Synthesized Cr/TiO₂ immobilized on pumice powder for photochemical degradation of acid orange-7 dye under UV/visible light: influential operating factors, optimization, and modeling

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Abstract

The current study aimed to investigate the removal efficiency of acid orange-7 (AO7) using synthesized Cr/TiO₂ immobilized on pumice powder under visible light and UV irradiation. The characterization of synthesized nanocatalyst examined by scanning electron microscope, X-ray diffraction, and Fourier transforms infrared. The optimum of experimental parameters including catalyst dosage, dye concentration, time and pH, D-optimal Design (DOD) along with response surface methodology obtained by R software. The initial and outlet concentration was measured using a spectrophotometer. Besides, Analysis of variance results for the quadratic model showed simple linear regression with high significance and provided as a predicting model. The differences less than 0.2 between multiple and adjusted R² in two models indicate that two examined models fitted suitably. The highest removal efficiency of AO7 was 95 and 74% under visible and UV irradiation, respectively. Therefore, the higher removal efficiency in visible light reduces the costs and energy, moreover, offers an environmentally friendly method. The results showed that the removal efficiency of AO7 increased considerably with rising catalyst dosage and time, as well as minimizing dye concentration, and pH.

Keywords Acid orange-7 · Cr/TiO₂ · UV light · Visible light · Pumice

Introduction

The effluent of the textile industries is one of the most significant types of water pollution worldwide due to the prominent demand for textile products. Besides, more than 17–20% of industrial water pollution produce in various processes of textile manufactures and produces colored wastewater [1, 2]. In these industries, azo dyes are significant and extensively used,

which demonstrate relatively 70% of dyes consumption in the world [3, 4]. Beside, among azo dyes, methyl orange is widely used as a pH indicator (pK_a = 3.5) as well as in textiles, food, paper, and leather industries. This compound creates serious health risks for humans and animals due to toxicity, cancer, genetic mutation, and low biodegradation [5]. Furthermore, methyl orange is stable to visible light and ultraviolet light because of its very short excited-state lifetime [6].

General treatment processes such as coagulation and activated sludge processes are not suitable in removing dyestuff due to their solid wastes generation [7, 8]. Therefore, new technology to reduce this effluent problem with minimum impact on the surrounding environment is required. So far, photocatalytic processes considered an effective alternative method to treat dye compounds in wastewater because of their excellent degradation and mineralization potential of organic pollutants [9–11]. According to the low cost, non-toxicity, chemical stability, and high-efficiency properties, TiO₂ is extensively used as an efficient catalyst to remove organic pollutants in water [12–14]. Though, TiO₂ has some disadvantages including bulky band-gap energy, which only response to UV light and leads to a higher electron-hole recombination

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level, consequently it cannot produce an adequate amount of $\bullet\text{OH}$, on the surface area [15].

Therefore to overcome this problem, several studies concentrating on TiO_2 surface modification by incorporation transition metals dopants such as Fe, V, Mo, Mn, and Cr into the TiO_2 crystal lattice, which improve the TiO_2 photo-response by lessening the band-gap energy [15–18]. In this study, to modify the photocatalytic activity of TiO_2 , chromium has been selected as a suitable dopant into TiO_2 , because chromium could repress the recombination of photo-generated electron-holes and rising the charge separation, which increases the wavelength response range [19, 20]. TiO_2 and other nanoparticles have adverse impacts on aquatic organisms, while the main challenge in treatment processes is to use low-cost and stable nanoparticles, which has a low affect on the environment [21]. Furthermore, agglomeration of suspended nanoparticles in liquid solution decreases the efficiency of photocatalytic degradation, and its recovery from aqueous solution is difficult [22, 23]. It reported that the porous supports could simultaneously increase photocatalytic degradation and adsorb pollutants [24].

In recent years, the researchers used pumice powder for removing cadmium, disinfection byproducts, heavy metals, phenol, various dyes, and sulfur dioxide from aqueous solution. Besides, Pumice powder as a porous media confirmed as excellent support according to low cost, micro-porous structure, large surface area, and plentifully availability in the earth's crust [25, 26]. In the present study, immobilized doped Cr/ TiO_2 nanoparticles on pumice powder synthesized by the sol-gel method, and the photocatalytic activity for AO7 removal from aqueous solution evaluated under both UV and visible light.

