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Photocatalytic mineralization of azo dye Acid Orange 7 under solar light irradiation

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ABSTRACT

The objective of this study was to investigate mineralization of hazardous water soluble azo dye Acid Orange 7 (AO7) under photocatalytic process. In this experiment, sunlight was used as the source for UV irradiation and titanium dioxide, TiO_2 as catalyst. The effects of some process variables on decolorization such as amount of TiO_2, azo dye concentration and dosage of hydrogen peroxide (H_2O_2) were examined. TiO_2-based photocatalytic degradation is an effective, economic and faster mode of removing azo dye AO7 from aqueous solution. The presence of sunlight enhanced the decolorization rate of AO7 and mineralized the intermediate products completely. The mineralization of AO7 was supported by the UV–Vis and ion chromatography analysis. The addition of proper amount of H_2O_2 could optimize the decolorization rate of AO7. The photocatalytic degradation of AO7 followed first-order kinetic model.

Keywords: Azo dye; Acid Orange 7; Photocatalytic process; Sunlight; Decolorization; Kinetic study

1. Introduction

Wastewaters from textile industry contain large amounts of organic dyes, representing a major threat to the environment due to their toxicity and potentially carcinogenic nature [1]. Azo dyes represent the most significant group of dyes used in the textile industry today. Many of these synthetic dyestuffs cannot be treated successfully by conventional methods due to their complex poly-aromatic structure and hence cause health problems [2]. There are numerous physical and chemical treatment techniques such as coagulation and flocculation, precipitation, oxidation and adsorption, have been used for decolorization of textile effluents [3–5]. The disadvantage of those methods of wastewater purification is the fact that they are not destructive but only transfer the contamination from one phase to the other. Most of azo dyes are recalcitrant to microbial degradation because they have complex aromatic molecular structures, thus conventional biological treatment methods are ineffective in decolorization and degradation. In addition, most of the dyes is only adsorbed on the sludge and is not degraded, thus causing generation of second pollution.

New technologies of wastewater purification leading to the complete mineralization of organic pollutants are now considered as the most suitable solution of the problem connected with more and more drastic requirements concerning the contamination level in water and wastewater [6]. Advanced oxidation processes (AOPs),

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particularly photocatalytic oxidation technology, provide a convenient way of treating undesirable chemicals, for instance pesticides, halogenated benzenes and dyes. AOPs were based on the generation of very reactive species such as hydroxyl radicals (•OH) that oxidize a broad range of pollutants quickly and none selectively [7]. They are notably known to discolor several structurally different sulfonated hydroxyl azo dyes [8]. The main advantage of these processes is that they can destroy organic molecules, leading to their complete mineralization or to biodegradable intermediate compounds [9].

Photocatalytic process can provide a low operating cost due to the use of sunlight as the source of irradiation, also implying as an environmental cleaning process. TiO_2-based photocatalytic systems have become emerging technology for destroying the organic dye pollutants because the TiO_2 photocatalyst is largely available, inexpensive, and non-toxic, and show relatively high chemical stability [10–12]. Acid Orange 7 is a water-soluble dye employed mostly in the textile industry and it was used as the model for photocatalytic decolorization in this study. The objective of the study was to investigate the TiO_2-based photocatalytic process in mineralization of AO7-containing wastewater under solar light irradiation.

2. Materials and methods

2.1. Chemical

Acid Orange 7 (AO7) with the molecular formula $C_{16}H_{11}N_2NaO_4S$ was supplied by Acros Organic. The formula structure is shown in Fig. 1. Commercially available TiO_2 powders, which is well-known to possess very high photocatalytic activity was selected for study of the mineralization of AO7. AEROXIDE TiO_2 P-25 from Evonik Industries was provided by Jebsen and Jessen. Hydrogen peroxide (35% w/w) is a strong oxidizing agent and widely use in decolorizing process was supplied by Bendosen Laboratory Chemicals. All chemicals were of analytical grade and used without further purification. Deionized water was used throughout this study.

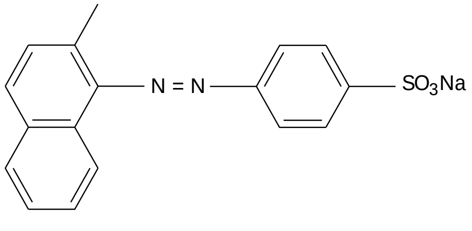

Fig. 1. Molecular structure of Acid Orange 7.

