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Photocatalytic removal of acid orange 7 azo dye by suspended and immobilized zinc oxide

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ABSTRACT

Acid Orange 7 (AO7) is one of the most widely used azo dye for textile industry and not easily removed via conventional biological wastewater treatment process. The photocatalytic process combining ultraviolet (UV) and zinc oxide (ZnO) in the suspended state or immobilized on the concrete plate was used to remove AO7 in this study. The effects of initial pH (2–11), UV lamp power (8–40 W), ZnO dosage (2.58–25.8 g/L for suspended reactor and 20–200 g/m^2 for immobilized reactor) and initial AO7 concentration (10–200 mg/L) on AO7 removal were systemically investigated in batch tests. Under the optimum conditions (neutral pH of 7, UV lamp power of 32 W, ZnO dosage of 10.32 g/L for suspended reactor and 80 g/m^2 for immobilized reactor, initial AO7 concentration of 50 mg/L), AO7 removal reached 97% and 98% after 60 and 360 min for suspended and immobilized reactors, respectively. AO7 removal followed by first-order reaction kinetics with decreasing rate constant and energy consumption with increasing initial AO7 concentration for both reactors. The photocatalytic efficiency of UV/ZnO in the immobilized reactor was significantly lower than in the suspended reactor but could be improved via increasing ZnO coated concrete plate area (i.e., ZnO active surface area).

Keywords: Suspended and immobilized ZnO; Initial pH; UV lamp power; ZnO dosage; Initial dye concentration

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1. Introduction

Artificial organic dyes are widely used for dyeing purposes in some industries (e.g., textile, paint, plastics, rubber) and partially discharged in the industrial wastewater. Among them, azo dyes containing azo group (–N=N–) in their molecular structure, are ones with a maximum number of individual species and mostly used in textile dyeing process. Due to their high structural stability and carcinogenic potential, azo dyes have to be removed from wastewater to avoid their release into the aquatic environment [1]. Some physical processes such as adsorption [2], membrane filtration [3,4], coagulation and electric floatation [5], have been used to remove azo dyes. However, these physical processes just separate/transfer the dyes from wastewater into another phase (solid or brine) rather than real removal via biological/chemical mineralization. Some biological processes such as the conventional activated sludge process [6], sequential batch reactor [7] and phytoremediation [8], are also tested to remove azo dyes but show limited performance due to their toxicity and stability from aromatic structures [9]. Chemical oxidation processes such as sun lysis [10], ozonation [2], oxidizers such as potassium permanganate [11], persulfate [12], electrochemical oxidation [13] and Fenton [14] are employed to remove azo dyes in recent years due to their high removal efficiency.

Almost all advanced oxidation processes are based on the production or use of active species (e.g., radical hydroxyl $^{\bullet}$OH), which oxidizes a wide range of pollutants effectively and quickly [15]. There are different methods for

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producing •OH including photochemical or photocatalytic reaction, catalysis, Fenton, radiation of an energetic electron beam and lysis [16]. Among them, photocatalytic processes using ultraviolet (UV) light and oxide catalyst have been used for dyes removal [17,18]. As a cheap semiconductor material without toxicity, zinc oxide (ZnO) has been widely used for photocatalytic oxidation. Due to the straight band of about 3.3 eV at room temperature and high oxygen binding energy of approximately 60 meV, ZnO has high photocatalytic efficiency. ZnO can be activated with UV radiation, which results in electron transfer from the valence band to the conduction band, forming holes (ZnO surface h^+) and free electrons (ZnO surface e^-). ZnO surface h^+ with high oxidizing ability leads to direct oxidation of organic pollutants [19]. One study showed complete removal of acid red 18 dye by ZnO particles in suspended photocatalytic reactor after an hour [20]. In another research on immobilized ZnO continuous photocatalytic reactor for acid red 27 dye removal, the removal efficiency was reported to be about 90% after 72 min [21].

From the viewpoint of the catalyst's state in photocatalysis, suspended state might be more efficient than the immobilized state in reaction rate and light energy utilization due to its high mass transfer efficiency, while immobilized state is better than the suspended state for preventing the loss of catalyst (especially the fine nanoparticles). Thus, it is very beneficial to compare the efficiency between the immobilized state and the suspended state from the industrial approach. As one of the azo dyes, acid orange 7 (AO7) is of great importance to environmental issues due to its huge consumption in the textile industry [22,23]. Some studies have been done to remove this dye in different ways including coagulation and flocculation [24], adsorption [2,17], UV/H_2O_2 [25], photocatalysis using TiO_2 [23,26], membrane aerated biofilm [27]. However, there is little information about the use of UV/ZnO photocatalysis to remove this dye.

The purpose of this study was to evaluate the capability of AO7 removal by UV/ZnO photocatalytic process in suspended and immobilized ZnO state. The effects of initial pH, UV lamp power, ZnO dosage, initial dye concentration on dye removal were investigated systemically in photocatalytic batch tests. The reaction kinetics and energy consumption for dye removal were also investigated.