Materials and methods

Synthesis and characterization of immobilized Cr-doped TiO_2 nanoparticle

For preparing pure TiO_2 nanocatalysts, sol-gel method used as follows: First, Solution A prepared beforehand by dissolving titanium isopropoxide (3.96 mL, 97%, SIGMA-ALDRICH) in 2-propanol (100 mL, Merck, Germany); Secondly, solution B provided by mixing distilled water (39 mL, Merck, Germany) in 2-propanol (39 mL, Merck, Germany); then, by adding glacial acetic acid (Merck, Germany) the pH of the solution adjusted to 2. In the next step, Solution B added drop-wise to solution A in a vigorous stirring for 2 h, then placed in a dark place for 2 days. After that, the pH of the solution was increased using ammonia and kept for one day for separation. Later, the obtained supernatant drained and settled particles dried at 80 °C in an oven. Finally, the sample was calcined in a muffle furnace at 400 °C for 2 h.

TiO_2 nanoparticles doped by chromium (Cr- TiO_2) were also synthesized by the same method of pure TiO_2 , except adding different amount of chromium nitrate 3(9 H_2O) (99%, SIGMA-ALDRICH) (at 0.5, 1, 3, 5, 10% of Cr to TiO_2) to the solution B, and dissolved in deionized water to obtain doped TiO_2 nanoparticles. In this stage, to remove the nitrate in the chromium nitrate structure, the resulting solution mixed with methanol (Merck, Germany) before drying, so the nitrate enters into the methanol. Then, the solution centrifuged for draining the methanol.

To Immobilization of Cr- TiO_2 on pumice powder, the pumice powder sieved with 50#, and to remove the impurity of pumice powder, the particles washed with distilled water for several times and kept in hydrogen chloride solution (1 normality, Merck, Germany) for 24 h, washed with distilled water again until the pH reached neutral. Immobilizing the Cr- TiO_2 on pumice, prepared with the same procedure of Cr- TiO_2 synthesized, except after removing methanol, 3 g of pumice powder was added and stirring for 2 h.

Characterization

The structure and phase composition of prepared samples determined by the X-ray diffraction (XRD) using Diffractometer Bragg-Brentano (Philips poster), reflection type in 30 mA and Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) at 40 kV, and the diffraction angles of 2θ in the range of 10–80°. The shape and surface morphologies of prepared samples characterized by a high-resolution scanning electron microscopy, SEM (Czech TESCAN company). Furthermore, the optical transmittance of samples determined by UV–vis light diffused reflectance spectroscopy (DRS) (the Avantes Spectrometer - Avaspec-2048-TEC model with Ava Lamp DH-S Setup) in the range of 300 to 900 nm wavelength. Moreover, the potential of functional groups on the surface of synthesis and immobilized Cr- TiO_2 nanoparticles recorded by FTIR using KBr pellets in the range of 400 to 4000 cm^{-1} on FT-IR a Bruker- Tens-OR 27 spectrophotometers.

Experimental setup for evaluating the AO7 removal efficiency

The experimental setup for measuring the removal efficiency of AO7 presented in Fig. 1. The setup including a Pyrex-glass reactor with the diameter and working volume of 10 cm and 100 mL, respectively. In addition, a 6 watts low-pressure lamp (Philips) with a length and diameter of 10 and 2 cm, respectively, placed at a 1 cm distance from the solution surface to implement UV irradiation, although visible light provided by sunlight. The sunlight intensity carefully recorded with UV-meter (Lurton), which was 17.2 W/m^2 .

In the current study, the effect of four factors including nanoparticle dosage (0.5–5 g/L), initial concentration of dye

Fig. 1 The schematic diagram of photocatalytic reactor used for acis orange-7 removal: **a** UV **b** visible light [27]

(5–50 mg/L), contact time (30–100 min), and initial pH of 3–9 on AO7 (Merck, Germany) removal investigated (Table 1). According to Table 1, coded values for the factors range considered from +1 to −1, which, zero code represents the center point. For carrying the photocatalyst experiments in the reactor, 50 ml of a specified concentration of AO7 solution with a certain amount of each variable, constantly stirred for determined contact time.