2.2. Photocatalytic process

The photodegradation of AO7 in aqueous solution under solar light irradiation was investigated under various conditions. All experiments were carried out in 500 mL beakers, which were placed on a magnetic stirrer. In each experiment, an appropriate amount of AO7 from stock solution was diluted to 300 mL with deionized water. A desired amount of TiO_2 was added into the beaker and the reaction will be started. Two sets of experiment were run simultaneous, one set was exposed to the sunlight and the other one was done in laboratory, to evaluate the effect of solar light irradiation on the decolorization rate. The solutions' pH, which was 7 ± 0.5, was not adjusted. Sample was withdrawn with syringe at certain time intervals. Then, it was filtered with 0.45 μm membrane filter to remove the TiO_2 particles and the obtained filtrate was taken for an analysis of AO7 concentration by the absorbance measurement. Two different dosages of AO7, 50 and 150 mg/L, were used to investigate the effects of AO7 concentration on the decolorization rate. In order to study the effects of H_2O_2 on photocatalytic degradation of AO7, four different dosages, 1, 3, 4 and 5 mL, were added to the beakers.

2.3. Analytical procedure

The UV–Vis spectra of AO7 were recorded from 200 to 800 nm using a UV–Vis spectrophotometer (Hitachi U-2800, Japan). The maximum absorbance wavelength (λ_{max}) of AO7 was found at 480 nm. The concentration of AO7 from photocatalytic process at certain time intervals can be determined by measuring the absorption intensity at λ_{max} 480 nm. The efficiency of decolorization was calculated as follows:

$$\text{Decolorization efficiency (\%)} = (1 - C_t/C_0) \times 100\% \qquad (1)$$

where C_t is the AO7 concentration at reaction time t (min) and C_0 is the initial AO7 concentration.

2.4. Kinetic study

The most widely used kinetic expressions to represent the photocatalytic process are the first-order (2) and Langmuir–Hinshelwood (3) kinetics. The Langmuir–Hinshelwood expression is approximated to first-order expression by several researchers for photocatalytic degradation of dyes

$$\text{Rate} = -(\mathrm{d}C/\mathrm{d}t) = k_1C \qquad (2)$$

$$\text{Rate} = -(\mathrm{d}C/\mathrm{d}t) = kKC/(1 + KC) \qquad (3)$$

where C is concentration at any time (mg/L); k_1 is first-order constant (min^{-1}); k and K the limiting rate constant of reaction at maximum and equilibrium constant for adsorption.

3. Results and discussion

3.1. Effect of solar light irradiation on degradation of AO7

Acid Orange 7 (AO7) is an anionic monoazo dye having sulfonate (SO_3^-) groups and the degradation of AO7 was carried out under the sunlight using TiO_2 as photocatalyst. The decolorization rate was recorded in terms of change in intensity of characteristic peak at 480 nm. Fig. 2 shows the decolorization and kinetic study of 50 mg/L AO7-containing wastewater with and without the presence of sunlight. The AO7 removal efficiency achieved 90% after 240 min exposed to the sunlight in the presence of TiO_2 as catalyst. On the other hand, the concentration of AO7 only reduced about 3% in the case of without sunlight. It was observed that the photocatalytic degradation of AO7 followed first-order kinetic model. As shown in Fig. 2(b), the decolorization rate constant increased from 2×10^{-4} min^{-1} to 77×10^{-4} min^{-1} when the experiment was carried out under sunlight irradiation. In the presence of sunlight, TiO_2 absorbs UV light and generates hydroxyl radicals (•OH) [13]. The •OH radicals formed on the illuminated TiO_2 surface are extremely powerful oxidizing agents that none selectively attack the adsorbed azo dye AO7 or those close to the catalyst surface, thus, resulting to their mineralization [1]. TiO_2-assisted photocatalytic degradation of pollutants using solar light has been successfully used being an economically viable process that can replace artificial light sources which are costly and hazardous.

