



UV irradiation catalyzed persulfate advanced oxidation process for decolorization of Acid Blue 113 wastewater

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ABSTRACT

A UV/persulfate advanced oxidation process was proposed to decolorize and mineralize a synthesized Acid Blue 113 (AB113) dyeing wastewater. Various operating parameters which affected the removal efficiencies of dye and total organic carbon (TOC) such as reaction time, persulfate dosage, initial dye concentration, initial pH, and UV intensity were studied. Results presented effective removal of AB113 azo dye by UV/persulfate process based on both color and TOC indicators. However, reaction with either UV irradiation alone or persulfate alone can reach low-removal efficiency of AB113. In UV/persulfate process, the higher the persulfate dosage applied, the higher the color and TOC removal efficiencies can be obtained up to 6.3 mM persulfate concentration. The color removal efficiency and reaction rate constant decreased with increase in the initial dye concentration. The initial pH was shown no significant effect on removal efficiency. UV intensity affected AB113 removal efficiency significantly when the persulfate dosage was as low as 1.05 mM. Results of UV-Visible spectrophotometry indicated the diminishing of chromophore group of AB113 at 566 nm and naphthalene rings at 272 nm.

Keywords: Persulfate; UV; Decolorization; Mineralization; Azo dye

1. Introduction

In the last couple of decades, treatment technologies dealing with effluents from dyeing-related industries draw much attention from research communities and industries [1–4]. According to their refractory to traditional treatment technologies as well as pollution properties to the discharged water bodies, wastewater effluents from dyeing-related textile industries receive

much challenging tasks from public awareness and government enforcements [5]. After applying to the dyeing processes, certain amount of residual dyestuff was discharged with wastewater to the traditional treatment facility utilizing coagulation and activated sludge processes. In this case, coagulation can hardly remove color caused by dyestuff but produces sludge needed further treatment. On the other hand, activated sludge process suffered by complicate property of dyestuff and its toxicity which causes recalcitrant to

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the micro-organisms in the activated sludge process [6]. To solve the serious color problem and meet the stringent color discharge standard, the operators from treatment facilities apply perchlorate to decolorize this kind of trouble wastewater. However, using perchlorate to the dyeing wastewater causes the formation of carcinogenic chlorinated organic compounds [5]. In this category of dyeing industrial wastewater, azo dyes with nitrogen double bond ($-N=N-$) are the largest class of commercial dyestuffs used in the textile industries. Therefore, many studies reported their efforts on investigating various technologies for decomposition of azo dye compounds [7–16]. Since the decolorization of dyestuffs is a challenging task for research communities, textile dyeing industries should pursue more efficient technique to be the pre-treatment or polishing processes to dealing with this type of highly colored and complicated wastewater.

Advanced oxidation processes (AOPs) employ UV irradiation, ozone, hydrogen peroxide, Fenton reagents, and TiO_2 and ZnO photocatalysts combinations to produce hydroxyl radicals for non-selectively degradation of recalcitrant organic compounds. The common point of these AOPs is the production of hydroxyl radicals which is most powerful oxidant applied in the pollutant treatment. Thus, AOPs have the potential ability to mineralize most of the organic contaminants into carbon dioxide and water. AOPs such as UV/H_2O_2 [7–9], UV/O_3 [10,11], and Fenton reaction [12,13] were reported to decolorize and mineralize azo dye wastewater successfully. Furthermore, photocatalytic processes utilizing TiO_2 and ZnO catalysts with UV irradiation were also reported to be effective in decolonizing azo dye wastewater [14–16]. Recently, alternative AOPs based on the formation of sulfate radicals ($SO_4^{\cdot-}$) were also developed for the degradation of organic pollutant. Firstly, persulfate was used as oxidant for *in situ* chemical oxidation (ISCO) technology to remedy groundwater and soil contaminants. Through thermal or chemical activation, persulfate can be transformed into sulfate radicals with more powerful oxidation potential to degrade refractory pollutants in groundwater or soil [17–20]. With success of ISCO soil and groundwater remediation, sulfate radical-based AOPs were emerging applied to the wastewater treatment purpose. Persulfate anion can be UV photo-activated to form sulfate radicals as follows:



The sulfate radicals are relatively more stable than hydroxyl radicals in aqueous [21]. Although,

persulfate is an oxidant with high-redox potential of 2.01 V, but it is less reactive to the pollutants at room temperature [22]. When activated by UV, ultrasound, thermal, transition metal anion, and zero-valent iron, persulfate will further produce sulfate radicals with even higher redox potential [23–26]. Sulfate radical and hydroxyl radical are both strong oxidants with similar oxidation power presented by redox potential of 2.6 and 2.8 V, respectively [22,27].

