

# The evaluation of improved degradation of Acid Black ATT dye in aqueous solution by hybrid photo-ozonation peroxymonosulfate process

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## Research Article

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# Abstract

The present study was designed and conducted to simultaneously produce two sulfate and hydroxyl radicals for the decomposition of Acid Black ATT dye, which showed that UV radiation and ozonation alone cannot decompose and break down this dye compound completely. The UV/O<sub>3</sub>/PMS process is able to completely remove all dye concentrations from 10 to 30 mg / L in 10 minutes. Then, the effect of parameters such as contact time, pH, initial dye concentrations, different doses of persulfate, and ozone under ultraviolet radiation on dye removal was studied. Based on the results of this experiment, the optimal concentrations of variables include pH, ozone concentration, and persulfate concentration, and initial dye concentration includes 10, 20 mg / min, 0.4 mM L<sup>-1</sup>, and 20 mg/ L, respectively. For every 0.1 mM increase in PMS concentration, the amount of dye removal increased by 14%. Based on the findings of this study, the combined UV/O<sub>3</sub>/PMS process can be concluded that the environmentally friendly hybrid technology of advanced sulfate-based oxidation removes contaminants resistant to aqueous media.

## 1. Introduction

As the most commonly used dyes, azo dyes, which contain one or more azo groups (-N = N-) in their chemical structure [1], are widely used in various industries such as textiles, paper, food, pharmaceuticals, etc. [2]. About 700,000 tons of dyes are currently produced annually, of which 10–15% end up in wastewater [3]. Without proper treatment, these released Azo dyes are toxic to wildlife and even more toxic to animals. They also prevent sunlight from penetrating deep-water layers and reduce oxygen solubility [4]. Discoloration and degradation of azo dyes have long been an environmental problem [5]. Many methods have been used to treat such wastewater from Azo dyes, including absorption, precipitation, ion exchange, and chemical oxidation [6]. Microbial degradation has been identified as an economical, effective, and energy-efficient strategy for decolorizing and degrading azo dyes [7]. Although numerous papers have been published on dye decolorization and microbial degradation, few of these organisms have been confirmed to have the ability to survive in high salt concentrations. Moreover, the discoloration activity of Azo dyes isolated under freshwater conditions decreased dramatically with increasing environmental salinity. Therefore, decolorization technology for colored wastewater is becoming more and more important [8, 9]. Industrial production of azo dyes and textile finishing processes produce wastewater streams contaminated with azo dyes. In addition, the use of membrane separation technology retains almost all dyes and salts in dye waste treatment, resulting in even higher salinity and chemical oxygen demand (COD) in dye waste discharge. Some azo dyes are difficult to treat with conventional wastewater treatment methods [10]. Several studies have shown that azo dyes are very difficult to biodegrade under aerobic conditions [11–13]. Dye effluents can typically be broken down by conventional treatments such as coagulation with hydrolytic metals, followed by flocculation and filtration. However, this traditional method produces a large amount of sludge that needs further treatment. On the other hand, adsorption to activated carbon is also an effective decolorization method. However, activated carbon can have a very short life depending on the initial dye level and type of dye [14,

15]. Regeneration of activated carbon is inefficient and very expensive. Other treatment methods such as membrane filtration are also effective, but very expensive. The operating costs of secondary wastewater disinfection by membrane filtration were much higher than ozone, UV, or chlorine [16].

Advanced oxidation processes (AOPs) such as  $O_3$ , UV/ $O_3$ , and UV/ $H_2O_2$  are commonly used to destroy organic matter in industrial wastewater and groundwater [17]. Extensive literature in this area has been published. These processes can mineralize most organic pollutants to carbon dioxide and water. In AOP systems, free radicals ( $\cdot OH$ ) are the major species contributing to the decomposition of organic matter in wastewater. In these methods, hydrogen peroxide or ozone is activated with UV light to produce hydroxyl radicals with a higher oxidation potential (2.8 V) than that of hydrogen peroxide (1.78 V) [18]. The general chemical reaction which is given by Eq. (1) shows the mechanism of this phenomenon [19].



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Over the past decade, many studies have been reported successfully using UV/ $H_2O_2$  processes to treat dye effluents. Gül et al. studied the Degradation of Reactive Red 194 and Reactive Yellow 145 azo dyes by  $O_3$  and  $H_2O_2$ /UV processes and showed the removal efficiency of organic contaminants after UV irradiation. Their results showed that the efficiency of the combined ozonation process exhibits faster kinetics than the individual  $O_3$ / $H_2O_2$ /UV processes due to synergistic effects [20]. Izadifard et al investigated the degradation process of sulfolane using activated persulfate with UV and UV/ $O_3$ , this study investigates the main effects and synergies of hybrid AOPs for improving the treatment of wastewater [21]. In a study done by Benami et al in 2021, the efficiency of elimination of cyanide in polluted industrial water was used by synthesizing and coupling manganese oxide (MgO) and persulfate (MgO/ $O_3$ /persulfate process) to destroy and eliminate, according to the findings of the investigation and degradation pathways, it can be concluded that catalyzed ozonation process with MgO nanoparticles and persulfate is a reliable advanced oxidation process for removal of cyanide from industrial wastewater [22]. Recently, there have been ways to increase photocatalytic efficiency, which has significantly degraded environmental and pharmaceutical pollutants. For example, the synthesis of complex Ga ( ) and addition to  $TiO_2$ /rGO nanocomposite have caused the destruction of pharmaceutical pollutants such as acetaminophen (ACT) [23]. And also, the synthesis of magnetically and reusable steel slag/ $TiO_2$  has caused the elimination of bipyridylum herbicides pollutants such as paraquat for controlling the aquatic weed in agricultural water [24]. Shu et al. stated that the UV/ $H_2O_2$  process was C.I. Acid Black 1 can be decolorized with a UV/ $H_2O_2$  process [25]. Azam et al. showed the advanced oxidation treatment using the UV/ $H_2O_2$  process in order to apply on decolorization of the azo dye C.I. Acid Orange 7 (AO7) in an aqueous solution in a batch photoreactor. The effects of the reactor gap size and UV dosage on the decolorization of dye have been investigated. The method of study involved monitoring the rate of dye solution decolorization during irradiation [26]. Dadban Shahamat et al. investigated the effect of  $O_3$ /UV on the Azo red 60 dye and experimentally and theoretically confirmed the removal of the dye from

the textile effluent by the Box-Behnken design [27]. The Combined biological and physicochemical processes were selected by Zoroufchi Benis et al, for the treatment of laundry wastewater. The effluent from the biological process was injected into the UV/O<sub>3</sub> process to completely remove residual COD and surfactants. Microfiltration and ultrafiltration were used to remove any residual suspended solids, Finally, the proposed combination of biological and physicochemical processes could be a promising and highly efficient process for the treatment and reuse of laundry wastewater [28]. Based on the works of literature above, advanced oxidation processes have been proven to be effective treatments for decolorizing azo dyes. This study aimed to determine the feasibility of using O<sub>3</sub>, UV/O<sub>3</sub>, and UV/O<sub>3</sub>/PMS processes in the presence of PMS as alternative treatment techniques for azo dye wastewater in a pilot-scale nuclear reactor. Operational parameters such as O<sub>3</sub> dosage, PMS concentration, Acid Black ATT dye concentration, reaction time, and pH were evaluated to find the optimal conditions for the UV/O<sub>3</sub>/PMS process.

## 2. Materials

Acid Black ATT (AB-ATT) was reached by Alvan Sabet Company (Iran) and used to prepare synthetic samples without any purification. HCl and NaOH were purchased from Merck company (Germany) and were applied for adjusting the pH of the sample. PMS was provided from Potassium peroxymonolufate by Sigma-Aldrich (CAS number 70693-62-8).

