method, the COD values were measured. This method, in brief, is described as follows: Under acidic conditions, the organic matter is oxidised using potassium

dichromate. The BOD₅ value was estimated by determining the oxygen consumption by titrating with sodium thiosulphate, post incubation for five days. The intensity of colour was measured at 400 nm, as the maximum wavelength using a UV-Vis spectrophotometer (Hach DR5000). To determine the quantity of decomposed organic carbon, a measuring device (TOC model (Multi NC3100, made in Germany) was used.

3. Results and Discussion

3.1 Effect of pH

One of the very important parameters in pollutant degradation that alters the performance of the AOP process most of the time is the pH of the solution. The effects of pH at the values of 3, 5, 7, 9, and 11 for the UV/PS, UV/H₂O₂, and UV/PS/H₂O₂ systems were considered in this study and the results are shown in Fig 1a. The experiments were performed at a contact time of 60 min at an initial concentration of 25 mg/L and radiation intensity of 36 watts and a concentration of oxidants of 15 mmol. For the UV/PS system, the best performance for dye degradation is achieved at pH of 7. Although no significant difference is noted between the removal efficiency at pH of 5 and 7, that is in acidic and alkaline pH, the efficiency shows a reduction, which in corresponding reports acknowledges that the best pH while employing UV/PS to eliminate the pollutants was within the almost neutral range (Ahmed et al., 2012; Yang et al., 2016). At alkaline pH, the $\text{SO}_4^{\circ-}$ species reacts with the OH^- to produce OH° radicals, according to Equation 5. Despite the conversion of the $\text{SO}_4^{\circ-}$ to SO_4^{-2} and the generation of the OH° radicals with a redox potential of 2.8 V, a slightly higher value than the redox potential of the $\text{SO}_4^{\circ-}$, the presence of the SO_4^{-2} ions can inactivate the OH° and $\text{SO}_4^{\circ-}$ species (Zhang et al., 2016). Besides, the CO₂ from the mineralisation of organic matter can result in the formation of bicarbonates and carbonates (as radical scavengers) under alkaline conditions. On the other

hand, at an acidic pH, additional $\text{SO}_4^{\circ-}$ can be produced under acid catalysis, according to the equations 6 and 7 (Zhang et al., 2016; Yuan et al., 2011).

When excess PS radicals are generated, it can increase the concentration of the radicals which may react with each other, instead of reacting with the organic pollutants (Yang et al., 2016).

For the UV/ H_2O_2 process, the best removal efficiency was observed to occur at pH of 5, showed a decline in performance as the pH increased. At alkaline pH, the redox potential of the OH° radical was reduced. Also, H_2O_2 may be decomposed into water and oxygen at high pH levels, as shown (Yao et al., 2013):

Further, in a low acidic environment, the H_2O_2 molecules react with the excess H^+ ions to form oxonium ions (H_3O_2^+) which are stable and cannot form the OH° radicals under ultraviolet radiation. At the same time, the excess H^+ ions may scavenge the generated OH° radicals. For the UV/PS/ H_2O_2 , the best pH was identified as 5, the reasons for which have been stated above and also mentioned in various articles (Wu et al., 2015; Xie et al., 2015).

3.2 Effect of oxidant concentration

The effects of the H_2O_2 and PS concentrations on the rate of the removal of the AB80 dye were investigated and the results are listed in Figure 1b. The experiments were performed at a contact time of 60 min at an initial concentration of 25 mg/L and radiation intensity of 36 watts and a pH of 7. As is evident, the rate of dye removal increased as the PS concentration surged up to

15 mmol, caused by the production of the $\text{SO}_4^\bullet$ radicals in response to the rise in the PS concentration. Also, with the increase in the concentration of 15 mmol, the removal rate declined, the reason being clarified as follows: the $\text{SO}_4^\bullet$ radical is converted to the PS radical according to equations 9 and 10 with lower reduction-oxidation potential than the $\text{SO}_4^\bullet$ radical (Yan et al., 2015). On the other hand, the $\text{SO}_4^\bullet$ radical acts as a scavenger radical and becomes a factor that facilitates the conversion of the $\text{SO}_4^\bullet$ radical to PS (Yan et al., 2011).

Therefore, an increase in the concentration of H_2O_2 to 15 mmol also improves the removal efficiency, caused by the production of the $\text{OH}^\bullet$ radicals; however, with further increase in the H_2O_2 levels, the removal efficiency decreases, due to the scavenging of the $\text{OH}^\bullet$ radicals available and the formation of hydroperoxyl ($\text{HO}_2^\bullet$); these are the weaker radicals, less active than the $\text{OH}^\bullet$ radicals (Sun et al., 2016).

