Photocatalytic Degradation of Anionic Azo Dyes Acid Orange 7 and Acid Red 88 in Aqueous Solutions Using TiO₂-containing Hydrogel

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The photocatalytic degradation of two anionic azo dyes Acid Red88 (AR 88) and Acid Orange 7 (AO7) was investigated in aqueous solution using a TiO₂-containing hydrogel and UV light. The pH-sensitive hydrogel poly (styrene-alt-maleic anhydride) (PSMA), was synthesized and crosslinked in the presence of melamine and TiO₂ nanoparticles which results in entrapment of TiO₂ into the melamine-grafted PSMA (M-*g*-PSMA) hydrogel. Potential application of this nanocomposite for removal of azo dyes from wastewater was studied and the effective parameters on degradation process including time, initial pH value of the solutions, temperature and amount of added nanocomposite were optimized. The optimized values for effective parameters are as follows: time: 30 min, initial pH of the solutions: 5.23 for AO7 and 5.3 for AR88, temperature: 24 ºC and amount of added nanocomposite: 250 mg. Results showed that in optimum experimental conditions the removal percentages are about %94 for AR88 and %71 for AO7 indicating good removal performance toward the method whilst pH-sensitivity of the nanocomposite facilitates retrieval of nanocatalyst at the end of the reaction.

Keywords: Photocatalytic degradation, Hydrogel, TiO₂, azo dye, Acid Red 88, Acid Orange 7

INTRODUCTION

Dyeing and textile industries are among biggest water-consuming and wastewater-producing industries. Wastewaters produced by these sources are contaminated by different components, that dyes are an important part of them. About %10-15 of dyes consumed by industries are discharged as wastewater into the environment [1,2] penetrating to ground and surface waters. Azo dyes are a class of synthetic colorants containing about %50 of all synthetic dyes that represent about %70 of colorant markets [3,4]. Variety of available colors, ease of use, excellent stability and low energy consumption during dyeing process are the basic reasons for their extensive applications [3]. Presence of aromatic moieties in the structure or degradation products of azo dyes is the main reason for their

carcinogenic and mutagenic properties. On the other hand, the change in the color of water resources caused by these materials besides high oxygen demand of their degradation process, which are usually non-biodegradable in environment, are huge environmental problems. Hence, a large number of efforts have been accomplished for removal of azo dyes from wastewaters and different methodologies have been employed by researchers [5-13].

Acid Orange 7 (AO7) is a water-soluble azo dye which has been used for coloring of a wide variety of materials such as nylon, aluminum, detergents, cosmetics, silk and wool. This dye and its degradation products (aromatic amines) have carcinogenic properties and cause following symptoms in the case of poisoning: eye, skin, mucous membrane and upper respiratory tract irritation, headaches, nausea, water-borne diseases such as dermatitis and loss of bone marrow leading to anemia [14]. Acid Red 88 (AR88) is used in textile industries for silk, nylon, wool and leather

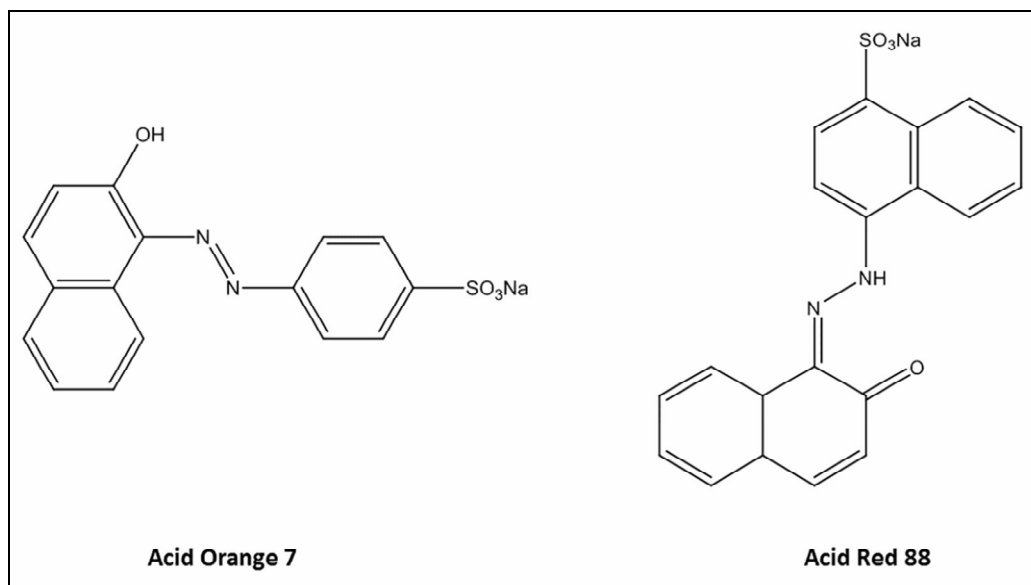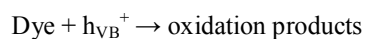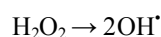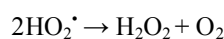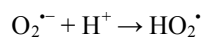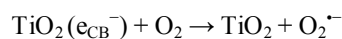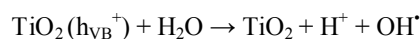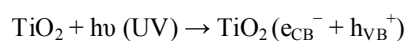*Corresponding author. E-mail: m.bahram@urmia.ac.ir