### 1–2. Photo-Ozonation persulfate experiments

Assessment of the degradation of Acid Black ATT dye under UV irradiation, UV/O<sub>3</sub>, and UV/O<sub>3</sub>/PMS and effective parameters such as O<sub>3</sub> concentration, pH, initial dye concentration, and PMS dosage were conducted in an experimental setup scheme as shown in Fig. 1. From the figure a photochemical reactor with the internal diameter of 25 mm and height of 400 mm with the volume of 120 mL was used to the photochemical treatment of the dye. At the center of the photochemical reactor, a quartz pipe with a diameter of 15 mm is fixed to protect the UV lamp. Inside the quartz pipe, a Phillips-made low-pressure mercury UV lamp with an irradiation wavelength of 254 nm and power of 9 watts is installed as a UVC source. The photo reactor was equipped with a peristaltic pump model YZ1515X to circulate the synthetic wastewater. An ozone generator (Arda, Ozoneuf, Model COG 40A, France) Was used to in situ providing O<sub>3</sub>. To evaluate the amount of reacted ozone the exhausted O<sub>3</sub> gas from the reactor was trapped in a potassium iodide (KI) solution. Through this study, the concentration of the dye was determined by measuring the absorbance at the maximum characterized wavelength of 618 nm using a DR 5000 spectrophotometer.

### 2–2. Analytical Methods

The concentrations of COD and TOC were determined according to the standard methods [16]. COD values were determined using the colorimetric method by a spectrophotometer (Hach, DR 5000). ADMI (American Dye Manufacturers Institute) method was employed to determine the dye value in the synthetic wastewater and treated effluents [29]. Ammonia was measured based on the Nessler method using Hach reagents [30]. TOC was determined with a TOC analyzer (Liqui TOC II, Elementar, Germany). pH was measured by pH meter (model E520) and the solution pH was adjusted by sodium hydroxide (0.1 M) and Hydrogen Chloride (0.1 M). Measurement of inlet and outlet of ozone to hybrid photo-ozonation persulfate system well done by iodometric method [31]. The removal efficiency of each parameter was found by using the following equation:

$$\%R = \frac{C_i - C_f}{C_i} \times 100$$

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where,  $C_i$  and  $C_f$  are the initial and final concentrations of each parameter before and after the reaction time, respectively.

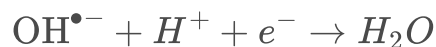
### 3. Result and discussion

Since the aim of this study was the assessment of the effect of PMS on dye degradation by the UV/ozone process, different experiments were conducted to assess the extent of degradation of the dye in the presence of UV light alone, ozone alone, UV/O<sub>3</sub>, and UV/O<sub>3</sub>/PMS then effective parameters such as pH, initial dye concentration, reaction time, and PMS dosage were optimized for hybrid process. For the assessment of the rate of the decolorization, the rate of decolorization, COD removal efficiency, and finally total organic carbon (TOC) were monitored in treated effluents [32].

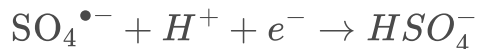
#### 1–3. Effect of pH

pH is one of the most important parameters in AOPs which is due to its effect on the form of substrate, oxidant ionization, formation of reactive oxygen species, redox potential, and treatment efficacy [33]. The pH not only causes radical oxidizing power but also the rate of radical generation and reaction between radicals and organic matter. Moreover, the activity and solubility of the oxidant and active species increase since the production rate of the radicals (SO<sub>4</sub><sup>•-</sup> and HO<sup>•-</sup>) is controlled by solution pH. Since the aim of this study was the assessment of the effect of PMS on dye degradation by UV/O<sub>3</sub> process to determine the optimum pH for the process, dye degradation was studied under different pH conditions and the lowest PMS dosage of 0.4 mM L<sup>-1</sup>. The effect of pH on removal efficiency at different reaction times is shown in Fig. 2 (a). According to Fig. 2 (a), the dye removal efficiency dropped at acidic conditions, while the highest removal efficiency was reached at the alkaline pH value. Figure 2(a)

confirms the highest efficiency at pH of 10. Furthermore, under the acidic condition, high concentrations of  $H^+$  have a detrimental effect on generated free radicals and the degradation rate may be limited.



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In fact, sulfate radicals and hydroxyl radicals are converted to ineffective and neutral species of  $HSO_4^-$  and  $H_2O$  in an acidic atmosphere. At alkaline solution pH, hydroxyl radical can be generated through the reaction of sulfate radicals with  $OH^-$  based on the electron transfer mechanism [34]. Consequently, the sulfate radical proportion is reduced in higher pH values.

with the various pH values, there is no significant change in process efficiency. PMS activation by UV irradiation is a pH-independent process with a quantum yield of 0.52, so the generation of radical oxidative species by PMS precursor results in providing both  $OH^-$  and  $SO_4^{\bullet-}$  and more removal efficiency with no pH dependency which can be obtained from the results of this study [26, 35, 36]. This is definitely an important benefit of this process since it can be used without pH adjustment and the use of additional chemicals to pH adaptation of the wastewater can be avoided. On the other hand, according to the results, the efficiency of the process in alkaline conditions shows a slight increase that could be because of the generation of  $OH^-$  in alkaline conditions by sulfate radicals according to Eq. 1 which increased the efficiency of the process.



The PMS function was monitored during 15 min reaction time at different pH values. Although the increase of pH enhances the molar absorption coefficient ( $\epsilon_{PMS}$ ) [37], the presence of several organics in a real matrix may reduce the absorption of UV by PMS.

In the UV/ $O_3$ /PMS process, sulfate radical and hydroxyl radical can be concurrently present in the solution [21]. It has been shown that the proportion of  $SO_4^{\bullet-}$  and  $HO^{\bullet}$  is a pH-dependent process. Indeed, the reduction or increase of initial pH value would dominate sulfate radicals or hydroxyl radicals in which at low pH, sulfate radicals are the predominant radicals while at high pH, hydroxyl radicals dominate as reactive radicals.

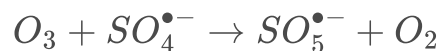
## 2–3. Effect of PMS dosage

Figure 3 shows the effect of different dosages of PMS on AB-ATT dye degradation through UV/ $O_3$ /PMS process. According to the figure, the photocatalytic degradation efficiency was 100% at the optimum

dosage of PMS ( $0.4 \text{ mM L}^{-1}$ ). The degradation efficiency of AB-ATT dye increased linearly from 43.28–100% with increasing PMS dosage from 1 to 5 min. Increased generation of activated radicals, i.e.,  $\cdot\text{OH}$  and  $\text{SO}_4^{\cdot-}$  because of enhanced PMS activation by  $\text{O}_3$  and UV led to a higher degradation of AB-ATT dye. According to the results with the increase of PMS concentration to  $0.4 \text{ mM L}^{-1}$ , the rate of degradation increased and COD removal efficiency reached 100% after 5 minutes. It was found that the rate of degradation decreased with increasing PMS concentration to amounts more than  $0.4 \text{ mM L}^{-1}$ . The reason could be the inactivation of Sulfate radicals due to the reaction of excess sulfate radicals with i) each other, ii) hydroxyl radicals, and iii) extra PMS. Nevertheless, Izadifard et al. [25] reported the removal of sulfolane between  $1$  to  $3 \text{ g L}^{-1}$  by the combination UV,  $\text{O}_3$ , and PDS. It is also reported that  $2 \text{ g L}^{-1}$  of PDS as an optimal value has been required. Moussavi et al. [38] reported that increasing the sulfate radical precursor leads to the enhancement of process performance until  $200 \text{ mg L}^{-1}$ . However, a further increase in the initial concentration of PMS or PDS lowers the removal efficiency. The above points lead us to a self-quenching effect in a reactor containing  $\cdot\text{OH}$  and  $\text{SO}_4^{\cdot-}$  due to higher concentration of the source of sulfate radicals, while this phenomenon is negligible under lower concentrations of PMS or PDS [39, 40].

### 3–3. Effect of Ozone (O) concentration

To assess the extent of dye degradation by ozonation the operating parameters were set at the initial AB-ATT concentration of  $20 \text{ mg L}^{-1}$  and pH 10 and then different concentrations of 10, 15, 20, and  $25 \text{ mg min}^{-1}$  ozone were injected into the reactor and the rate of dye decay and COD removal efficiency were evaluated. According to the results in Fig. 4, the highest dye decay (70%) and COD removal efficiency (47%) were obtained using  $\text{O}_3/\text{UV}/\text{PMS}$  after 40 min of treatment. It means not only ozonation alone can decay the AB-ATT dye in the solution, but also the rate of COD removal by this process is insignificant. The concentration of the hydroxyl radicals increases with an increase in the ozone dosage. This pH-independent is due to the fact that in the early stage of the ozonation, chromophore groups decompose according to ozone oxidation. In contrast, intermediate products of oxidation need more time to degrade [26, 41]. As a result, more free radicals can be generated after ozone contact with PMS in the solution. Despite the maximum decolorization at  $25 \text{ mg/min}$ , the optimum ozone concentration was selected as  $20 \text{ mg min}^{-1}$  without significant sacrifice. That may affect the amount of effective free radicals and act as scavengers [42].