To determine the highest removal efficiency of Cr-TiO₂ nanoparticles, among the different percentages of Cr-TiO₂, a stock solution of 8 mg/l was prepared by nano-catalyst powder and investigated for AO7 dye removal in both UV and visible light sources. For this purpose, 0.2 g of nanoparticles were dissolved in 25 ml of deionized water and mixed for 5 min, then irradiated in a 40 kHz frequency of ultrasonic waves for 10 min to homogenize the solution. For removal efficiency analysis, the specific value of the stock and other variables added to the reactor, the resulted suspension centrifuged (5000 rpm), and filtered by 0.2 μm cellulose acetate membrane filter after a contact time. The initial and residual dye concentration of the solution was analyzed by spectrophotometer at 485 nm. Afterward, the catalyst with maximum removal efficiency, which was 10% Cr/TiO₂ (Fig. 2) selected to stabilize on pumice powder. All of the experiments were carried out by 10% Cr/TiO₂ immobilized on pumice powder.

The percentage of AO7 degradation efficiency can calculate as follows:

$$DE\% = \frac{c_0 - c}{c_0} \times 100\% \quad (1)$$

Table 1 Experimental ranges and independent variable levels used in CCD design

Variables	Symbol	Coded levels		
		−1	0	+1
		Real values		
Nanoparticle doses	×1	0.5	2.58	5
Initial concentration of dye	×2	5	26.77	50
Contact time	×3	30	69.28	100
pH	×4	5	7	9

Where C_0 is the initial concentration of AO7 (mg/L); C is the remaining concentration of AO7 (mg/L) at given time.

Design of experiment using DOD

In the current study, the design of the experimental of AO7 removal carried out by D-optimal Design (DOD). Furthermore, RSM applied to determine the quadratic effects of independent variables on the AO7 dye removal (response variable) and the interaction effects of each considered factors including nanoparticle dosage (×1), initial concentration of dye (×2), contact time (×3), initial pH (×4) on the AO7 removal efficiency (Y). Collectively, 28 runs performed in each visible and UV illumination source. The analysis variances (ANOVA) (R^2 , adjusted R^2 , Predicted R^2 , F-test, and t-test), plots, and residuals analysis applied to examine the results and to confirm the statistical significance of the fitted quadratic models [28]. After obtaining the responses, the relationship between the response (Y) and the independent variables in the D-optimal design calculated by the following model Eq. (2) [29]:

$$y = B_0 + \sum_{i=1}^n B_i X_i + \sum_{i=1}^n B_{ii} X_i^2 + \sum_{i < j} B_{ij} X_i X_j + \varepsilon \quad (2)$$

Where y is the response (AO7 removal efficiency), B_0 is the constant response whenever all variables set at the center point, B_i , B_{ii} and B_{ij} indicates the linear coefficient, quadratic coefficient, and interaction coefficient, respectively; x_i the variables coded values and n is the independent variables number.

Result and discussion

Structural properties of immobilized Cr/TiO₂ nanoparticle

Figure 3 compares the phase structures of immobilized Cr/TiO₂ nanoparticle described by XRD patterns. As provided in the Fig. 3, prepared composites have several diffraction peaks at 38/69° attributed to Anatase Phase (JCPDS card no.

Fig. 2 AO7 removal by 0.5, 1, 3, 5, 10% Cr/TiO₂ and commercial TiO₂ under UV and visible light

21-1272), 29/59°, 56/33°, and 78/33° in Brookite Phase (JCPDS card No. 29-1360), and 41/49°, 56/33°, 64/38°, and 74/42° correspond to the Rutile phase (JCPDS card no. 21-1276) of titanium oxide. Furthermore, 35/40°, 41/49°, 74/42° peaks belong to the chromium as the dopant element (JCPDS card no. 06-0532), which confirms the successful dope of Cr on TiO₂.