Fig. 1. Molecular Structures of Acid Red 88 and Acid Orange 7.

dyeing as well as a food colorant [15]. Same as AO7, this dye also shows carcinogenic behavior. The structures of both so-called azo dyes is shown in Fig. 1.

Various techniques have been developed for removal of these azo dyes; such as electrochemical oxidation [16-19], and using catalysts [20-28] and living organisms like bacteria [29-31], *etc.*

Photocatalysis is one of the appealing methods for wastewater treatment which uses semiconductor catalysts in the presence of a light source (UV or Visible light depending on the type and nature of the catalyst) for degradation of organic pollutants. Semiconductor materials used as catalysts are relatively inexpensive and have the ability to mineralize a wide range of organic compounds [32]. Various types of catalysts have been investigated in degradation studies including TiO_2 [1,4,23,26,27], Ce_2O [20,24], Cu_2O [24,33], SnO_2 [34,35], WO_3 [36] and ZnO [37,38]. Among those, TiO_2 has attracted much more attention for application as a catalyst in wastewater treatment because of non-toxicity, high oxidative power and great photostability alongside commercial availability of its nanoparticles with different sizes [39,40]. The mechanism of photocatalytic degradation of organic dyes by TiO_2 is shown below [39,40,46]. Irradiation of TiO_2 with UV light

in solution results in production of electron-hole pairs (e_{CB}^- and h_{VB}^+) which will promote degradation process by generation of powerful non-selective oxidation agent $OH^{\bullet}$:

$$TiO_2 + h\upsilon \, (UV) \rightarrow TiO_2 \, (e_{CB}^- + h_{VB}^+)$$

$$TiO_2 \, (h_{VB}^+) + H_2O \rightarrow TiO_2 + H^+ + OH^{\bullet}$$

$$TiO_2 \, (h_{VB}^+) + OH^- \rightarrow TiO_2 + OH^{\bullet}$$

$$TiO_2 \, (e_{CB}^-) + O_2 \rightarrow TiO_2 + O_2^{\bullet-}$$

$$O_2^{\bullet-} + H^+ \rightarrow HO_2^{\bullet}$$

$$2HO_2^{\bullet} \rightarrow H_2O_2 + O_2$$

$$H_2O_2 \rightarrow 2OH^{\bullet}$$

$$Dye + OH^{\bullet} \rightarrow degradation \, products$$

$$Dye + h_{VB}^+ \rightarrow oxidation \, products$$

$$Dye + e_{CB}^- \rightarrow reduction \, products$$

TiO_2 nanoparticles are in powder form which may limit their usage because of some difficulties including the necessity of stirring the solution during usage and problems associated with separation of catalyst from reaction medium after utilization. Filtration, sedimentation and centrifuging are solutions for addressing the latter but they may be inefficient in the case of using nanoparticles with smaller size. Using supported TiO_2 nanoparticles is an alternative solution for this problem. These supports allow contact between TiO_2 surface and degradable material in solution, however, they avoid the catalyst to make suspensions during usage which in turn makes separation of catalyst much more convenient at the end of process [39]. Zeolites [41], activated carbon [42], silica [43], carbon nanotubes [44] and hydrogels are common supporting substrates.