## 4 – 3. Dye photodegradation through UV irradiation

For the investigation of the rate of the decolorization by UV irradiation the synthetic solution with the concentration  $20 \text{ mg L}^{-1}$  of Acid Black ATT and pH 10 was injected into the reactor and the rate of dye decay and COD removal efficiency were obtained by sample withdrawal in different time intervals. The reaction time was counted since the UV lamp turned up. Figure 5 shows the results of the photodegradation of AB-ATT. According to the results after 40 min of UV irradiation, only 64% removal efficiency was obtained and COD was insignificant. These results imply that photodegradation of dye molecules only breaks their chromophore bonds to disappear the dye but does not affect the COD removal significantly [43]. It also can be a result of the reduction of irradiation intensity in AB-ATT solutions.

## 5 – 3. Integrated UV and O process

Figure 6 demonstrated the results of the decolorization and COD removal efficiency through the UV and  $\text{O}_3$  processes. The observed acceleration in dye and COD removal is due to the increased  $\bullet\text{OH}$  generation as a result of  $\text{O}_3$  decomposition by UV to  $\text{OH}\bullet$  precursors. Based on the various combinations of processes and results, the accelerations observed with simultaneous application of ozonation and UV irradiation are the result of increased mass transport of ozone and increased OH production (due to UV decomposition of  $\text{O}_3$  and  $\text{H}_2\text{O}_2$ ), respectively. The degradation efficiency of naproxen by the UV oxidation process was investigated and the removal efficiency of naproxen was 84%, confirming that the integrated UV process is very effective in the degradation of naproxen [44]. The  $\text{Mn}_2\text{O}_3/\text{Fe}_2\text{O}_3$  @ monopersulfate (MPS) was synthesized easily and its activation process on the degradation of ciprofloxacin (CIP) was investigated. The MPS could remove 92% of CIP under optimized conditions [45]. Cuerda-Correa et al. reviewed advanced oxidation processes for removing antibiotics with different oxidation processes [46]. Considerable synergy was observed when reactions were performed via an integrated system. Qin et al. The UV/ $\text{O}_3$ /PDS method was found to be superior to other methods in degrading clofibric acid (CA). They reported that the integrated UV/ $\text{O}_3$ /PDS process increased the CA destruction rate from 1.7 to 1.9 [47].

## 6 – 3. Effect of the time on UV/O/PMS process

Reaction time is one of the important parameters in the water and wastewater treatment process so less reaction time results in lower investment costs. A longer reaction time results in the generation of radical species and improves the degradation of intermediate products from pollutants. Based on the results in Fig. 7, the UV/ $\text{O}_3$ /PMS process is able to degrade  $20 \text{ mg L}^{-1}$  of AB-ATT dye in 5 minutes under optimum conditions. However, at this time the rate of COD removal reached 69% (Fig. 7). The photolytic process produces fewer hydroxyl radicals, resulting in lower decomposition power. Therefore, this dye exhibited high resistance to UV degradation. However, ozone treatment resulted in 94% and 53% removal of dye discoloration and TOC, respectively, at the end of the 1-hour reaction time. For the  $\text{O}_3$ /UV process, dye discoloration and TOC removal at the end of reaction time were 100% and 74%, respectively. The  $\text{O}_3$ /UV system enhanced the decomposition of ozone molecules and produced more free radicals [48]. Therefore,



the highest removal efficiency occurs with photo-oxidation ( $O_3$ /UV) processes, followed by  $O_3$  and photolysis (UV) systems. The results also showed that the  $O_3$  and UV processes were synergistic with each other, reaching a maximum at a reaction time of 30 min, equivalent to 8%. Similar studies have also reported a synergistic effect between ozone and other free radical generators [49]. In a study by Castro et al. For the removal of azo dyes from wastewater, the efficiency of AOPs has been compared and compared to other AOPs such as Fenton and UV, the ozonation process removes higher organic pollutant loads in a shorter time. But the TOC-related elimination rate was not high. Additionally, using ozonation alone increases operating costs. Satisfactory results were obtained by combining ozonation with a biological aerobic system, which not only improved the degradability of organic materials but also reduced the cost of wastewater treatment [50].

## **7 – 3. Effect of initial AB-ATT concentration**

According to Table 1, the removal efficiency of dye degradation decreased with the increase of the initial concentration of AB-ATT. The result shows the constant concentration of oxidant with the increase of dye concentration few molecules react with oxidant. On the other hand, with increasing dye concentration dispersion of UV light decreased, and consequently, fewer radical species are generated, and also the rate of the photolysis of the dye decreased. It was assumed that the number of active radicals produced in the combination of UV,  $O_3$ , and PMS was constant as the  $O_3$ , PMS dosage, and pH were controlled at the optimum level in the reactor. Thus, the ratio of active radicals to AB-ATT decreased at higher initial concentrations in the present process. The findings revealed that the combined UV/ $O_3$ /PMS process employed an efficient operation for eliminating wide concentrations of organic pollutants due to its superlative oxidation nature. In the dye ozonation process, a portion of the soluble ozone is used in the reaction to generate active radicals that are highly capable of degrading the dye into mineral and hydroxyl intermediates [52]. Since the dye is effectively removed in the ozonation process, the amount of dye used in the process is an important parameter that contributes to the efficiency of the process. Thus, the initial concentration of contaminants plays an important role in the efficiency of oxidation and its removal by his AOP. Therefore, the removal rate is directly related to the amount of ozone, the production of hydroxyl radicals, and their interactions with the number of contaminants [52]. Mehdizadeh et al. Results obtained by evaluating the effect of dye concentration on the ozonation process show that the highest dye discoloration (98%) and TOC removal (53%) was achieved at a concentration of 50 mg/L at the end of the reaction time. Increasing the dye concentration to 300 mg/L reduced the color change and TOC efficiency to 68% and 19% at the end of the reaction time (60 min). AOP produces only a certain number of active radicals under similar conditions. These types of processes are capable of oxidizing and removing a certain number of organic compounds. Therefore, it is clear that increasing the concentration of contaminants decreases cleaning efficiency. Because the number of hydroxyl radicals produced is less than the number of dye molecules, these radicals are not enough to decompose all contaminant molecules [53].

Table 1

The results of Acid Black concentration (pH:10,  $O_3$ :20 mg min<sup>-1</sup>, PMS: 0.4 mM/L)

Concentration (mg L <sup>-1</sup> )	Time (S)					
	30	1	2.5	5	7.5	10
10	52.36	79.06	100			
20	25.42	43.28	82.96	100		
30	16.92	32.92	61.44	88.15	95.25	100
40	9.98	20.16	45.59	66.13	75.41	86.1

### 8 – 3. Effect of the presence of anions and radical scavengers

Considering that different anions can affect advanced oxidation processes and, in some cases, it reduces removal efficiency. Therefore, in this study, the effect of the presence of different anions was investigated. For this purpose, sample water was used as a sample that contains almost all anions. In order to determine the dominant oxidizing species in the UV/ $O_3$ /PMS process, phenol and nitrobenzene radical scavengers were used with a concentration of 2000 mg L<sup>-1</sup>, and a severe drop in removal efficiency was observed under these conditions. Figure 8 shows the results of this part of the study. Considering that anions are present in all water samples, therefore they can be effective in the performance of advanced oxidation processes and enter into chemical reactions. Based on the results, there is no significant difference in the removal efficiencies when anions are present and when there are no anions in the water sample. This shows the stable and appropriate performance of the UV/ $O_3$ /PMS process in the decomposition of ATT acid black dye under different conditions. Anions such as nitrate in water can lead to a decrease in process efficiency. Such anions by absorbing the emitted spectrum can reduce the percentage of PMS activation with UV radiation and ultimately lead to a decrease in process efficiency [54]. Radical scavenging tests were used to prove the existence of radical oxidizing species such as sulfate and hydroxyl radicals. Radical scavengers used in this study are phenol and nitrobenzene. The presence of these compounds in the UV/ $O_3$ /PMS process led to a significant drop in AB-ATT removal efficiency. This indicates the presence of radical species in the dye oxidation process. Table 2 shows the reaction rate constant of hydroxyl and sulfate radicals with phenol and nitrobenzene. Based on the efficiency of AB-ATT dye removal and the rate constant of the reactions presented, it is possible to identify the radical species present in the AOPs process [55]. According to the obtained results, the highest decrease in dye removal efficiency was obtained in the presence of phenol. The reaction rate constant of phenol with sulfate radical is more than 1000 times the reaction rate of nitrobenzene with sulfate radical. On the other hand, the rate of reactions of both scavenging radicals with hydroxyl radicals is almost equal. Also, considering the speed constants mentioned, it can be