The shape and morphology of nanoparticles stabilized on the pumice showed in Fig. 4 at two scales (1 μm and 500 nm). The figure shows an irregular surface in coated pumice, which some of the pumice pores filled by the nanoparticles, moreover, on the nanometric scale, the roughness of the pumice surface increased. The EDAX analysis (Fig. 3) also show a small percentage of titanium (1.96%) in the pure pumice, while chromium is generally absent. In the coated sample, titanium and chromium increase by 25.49% and 2.07%, respectively. These changes confirm the successful coating of

TiO₂ containing chromium on the surface of the pumice. As a result, more catalyst activity is likely to be within the visible light range.

DRS of samples recorded with Avaspec-2048-TEC Avantes Spectrometer with AvaLamp DH-S Setup. Figure 5 shows the spectra of commercial TiO₂ and 10% Cr-TiO₂. The pure TiO₂ absorption edge is about 420 nm, that increased to 670 nm, by adding 10% chromium to the nanoparticle, which leads to the enhancement of the activity of the nanoparticles in visible light. Therefore, these nanoparticles are active in both light sources. The light adsorption intensity in Cr-TiO₂ is higher than pure TiO₂, resulting in the production of more electron-holes and higher catalytic activity. Therefore, it is likely that nanoparticles containing 10% chromium will be more effective in removing AO7 dye from aqueous solutions in both light sources.

Fig. 3 XRD pattern for Cr-TiO₂

Fig. 4 SEM images and IDAX of **a**, **b** raw and **c**, **d** coated pumice

Figure 6 shows the FTIR spectrum of bare pumice and Cr-TiO₂ immobilized on pumice. In the pumice sample, the major peaks are 3431.84, 2923.94, 2373.51, 1637.88, 1385.2, 1044.37, and 468.3 cm⁻¹, which correspond to the functional groups of B-N-H, -O-H, C-N, P-H, -NH₂, C-H, and C-O-C, respectively. On the other hand, in coated pumice, the absorption intensity at 3431.84, 1637.88, and 1044.37 cm⁻¹

increased, while a new peak at 731.75 cm⁻¹ appears, which corresponds to the SO₂.

Model fitting and statistical analysis

The experimental data implied for AO7 removal by UV and visible light and predicted response related to the

Fig. 5 DRS of commercial TiO_2 and 10% Cr- TiO_2

corresponding model shows in Table 2. The AO7 removal efficiency was 4–82% and 5–92% for UV and visible light, respectively (Table 2). The effect of each factor ($\times 1$, $\times 2$, $\times 3$, $\times 4$ related to Dose, Dye concentration, Time, and pH, respectively) on AO7 removal under UV and visible light compared in Table 3. The result reveals that in both light sources, all the factors had a statistically significant effect on efficiency at the first-order model.

The dose and time were more significant than the dye concentration and pH in UV irradiation. On the other hand, in the visible light, the significance of pH was more compare to UV light, while it was lesser in case of time. It seems that the factors behave differently in various light sources. Increasing the dose and contact time will increase efficiency, but the dye concentration and pH reduce the removal efficiency. The dye concentration with the coefficient estimate and T-value of 5.67 and 3.23, respectively, had less adverse effects on removal efficiency than the pH factor (Table 3). In the interaction model, there is a meaningful correlation between dose and concentration in both light sources, but time and pH are only significant in UV light. According to the results, the quadratic

model was chosen for prediction because it properly fits with the results.

The significance of AO7 dye removal evaluated by the ANOVA and several regression analyses with quadratic models used to calculate and fit the results (Table 4). The $R^2 > 0.99$ obtained for AO7 dye removal in both UV and visible light sources. The values of adjusted regression ($R^2\text{-Adj}$) for examined dye were 0.97% and 0.98% in UV and visible light, respectively, their difference with R square is less than 0.2 indicate the appropriate relationships between the response and variables. On the other hand, in the given model, the p value < 0.0027 and < 0.0001 obtained under UV and visible light irradiation, respectively. Conclusively, the model is significant in the dye removal process [30].