In this study, the degradation of azo dye C.I. Acid Blue 113 (AB113) using a batch homogeneous photocatalytic reactor in which the UV 254 irradiation on persulfate to produce sulfate radicals was investigated. Operating parameters such as persulfate dosage, initial dye concentration, initial pH, and UV intensity that may affect the degree of the dye degradation were studied. Changes in color intensity, total organic carbon (TOC), pH, and oxidation reduction potential (ORP) were monitored.

2. Materials and methods

2.1. Materials and apparatus

A dis-azo dye, C.I. AB113 was selected as target compound for this UV/persulfate AOP decolorization study. AB113 ($C_{32}H_{21}N_5Na_2O_6S_2$, C.I. 26360, characterized wavelength at 566 nm, molecular weight of $681.66 \text{ g mol}^{-1}$, 50% purity) was purchased from Sigma-Aldrich, Inc. and used as received without further purification. The chemical structure of AB113 can be obtained from our previous study [7]. Reagent grade Sodium Persulfate with 550 g l^{-1} solubility was purchased from Merck, Inc.

A Thin Gap Annular Photooxidation Reactor (TGAPR) utilized a low-pressure mercury arc UV lamp (Sterilight made, wavelength 253.7 nm, input power of 14 W) was conducted in the experiments. The photooxidation reactor setup was also presented in our previous work [7]. In this reactor, UV lamp was protected by central inner quartz tube and wastewater with AB113 was pumped through the thin gap between quartz tube and outer stainless shell. Fig. 1 is a schematic drawing of the TGAPR employed in this work. The outside diameter of the quartz tube was 2.2 cm. The inside diameter of stainless shell was designed to be 3.20 cm. Thus, the annular gap size was 0.5 cm. While the dye wastewater flowed through the reactor from its inlet to outlet, the effluent was then recirculated back to the stirred storage tank, and then pumped back to the reactor continuously. The UV light intensity of 14 W yielded a surface light energy of 2.1 mW cm^{-2} measured at the outer surface of quartz tube. In each experimental run, 1,000 ml dye

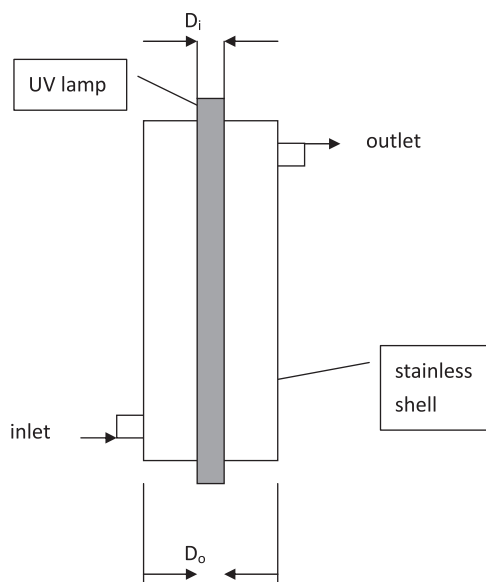


Fig. 1. The schematic drawing of the annular photooxidation reactor employed.

solution was introduced to the TGAPR and recirculated. The temperature was monitored to be slightly increased around room temperature (21.4–25.8°C) which can influence the reaction kinetics insignificantly.

2.2. Experimental procedure and analysis

AB113 azo dye solution at various concentrations was prepared with deionized water. The experimental variables studied included reaction time, persulfate dosage, initial dye concentration, initial pH, and UV intensity. At a predetermined reaction time, an aliquot of the solution was withdrawn and analyzed for residual dye concentration, TOC, and color intensity. In the case of pH effect study, the experiments were conducted by adjusting the initial pH value of 5.2 to the range of 2–10 using HCl and/or NaOH with initial AB113 concentration of 50 mg l⁻¹ and persulfate dosage 6.3 mM. Dye concentration was determined by measuring the absorbance at characterized wavelength of 566 nm using Hitachi U-2000 spectrophotometer. Color intensity was determined based on the American Dye Manufacturers Institute standard color measurement by applying the Adams–Nickerson color difference formula following method 2120E of the Standard Methods. The pH and redox potential (ORP) were monitored by a Eutech PH5500 dual channel pH/ion meter with specific probes. TOC was obtained with a Total Organic Carbon Analyzer from O.I. Analytical Aurora, model 1030.