concluded that phenol mainly deactivates the hydroxyl radical, while nitrobenzene deactivates the sulfate radical in addition to the hydroxyl radical. Therefore, decreasing removal efficiency in the presence of phenol is greater than nitrobenzene, it can be concluded that in addition to the hydroxyl radical, sulfate radical is also present in the environment. The results demonstrate phenol leads to a drop in the efficiency of AB-ATT removal by about 39%, while nitrobenzene has a drop in efficiency of about 53%. Therefore, it can be concluded both hydroxyl and sulfate radical oxidizers are present in UV/O<sub>3</sub>/PMS process. Mousavi et al. used VUV radiation to activate persulfate, and in this study, the co-production of sulfate and hydroxyl radicals has been proven by scavenging radical tests [38].

Table 2

Reaction rate constant of various radical scavengers with hydroxyl and sulfate radicals

Scavengers	$\text{SO}_4^{\bullet} \text{ (g L}^{-1}\text{)}$	$\text{HO}^{\bullet} \text{ (g L}^{-1}\text{)}$
Phenol	$8.8 \times 10^9$	$6.6 \times 10^9$
Nitrobenzene	$10^6$	$3.0\text{-}3.9 \times 10^9$

### 9 – 3. Mineralization of AB-ATT dye in the UV/O/PMS process

Mineralization of organic compounds indicates the end of the oxidation path of an organic compound. Therefore, in this study, in order to determine the rate of mineralization in the UV/O<sub>3</sub>/PMS process, residual TOC was measured at different times. Figure 9 shows the mineralization rate of 20 mg L<sup>-1</sup> dye at various times. Results of mineralization rate evaluation of AB-ATT with UV, O<sub>3</sub>, UV/O<sub>3</sub>, and UV/O<sub>3</sub>/PMS processes show that 20 mg L<sup>-1</sup> of AB-ATT dye is completely removed in 5 minutes with the UV/O<sub>3</sub>/PMS process, while at the moment of removal of all the dye, only 53% of the sample has been mineralized. In addition to removal dye, have achieved 7.5, 21.4, and 36.2% mineralization, respectively. In the advanced oxidation process, the desired organic compound is first decomposed, and this decomposition may occur by breaking a bond of this compound, and another organic compound is produced, and even in some cases, this secondary compound can be far more toxic than the compound. If the process continues and there are oxidizing species, this secondary compound can also be decomposed and finally turn into CO<sub>2</sub> and H<sub>2</sub>O, in which case complete mineralization occurs. This shows that secondary organic products are also produced in this process, which leads to the observation of TOC in the output samples. In many advanced oxidation studies, mineralization of the sample along with the complete removal of the pollutant from the water environment was not done and only a part of the pollutant was mineralized [56, 57].

## 10 – 3. Kinetics of AB-ATT dye decomposition

In order to determine the rate constant of the dye decomposition reaction in the UV/O<sub>3</sub>/PMS process, pseudo-first-order kinetics was used [58]. Decomposition kinetics in ozonation and UV radiation processes, as well as dye decomposition kinetics in the UV/O<sub>3</sub> process, were evaluated, and the results are shown in Fig. 10. As it is clear in this graph, the R<sup>2</sup> coefficient for UV/O<sub>3</sub>/PMS was obtained at 0.98, which indicates that the decomposition of ATT black acid dye follows the first-order kinetics. Also, the reaction rate constant is equal to 0.795 min<sup>-1</sup> based on the equation of the fitted line and indicates that the decomposition of ATT acid black dye follows this kinetic model. Also, the rate constant obtained from this kinetic model shows that the decomposition reaction of 20 mg L<sup>-1</sup> dye in the UV/O<sub>3</sub>/PMS process with a rate constant of 0.795 min<sup>-1</sup> has a relatively higher rate compared to similar studies. Another point regarding the rate constant of reactions is the partial decrease of the rate constant with the increase in pollutant concentration, this can justify the functionality of the UV/O<sub>3</sub>/PMS process in the decomposition of the dye easily in high dye concentrations economically.

## 4. Conclusion

The degradation of AB-ATT via the UV/O<sub>3</sub>/PMS process under the conditions of PMS dosage: 0.4 mM L<sup>-1</sup>, O<sub>3</sub> dosage: 20 mg min<sup>-1</sup>, pH: 10, and T: 5 min were comprehensively investigated. The UV/O<sub>3</sub>/PMS process indicated complete degradation of AB-ATT in 40 min. The UV/O<sub>3</sub>/PMS caused significant TOC and COD removal up to 53% and 69.56%, respectively. Primary active species that contributed to the AB-ATT degradation were the <sup>•</sup>OH and SO<sub>4</sub><sup>-•</sup>. Additionally, various radical scavengers such as Phenol and nitrobenzene proved that <sup>•</sup>OH and SO<sub>4</sub><sup>-•</sup> species were the main oxidizing radicals for AB-ATT removal. The mineralization results illustrated that hydroxylation and decarboxylation were the main pathways in AB-ATT degradation in the UV/O<sub>3</sub>/PMS reactor. Besides, the decomposition of AB-ATT under UV/O<sub>3</sub>/PMS radiation was best fitted with pseudo-first kinetic.

## Declarations

The authors declare no potential conflict of interest.