2. Materials and methods

2.1. Experimental set-up

During the study, AO7 dye (Chemical Abstract Service number 633-96-5) with molecular formula $C_{16}H_{11}N_2NaO_4S$, the molecular weight of 350.3 g/mol and pKa of 8.26 under 25°C was used to prepare dye solution with different concentrations. ZnO powder with an isoelectric point of 8.7–10.3 was purchased from Lima Company (Tehran, Iran). The plastic batch reactors had dimensions of (23 cm × 15 cm × 12 cm) with an effective solution volume of 1.7 L for both suspended and immobilized state (shown in Fig. 1). For the suspended reactor, ZnO powder was added in the dye solution and mixed homogenously by a magnetic stirrer. For the immobilized reactor, ZnO powder was coated on the surface of a concrete plate (detailed fabrication shown in the section below), which was immersed in the dye solution. Depending on the required UV radiation intensity, 1 to 5 Philips UV-C Backlight 8W lamps (Eindhoven, Netherlands) were hanged up 10 cm above the water level in the reactor. Around the reactor was covered with a layer of thick aluminum sheet to protect the safety and to increase the reflection and efficiency of UV light.

2.2. Immobilized ZnO catalyst preparation

As a widely used and cheap material, a concrete plate (dimensions of 23 cm × 15 cm × 0.5 cm) was fabricated to support ZnO powder. To construct concrete plate based on the American Concrete Institute regulations, fine aggregates of less than 5 mm, type 5 types of cements (anti-sulfate cement widely used in municipal and industrial wastewater treatment plants) and tap water were used. For the smooth and uniformity of the concrete surface, more cement in concrete than standard dosage was used to prevent the formation of fine-grained concrete cracks. Concrete plates were kept in cool water for more than 20 d for stabilization before coating ZnO powder.

According to the results from the previous study [28], the water sealer method using a water concrete adhesive solution was employed to coat ZnO powder onto concrete plates. Firstly, the mixture of ZnO powder, concrete glue and tap water with a matching ratio of 1 g, 10 ml, and 100 ml,

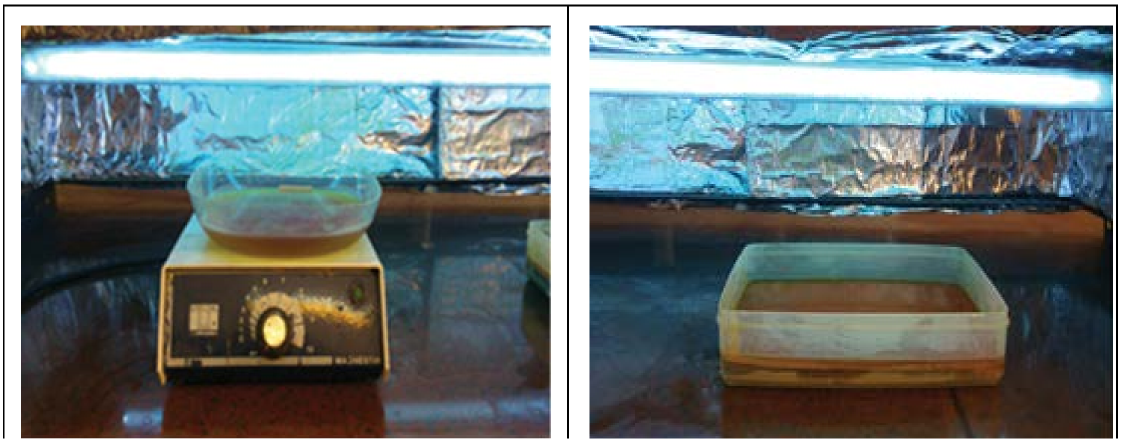


Fig. 1. UV/ZnO photocatalytic set-up. (a) Suspended reactor and (b) Immobilized reactor.

respectively, was stacked in ultrasonic apparatus for 5 min to separate powder. Then, the mixture with different volumes depending on the surface coating density was poured onto the concrete surface and placed at room temperature for 24 h until the soluble water evaporated. To ensure proper coating of ZnO powder on concrete surfaces, scanning electron microscopy (SEM) images were prepared. As shown in Fig. 2, the uniformity layer was formed and there were only black holes in some places (lack of ZnO particles) on the concrete surface. The results of the surface analysis using the energy dispersive X-ray (EDX) confirmed the existence of ZnO at the shooting location as shown in Fig. 3.