3. Results and discussion

3.1. Synergic effect of combining UV 254 irradiation and persulfate oxidant

The AB113 oxidative removal was first compared for three degradation processes, i.e. persulfate alone, UV/persulfate, and UV irradiation alone, at the initial AB113 concentration of 50 mg l⁻¹, persulfate dosage of 4.2 mM and UV light intensity of 14 W l⁻¹ at wavelength of 254 nm in 120 min of reaction in the TGAPR. Fig. 2(a) shows results of AB113 (color) removal by various systems. Similar photooxidation of AB113 azo dye by UV/H₂O₂ was presented very effective as shown in our previous study [7]. In this work, the results indicated that the system of persulfate alone was able to remove AB113 in a moderate level, in this case about 65% AB113 removal in 120 min. UV irradiation alone was less effective than persulfate alone process to remove only 50.3% AB113. On the other hand, AOP utilizing both persulfate and UV 254 irradiation was shown to remove AB113 effectively with almost 100% removal, in 120 min. It was also observed that the pH changed towards acidic conditions during the persulfate and UV/persulfate oxidation (data not shown). The pH value of UV/persulfate process changed significantly from initially pH 5.0 to pH 2.2 at the end of the decolorization reaction. This was due to the formation of organic acid by-products and sulfate ions. This was expected as persulfate is a known strong oxidant that upon irradiation with UV light can generate sulfate radicals, stronger oxidation agents that can oxidize a wide group of organic compounds non-specifically. As for persulfate alone process, the pH change was less in comparison to UV/persulfate process, according to less powerful reaction and less organic acid by-products formation. ORP is an important parameter which should be monitored during AOP reaction. Higher solution ORP can be obtained for UV/persulfate process than that of persulfate alone process as shown in Fig. 2(b). The ORP of a solution is a measure of the oxidizing or reduction power of the solution. In an oxidizing environment with presence of an oxidizing reagent, a higher ORP with positive value will exist. On the other hand, a lower ORP presents a more reducing environment [28]. Kim et al. reported the use of ORP measurement and control to ensure the efficiency of wastewater treatment by Fenton process. They presented an increase of ORP from 560 to 640 mV by addition of Fenton's reagent. At the same time pigment concentration decreased by oxidation with OH radicals. Then the ORP decreased due to the depletion of Fenton's reagent to produce OH radicals [29].

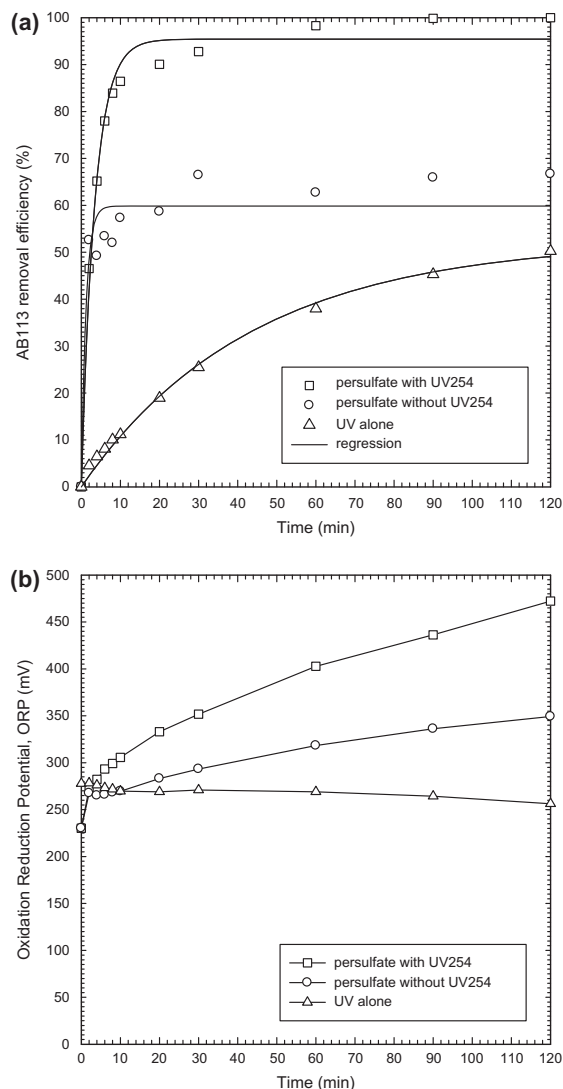


Fig. 2. UV synergistic effect of persulfate alone, UV/persulfate and UV irradiation alone processes on (a) AB113 removal efficiency, (b) ORP. The conditions were initial dye concentration of 50 mg l^{-1} , sodium persulfate dosage 4.2 mM , UV dosage 14 W l^{-1} and reaction time during 120 min.