Hydrophilic polymeric structures of hydrogels can be synthesized in such a way that entrap catalyst nanoparticles [4,45-47]. The main advantage of hydrogels is that they can undergo volume changes in response to different stimuli such as pH, temperature, light and so on based on their pendant functional groups which facilitates their application and separation in dye degradation studies using nanocatalysts [4,47].

In this study, the pH-sensitive hydrogel, melamine-grafted poly(styrene-*alt*-maleic anhydride) (M-*g*-PSMA), is synthesized as a support for entrapment of TiO_2 nanoparticles by grafting PSMA in the presence of melamine and TiO_2 nanoparticles and is used for photocatalytic degradation of frequently and extensively used anionic azo dyes AR88 and AO7 in wastewater. Obtained results show the high capability of used nanocomposite toward removal of the investigated azo dyes besides its ability to facilitate removal of nanocatalyst residues from reaction medium after utilization because of its pH-sensitive nature.

EXPERIMENTAL

Materials

Tetrahydrofuran (THF), maleic anhydride, Acid Red 88, Acid Orange 7, HCl and NaOH were purchased from Merck and used without further purifications. Benzoyl peroxide (BPO) was also purchased from Merck, dissolved in boiling methanol, filtered and recrystallized by cooling down to room temperature. Styrene monomer was kindly donated by Tabriz Petrochemical Company (TPC) and distilled under reduced pressure before use. Titanium Oxide Nanopowder (TiO_2) with particle size of 10-25 nm was purchased from US Research Nanomaterials, Inc. and used as received. 1.0×10^{-5} M stock solutions of AR 88 and AO7 was prepared by dissolving proper amounts of dyes in water. 0.1 M solutions of HCl and NaOH was used for pH adjustments. Double distilled water was used throughout the experiments.

Instruments

Initial pH value of the solutions was adjusted using a Hanna instruments pH 211 Microprocessor pH-meter. FT-IR spectra was recorded using a Nexus-670 ThermoNicolet FT-IR spectrophotometer (USA). A PG-Instruments T80+ UV-Vis spectrophotometer was used for recording the absorbance of solutions at selected wavelengths. A 15w Phillips TUV15t8 UV lamp was utilized for irradiation of solutions at 254 nm in UV region.

Methods

Synthesis of poly(styrene-*alt*-maleic anhydride) (PSMA). PSMA was synthesized as described in the literature [48]. In a 100 ml two-necked round-bottom flask equipped with magnetic stirring bar, maleic anhydride (4.9 g), BPO (%0.01 mol), dried THF (50 ml) and styrene (5.73 ml-0.005 mol) were added, respectively. The reaction mixture was degassed with argon for 20 min using capillary and then stirred under inert atmosphere at 80 °C overnight. Then, the flask was cooled down to room temperature and the product was precipitated in n-hexane followed by filtering and washing several times with n-hexane. The final product dried at room temperature for 24 h.

Preparation of the M-*g*-PSMA hydrogel. In a typical method, the PSMA (1 g), melamine (0.62 g, 0.005 mol) and TiO_2 (0.2 g) were mixed in a 50 ml round-bottom flask containing 20 ml THF and 20 ml distilled water. The reaction mixture was stirred and kept under reflux overnight to prepare the hydrogel. Then, the product was filtered and washed several times with distilled water and dried at room temperature for 48 h.

Working procedure. In a 10 ml beaker a 5.0×10^{-6} M solution of AO7 or AR88 was prepared by adding 5 ml of

its stock solution and diluting up to 10 ml. The effects of four parameters on degradation efficiency including pH, amount of nanocomposite, time and temperature were investigated by "one variable at a time" method and following procedures:

- Effect of pH: The pH value of dye solutions with the so-called concentration were investigated at five levels from 2.54 to 9.82 including 2.54, 3.21, 5.23, 7.2 and 9.82. After pH adjustment, 250 mg of nanocomposite was added and resulting solution was irradiated by UV light for 30 min at 24 ℃.

- Effect of nanocomposite content: Selected levels for this factor include 50, 150, 250, 350 and 450 mg. pH value of solutions were set to 5.23 for AO7 and 5.3 for AR88 and resulting solutions were irradiated by UV light for 30 min at 24 ℃.

- Effect of time: The pH of dye solutions were set to 5.23 for AO7 and 5.3 for AR88 and after adding 250 mg of nanocomposite, irradiation of solutions was carried out at 24 ℃ while time varied from 0 to 60 min at five levels with 15 min intervals.