3.2. Effect of initial concentration of AO7 on decolorization rate

The initial concentrations of AO7 examined in this study were 50 and 150 mg/L. As shown in Fig. 3(a), the AO7 removal efficiency was 88% and 45% for initial AO7 concentration of 50 and 150 mg/L, respectively. It is obvious that AO7 with 50 mg/L concentration was decolorized more efficiently compared to 150 mg/L. The concentration for AO7 regardless their initial concentration will be decreased with time. It is because that there was the reaction going on in the decolorization process with TiO_2 as catalyst in the presence of sunlight. The

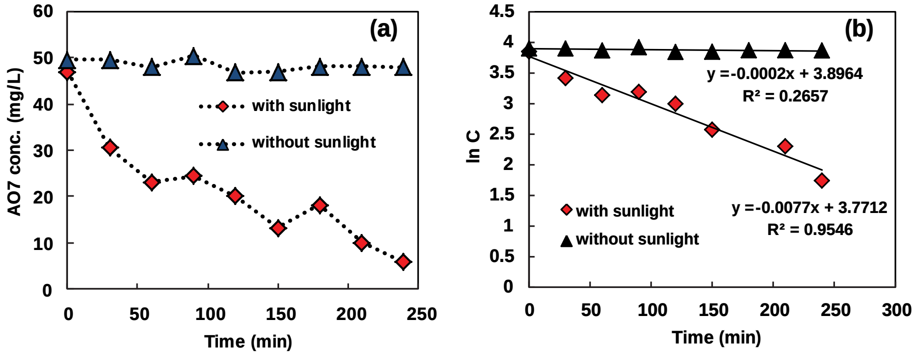

Fig. 2. Photocatalytic degradation of AO7 with and without the presence of sunlight (a) and kinetic study (b).

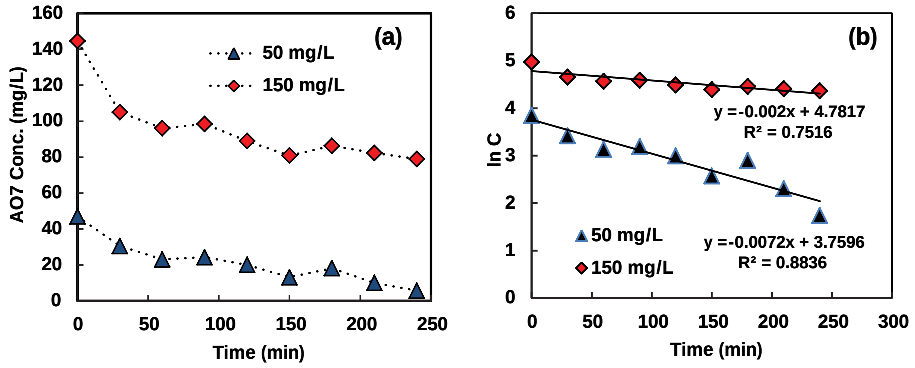

Fig. 3. Photocatalytic degradation of AO7 in different concentrations with 0.3 g TiO_2 as catalyst (a) and kinetic study (b).

forming of •OH radicals can attack the azo dye AO7. The AO7 will be further decolorized with the breaking down of the azo bond by the •OH radicals. The cleavage of the azo bond in AO7 can lead to the formation of naphthalene and benzene, which can then be consequently mineralized through photocatalytic process [14–16].

As shown in Fig. 3(b), the photocatalytic degradation rate constants were 7.2 × 10^{-3} min^{-1} and 2 × 10^{-3} min^{-1} for initial AO7 concentration of 50 and 150 mg/L, respectively. The high degradation rate for 50 mg/L AO7 compared to the one with 150 mg/L can be supported with the research that stating the reactivity of the reaction is generally high at low pollutants concentrations [17]. Higher AO7 concentration meaning that there is less amount of the catalyst available for the degradation process. With low concentration AO7, the catalyst can degrade the dye faster to become decolorized since there were enough amounts of the •OH radicals for degradation of dye. Besides, higher dye concentration will decrease the path length of photons entering to the dye causing them to absorb more UV radiation from the sunlight rather than the catalyst and thus reducing the catalytic efficiency [18]. Azo dye AO7 with 150 mg/L will receive more photons from the sunlight and not the TiO_2. Hence, the catalyst cannot perform well in degrading the dye. However, dye with lower concentration, which is 50 mg/L can react with catalyst more efficient since the catalyst is able to receive more photons from sunlight.