In this set of experiments, the highest ORPs can be reached up to 472 and 349 mV for UV/persulfate and persulfate alone processes, respectively. This observation explains UV/persulfate process performed more powerful oxidative decolorization than persulfate alone process due to the formation of sulfate radicals. However, under UV irradiation alone the ORP was relatively unchanged because no oxidant was added and no free radicals were formed.

The effectiveness of mineralization of AB113 solution was evaluated by UV/persulfate and persulfate

alone processes. The TOC is an indicator of mineralization. With the limitation of TOC measurement instrument, large azo dye molecules resist to be oxidized by persulfate oxidant in TOC analyzer. Thus, at beginning of the oxidation reaction, solution TOC cannot be destroyed easily. At this time region, large molecules were degraded to lower molecule weight intermediates which still contributed to TOC measurement. Therefore, at first 40 min, TOC removal may remain still or present negative values. It is interesting to observe that TOC removal efficiency presents negative value up to -20% during the first 40 min for UV/persulfate process. Since the TOC analyzer used in this work was a wet oxidation type instrument, it has no catalyst to convert organic carbon into carbon dioxide. This explains the negative TOC removal efficiency happened at beginning of the reaction. Similar observation of negative TOC removal was discussed in our previous study [30]. After this lag phase (40 min), TOC can be removed significantly. The mineralization of AB113 solution by persulfate was rather difficult, which took 120 min to obtain as low as 41% of TOC removal that the original TOC of 50 mg l^{-1} AB113 solution is $18.1 \pm 0.2 \text{ mg l}^{-1}$ for both processes. From the results, UV/persulfate was the better TOC removal process with 92% TOC removal efficiency than persulfate alone process (TOC data not shown).

3.2. Effect of persulfate dosage

In order to investigate the effect of persulfate dosage on this UV/persulfate system, the effect of persulfate dosage on the photooxidation of AB113 was studied at initial concentrations of 50 mg l^{-1} , persulfate dosage of 0.21 – 6.3 mM , and 14 W l^{-1} UV light intensity for a period of 120 min in the TGAPR. Fig. 3(a) shows the removal of AB113 as a function of persulfate dosage under 14 W l^{-1} of UV irradiation. Results indicated that the AB113 removal efficiency increased from 72.5 to 99.5% in 60 min when the persulfate dosage increased from 0.21 to 6.3 mM . From the results, the higher the persulfate dosage reached higher AB113 removal efficiency. Similar observation was obtained by Yang et al. for Acid Orange 7 at 200 – $2,000 \text{ mg l}^{-1}$ (0.84 – 8.4 mM) persulfate dosage and Kamel et al. for Congo red dye at 1.0 – 2.0 mM persulfate dosage [24,31].

As mentioned prior to this section, TOC removal efficiency presented a lag phase. Therefore, through 120 min reaction time, one can observe the effect of persulfate dosage on TOC removal efficiency under UV/persulfate process as shown in Fig. 3(b). The TOC removal efficiency increased exponentially while