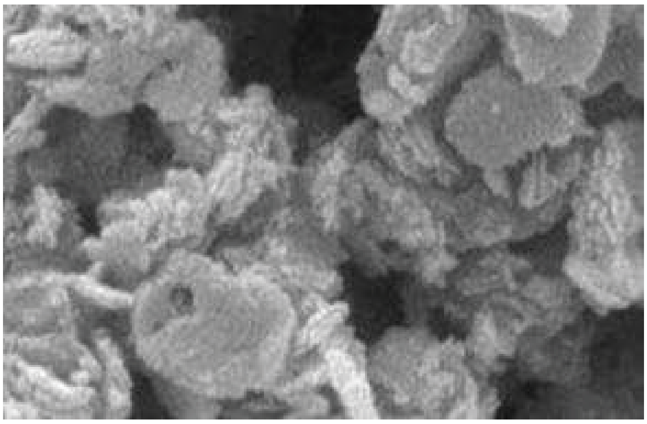


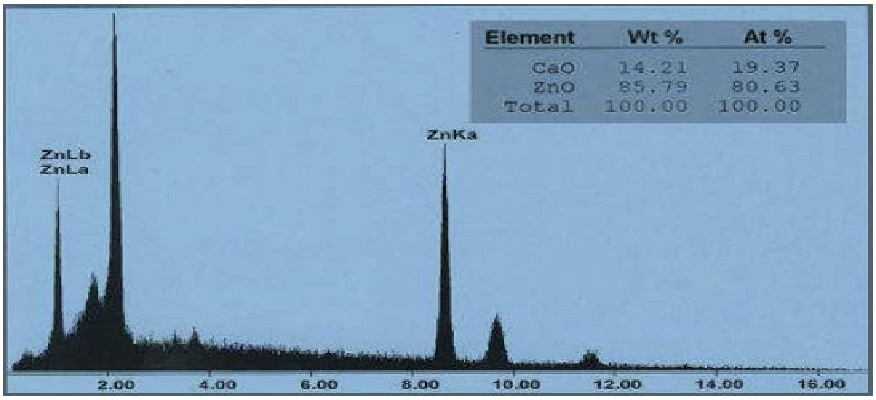
Fig. 2. SEM images of concrete plates after coating ZnO (30,000 times).

2.3. Photocatalytic batch tests protocol

The control tests with dye only, dye and UV, dye and ZnO for both suspended and immobilized reactors to check the background effects before photocatalytic tests. From Table 1, all dye removals were negligible in control tests, indicating the plastic container and concrete plate had no adsorption capability on the dye while UV or ZnO alone had nearly no dye removal. Thus, the dye removal could be only attributed to photocatalysis by combined UV/ZnO in this study. The photocatalytic batch tests were conducted under different initial pH (2–11), initial dye concentration (10–200 mg/L), ZnO dosage (2.58–25.8 g/L for suspended state and 20–200 g/m^2 for immobilized state) and UV light power (8–40 w) to explore the optimum conditions for dye removal under both suspended and immobilized state. All experiments were done in triplicate at room temperature of 22°C–24°C, where the relative standard deviations of data with a value of less than 2.33% indicated high repeatability in this study.

2.4. Analytical methods

All samples were pre-filtered via a 0.45 μm syringe filter to remove particles for measurements. AO7 was quantified by spectrophotometry under the maximum absorbance wavelength of 485 nm. Chemical oxygen demand (COD)



Element	Wt %	At %
CaO	14.21	19.37
ZnO	85.79	80.63
Total	100.00	100.00

Fig. 3. EDX results of concrete coated by ZnO.

Table 1
Results of control tests (initial dye concentration 50 mg/L, initial pH 7, UV lamp power 32 W, ZnO dosage 10.32 g/L for suspended reactor and 80 g/m^2 for immobilized reactor, test time 8 h)

Test conditions	Dye removal (%)	
	Suspended reactor	Immobilized reactor
Dye only (dye in a container for suspended reactor, dye and uncoated concrete plate in a container for immobilized reactor)	1.1	1.6
Dye and UV (UV lamps on, no ZnO)	2.0	2.8
Dye and ZnO (UV lamps off, ZnO addition)	5.2	3.1

measurement was based on rapid digestion followed by titration according to the standard method 5220D [29]. Major devices used in this study included spectrophotometer (DR1900, Hach, Colorado, United States of America), centrifuge made by Sigma (Shropshire, United Kingdom), E-Fung 6SFD ultrasonic bath (40 kHz), COD digestion reactor (DRB200, Hach, Colorado, United States of America), pH meter (Met Rohm, Herisau, Switzerland) and digital balance (PLS360-3, Kern, Balingen, Germany). Major materials included ZnO nanopowder made by Nano Pars Lima (Tehran, Iran), AO7 by Alvan Industries Company (Tehran, Iran), super concrete adhesive by Optimum Concrete Chemistry Company (Tehran, Iran), HCl and NaOH for pH adjustment, potassium dichromate, silver sulfate, mercury sulfate and sulfuric acid product of Merck Company (Darmstadt, Germany) for COD testing and distilled water for dilution.