The use of two oxidants was simultaneously investigated, and the 12 mmol concentration was selected as the optimal concentration of the oxidants in the combined process, although not much difference in the scavenging activity is observed between the 8 and 12 mmol concentrations, and the high concentrations (Tan et al., 2014).

3.3 Effect of radiation intensity

One of the most important parameters in this study of the process of photolysis is the radiation, given at intensities of 8, 5, 24, and 36 W, in the combined process of UV/PS/ H_2O_2 ; when the radiation intensity was increased from 8 to 36 W, the removal efficiency was also seen to rise, so that in 60 min, the removal rate was 74.6% at the radiation intensity of 8 W. However, at the same time, at the radiation intensity of 36 W, the removal rate was 98.2% (Fig 1c). This

increase in the removal rate induced by the increase in the intensity of the irradiated radiation resulted in an increase in the number of excited electrons, which ultimately enhanced the generation of active OH° or $\text{SO}_4^{\circ-}$ (Yuan et al., 2014). The experiments were performed at a initial concentration of 100 mg/L and pH of 7 and a concentration of oxidants of 15 mmol.

3.4 Effect of initial AB80 dye concentration and irradiation time

The effect of the initial dye concentration at concentrations of 10, 25, 50, and 100 mg/L on the combined process was performed using the optimal quantity of oxidants and pH, and the results are shown in Figure 1d. The experiments were performed at a pH of 7 watts and a concentration of oxidants of 15 mmol. As depicted, at the 25 mg/L concentration, the highest removal efficiency (98.2%) was obtained, which declined in response to the increase in concentration. The reason for this occurrence is explained as follows: Although the initial concentration of the dye is increased, the production rate of OH° or $\text{SO}_4^{\circ-}$ is remains constant during the process (Kwon et al., 2015). Further, the UV absorption by the dye molecules shows a surge in response to the increase in the dye concentration, thus preventing the activation of the oxidants (Wols et al., 2015).

Irradiation time and contact time are other crucial parameters that were examined and shown in Figure 1d, and as is obvious, when the irradiation time increases from 10 to 60 min, the removal rate also rises significantly. In terms of irradiation time, the exposure of the oxidants of H_2O_2 and PS to ultraviolet light activates them. Therefore, as the radiation time increases, more electrons are produced, which thus generate more OH° and $\text{SO}_4^{\circ-}$ radicals and provides great opportunity for the active OH° and $\text{SO}_4^{\circ-}$ radicals to degrade the AB80 dye (Rastogi et al., 2009).

3.5 Comparison of the dye removal by different processes

After determining the optimum conditions in the earlier steps, the effect of each oxidant alone and the effect of their simultaneous use during the different processes involved in the removal of the AB80 dye was studied, the results of which are shown in Figure 1e. Considering the results of the prior steps, the study was performed in 10-60 min of contact time under the optimum values of the parameters, including the 15 mmol doses of PS and H₂O₂, 36 W of radiation intensity, and 25 mg/L of dye concentration, at pH of 7. As observed, the process efficiencies of the H₂O₂, UV/H₂O₂, UV, UV/PS, PS, and UV/PS/H₂O₂ in dye removal are different, with very low efficiency of the H₂O₂, UV and PS processes. Moreover, from these results, the UV/PS/H₂O₂ process reveals the highest removal efficiency, eliminating 98.2% of the AB80 dye in 60 min. This increase in efficiency for the combined process can be attributed to the UV-induced activation of S₂O₈²⁻ or H₂O₂ because the UV light, according to equations 1 and 2, produces the OH[•] or SO₄^{•-} radicals, considered the strongest oxidants (Wols et al., 2014; Wols et al., 2015).

Figure 1. The effect of pH (a), concentrations of PS and H₂O₂ (b), UV light intensity (c), initial concentration of AB80 dye (d), and various processes (e) on the photochemical degradation efficiency of AB80 dye

3.6 Mineralisation assessment

The TOC analysis can offer a measure of the degree of mineralisation of the AB80 dye. The quantity mineralised occurred under the optimal conditions obtained from the previous steps, where the AB80 dye concentration at this stage of the study was considered to be 100 mg/L, and the quantity mineralised was determined at different times. The initial TOC level for 100 mg/L concentration was found to be 65.6 mg/L.

The TOC results for a comparison of the three UV/PS/H₂O₂, UV/H₂O₂, and UV/PS systems are shown in Figure 2a. Note that the efficiency based on TOC for this case is defined as follows (Zhang et al., 2014):

$$\% \text{TOC Removal} = \frac{\text{TOC}_0 - \text{TOC}_t}{\text{TOC}_0} \times 100 \quad (11)$$

Where TOC_0 and TOC_t are the TOC concentrations measured at the beginning and after a specific time of the degradation process, respectively.