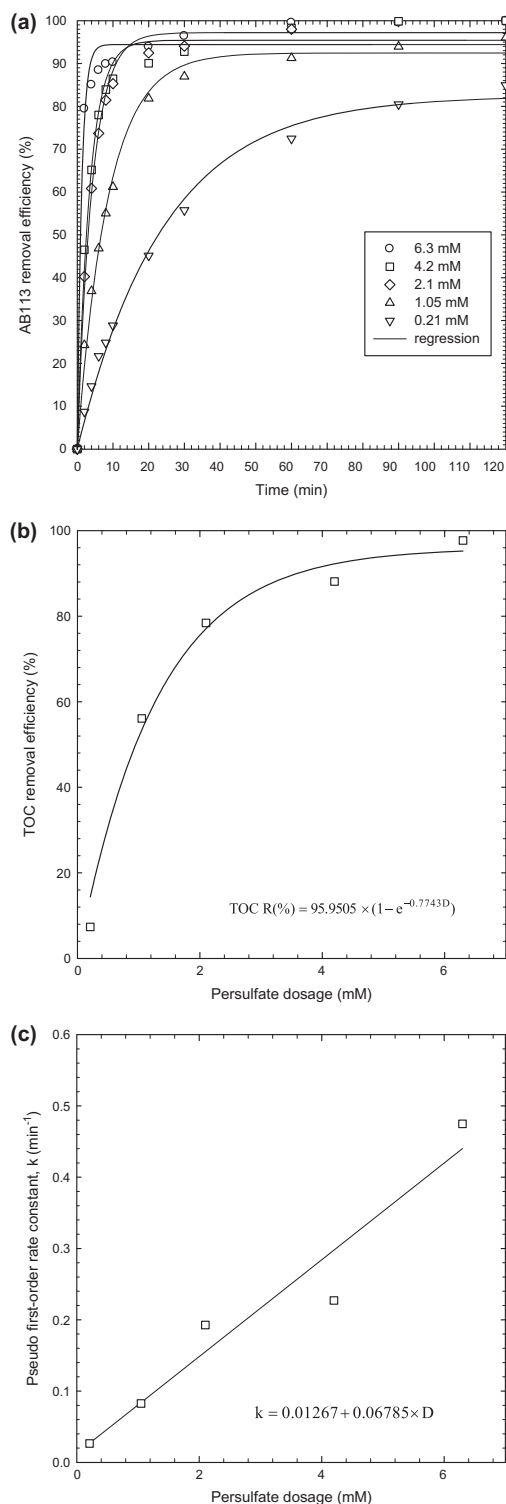


Fig. 3. Effect of persulfate dosage on (a) AB113 removal, (b) TOC removal, (c) pseudo first order rate constant (k), by UV/persulfate AOP. The conditions were initial dye concentration of 50 mg l^{-1} , UV light intensity of 14 W l^{-1} and reaction time during 120 min.

persulfate dosage increasing. An empirical equation as follows can be used to predict the TOC removal efficiency (TOC $R\%$) with known persulfate dosage (D , in mM):

$$\text{TOC } R(\%) = 95.9505 \times (1 - e^{-0.7743D}) \quad (2)$$

where TOC $R(\%)$ denotes the removal efficiency of TOC (%), D is the persulfate dosage (mM). In this set of experiments, the UV intensity was fixed as a constant. Since, UV intensity is an important parameter which can affect the performance of the UV/persulfate system. Thus, the Eq. (2) only applicable for highest UV intensity of 14 W l^{-1} . Further modification is needed for applying in various UV intensities.

From Fig. 3(b), the TOC removal was 7.4% for persulfate dosage of 0.21 mM and increased up to 97.7% for persulfate dosage of 6.3 mM. Results indicated that the TOC removal was more sensitive to persulfate dosage than that of AB113 removal. To decolorize and mineralize simultaneously, one should choose higher persulfate dosage to fulfill both AB113 dye and TOC removal requirements.

The initial stage of AB113 degradation under UV/persulfate process follows pseudo-first-order reaction, and can be described as follows:

$$C_{\text{AB113}} = C_{\text{AB113},0} \times e^{-kt} \quad (3)$$

where k denotes the pseudo-first-order reaction rate constant (min^{-1}), t is the reaction time (min), $C_{\text{AB113},0}$ designates the initial concentration (mg l^{-1}) of AB113, and C_{AB113} is the concentration (mg l^{-1}) of AB113 at time t . The curve fitting of experimental results by Eq. (3) can be used to obtain rate constants. The rate constants followed similar trend as AB113 removal efficiency; the observed pseudo-first-order rate constants were 0.0265, 0.0826, 0.1927, 0.2271, and 0.4749 min^{-1} at persulfate dosage of 0.21, 1.05, 2.10, 4.20, and 6.30 mM, respectively. The results agree with other work, where the first-order rate constants were in the same range of 0.0908 min^{-1} for Cibacron Brilliant Yellow 3 dye reported by Yeber et al. [32]. The results were shown in Fig. 3(c). From this figure, under persulfate dosage of 0–6.3 mM, the rate constant presented a proportional linear relationship with persulfate dosage. The equation (shown as following) can be used to predict pseudo-first-order rate constant for UV/persulfate process to decolorize AB113 solution.

$$k = 0.01267 + 0.06785 \times D \quad (4)$$

where k denotes the pseudo-first-order reaction rate constant (min^{-1}), D is the persulfate dosage (mM). Same limitation is applied as Eq. (2).

3.3. Effect of initial dye concentration

To present the effect of initial AB113 concentration on this UV/persulfate system, the effect of initial dye concentrations on the photooxidation of AB113 was studied at initial concentrations of 10–100 mg l^{-1} , persulfate dosage of 6.3 mM , and 14 W l^{-1} UV light intensity for a period of 120 min in the TGAPR. Fig. 4(a) shows results of AB113 photodegradation as a function of reaction time at various initial dye concentrations. Results indicated that the rate constant of dye removal decreased from 0.4499 to 0.1536 min^{-1} when the initial dye concentration increased from 10 to 100 mg l^{-1} as calculated from Fig. 4(a) and summarized in Fig. 4(b).