3. Results and discussion

3.1. Effects of pH on dye removal

One of the important parameters in photocatalytic reactions is the pH of the solution, which may affect the ionization state of dye molecules, the surface charge state of catalyst and the oxidative species. Dye removal under different initial pH in suspended and immobilized reactors was shown in Fig. 4. Dye removal was highest under neutral conditions in both reactors, indicating neutral pH favorable for photocatalytic reaction. Thus, the initial neutral pH 7 was selected in the following tests. Dye removal after 60 min reaction under strongly acidic conditions (pH 2.2 in suspended reactor and pH 3 in immobilized reactor) was very low (less than 5%). Under strongly acidic conditions, AO7 would be dominant in a neutral state and thus harder to adsorb onto the ZnO surface although ZnO surface positively charged and more protons would consume lots of hydroxyls directly, both reducing dye oxidation. With pH increased to neutral conditions (pH around 7), dye removal increased to the maximum value (95% and 27%) for suspended and immobilized reactors, respectively. With pH increased to alkali condition (pH 9–11), dye removal significantly decreased for both reactors. Under strong alkali conditions, both AO7 and ZnO would be negatively charged and thus hard for adsorption and more [OH$^-$] would directly occupy the surface positive holes of ZnO, both reducing dye oxidation. Under neutral conditions, AO7 would be partially negatively charged without negative effects from excessive [H$^+$] or [OH$^-$], thus oxidation rate would be highest [30–33].

3.2. Effects of UV lamp power on dye removal

UV lamps with different power of 8, 16, 24, 32 and 40 W were used to investigate the effect of UV radiation intensity on dye removal. For both suspended and immobilized reactors (shown in Fig. 5), dye removal after the same reaction time (10–60 min) firstly increased with UV lamp power (i.e., the number of photons emitted) from 8 to 32 W and then kept nearly constant with UV lamp power from 32 to 40 W. This indicated that UV lamp power of 32 W could meet the maximum energy demand for exciting ZnO in this study. Thus, the UV lamp power of 32 W was selected as the energy source for the following tests. After 60 min reaction under UV lamp power of 32 W, dye removal under initial AO7 concentration of 50 mg/L and ZnO dosage of 10.32 g/L in suspended reactor and 80 g/m^2 in immobilized reactor reached 97% and 35%, respectively.

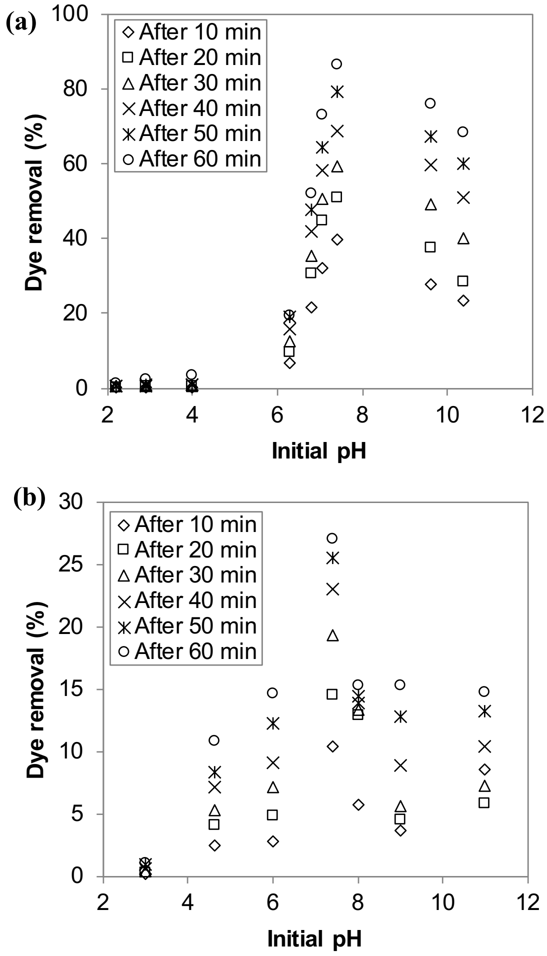


Fig. 4. Dye removal under different initial pH of dye solution. (a) Suspended reactor (initial dye concentration 50 mg/L, ZnO dosage 10.32 g/L, UV lamp power 32 W) and (b) Immobilized reactor (initial dye concentration 50 mg/L, ZnO dosage 80 g/m^2, UV lamp power 32 W).

3.3. Effects of ZnO dosage on dye removal

Different ZnO dosage of 2.58–25.8 g/L for suspended reactor and of 20–200 g/m^2 for the immobilized reactor was tested to investigate its effects on dye removal. From Fig. 6a for suspended reactor, dye removal showed a rapid increase with ZnO dosage from 2.58 to 10.32 g/L and a slow increase with ZnO dosage from 10.32 to 25.8 g/L. This indicated that the ZnO dosage of 10.32–25.8 g/L would make the solution more turbid and thus affect UV light penetration in this study. Thus, the ZnO dosage of 10.32 g/L was selected for the following tests. After 60 min reaction under ZnO dosage of 10.32 g/L, dye removal under initial AO7 concentration of 50 mg/L and UV lamp power of 32 W in the suspended reactor reached 96%.