The obtained lack-of-fit and F-value of 0.57 and 0.94 imply that the lack of fit was statistically insignificant for dye removal in both UV and visible light, respectively, which prove a significant model relationship between the variables and AO7 dye removal [31]. Moreover, the results of ANOVA indicated that the effect of all investigated variables on response was significant (P value < 0.05).

Effect of independent variables on AO7 removal

The combined effect of nanocatalyst dose and contact time at a pH of 5 and the initial concentration of 27.50 mg/L shown in Fig. 8a, b. The photocatalytic degradation increases with increases the catalyst dosage from 0.5 to 5 g/L and contact time from 30 to 100 min. Also, dye removal could be affected by the catalyst concentration, that might be due to the characteristic of heterogeneous photocatalysis [32]. As shown in this figure, the highest removal efficiency of 75.94% and 68.41% for AO7 dye found at a maximum dosage of Cr/ TiO_2 catalyst (5 g/L) and contact time of 100 min under both visible and UV

Fig. 6 FTIR spectra of pumice and pumice/Cr- TiO_2

Table 2 DOD experimental design for AO7 removal

Run	Coded levels of variables				Levels of variables				Response AO7 removal %	
	×1	×2	×3	×4	Dose (g/L)	Dye con. (mg/L)	Time (min)	pH	UV irradiation experimental	Visible light experimental
1	1.00	1.00	−1.00	1.00	5	50	30	9	47.32	73.54
2	1.00	−0.15	−1.00	−1.00	5	24.03	30	5	45.62	44.24
3	1.00	−1.00	0.00	1.00	5	5	65.06	9	65.67	31.88
4	0.24	0.25	0.11	−1.00	3.28	33.13	68.72	5	73.56	91.83
5	1.00	−1.00	−1.00	0.00	5	5	30	7	53.13	19.35
6	1.00	−1.00	1.00	0.00	5	5	100	7	67.85	48.77
7	0.16	−1.00	1.00	−1.00	3.1	5	100	5	79.29	54.77
8	1.00	1.00	−0.06	0.00	5	50	62.93	7	65.88	89.65
9	1.00	1.00	1.00	−1.00	5	50	100	5	70.54	92.28
10	−1.00	−1.00	1.00	1.00	0.5	5	100	9	56.40	16.08
11	−0.16	1.00	−1.00	−1.00	2.4	50	30	5	50.38	69.68
12	−1.00	0.15	1.00	−1.00	0.5	30.92	100	5	23.29	51.77
13	−1.00	−1.00	0.06	0.00	0.5	5	67.08	7	39.51	30.25
14	−1.00	1.00	−1.00	0.00	0.5	50	30	7	12.40	7.69
15	−1.00	−1.00	1.00	1.00	0.5	5	100	9	44.96	5.18
16	−1.00	−1.00	−1.00	−1.00	0.5	5	30	5	37.87	14.44
17	−0.13	−0.12	0.94	0.00	2.46	24.81	97.81	7	62.62	62.02
18	0.11	0.13	−0.81	0.00	3	30.35	36.56	7	31.28	60.49
19	−1.00	1.00	0.00	1.00	0.5	50	64.94	9	3.58	11.36
20	−1.00	0.15	1.00	−1.00	0.5	30.92	100	5	21.23	13.27
21	−0.53	−0.54	−1.00	1.00	1.55	15.36	30	9	23.22	20.32
22	−0.25	−0.31	0.23	1.00	2.19	20.46	72.92	9	51.42	60.08
23	0.53	0.54	1.00	1.00	3.95	39.62	100	9	76.58	70.88
24	0.16	−1.00	1.00	−1.00	3.1	5	100	5	82.02	52.59
25	1.00	1.00	−1.00	1.00	5	50	30	9	57.73	75.68
26	−1.00	−1.00	0.06	0.00	0.5	5	67.08	7	45.50	31.88
27	−1.00	1.00	1.00	0.00	0.5	50	100	7	15.10	13.81
28	−0.19	1.00	0.91	−1.00	2.33	50	96.72	5	63.55	77.76

light sources, respectively. The improvement of removal efficiency might be due to active hydroxyl radicals, because of a higher presence of active sites and surface area in higher nanocatalyst dosage [33]. Abdollahi et al. reported an 85% removal rate of AO7 from wastewater using reusable clinoptilolite–TiO₂ nanocomposite [34].