As observed from Figure 2a, the amount of mineralisation increases with the increase in degradation time, but when compared to the other two systems it was much higher for the combined system. In fact, around 92.1% of the TOC is removed by the combined system in 120 min, while only 50.95% is removed for the UV/H₂O₂ system and about 59.1% for the UV/PS system.

3.7 Improvement of biodegradability

Due to the toxicity of industrial wastewater, biological processes alone do not have the efficiency, adequate to treat industrial wastewater. The AOPs processes, on the other hand, are expensive when used only to treat the organic compounds. As they had the capacity to improve the effluent quality, the AOPs can be used to treat toxic and strong wastewater prior to submitting them to biological treatment (Yu et al., 2004). In order to evaluate the biodegradability of the treated effluent, the BOD₅/COD index is employed as a common index. The BOD₅/COD ratio was initially 0.19, which is indicative of the low biodegradability of coloured wastewater. It is significant that for biodegradability, this ratio should be greater than 0.4. Figure 2b shows the BOD₅/COD values after different processes within a photolytic time of 120 min. In the UV, PS, and H₂O₂ systems, the degree of biodegradability showed no significant change and increased from 0.19 to about only 0.23, which can normally be attributed to the COD and BOD₅ reduction in solution. Therefore, the wastewater continues to be non-biodegradable. But for the combined UV/PS/H₂O₂ system, this rate goes up to 52.4%, and the wastewater becomes biodegradable; therefore, in this system, it can be stated that the non-biodegradable materials have become simpler materials.

3.8 The role of radical species

To evaluate the contribution of the $\text{OH}^\bullet$ or $\text{SO}_4^{\bullet-}$ radicals to the efficiency of the UV/PS/ H_2O_2 process, two alcoholic radical scavengers, EtOH and t-BuOH, were added separately to the solutions. The EtOH can quench both $\text{OH}^\bullet$ or $\text{SO}_4^{\bullet-}$ radicals. However, the t-BuOH can destroy $\text{OH}^\bullet$ radicals principally and react weakly with the $\text{SO}_4^{\bullet-}$ radicals (Yu et al., 2003; Khan et al., 2014). Accordingly, the difference in efficiency in the presence of these scavengers can be considered the contribution of the $\text{SO}_4^{\bullet-}$ radicals. Therefore, in light of the efficiency of the system, coupled with these two scavengers, it is easy to understand the contribution of $\text{OH}^\bullet$ or $\text{SO}_4^{\bullet-}$ radicals. As Figure 2c shows, the addition of EtOH in different quantities reduced the efficiency much more than the t-BuOH. For example, the addition of 1.4% (V/V) EtOH or t-BuOH reduced the efficiency by 41% and 29%, respectively, when compared to the normal state without the scavengers. These observations mean that both the radical species are involved in the degradation of the AB80 dye. It noteworthy that for the electron transfer reactions, the $\text{SO}_4^{\bullet-}$ radicals are found to be more selective, but the $\text{OH}^\bullet$ radicals can quickly participate in the reactions related to either the addition or abstraction of hydrogen (Yu et al., 2004).

3.9 Reaction kinetics

In all the three systems, rapid rate of dye removal was seen, most likely due to the presence of the oxidants when the reaction commenced. To study the reaction rate, the pseudo-first-order kinetic model is most often used, (see formula given below) (Zhang et al., 2014):

$$\ln \frac{C_0}{C_t} = k \cdot t \quad (12)$$

Where the C_0 and C_t are the initial concentration and concentration post the photochemical reaction at time t , and k is the constant rate of the pseudo-first-order reaction (1/min). The reaction rate constant is obtained by plotting the $\ln C_t/C_0$ at time t . The diagram desired is

shown in Fig 2d. As is observed, the $\ln C_t/C_0$ diagram at time t is linear for all three systems, indicating a high regression coefficient and data adherence to the pseudo-first-order kinetics. Also, the reaction rate constant for the UV/PS/H₂O₂, UV/PS, and UV/H₂O₂ combined systems is 0.066, 0.026, and 0.02 min⁻¹, respectively; thus, it can be said that the reaction rate for the UV/PS/H₂O₂ combined system is greater than that of the other two systems.