- Effect of temperature: 250 mg of nanocomposite was added to dye solutions. The temperature was investigated at five levels including 10, 20, 24, 30 and 40 ℃ while pH values of solutions were fixed at 5.23 for AO7 and 5.3 for AR88 and irradiation time was 30 min.

For each experiment, the absorbance of solution was measured at λ_{max} of each dye (485 nm for AO7 and 504 nm for AR88) before (A_0) and after irradiation (A_t) and the values of dye removal percentage (%R) were calculated using Eq. (1) [5,12,13,25] which have been used for optimization of effective parameters.

$$\%R = \frac{A_0 - A_t}{A_0} \qquad (1)$$

RESULTS AND DISCUSSION

Preparation of Nanocomposite

Scheme 1 shows the reaction between styrene and maleic anhydride in the presence of BPO to prepare PSMA which its SEM image is shown in Fig. 2. This copolymer then underwent crosslinking with melamine (Scheme 2).
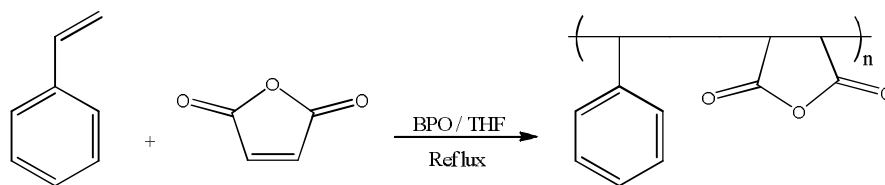
Figure 3 shows FT-IR spectra of PSMA and M-*g*-PSMA. In the spectrum A, related to PSMA, the absorption peaks around 1453, 1495 and 1630 cm^{-1} are related to the aromatic C-C bond stretch vibrations of styrene groups. Also, the absorption peaks around 1780 and 1855 cm^{-1} are assigned to the anhydride C-O bond stretch vibrations of maleic anhydride groups.

By grafting melamine to maleic anhydride groups of PSMA, an amide and a carboxylic acid will form [50] which is clearly observable in the FT-IR spectrum of M-*g*-PSMA (Fig. 3B). In this spectrum, the 1638 and the 1714 cm^{-1} absorption peaks are related to the amidic and acidic carbonyl groups, respectively. Also absorption peaks of the aromatic triazine ring of the melamine are shown between 2500 and 3500 cm^{-1} which are characterized by broad absorption peaks in this area. Presence of TiO_2 nanoparticles during grafting process will cause their entrapment in hydrogel structure which results in preparation of TiO_2-containing nanocomposite.

Optimization of Parameters Effective on Dye Removal Process

pH optimization. Initial pH of solution has a dual effect in photocatalytic dye removal process using TiO_2 and pH-sensitive hydrogel. In one hand, it affects the surface charge of TiO_2 nanoparticles which can result in amplification or debilitation of electrostatic attraction between nanoparticles and organic material present in solution. In this case, the catalytic reaction can be accelerated or decelerated because of increasing or decreasing number of collisions (and hence adsorption) between reactive components, respectively [21, 32]. On the other hand, the pH-sensitive nature of hydrogel makes it soluble in higher or lower than certain pH values based on its structure and pendant functional groups.
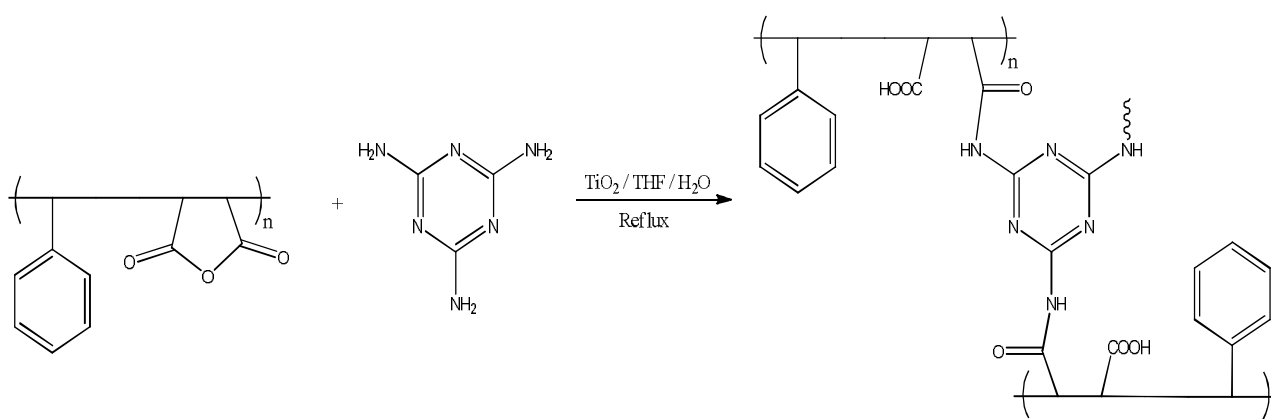
Figure 4 shows the effect of pH variation on the removal of AO7 and AR88 which both are anionic azo dyes. Higher pH values cause the surface charges of TiO_2 nanoparticles to be negative and the repulsion between negative charges of dyes and nanoparticles decreases the adsorption of dye on TiO_2 surface which results in decreasing of removal efficiency. Lower pH values will cause deswelling of hydrogel which in turn will decrease the contact between positively charged TiO_2 nanoparticle surfaces and anionic dyes, and hence will decrease removal efficiency by making