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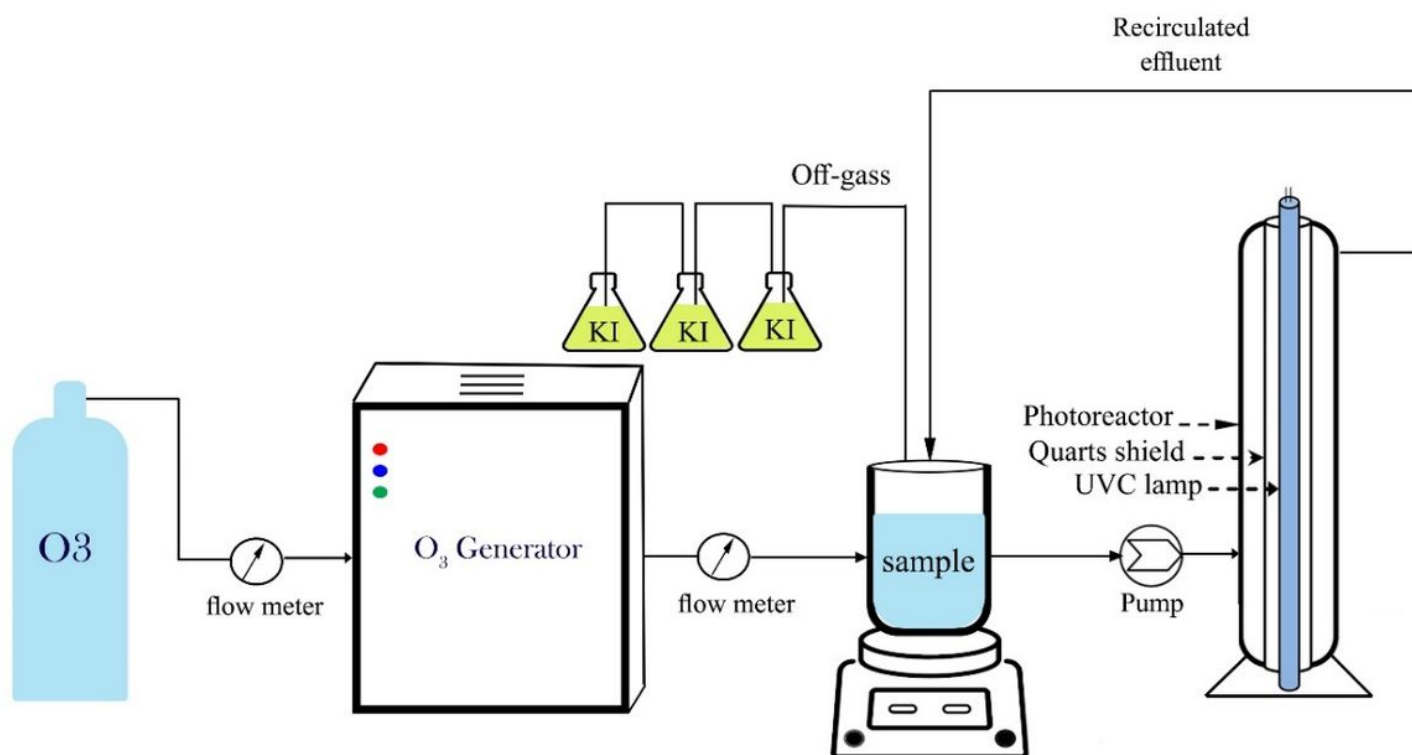
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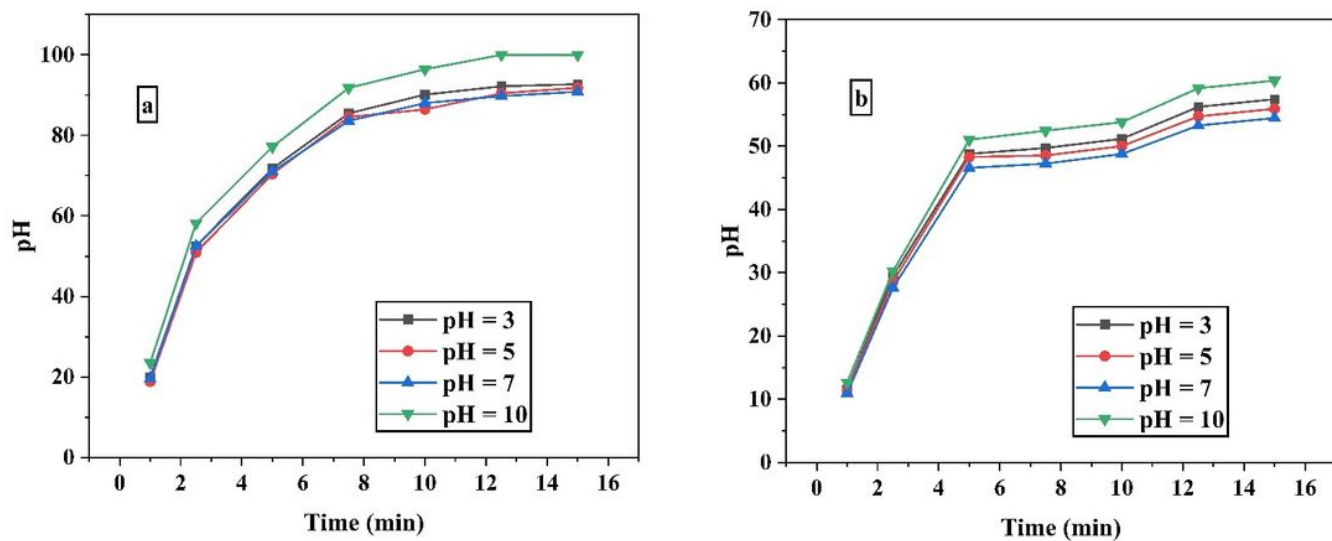
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## Figures



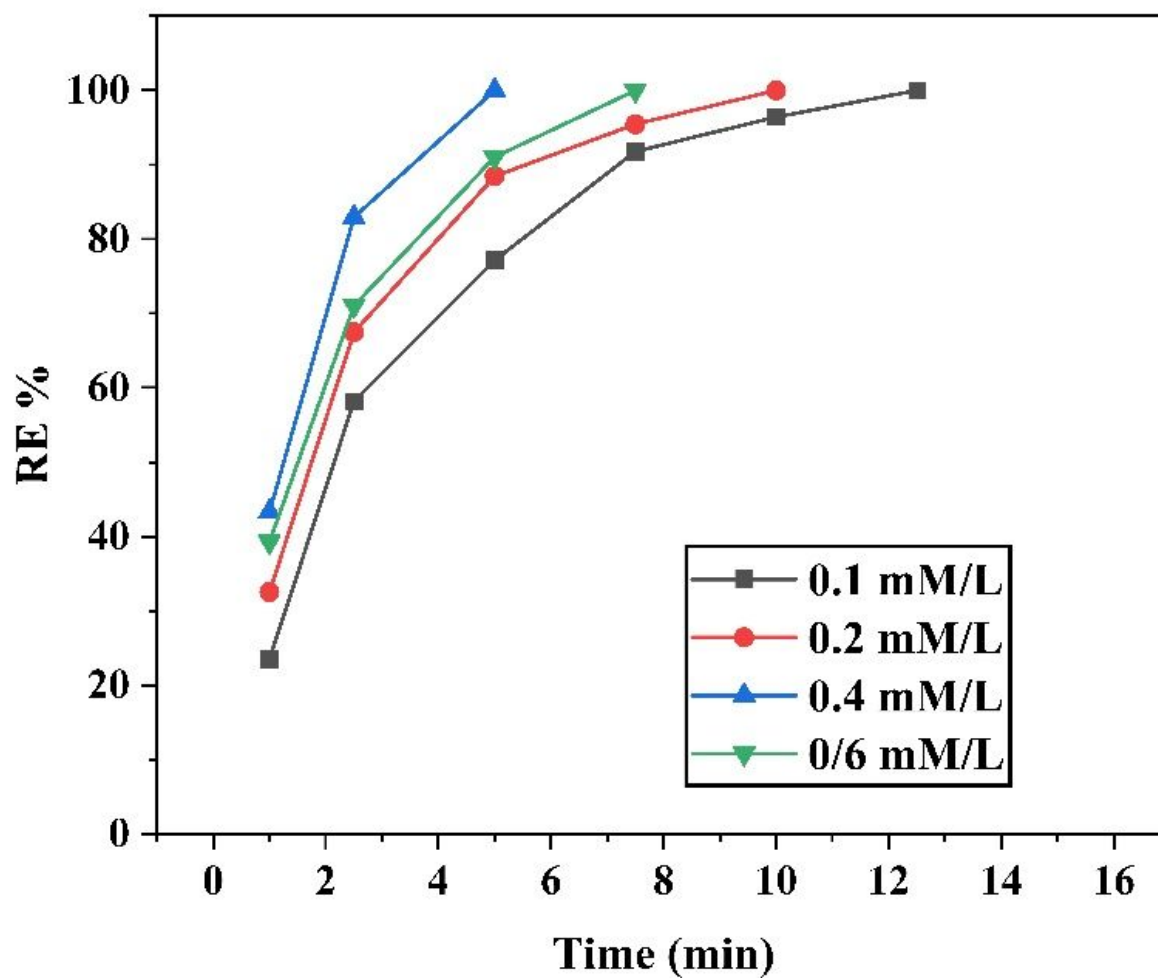
**Figure 1**

Schematic Photochemical Reactor of UV/O<sub>3</sub>/PMS



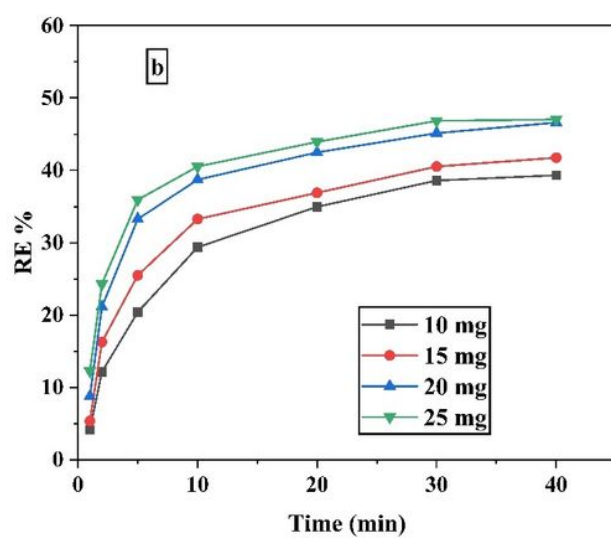
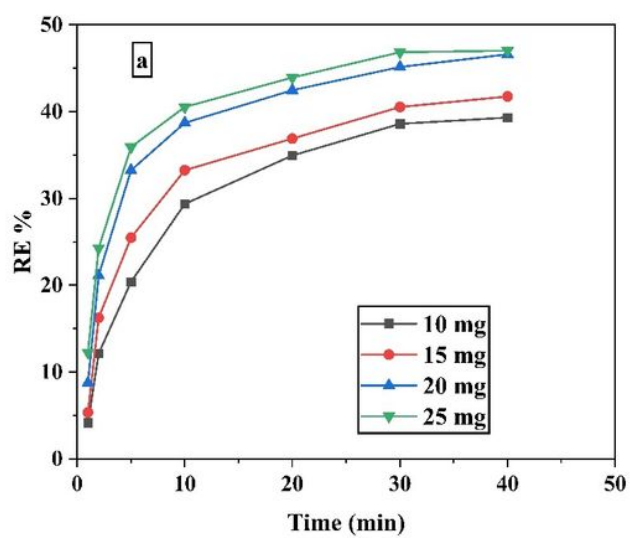
**Figure 2**