It is interested to find that pseudo-first-order rate constant, k , declines exponentially by raising initial dye concentration while UV intensity of 14 W l^{-1} . The results were similar to the observations by other investigators that the declining pseudo-first-order rate constants with respect to increasing initial dye concentrations [7]. The TOC removal were 85.4 and 97.5% in 120 min for initial AB113 concentration of 100 and 50 mg l^{-1} , respectively, and increased up to 100% for initial AB113 concentration less than 30 mg l^{-1} . Results indicated that the TOC removal was more sensitive to persulfate dosage than that of AB113 removal.

3.4. Effect of pH

Fig. 5(a) shows AB113 dye removal as a function of time at various pH values. Results indicated that at original pH the color removal reached 90.8% in 10 min of UV/persulfate reaction. At acidic pH of 2 the color removal rate of 90.3% was obtained. This implies that acidic pH provides no benefit for AB113 decolorization under UV/persulfate system. On the other hand, at alkaline pH of 9 and 10, the color removal rate increased up to 94.7 and 94.6%, respectively. However, the solution initial pH presented insignificant effect on AB113 degradation under UV/persulfate system. Fig. 5(b) shows the TOC removal efficiency as a function of pH value. Results indicated that at original pH 5.2 the TOC removal reached 100% in 120 min of UV/persulfate reaction. At acidic pH of 2 the TOC removal rate of 1.82% at 30 min increased to 90.1% at 60 min, then reached 97.5% at 120 min reaction time. The pH value of 9.4 demonstrated highest TOC

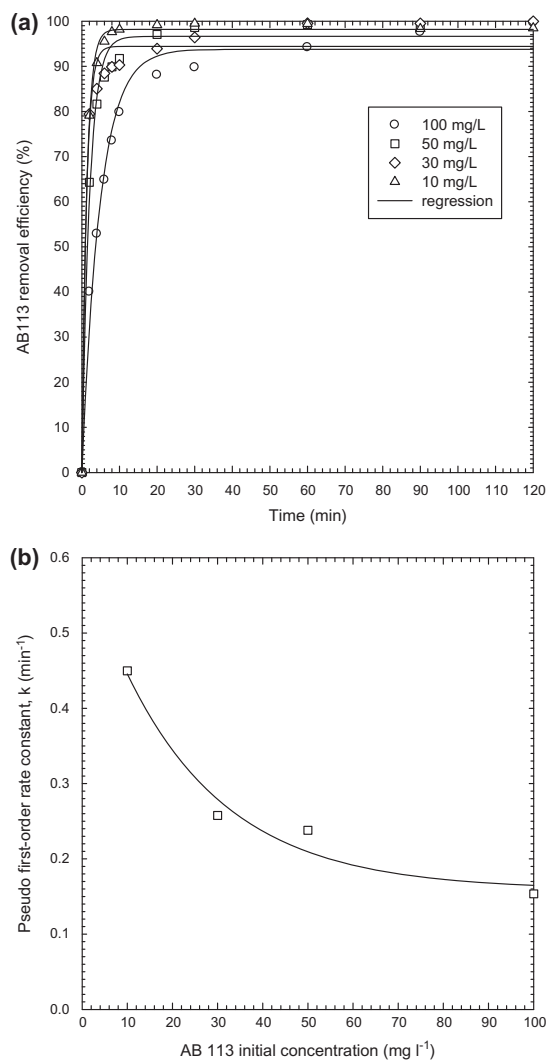


Fig. 4. Effect of initial concentration on (a) AB113 degradation and (b) pseudo-first-order rate constant. The conditions were persulfate dosage 6.3 mM , light intensity of 14 W l^{-1} , and reaction time 120 min.

removal efficiency at all reaction time periods. The results imply the TOC removal efficiency is rather stable in the range of 97.5–100% for pH range 2–10 in 120 min of reaction time.

3.5. Effect of UV light intensity

Theoretically, the higher the UV light intensity applied to a photocatalytic system, the faster the $\text{SO}_4^{\cdot-}$ free radical formation to obtain the higher dye decolorization and mineralization rate. Thus, the rate constant increases as UV intensity increasing, while the same persulfate dosage applied. Since, the photolysis of persulfate is enhanced to produce abundant $\text{SO}_4^{\cdot-}$