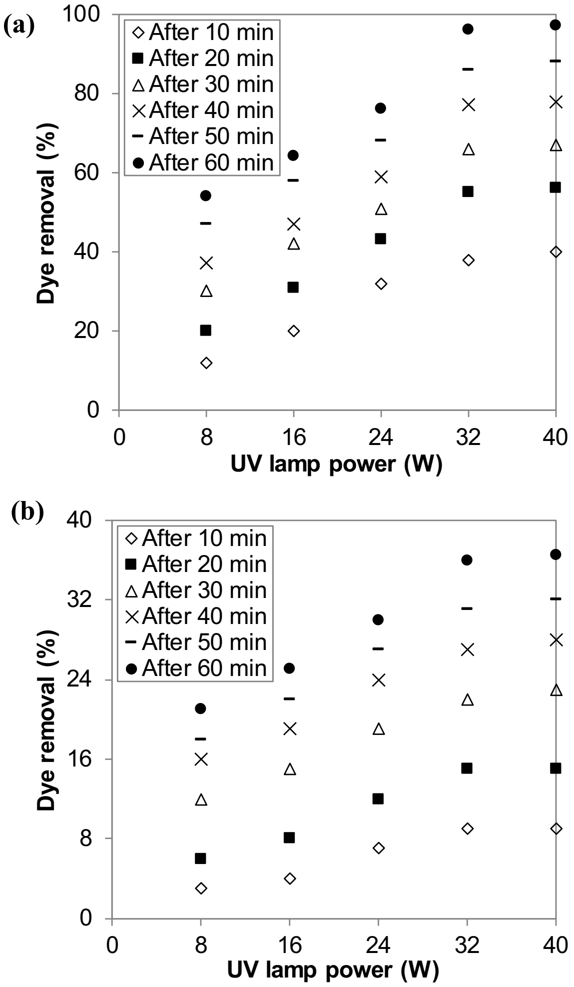


Fig. 5. Dye removal under different UV lamp power. (a) Suspended reactor (initial pH 7, initial dye concentration 50 mg/L, UV lamp power 32 W) and (b) Immobilized reactor (initial pH 7, initial dye concentration 50 mg/L, UV lamp power 32 W).

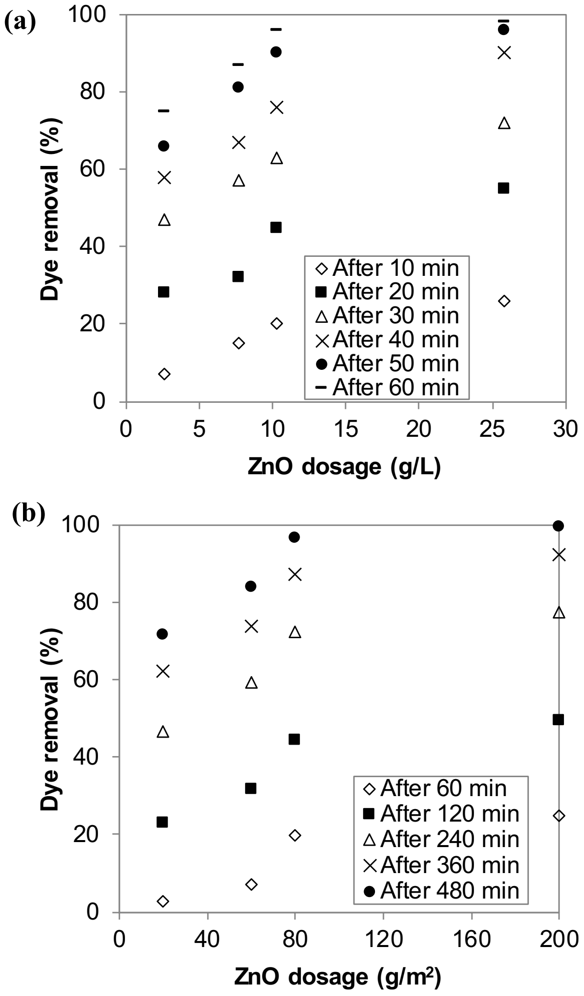


Fig. 6. Dye removal under different ZnO dosage. (a) Suspended reactor (initial pH 7, initial dye concentration 50 mg/L, ZnO dosage 10.32 g/L) and (b) Immobilized reactor (initial pH 7, initial dye concentration 50 mg/L, ZnO dosage 80 g/m^2).

From Fig. 6b for immobilized reactor, dye removal showed a rapid increase with ZnO dosage from 20 to 80 g/m^2 and a slow increase with ZnO dosage from 80 to 200 g/m^2. This indicated that the ZnO dosage of 80–200 g/m^2 could cover the concrete plate more than one layer and thus the effective ZnO surface area receiving UV light could reach the maximum value in this study [34]. Thus, the ZnO dosage of 80 g/m^2 was selected for the following tests. After a 480 min reaction under ZnO dosage of 80 g/m^2, dye removal under initial AO7 concentration of 50 mg/L and UV lamp power of 32 W in immobilized reactor reached 97%.