The rate of dye decay (a) and COD removal (b) in different pH by UV/O<sub>3</sub>/PMS Initial dye concentration 20 mg L<sup>-1</sup>, O<sub>3</sub>:20 mg min<sup>-1</sup>, PMS: 0.4 mM L<sup>-1</sup>



**Figure 3**

Rate of decolorization under different PMS concentrations through UV/O<sub>3</sub>/PMS Initial dye concentration: 20 mg L<sup>-1</sup>, pH: 10, O<sub>3</sub>: 20 mg min<sup>-1</sup>



**Figure 4**

The rate of AB-ATT dye decay (a) and COD removal (b) by  $O_3$  process Initial dye concentration:  $20 \text{ mg L}^{-1}$ , pH:10

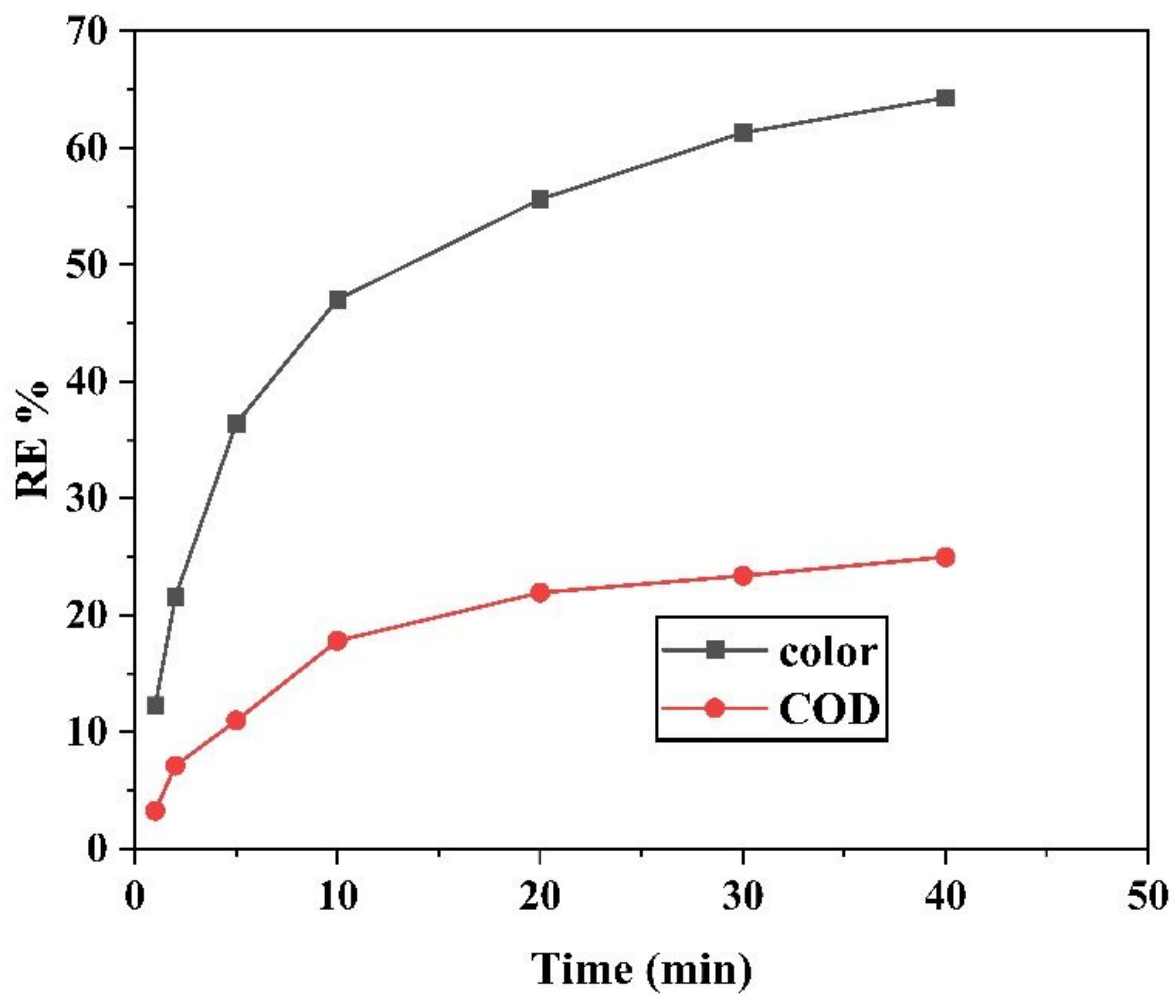
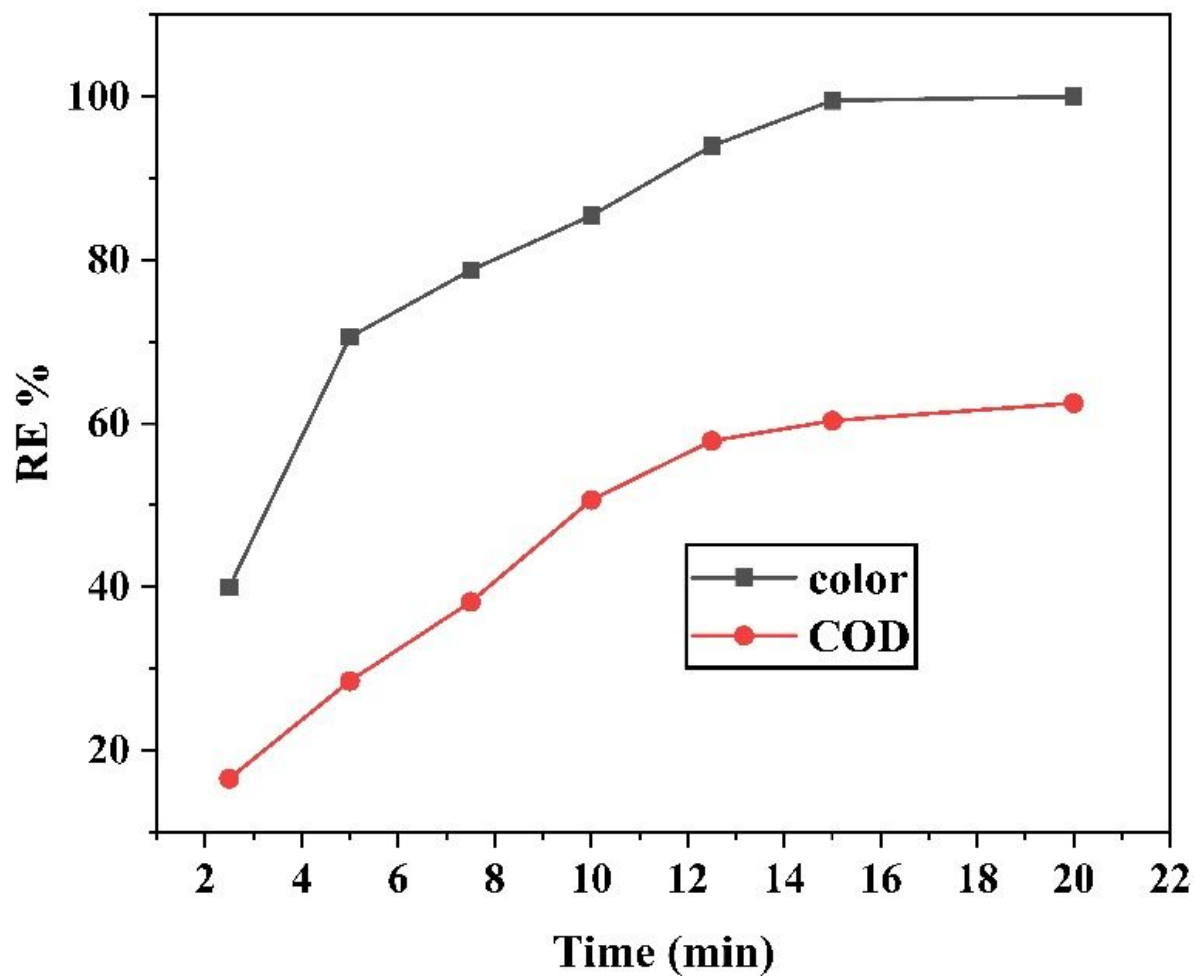