Scheme 1. Synthesis of PSMA

Fig. 2. SEM image of PSMA hydrogel.

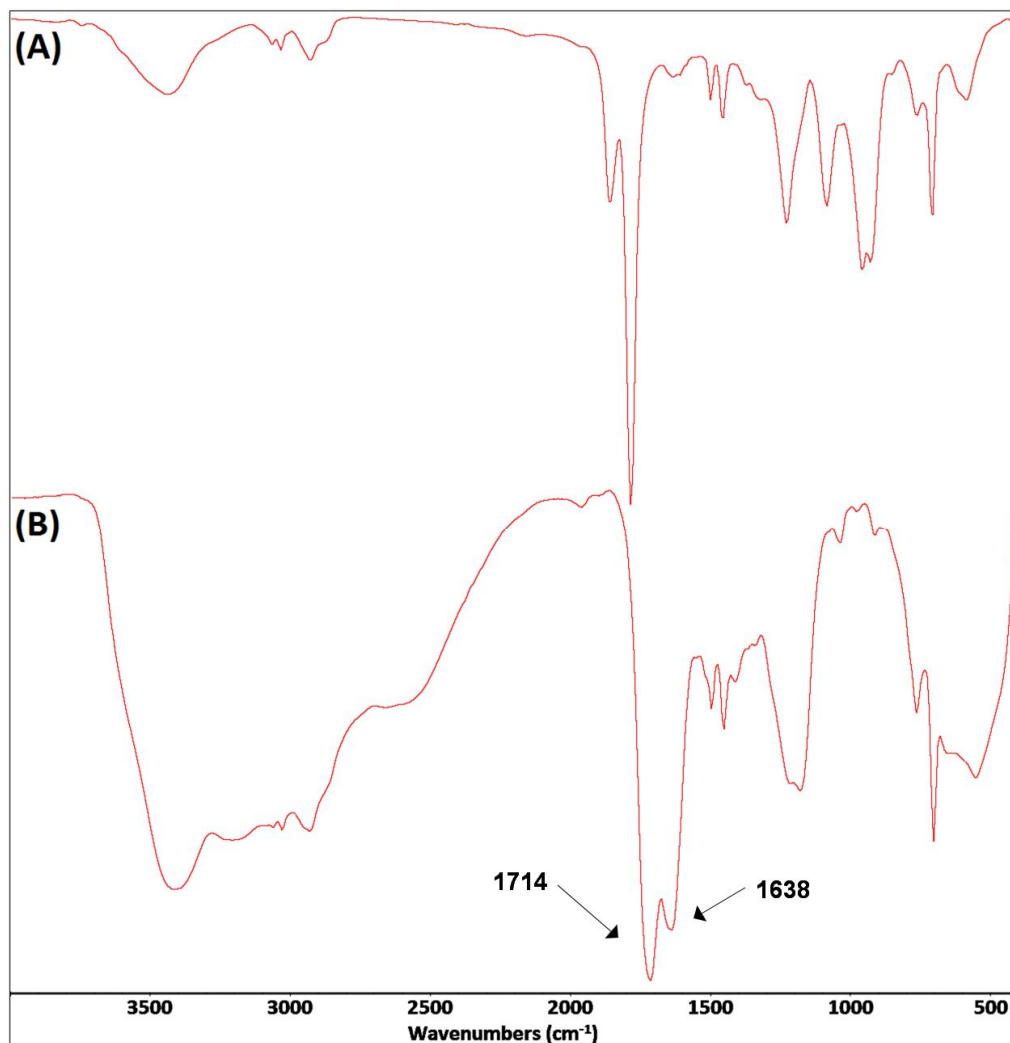*Scheme 2*. Preparation of M-*g*-PSMA

Fig. 3. FT-IR spectra of (A) PSMA and (B) M-*g*-PSMA.

nanoparticles inaccessible for organic material.

On the basis of experimental results, the maximum removal of dyes occurs at pH = 5.23 for AO7 and pH = 5.3 for AR88, and therefore these values were employed to perform degradation studies at optimal conditions.

Optimization of nanocomposite content. Figure 5 shows the effect of different amounts of nanocomposite on removal of dyes. Increasing the amount of nanocomposite will increase nanocatalyst content in solution which results in an increase of active sites of nanocatalyst surface facilitating the production of hydroxyl and superoxide