3.4. Dye removal, removal kinetics, and energy consumption under different dye concentration

Under the selected initial pH of 7, UV lamp power of 32 W and ZnO dosage of 10.32 g/L for suspended reactor and 80 g/m^2 for immobilized reactor based on the section of 3.1–3.3, different initial dye concentration of 10–200 mg/L was investigated to explore dye removal, removal kinetics, and energy consumption. From Fig. 7a for suspended reactor, dye removal reached more than 95% after 20, 30, 60, 80, 90, 110 min reaction under initial dye concentration of 10, 20, 50, 100, 150, 200 mg/L, respectively. From Fig. 7b for immobilized reactor, dye removal reached more than 95% after 90, 120, 300, 540, 780, and 1,020 min reaction under initial dye concentration of 10, 20, 50, 100, 150, and 200 mg/L, respectively.

For both reactors, dye removal showed a logarithmic increasing trend, indicating it might follow the first-order reaction kinetics ($dC/dt = -k_f \cdot C$, $\ln(C/C_0) = -k_f \cdot t$; where C is AO7 concentration at time t (mg/L), C_0 is initial AO7 concentration (mg/L), k_f is first-order rate constant (1/min), t is reaction time (min)). The good linear correlation (all correlation coefficient R higher than 0.98) between $\ln(C/C_0)$ and t (shown in Fig. 8) demonstrated that AO7 removal by UV/ZnO photocatalytic oxidation for both suspended and immobilized reactors followed the first-order reaction kinetics in this study.

The first-order rate constant under different initial dye concentrations for both suspended and immobilized reactors

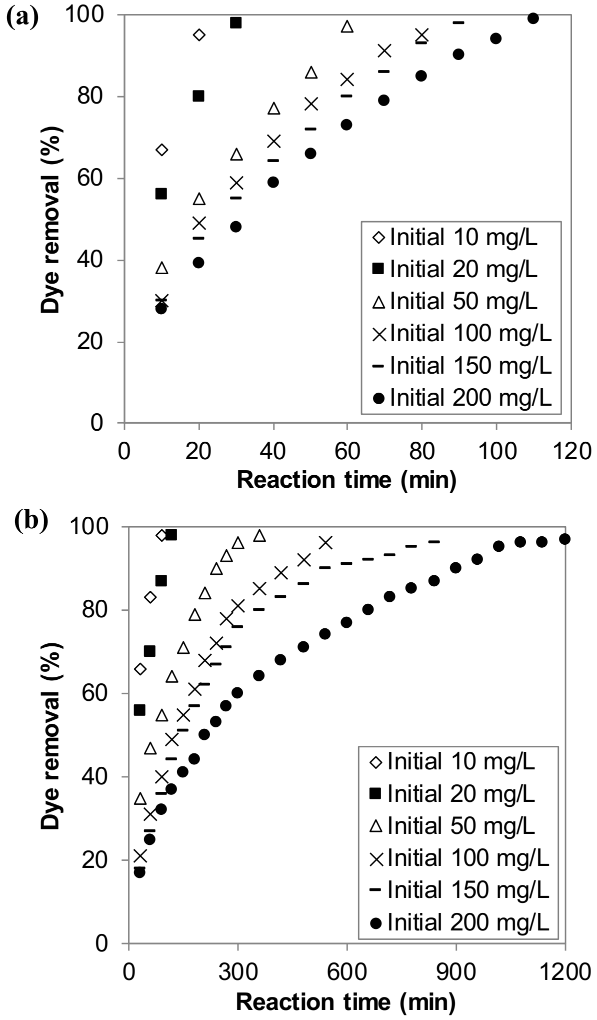


Fig. 7. Dye removal under different initial dye concentration. (a) Suspended reactor (initial pH 7, ZnO dosage 10.32 g/L, UV lamp power 32 W) and (b) Immobilized reactor (initial pH 7, ZnO dosage 80 g/m^2, UV lamp power 32 W).

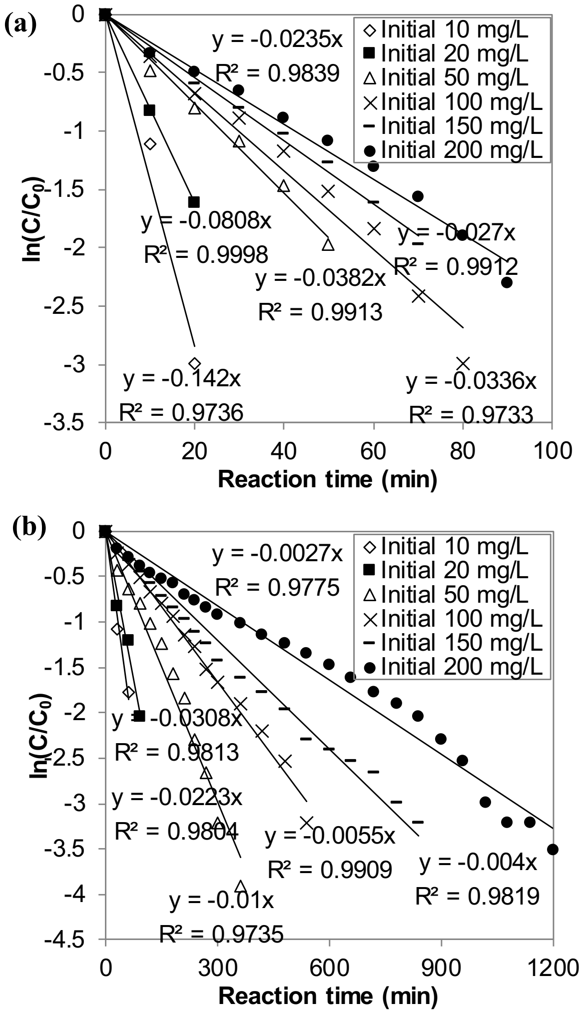


Fig. 8. First-order reaction kinetics correlation for dye removal under different initial dye concentrations. (a) Suspended reactor (initial pH 7, ZnO dosage 10.32 g/L, UV lamp power 32 W) and (b) Immobilized reactor (initial pH 7, ZnO dosage 80 g/m^2, UV lamp power 32 W).