Figure 2. TOC removal efficiency (a), BOD₅/COD rate for different processes (b), Effect of various scavengers (c), and pseudo-first order kinetics (d), for different removal methods

3.10 Energy consumption

One of the central parameters for the superiority of the technology used in wastewater treatment is the economic aspect, which most often is often critical. In this regard, electrical energy consumption (EEC) is the main share of the energy in the photochemical process. Here, the

EEC can be calculated in accordance with the proposal of the International Union of Pure and Applied Chemistry, using the following equation (Khan et al., 2013).

$$EEC = \frac{P \times t \times 1000}{V \times 60 \times \log\left(\frac{C_0}{C_e}\right)} \quad (13)$$

Where P is the electrical power (kW) of the photochemical system (generally targeting radiation energy), V is the volume of the solution in the reactor in litres, and t is the reaction time (min).

Therefore, the EEC required for the photochemical degradation of the AB80 dye solution employing the processes of UV/H₂O₂, UV/PS, and UV/PS/H₂O₂ are 61, 47.8, and 20.8 kWh/m³, respectively, and as observed, for the combined UV/PS/H₂O₂ system, the energy consumed is less than that in the other two systems. In a study conducted to ascertain the removal of atrazine using the photochemical process by UV/H₂O₂/Fe²⁺, the energy consumed is equal to 76.2 kWh/m³, which is higher than the energy consumed in this study (Khan et al., 2013). The expenditure involved for the electricity consumed was calculated according to industrial consumption and based on Iran, it is equal to US dollar 0.064 per 1 kWh for the combined system.

3.11 Toxicity test

The bioassay using *Daphnia magna* was used to test the solution toxicity. *Daphnia* was selected for this purpose due to its brief reproduction time, high sensitivity, simplicity of testing, and low laboratory costs, and most important, for its parthenogenesis, ranking high among the most crucial factors in the validity of the results drawn from a bio-experimental experiment (Sun et al., 2016). In this study, the *Daphnia* neonate was used instead of the adult *Daphnia*. When the adult *Daphnia* was used, it was possible to reproduce and increase the number of *Daphnia* in the samples under investigation, which would interfere with the test results and their uncertainty. To perform the toxicity test, a concentration of 25 mg/L of the AB80 dye solution

was prepared. In the bioassay, the next step was to collect the three to four-day-old *Daphnia* neonates from the culture medium and dilute them up to three times in water, and wash for five minutes. Then, 10 *Daphnia* were dropped by pipette into each of the containers for testing. The number of *Daphnia* was counted after a contact time of 24 hours. No live *Daphnia* were found for the solution at 25 mg/L concentration after 24 hours, while for the control solution (without dye), all ten *Daphnia* were alive. After using the combined process of the UV/PS/H₂O₂ and removal of the dye from the solution, the number of live *Daphnia* was 9 after 24 hours, showing that only one *Daphnia* was eliminated during this process. Therefore, it can be concluded that the effluent toxicity was reduced by 90%. Also, the NOEC value (the concentration at which no effect was observed after 24 hours) was tested for AB80 dye; its value was observed to be 1.5 mg/L. Further, the concentration at which 50% of the laboratory samples were destroyed, the so-called LC50 was established as 4.7 mg/L for the dye solution.

4. Conclusion

In this study, the performance of the UV/PS/H₂O₂, UV/H₂O₂, and UV/PS systems for the removal of the AB80 dye was evaluated, and these systems were compared in terms of energy consumption, mineralisation, toxicity, and reaction kinetics and biodegradability. The results of the study indicate that the parameters of pH, oxidant concentration, system type, AB80 dye concentration, as well as reaction time show remarkable involvement in the production of the OH[•] or SO₄^{•-} radicals during the photochemical-oxidation processes based on the H₂O₂ and PS. In this photochemical system, an increase in the time and a decrease in the initial dye concentration and pH, produced the desired efficiency in the removal of the AB80 dye. The combined UV/PS/H₂O₂ process showed the capacity to remove 98.2% of the dye solution and minimise the toxicity of the effluent caused by *Daphnia*. As this system converts non-biodegradable wastewater into biodegradable effluents, it is proposed that this system be used in the treatment of industrial wastewater prior to the biological systems. Reaction kinetics are

pseudo first-order kinetics and the reaction rate is higher for the UV/PS/H₂O₂ system than for any other systems. Also, in this study, mineralisation was accomplished using TOC, and from the results it is evident that mineralisation has been performed as well.

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Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare no competing interests.

-Authors Contributions

All authors contributed to the study conception and design. Material preparation, data collection, and analysis were performed by Tariq J. Al-Musawi, Murat Yilmaz and Samaneh Mohebi. The first draft of the manuscript was written by Amir Hossein Mahvi and Davoud Balarak; all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials

The datasets used and analyzed during the current study are available from the corresponding author on reasonable request.

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