3.3. Effect of TiO_2 dosage on degradation of AO7

Fig. 4 shows the removal efficiency of AO7 with 0.3 g and 0.6 g of TiO_2 reacted with 50 mg/L AO7. The decolorization efficiency of AO7 was higher in the case with 0.6 g of TiO_2 as catalyst (93%) than 0.3 g (83%) of TiO_2. The data obtained was well fitted with the first-order kinetic model and the photocatalytic degradation rate constant increased from 6.7 × 10^{-3} min^{-1} to 10.9 × 10^{-3} min^{-1} with TiO_2 dosage from 0.3 to 0.6 g, respectively. This indicated that higher amount of TiO_2 will have higher removal efficiency because the more TiO_2 is added, the more •OH radicals been produced. Consequently, it can directly attack and destroy organic chemicals because it react rapidly and none selective with nearly all electron rich organic compounds and the final products are carbon dioxide and water. As the amount of TiO_2 increase, the amount of •OH radical generated also increased. Therefore, there will be more and sufficient of •OH radical to attack the AO7 in this experiment. However, when TiO_2 was overdosed, the intensity of incident UV light was attenuated because of the decreased light penetration and increased light scattering, which embedded the positive effect coming from the dosage increment and therefore the overall performance reduced [19].

3.4. Effect of H_2O_2 dosage on degradation of AO7

As shown in Fig. 5, the presence of H_2O_2 caused drastic decolorization of AO7 compared to the reaction without H_2O_2. This indicates that with the presence of H_2O_2, removal efficiency was higher compared to the reaction that without H_2O_2. This clearly implies that H_2O_2 is significant in enhancing efficiency of azo dye removal. Addition of 1 mL H_2O_2 boosted the degradation rate of AO7 as shown in Fig. 5. Initially, H_2O_2 that contained of O–O bond was separated by the UV radiation and produced •OH radicals. Consequently, the higher amount of •OH radicals generated attacked the AO7 with higher rate of reaction, thus removal efficiency of azo dye increased. As shown in Fig 5(b), the photocatalytic degradation rate constant increased from 8.3 × 10^{-3} min^{-1} to 25.4 × 10^{-3} min^{-1} as 3 mL of H_2O_2 was added into the AO7 solution. However, further increase in H_2O_2 concentration lowered the degradation rate. The photocatalytic degradation rate constant decreased to 19.1 × 10^{-3} min^{-1} with the addition of 5 mL

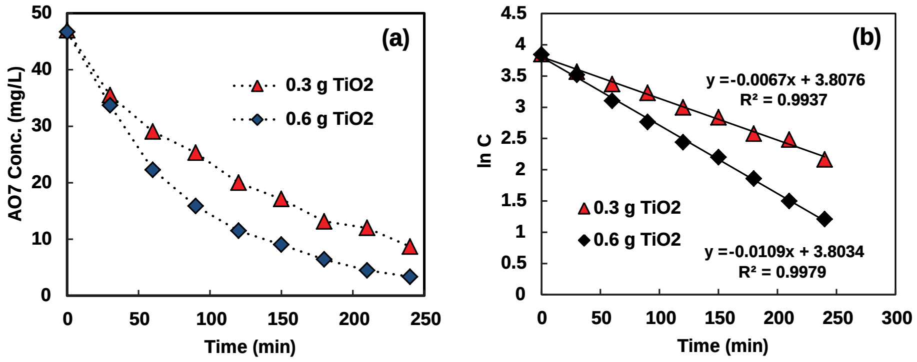

Fig. 4. Photocatalytic degradation of AO7 with different amount of TiO_2 as catalyst (a) and kinetic study (b).