was shown in Fig. 9. For suspended reactor, the first-order rate constant showed a rapid decrease from 0.142 to 0.0382 1/min with initial dye concentration from 10 to 50 mg/L and then a slow decrease from 0.0382 to 0.0235 1/min with initial dye concentration from 50 to 200 mg/L, which were similar to a previous study [35]. Similarly, for the immobilized reactor, the first-order rate constant showed a rapid decrease from 0.0308 to 0.01 1/min with initial dye concentration from 10 to 50 mg/L and then a slow decrease from 0.01 to 0.0027 1/min with initial dye concentration from 50 to 200 mg/L. Under lower initial dye concentration, both UV light intensity and ZnO active surface area were excessive, thus resulting in a higher photocatalytic reaction rate. With increasing initial dye concentration, ZnO active surface area and UV light intensity gradually became the limiting factor penetration [5,36], thus resulting in decreasing photocatalytic reaction rate in this study.

Based on dye removal with reaction time in this study, energy consumption per removed dye could be calculated ($E_t = P\cdot t/(V\cdot(C_0-C_t))/60$; where E_t is energy consumption per removed dye at reaction time t (Wh/mg), P is UV lamp power (W), t is reaction time (min), V is reactor volume (L), C_0 is initial AO7 concentration (mg/L), C_t is AO7 concentration at time t (mg/L)). The energy consumption for dye removal of more than 95% in both suspended and immobilized reactors was shown in Fig. 10. For the suspended reactor, the energy consumption showed a rapid decrease from 0.65 to 0.38 Wh/mg with initial dye concentration from 10 to 50 mg/L and then a slow decrease from 0.38 to 0.17 Wh/mg with initial dye concentration from 50 to 200 mg/L. Similarly, for the immobilized reactor, the energy consumption showed a rapid decrease from 2.84 to 1.93 Wh/mg with initial dye concentration from 10 to 20 mg/L and then a slow decrease from 1.93 to 1.74 Wh/mg with initial dye concentration from 20 to 200 mg/L. In contrast with the reaction rate, energy consumption decreased with increasing initial dye concentration. More UV light were consumed directly for photocatalytic

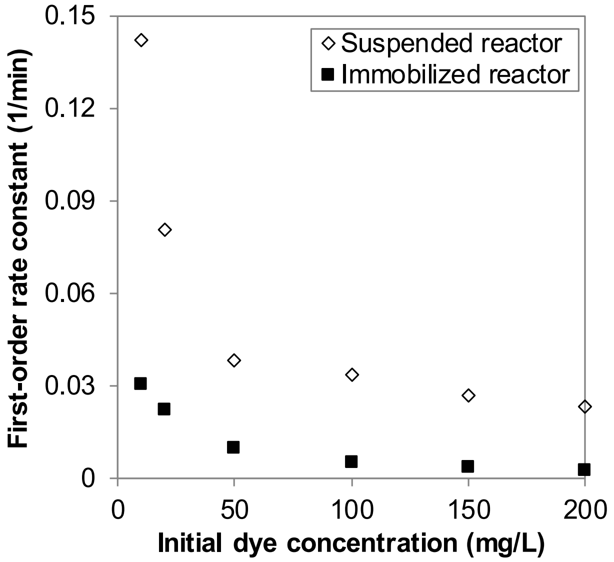


Fig. 9. First-order rate constants under different initial dye concentration (initial pH 7, UV lamp power 32 W, ZnO dosage 10.32 g/L for suspended reactor and 80 g/m^2 for immobilized reactor).

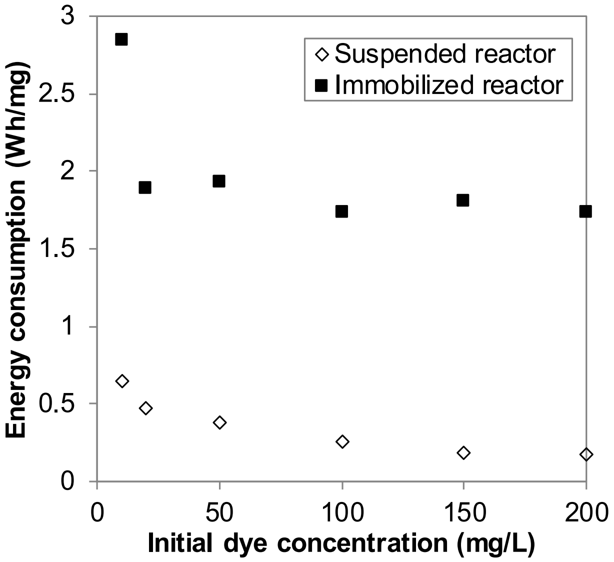


Fig. 10. Energy consumption per removed dye under different initial dye concentration (initial pH 7, UV lamp power 32 W, ZnO dosage 10.32 g/L for suspended reactor and 80 g/m^2 for immobilized reactor).

oxidation of dye under higher initial dye concentration, thus enhancing the energy efficiency for dye removal.