radicals responsible for decolorization process and hence higher rates of dye degradation process will be achieved. On the other hand, higher nanocatalyst contents cause the solution to be turbid preventing UV light to penetrate and interact with solution that is necessary for photocatalytic reaction to proceed. The result is a decrease in the rate of degradation process at higher nanocatalyst contents. On the basis of experimental results and as depicted in Figure5, the maximal degradation percentage for both dyes is observed when the nanocomposite content in solution is equal to 250 mg so this value was selected as optimal point for this
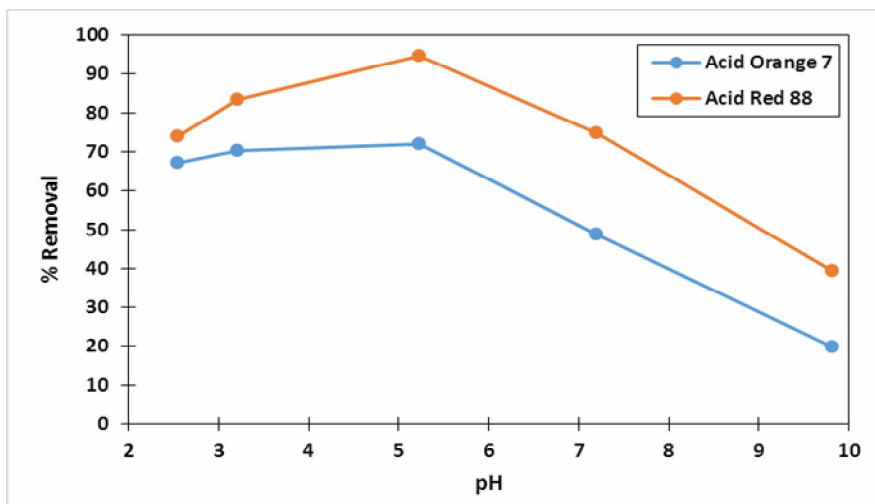
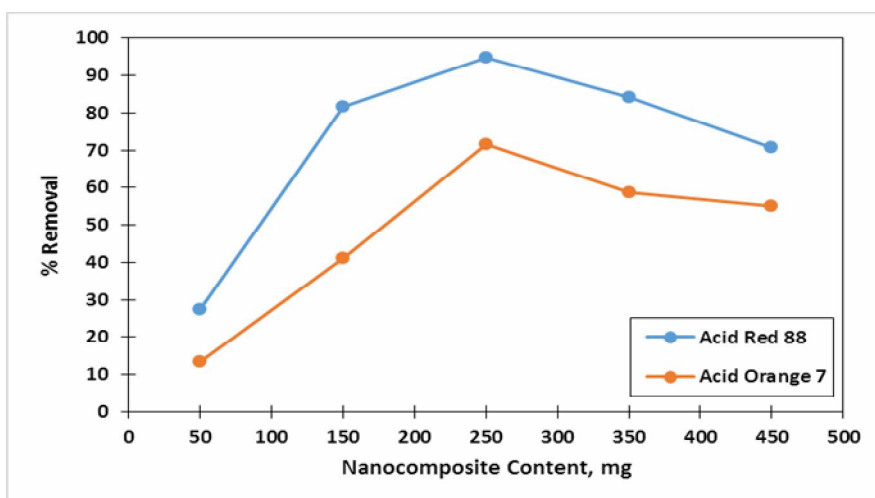**Fig. 4.** Effect of pH on removal of Acid Red 88 and Acid Orange 7.