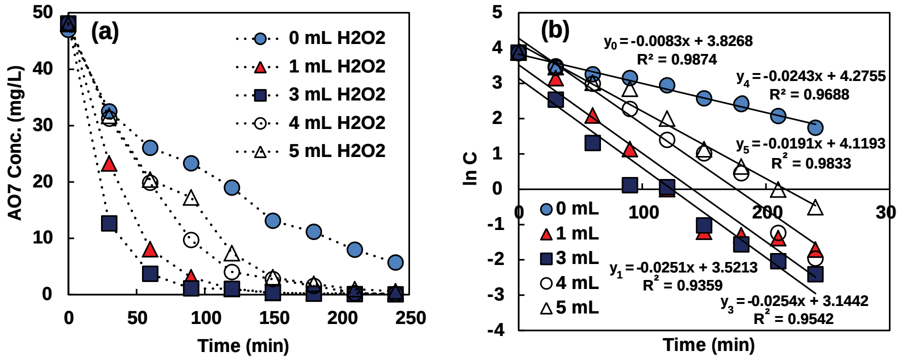

Fig. 5. Photocatalytic degradation of AO7 with and without the presence of H_2O_2 (a) and kinetic study (b).

H_2O_2. Our result showed that, for the usage of 1 mL and 5 mL of H_2O_2, the removal efficiency was 99% and 97%, respectively. Five milliliter of H_2O_2 indicates lower removal efficiency although the concentration of H_2O_2 was higher. This is because of the excess H_2O_2 reacts with the •OH radicals earlier formed and hence acts as an inhibiting agent of degradation by consuming the •OH radicals responsible for degrading the pollutant molecule [20–22]. Excessive H_2O_2 leads to formation of perhydroxyl radical ($HO_2\cdot$) which is not as reactive as •OH radicals to decolorize AO7.

3.5. Spectrum analysis for photodegradation of AO7

Time dependent UV–Vis spectral changes during photocatalytic degradation for typical run performed with 0.3 g of TiO_2 as catalyst in 30 mg/L of AO7 is shown in Fig. 6. Complete removal of the initial orange color was observed after 4 h of solar light irradiation. The spectra of AO7 show peaks at 220, 260 and 310 nm in UV region and maximum absorbance at 480 nm in visible region. The absorbance peak at 220 and 310 nm are attributed to the benzene and naphthalene ring [17], and the absorbance peak at 480 nm is due to the azo linkage of AO7. The absorption of the visible band at 480 nm decreased with time indicated the cleavage of ado bond leading to decolorization.

Fig. 7 shows the absorbance ratio of AO7 samples throughout the irradiation time. It was observed that the absorbance ratio at 220 nm/480 nm increased until reaching a maximum level and then decreased drastically. This trend may suggests that, the photocatalytic degradation of AO7 involved the cleavage of ado bond in the first period, creating an aromatic amine and a naphthalene group, thus the ratio of absorbance at 220/480 increased. On the other hand, the absorbance ratio at 310 nm/480 nm only increased slightly which indicates unstable of the naphthalene group and easily being degraded to aromatic amines. After 5 h of solar light irradiation, the bands at 220, 260, 310 and 480 nm were disappeared indicating mineralization of AO7 under photocatalytic process. As reported by Bansal et al. [17], the probable pathway for photocatalytic degradation of AO7 involved the symmetrical cleavage of azo bond to yield the intermediate 2-hydroxyl sulfanilic acid and 2-hydroxy-1,4-napthquinone. Azo bond is more

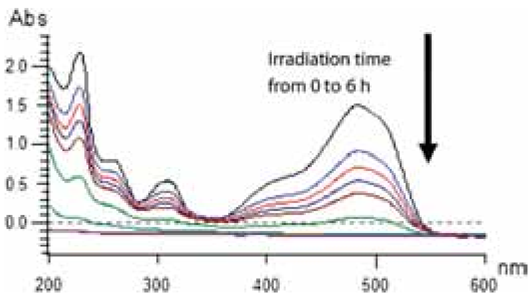

Fig. 6. UV–Vis spectral changes of AO7 in aqueous solutions with the increasing irradiation time.