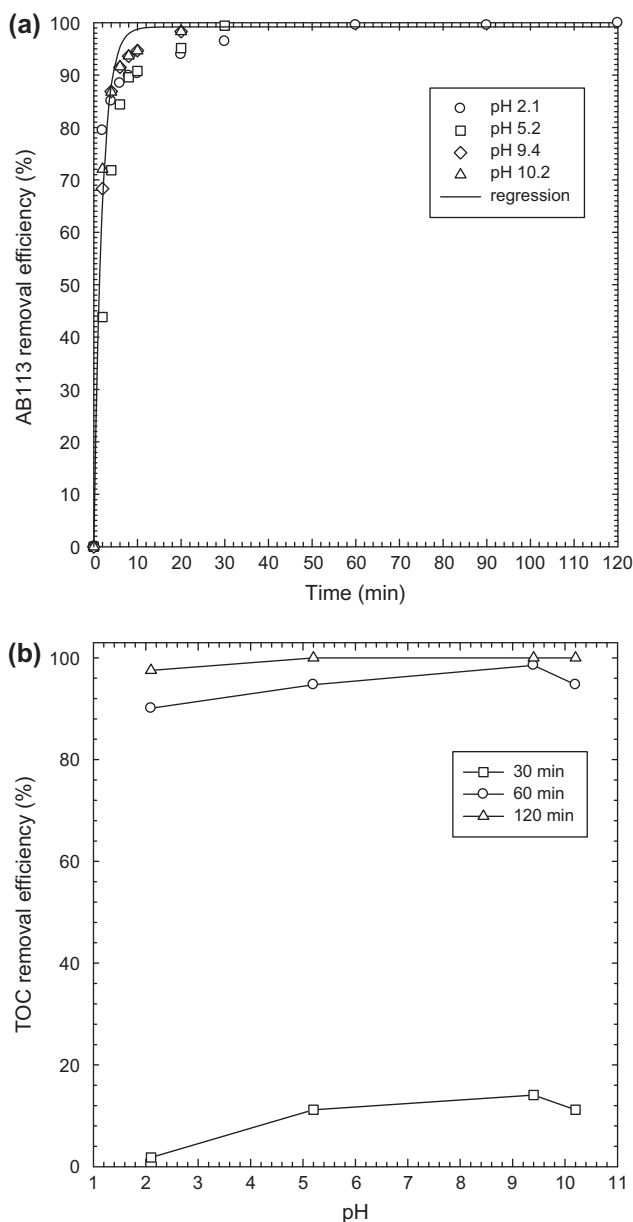


Fig. 5. Effect of initial pH on (a) AB113 degradation and (b) mineralization under UV/persulfate system. The conditions were initial dye concentration of 50 mg l^{-1} , persulfate dosage 6.3 mM , light intensity of 14 W l^{-1} , and reaction time during 120 min.

free radical in the dye solution to be used for decolorization. It is obvious that the more UV intensity employed to the system, the faster the dye decolorized. Fig. 6 shows the removal of color as a function of UV intensity for 1.05 and 6.3 mM persulfate dosage. Results indicated that at low-persulfate dosage of 1.05 mM, the color removal increased from 61.2 to 87.9% in 10 min when the UV intensity

increased from 14 to 30 W l^{-1} , respectively. As reaction time increased up to 60 min the AB113 removal efficiencies were closer in 5% range. On the other hand, for highest persulfate dosage of 6.3 mM, the AB113 removal efficiencies were very close during whole reaction period. The mineralization of AB113 was thoroughly when highest persulfate dosage of 6.3 mM was applied both high and low-UV dosages can reach 100% mineralization in 120 min. From the results, an observation that persulfate dosage played more important role on AB113 degradation and mineralization than that of UV intensity can be concluded. Due to the limitation of experimental setup, few previous works reported the effect of UV intensity on the decolorization of azo dye by UV/persulfate process. Salari et al. used an annular photo-reactor with constant volumetric flow of 500 ml min^{-1} and adjustable UV intensity from 5.5 to 40 W m^{-1} to treat Basic Yellow 2 dye with a persulfate dosage of 5 mM. They reported that with increasing light intensity the decolorization rate of dye increases which is consistent with this work [33].

3.6. The diminishing of UV-Visible spectra absorption peaks

The change of absorption peaks of AB113 azo dye after UV/persulfate photocatalytic treatment was