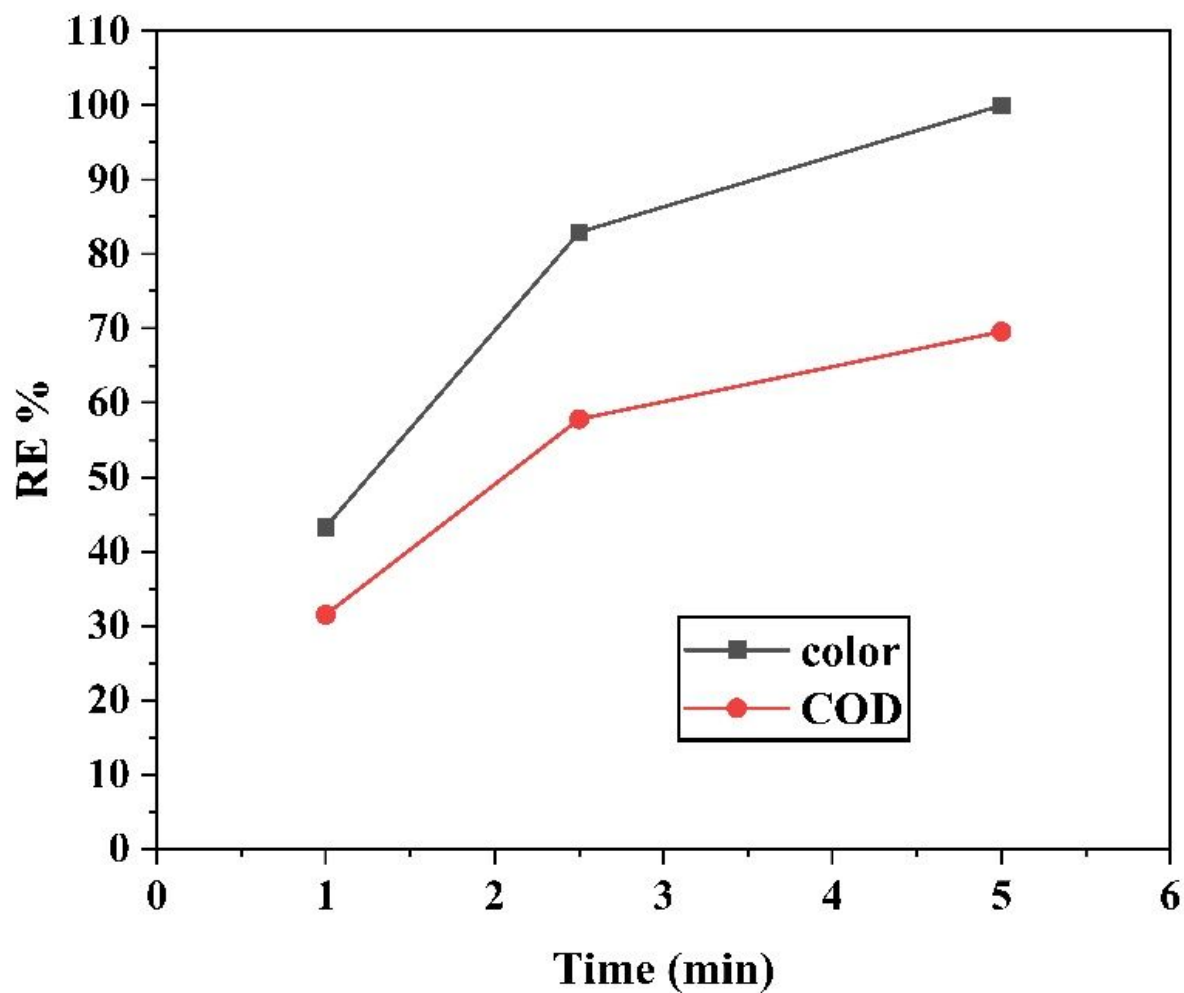
Figure 5

The rate of dye decay and COD removal by UV Irradiation. Initial dye concentration  $20 \text{ mg L}^{-1}$ , pH:10



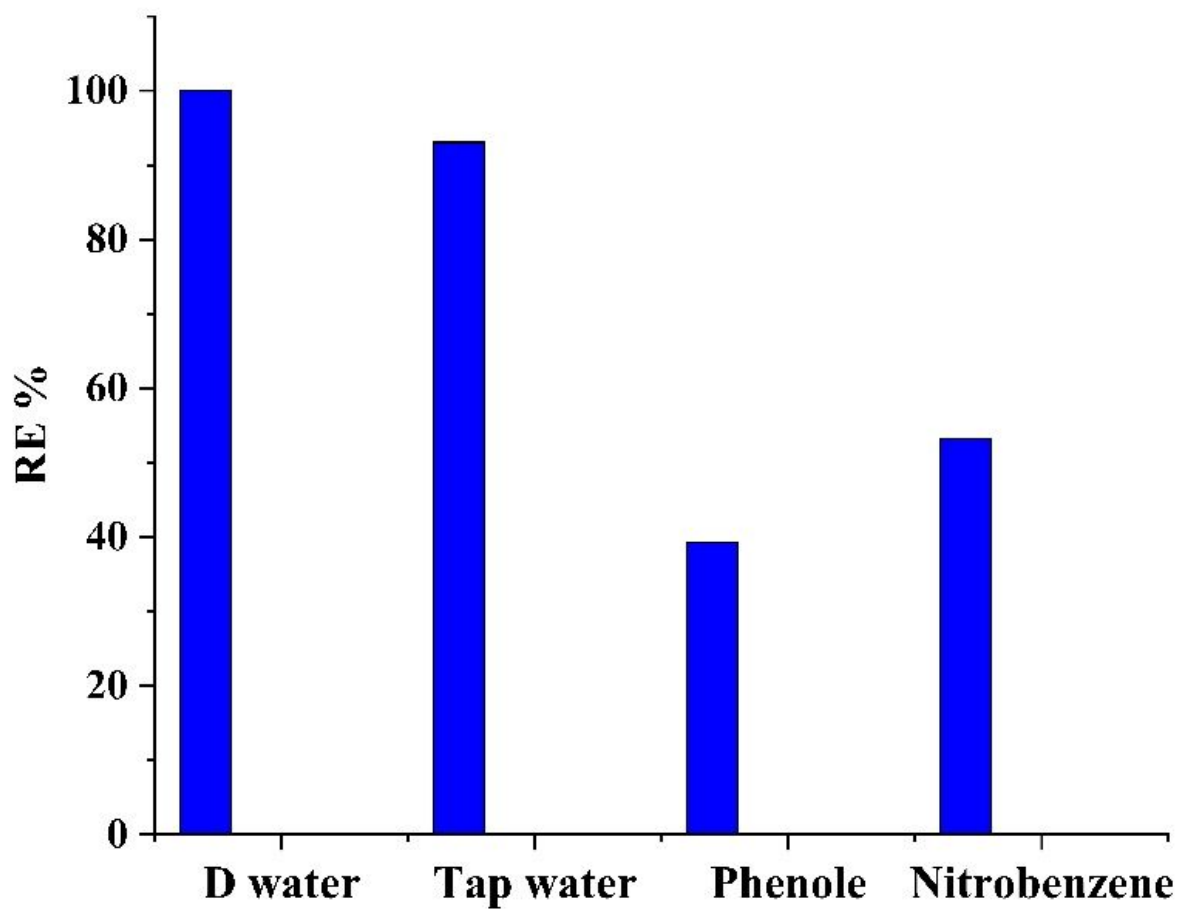
**Figure 6**

The rate of dye decay and COD removal through UV/O<sub>3</sub> Initial dye concentration: 20 mg L<sup>-1</sup>, O<sub>3</sub>: 20 mg min<sup>-1</sup>, pH:10