Fig. 5. Effect of nanocomposite content on removal of Acid Red 88 and Acid Orange 7.

parameter in the removal of both AO7 and AR88 dyes at optimum degradation conditions.

Optimization of temperature. Temperature has an inevitable effect on chemical reactions. Photocatalytic reactions are also affected by temperature in some extents. Figure 6 shows results obtained from dye removal experiments performed at different temperatures. As it is seen, a slight increase in degradation is observed at temperatures up to 24 ºC but as the temperature exceeds this

value, the rate of degradation process is apparently decreased that can be attributed to the increase in recombination of electron-hole pairs (charge carriers) and also desorption of adsorbed azo dyes from TiO_2 nanocatalyst surfaces [32]. Therefore, on the basis of obtained results, it was found that 24 ºC is the optimum temperature for removal of both AO7 and AR88 at experimental conditions.

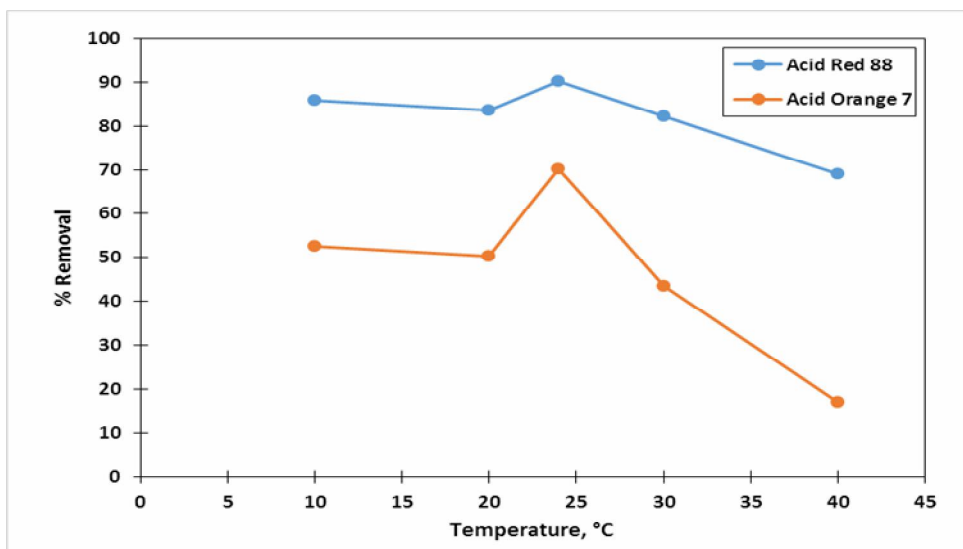**Optimization of irradiation time.** It is observed in

Fig. 6. Effect of temperature on removal of Acid Red 88 and Acid Orange 7.
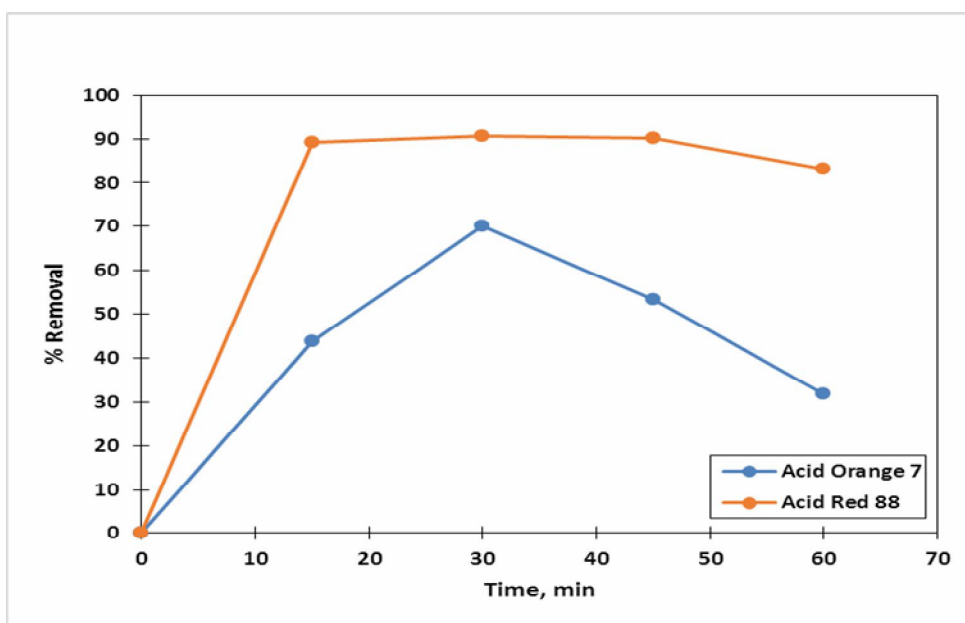