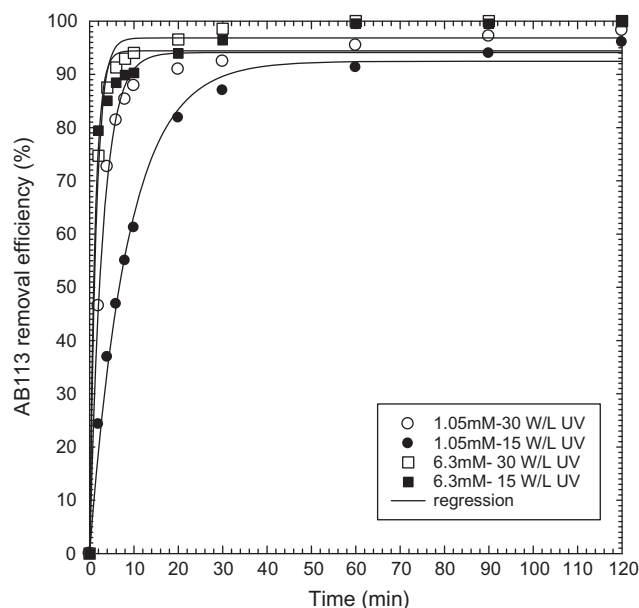


Fig. 6. Effect of UV light intensity on AB113 degradation under UV/persulfate system. The conditions were initial dye concentration of 50 mg l^{-1} , persulfate dosage 6.3 mM , light intensity of $14\text{--}30 \text{ W l}^{-1}$, and reaction time 120 min.

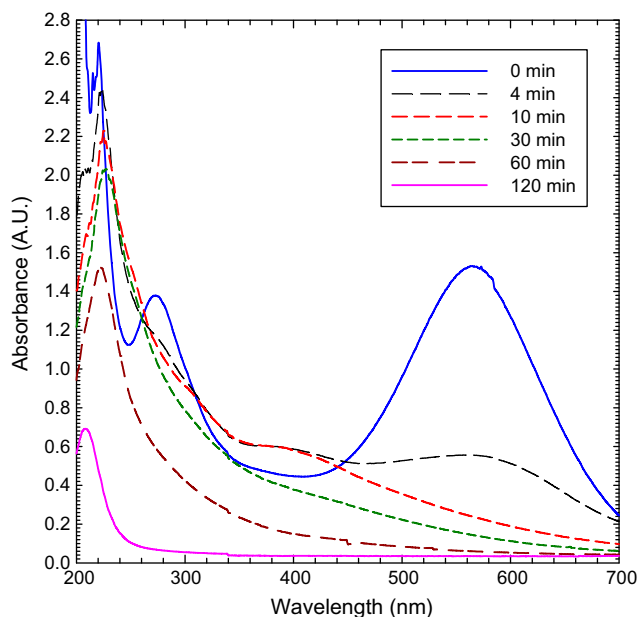


Fig. 7. The UV-Visible spectra for AB113 degradation under UV/persulfate system. The conditions were initial dye concentration of 50 mg l^{-1} , persulfate dosage 6.3 mM , light intensity of 14 W l^{-1} , and reaction time 120 min.

surveyed. The initial dye concentration was 50 mg l^{-1} and was treated with a persulfate dosage of 6.3 mM and reaction time of 0–120 min under 14 W l^{-1} UV irradiation. The UV-Visible absorption spectrum (showed in Fig. 7) for AB113 before reaction showed three peaks at 220, 272, and 566 nm wavelengths. At first 4 min, the absorbance of characteristic wavelength 566 nm decreased significantly from 1.530 to 0.555 A.U. After 90 min of reaction, the absorbance at 566 nm reached 0.036 A.U. which was only 2.35% of original absorbance. The absorption peak at 566 nm represented chromophore group of AB113 azo dye. Therefore, the degradation of AB113 can be measured by absorbance of this peak. Accordingly, the dye molecule was degraded and decolorized during the reaction. The absorption peaks of 272 nm represented naphthalene rings also diminished fast during reaction from 1.377 to 0.039 A.U. for 120 min of reaction time. Absorption peak of 220 nm attributed to the benzene rings remained slightly change for first 30 min. After 60 min of reaction, the absorption peak decreased to a rather small absorbance.

4. Conclusions

UV/persulfate AOP was proven to be a promising treatment technology for decolorization and minerali-

zation of AB113 wastewater. The persulfate dosage was shown to be most effective parameter to influence the AB113 and TOC removal rate amount all operating parameters studied. For persulfate dosage from 1.05 to 6.3 mM , the higher the persulfate dosage applied, the higher the removal efficiency can be obtained. The rate of AB113 removal increased with UV intensity increasing at lower persulfate dosage of 1.05 mM . However, at higher persulfate dosage of 6.3 mM , the enhancement of AB113 removal by UV intensity was shown insignificant. The initial pH was shown to be less effective on the AB113 decolorization. Based on the spectra of UV-Visible photometry analysis, the absorption peak of 566 nm represented the chromophore and peak of 272 nm represented naphthalene rings were diminished during the reaction. This implies the major structure of AB113 dye was destructed thoroughly.

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