**Figure 7**

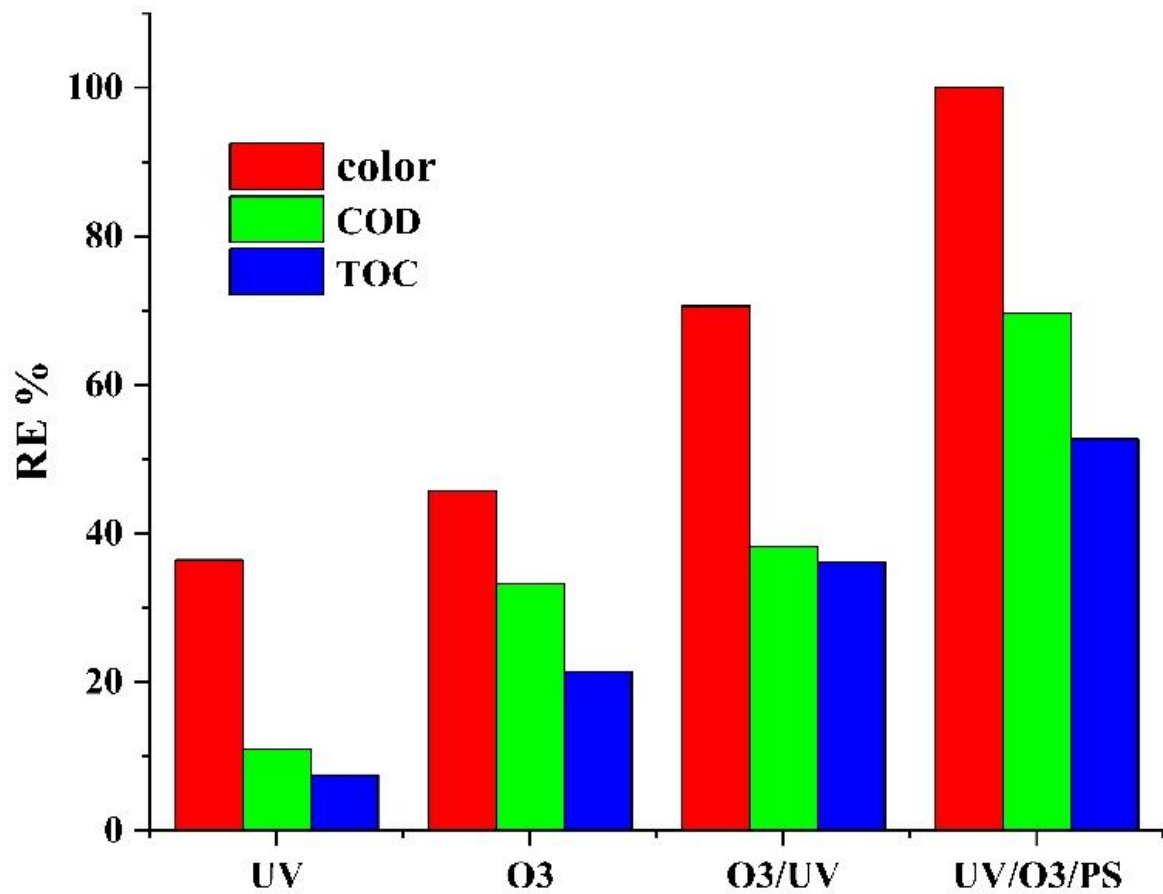
The effect of the time of the reaction efficiency of the UV/O<sub>3</sub>/PMS process Initial dye concentration:20 mg L<sup>-1</sup>, pH:10, O<sub>3</sub>:20 mg min<sup>-1</sup>, PMS: 0.4 mM L<sup>-1</sup>



**Figure 8**

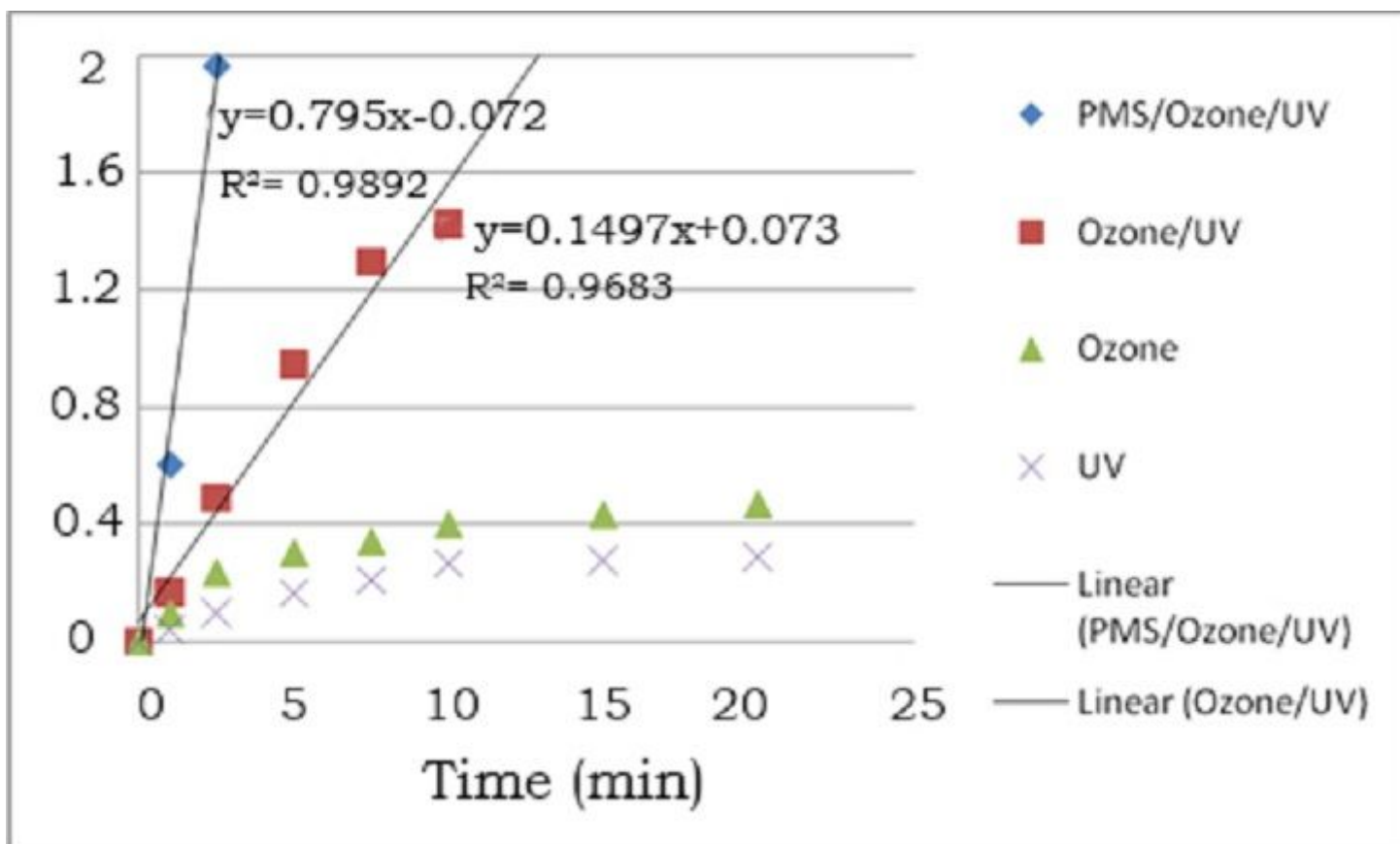
Investigating the effect of radical scavengers on the performance of the UV/O<sub>3</sub>/PMS process dye concentration: 20 mg L<sup>-1</sup>, pH: 10, O<sub>3</sub>: 20 mg min<sup>-1</sup>, time:5 min, PMS: 0.4 mM L<sup>-1</sup>, Scavengers: 2 g L<sup>-1</sup>





**Figure 9**

Comparison of removal efficiency and mineralization of AB-ATT dye in UV/O<sub>3</sub>/, UV/O<sub>3</sub>, UV, and O<sub>3</sub> PMS processes



**Figure 10**

Investigating the kinetics of ATT black acid dye decomposition in UV/O<sub>3</sub>/, UV/O<sub>3</sub>, UV, and O<sub>3</sub>/PMS processes