3.5. Comparison between suspended and immobilized reactor

Based on the balance between reaction rate and energy consumption, the optimum initial dye concentration would be 50 mg/L for both suspended and immobilized reactors. The summarized results for both suspended and immobilized reactors under the optimum conditions (initial pH 7, UV lamp power 32 W, initial dye concentration 50 mg/L, ZnO dosage 10.32 g/L and 80 g/m^2) are shown in Table 2. For suspended reactor, dye and COD removal after 60 min reaction reached 97% and 72%, respectively. For immobilized reactor, dye and COD removal after 360 min reaction reached 98% and 74%, respectively. The difference between dye and COD removal indicated that some intermediate products occurred during photocatalytic oxidation of AO7 and could be eventually mineralized with prolonged reaction time.

From the experimental protocol, only one concrete plate with ZnO coated one side was used for the immobilized reactor, resulting in that the real ZnO mass was 0.69, 2.07, 2.76 and 6.9 g corresponding to ZnO dosage of 20, 60, 80 and 200 g/m^2, respectively. For the suspended reactor, the real ZnO mass was 4.45, 13.35, 17.8 and 44.5 g corresponding to ZnO dosage of 2.58, 7.74, 10.32 and 25.8 g/L, respectively. Thus, the strict comparison between suspended and immobilized reactors was not available due to that the ZnO mass was not the same in both reactors even under the same other conditions (i.e., initial pH, UV lamp power, initial dye concentration). However, the ZnO mass of 4.45 g corresponding to ZnO dosage of 2.58 g/L for the suspended reactor was just fallen between 2.76 and 6.9 g corresponding to the ZnO dosage of 80 and 200 g/m^2, respectively, for immobilized reactor. Thus, a direct comparison between suspended and immobilized reactors could be made from Fig. 6. After 60 min reaction, dye removal reached 75% under ZnO dosage of 2.58 g/L for suspended reactor (Fig. 6a) while dye removal reached 19.7% and 24.8% under ZnO dosage of 80 and 200 g/m^2, respectively, for immobilized reactor (Fig. 6b). This indicated that dye removal in the suspended reactor was 3–3.8 times of dye removal in an immobilized reactor under the same conditions. Much less active surface area of ZnO in immobilized reactor than suspended reactor could be the main reason for lower dye removal in immobilized reactor than suspended reactor. This was the natural drawback for immobilized catalysts and could be improved via increasing concrete plate area (still receiving UV light) in the reactor (e.g., multiple inclined concrete plates). Thus, it was possible to make an immobilized reactor reach the comparable photocatalytic efficiency to the suspended reactor.

Table 2
Optimum conditions for suspended and immobilized reactor in this study

Parameters	Suspended reactor	Immobilized reactor
ZnO dosage	10.32 g/L	80 g/m^2
AO7 concentration	50 mg/L	50 mg/L
pH	7	7
UV lamp power	32 W	32 W
Optimum reaction time	60 min	360 min
Dye removal	97%	98%
COD removal	72%	74%

4. Conclusions

This study investigated systemically AO7 removal by combined UV and ZnO (suspended or immobilized on concrete plate) photocatalytic batch tests under different initial pH of 2–11, UV lamp power of 8–40 W, ZnO dosage of 2.58–25.8 g/L for suspended reactor and 20–200 g/m^2 for immobilized reactor, and initial AO7 concentration of 10–200 mg/L. The optimum reaction conditions for AO7 removal were as follows: neutral pH of 7, UV lamp power of 32 W, ZnO dosage of 10.32 g/L for the suspended reactor and 80 g/m^2 for the immobilized reactor. AO7 removal under different initial AO7 concentrations of 10–200 mg/L could reach over 95% after 20–110 min and 90–1,020 min reaction time for suspended and immobilized reactors, respectively. AO7 removal followed by first-order reaction kinetics with decreasing rate constant (0.142–0.0235 1/min for suspended reactor and 0.0308–0.0027 1/min for immobilized reactor) and energy consumption (0.65–0.17 Wh/mg for suspended reactor and 2.84–1.74 Wh/mg for immobilized reactor) with increasing initial AO7 concentration from 10 to 200 mg/L. Although the photocatalytic efficiency in the immobilized reactor was significantly lower than in the suspended reactor, it could be improved via increasing the ZnO coated concrete plate area (i.e., ZnO active surface area).

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