The influence of different nanocatalyst doses (from 0.5 to 5 g/l) on the photocatalytic degradation of AO7, studied at different pH values of (5, 7, and 9) under both visible and UV light, whereas the initial concentration and reaction time were fixed at 27.5 mg/L and 65 min, respectively. The pH of the solution is an important parameter, which affects the photocatalytic degradation activity. The difference of pH in the solution switches the TiO₂ surface charge and changes the catalytic reaction abilities. Therefore, the dye adsorption on the surface altered, resulting in changing the reaction rate. So, in acidic or alkaline form the TiO₂ surface could be protonated or deprotonated as follows [35]:

Therefore the surface of TiO₂ will be positively charged in the acidic situation and negatively charged in alkaline conditions. The surface charge of the TiO₂ catalyst is positive, which acts as a strong acid. On the other hand, the anionic dye behaves as a strong base, which can significantly adsorb on the positively charged catalyst surface. Therefore, this process is not favorable in the alkaline situation due to the completion of hydroxyl ions with the dye molecule, and also the electrostatic force of attraction with the dye molecule according to the negatively charged catalyst [36]. Photocatalytic degradation is related to the initial dye concentration, chemical structure of the dye, photocatalyst surface, and the solution pH. The effect of pH depends on the properties of catalyst surface-charge, which described as the point of zero charges

Table 3 Estimated regression coefficients for experimental AO7 removal %

Model term	Coefficient estimate	Standard error coefficient	T-value	P value	Significant level
UV irradiation					
(Intercept)	53.361903	4.4740606	11.926951	2.25E-08	****
×1	19.323634	1.7979412	10.747645	7.75E-08	****
×2	−5.6735134	1.7539652	−3.2346784	0.0065176	***
×3	10.443975	1.8295282	5.7085621	7.19E-05	****
×4	−3.6937227	1.8958732	−1.9482962	0.0732986	*
×1:×2	7.9171229	1.9852055	3.9880621	0.0015465	***
×1:×3	0.7276531	2.2991962	0.3164815	0.7566615	Non-significant
×1:×4	3.5994664	2.3800959	1.5123199	0.1543765	Non-significant
×2:×3	−1.7618433	2.1828537	−0.8071284	0.434112	Non-significant
×2:×4	−0.7900556	2.2709206	−0.347901	0.7334832	Non-significant
×3:×4	5.0582849	2.1974447	2.3018941	0.0385232	**
×1 ²	−18.825954	3.8776932	−4.8549366	0.0003144	****
×2 ²	12.225056	3.8813767	3.1496699	0.0076765	***
×3 ²	−3.824738	3.5392932	−1.0806502	0.2994933	Non-significant
×4 ²	2.4721369	3.2212727	0.767441	0.4565325	Non-significant
Visible light					
(Intercept)	53.361903	4.4740606	11.926951	2.25E-08	****
×1	19.323634	1.7979412	10.747645	7.75E-08	****
×2	−5.6735134	1.7539652	−3.2346784	0.0065176	****
×3	10.443975	1.8295282	5.7085621	7.19E-05	**
×4	−3.6937227	1.8958732	−1.9482962	0.0732986	***
×1:×2	7.9171229	1.9852055	3.9880621	0.0015465	***
×1:×3	0.7276531	2.2991962	0.3164815	0.7566615	Non-significant
×1:×4	3.5994664	2.3800959	1.5123199	0.1543765	Non-significant
×2:×3	−1.7618433	2.1828537	−0.8071284	0.434112	Non-significant
×2:×4	−0.7900556	2.2709206	−0.347901	0.7334832	Non-significant
×3:×4	5.0582849	2.1974447	2.3018941	0.0385232	Non-significant
×1 ²	−18.825954	3.8776932	−4.8549366	0.0003144	****
×2 ²	12.225056	3.8813767	3.1496699	0.0076765	Non-significant
×3 ²	−3.824738	3.5392932	−1.0806502	0.2994933	***
×4 ²	2.4721369	3.2212727	0.767441	0.4565325	Non-significant