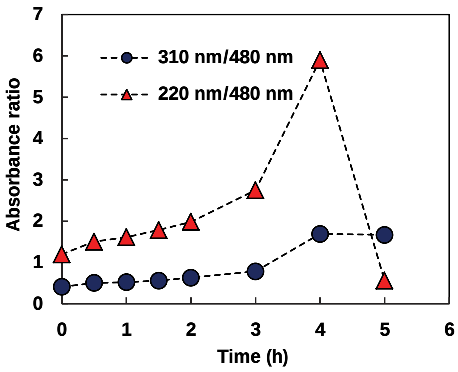

Fig. 7. Absorbance ratio monitoring in photocatalytic degradation of AO7.

easily to be reduced compared with the other groups in azo dye structure. Sulfanilamide and 1-amino-2-naphtol are the most probable products resulted from electrons or active hydrogen atoms reduction, among which 1-amino-2-naphtol is the most possible chemical susceptible to oxidative species [23]. On the other hand, biodegradation of AO7 under anaerobic condition generated two intermediate products, namely 1-amino-2-naphtol and sulfanilic acid [24], initiated by the broken down of azo bond. Stylidi et al. [25,26] also claimed that the first step in photocatalytic degradation of AO7 most probably involves cleavage of the dye molecule at the level of the very active azo bond, which is more liable to oxidation. After the cleavage of azo bond, various intermediate products being produced such as coumarin, 2-naphthol, 1,2-naphthoquinone, 2-hydroxy-1,4-naphthoquinone, phthalic acid, phthalic aldehyde, 2-formyl-benzoic acid, 2-acetyl-benzoic acid and 2-hydroxy-benzoic acid and others aliphatic acids [25,26]. From UV–Vis analysis, our result is agreed with their outcomes [17,23–26] that the photocatalytic degradation of AO7 was initiated with the cleavage of azo bond and formed two intermediate products.

Mineralization of 50 mg/L AO7 under photocatalytic degradation process was evaluated by monitoring the evolution of NO_3^- and SO_4^{2-}. Previous works have shown that nitrogen atom in dye is mainly transformed into NH_4^+, NO_3^- and gas N_2 whereas sulfur atom is mineralized into SO_4^{2-} [27,28]. As shown in Fig. 8, the evolution of NO_3^- was observed after AO7 was irradiated with solar light for 200 min. The NO_3^- concentration monitored was increased up to 0.2 mg/L after 9 h of solar light irradiation. The evolution proportion of NH_4^+, NO_3^- and N_2 depends mainly on the initial oxidation degree of nitrogen, the substrate structure and on irradiation time [29]. The SO_4^{2-} can be detected after 1 h of photocatalytic degradation and this can be ascribed by an initial attack of •OH radicals on sulfonate group in AO7. The degradation pathway of AO7 under photocatalytic degradation can be in the sequence of azo dye, intermediate aromatic amines, aliphatic acid and mineral ions [17].

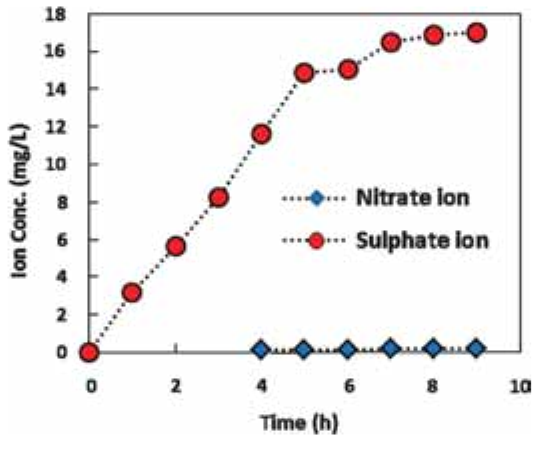

Fig. 8. Nitrate and phosphate ions monitoring in photocatalytic degradation of AO7

4. Conclusion

Decolorization rate increased tremendously in the presence of sunlight and the AO7 removal efficiency achieved 90% after 240 min exposed to the sunlight in the presence of TiO_2 as catalyst, whereas the AO7 concentration only reduced about 3% in the case of without sunlight. The presence of H_2O_2 caused drastic removal of AO7 compared to the reaction without H_2O_2. This indicates the importance of H_2O_2 for generating •OH radicals in photocatalytic process for mineralization of AO7. However, excessive of H_2O_2 concentration lowered the degradation rate. The photocatalytic degradation of AO7, in general, followed first-order kinetic model. The UV–Vis spectra analysis shows the photocatalytic process not only caused the decolorization of AO7, but the intermediate products generated also mineralized completely.

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