Fig. 7. Effect of Irradiation time on removal of Acid Red 88 and Acid Orange 7.

many studies that increasing the irradiation time in dye degradation processes involving semiconductor catalysts, will increase the removal of dyes. This is due to the formation of more electron-hole pairs in catalyst structure caused by incident UV light which in turn results in formation of the higher number of oxidation agents (Hydroxyl and superoxide radicals) in solution. However, as the number of catalyst molecules in solution are limited, increasing the irradiation time will just increase the rate and percentage of removal process to a specific constant value

and after that irradiation of solution for longer times has no effect on removal process. Also, from economical point of view it is preferred to perform removal studies in a meaningful time with an acceptable efficiency.

Figure 7 shows the effect of irradiation time on removal of AO7 and AR88 and as depicted by this figure, using irradiation times more than 30 min has no effect on removal efficiency. So, on the basis of experimental observations and considering economic aspects, this value was selected as the optimal time for degradation study.

The optimized values for parameters affecting the removal efficiency were used for studying the degradation of AO7 and AR88 at these conditions. The obtained values for removal percentage are %94 and %71 for AR88 and AO7, respectively, indicating lower removal rate for AO7 compared to AR88 at experimental conditions that can be attributed to differences in their structures leading to different amounts of dye adsorption on the surface of photocatalyst at specific pH and differences in photocatalytic performance of TiO_2 toward various degrees of adsorptions [49]. However, results showed the efficiency of the proposed method toward removal of anionic azo dyes from wastewaters and also represent the capability of the employed nanocomposite in separation from reaction medium after utilization, an inevitable advantage in wastewater treatment applications.

Based on the literature review, we found that there are just few reports related to employing of TiO_2-Containing hydrogels for removal of AO7 from wastewaters [45,51] and almost no report was found for degradation of AR88 using this type of nanocomposites. Obtained results for AO7 are comparable with those reported in the literature, however the key point is the significantly reduced time required for degradation of equal quantities of AO7 using M-g-PSMA compared to other utilized nanocomposites.

The solubility of M-*g*-PSMA in higher pH values, restricts its applications for removal of dyes at such conditions, but it can be structurally modified in such a way that can tolerate higher pH values as well as lower ones. It is estimated that a wide variety of anionic dyes can be removed using this nanocomposite since it is just a support for immobilization of TiO_2 nanoparticles which are the main agents responsible for degradation of organic matter in solution.

CONCLUSIONS

Acid Orange 7 and Acid Red 88 are among the most utilized azo dyes in various industries and many efforts have been performed for treatment of wastewaters contaminated by these carcinogenic pollutants. Among others, many researchers have paid much more attention to photocatalysis due to undeniable advantages of semiconductor catalysts including non-toxicity, recyclability and enhanced removal rates. However, some problems associated with usage of these materials like difficulties in separation from treated wastewater after utilization restrict their applications and lead to invention of the supported catalysts which stimuli-sensitive hydrogel supported-TiO_2 nanocomposites are among them. This study aimed to show the possibility of using M-*g*-PSMA as a pH-sensitive support for TiO_2 nanoparticles in the removal of AO7 and AR88 azo dyes. Obtained results showed comparable removal efficiencies and reduced degradation times at the optimized values of effective parameters using the proposed nanocomposite compared to others and indicate the capability of M-*g*-PSMA as a pH-sensitive support for TiO_2 nanoparticles as well as other nanocatalysts in dye removal processes provided that it retains its non-solubility in used pH conditions.

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