**** < 0.0001; *** < 0.001; ** < 0.01; * < 0.1

Table 4 Analysis of ANOVA for response surface quadratic model

Source	Sum of square		Degrees of freedom		Mean of square		F value		p value prob > F	
	UV	Vis	UV	Vis	UV	Vis	UV	Vis	UV	Vis
Model	12,143.69	19,738.81	16	17	758.98	1161.11	47.81	73.20	< 0.0001	< 0.0001
Residual	111.12	126.89	7	8	15.87	15.86	—	—	—	—
Lack of fit	33.10	61.48	3	4	11.03	15.37	0.57	0.94	0.6663	0.5232
Pure error	78.03	65.41	4	4	19.51	16.35	—	—	—	—
Cor Total	12,254.82	19,865.70	23	25	—	—	—	—	—	—

UV: R-Squared: 0.9909, Adj R-Squared: 0.9702, Adeq Precision: 22.829, C.V. %: 8.28

Vis: R-Squared: 0.9936, Adj R-Squared: 0.9800, Adeq Precision: 25.441, C.V. %: 8.50

Fig. 7 Contour plots for the effect of each factor on the AO7 removal by visible (**a, c, e**) and UV light (**b, d, f**), Time (min) versus catalyst dosage (g/L) (**a** and **b**), catalyst dosage (g/L) versus pH (**b** and **c**), dye concentration (mg/L) versus Time (min) (**e** and **f**)

Fig. 8 Normal plot of residuals and predicted versus actual under **a** visible light and **b** UV light sources

(PZC). At pH value lower and more than PZC, the photocatalyst surface gets positively and negatively charged, respectively. According to the nature of the dye, it will be adsorbed less or more on the catalyst surface in acidic and basic conditions. In acidic media, electrons reduction in transition band plays a significant role in dye photodegradation because of the reductive cleavage of azo bonds [37–39]. AO7 (anionic dye) indicated the highest degradation at acidic pH that could be due to more positive hydrogen ions, for adsorption on the catalyst surface, in acidic media, which leads to the restriction of the semiconductor particle excitation and free radicals production reduction. The AO7 dye removal rate is 40% and 65% at catalyst dosages of 3 and 5 g/L under visible light (pH = 5) (Fig. 8c, d). The higher degradation occurred at higher catalyst dosages, which is because of the more available sites [40].

Figure 8e, f revealed that the removal efficiency increases by increasing initial dye concentration, and the maximum removal rate (79.65%) observed in 50 mg/L after 100 min contact time under visible light. The decolonization rate decreases with increases the initial concentration under both light source, it might be due to some reasons including 1) reduces photo path-length entering the solution in photocatalyst surface, and 2) adsorbing more ions of AO7 by TiO₂ powder [41, 42], which decreases the •OH production, resulting less removal efficiency. The increase of removal percentage of AO7 by increasing initial concentration under visible light was higher than UV light irradiation (Fig. 7e, f). The highest degradation of AO7 under visible and UV light sources were 79.65% and 74.31% in the time of 100 min and initial dye concentration of 50 and 5 mg/L, respectively. Hamadianian et al.

Table 5 Variable values for optimum efficiency of AO7 in UV and visible light

Vaibles	Dose	Con.	Time	pH	Removal(%)
UV irradiation	3.155	6.62	76.34	6.946	74.275
	2.75	27.5	65	7	53.362
	3.155	6.62	76.34	6.946	74.275
Visible light	3.90875	45.32	68.955	6.382	94.714
	2.75	27.5	65	7	73.692
	3.90875	45.32	68.955	6.382	94.714

studied methyl orange degradation in aqueous solution by Cr-doped titanium oxide, which realized that Cr/TiO₂ increases the photocatalytic degradation more considerably under the visible light than the UV light source as a function of increases time irradiation [43]. Maria et al. found that decolorization of AO7 decreased under visible light with increasing irradiation time by photocatalytic degradation with undoped TiO₂ catalyst [44]. The more photocatalytic degradation of Cr/TiO₂ under visible light could be due to the ability of higher light absorption in visible light; the valuable influence of Cr doping might be due to the effective separation of photoexcited electrons and holes. Besides, the hydroxyl ions can convert to hydroxyl radicals as a result of trapped holes in Cr. Moreover, the ion species on the net surface of Cr/TiO₂ catalysts trapping the photoproduct holes and generates the OH radical [43]. Increasing the irradiation time did not lessen the electron excitement of nanocatalyst and the production of hydroxyl free •OH production. Though byproducts made as a result of organic materials degradation, so some of the free radicals used for these byproducts degradation, therefore AO7 degradation takes more time.

Figure 8 shows the valid correlation between the experimental results and the predicted value in visible and UV light sources. Also, the residual behavior conforms to a normal

Table 6 Pseudo-first-order rate constant for AO7 degradation with UV and visible light source

Concentration	Visible		UV	
	$k_{app} \times 10^2 (min^{-1})$	R^2	$k_{app} \times 10^2 (min^{-1})$	R^2
7	0.69	0.7243	0.95	0.9447
14	0.8	0.8455	1.85	0.9584
25	0.74	0.942	1.38	0.9865

distribution, which shows that the model is suitable for AO7 removal by immobilized Cr/TiO₂ catalysts.

Parameter optimization

To optimize the parameters in the process for the quadratic model, the steepest function of R software used to achieve the maximum removal performance of AO7 removal in both UV and visible light. According to Table 5, It is clear that the efficiency of the synthesized nanoparticles is much higher in the visible light even for a higher dye concentration compare to UV light, which illustrates the successful shift of the absorption edge to visible light, which can reduce energy consumption considerably.

Reaction kinetics

The kinetics of the reaction investigated at different concentrations of 7, 14, and 25 mg/L. According to previous studies, the photocatalytic reaction most follows the Langmuir–Hinshelwood kinetic model (Fig. 9 and Table 6).

Reaction energy consumption

EEO define as the number of kilowatt-hours (kWh) of electrical energy required to reduce the concentration of a pollutant

Fig. 9 photocatalytic degradation kinetics (4.2 g/L catalyst concentration, pH 5 in different dye concentration) **a** visible, **b** UV light source

by one order of magnitude unit volume of contaminated water (kWh/m³) and in the batch reactors is calculated according to the following equation:

$$E_{EO} = \frac{P \times t \times 1000}{V \times 60 \times \log\left(\frac{C_0}{C_t}\right)} \quad (5)$$

Where P is the input power (kW), t is the radiation time (min), V is the reactor volume (Liters), C₀ and C_t initial, and concentration at the time of t (mg/L), respectively. This parameter used to determine the efficiency of processes to treat organic contaminants [45]. In this study, the total consumed energy for the photocatalytic degradation of AO7 at optimized conditions was 431.5 and 1304.7 kWh/m³ for 53 and 74% removal efficiency, respectively. Shirzad et al. investigated the photocatalytic removal of acid 14 (AR14) by Nano ZnO nanoparticles fixed on snail shells, and the amount of EEO was 1078.4, 1668.05 and 185.03(kWh/m³) for UV, UV/ZnO and coated UV/ZnO, respectively [46]. On the other hand, in the visible source without using energy, the higher efficiency removal of AO7 has obtained.

Conclusion

According to the result, the AO7 dye removal by prepared immobilized Cr/TiO₂ on pumice from aqueous solution as an eco-friendly nanomaterial were feasible under both visible and UV light sources, in which increasing nanocatalyst dose and contact time, as well as decreasing dye concentration and pH resulted in improving removal efficiency of AO7. The maximum efficiency of AO7 removal under visible and UV light sources were 95 and 74% in the time of 76, 69 min, initial dye concentration of 45.3 and 6.6 mg/L, and 3.9 and 3.1 catalyst dosage, respectively.

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Conflict of interest The authors declare that they have no conflict of interest.

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