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Photocatalytic degradation of acid red 14 from contaminated water using immobilized TiO_2 nanoparticles on glass beads activated by UV/peroxydisulfate

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ABSTRACT

The present study investigates the photocatalytic degradation of C. I. acid red 14 (AR 14) as a textile dye, in aqueous medium using immobilized TiO_2 nanopowder on glass beads illuminated by a UV-C lamp (30 W). Photocatalytic degradation of organic pollutants is done with photogenerated holes as a result of UV light irradiation on surface of TiO_2 nanoparticles and generation of hydroxyl radicals as power oxidant. This process is performed under a set of variables (concentration of peroxydisulfate, AR 14, and temperature). AR 14 photocatalytic degradation increased with increasing peroxydisulfate concentration and temperature. The increase in dye concentration caused a decrease in removal efficiency. The progress of photocatalytic decolorization of the AR 14 was studied by measuring the absorbance at $\lambda_{max} = 514$ nm by UV–Vis spectrophotometer. The results indicated no observable loss of the color when the UV or UV/TiO_2 was applied in the absence of $S_2O_8^{2-}$. The results reveal that a considerable decrease in the concentration of the dye occurs when the sample was photocatalytic degraded by $S_2O_8^{2-}$.

Keywords: Advanced oxidation process; C. I. acid red 14; Immobilized TiO_2 nanoparticles; UV irradiation; Wastewater treatment

1. Introduction

The textile industry produces large quantities of highly colored effluents, which are generally toxic and resistant to destruction by biological treatment methods. Azo dyes, such as acid red 14 (AR 14), are widely used in the textile industry [1,2]. Various chemical and physical processes, such as chemical precipitation and separation of pollutants, coagulation, electrocoagulation, elimination by adsorption on activated carbon, are applied for color removal from textile

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effluents [3]. One difficulty with these methods is that they are not destructive but only transfer the contamination from one phase to another. In recent years, as an alternative to conventional methods, "advanced oxidation processes" based on the generation of very reactive species such as hydroxyl radicals have been proposed to oxidize quickly and non-selectively a broad range of organic pollutants. Also, many investigations in the area of photocatalytic degradation of pollutants have employed suspensions of the semiconducting particles [4]. However, from a practical point of view, it may not be possible to completely recover the photocatalysts used in the reactor. This needs either long settling times or filtration, which is an expensive process. Hence, many researchers have decided to study the feasibility of coating the photocatalyst on inert surfaces such as glass beads, activated carbon fiber, cotton material, and cement surface. Nano-TiO_2 photocatalysts have attracted a great attention due to their non-expensive, non-toxic, biocompatible, and high reactivity for the degradation of organic compounds [4,5]. Photocatalytic degradation of organic pollutants is done with photogenerated holes as a result of UV light irradiation on surface of TiO_2 particles (Eq. (1)). Also by these photogenerated holes, hydroxyl radicals are produced by the oxidation of OH^- or H_2O (Eqs. (2) and (3)), which are principally responsible for the degradation of organic species. Oxygen, as an efficient electron trap (Eq. (4)), is used for preventing the recombination of electrons and photogenerated holes. Eqs. (5)–(7) represent the other reactions of UV/TiO_2. If oxygen is limited, rapid recombination of photoproduced electrons and holes in TiO_2 lowers the efficiency of the photocatalytic reactions representing the other reactions of UV/TiO_2 [6,7].

$$TiO_2 + h\nu \rightarrow TiO_2(e_{CB-} + h_{VB+}) \quad (1)$$

$$TiO_2(h_{VB+}) + OH^- \rightarrow TiO_2 + OH^{\cdot} \quad (2)$$

$$TiO_2(h_{VB+}) + H_2O \rightarrow TiO_2 + H^+ + OH^{\cdot} \quad (3)$$

$$TiO_2(e_{CB-}) + O_2 \rightarrow TiO_2 + O_2^{-\cdot} \quad (4)$$

$$O_2^{-\cdot} + H^+ \rightarrow HO_2^{\cdot} \quad (5)$$

$$TiO_2(e_{CB-}) + H^+ + O_2^{-\cdot} \rightarrow TiO_2 + HO_2^- \quad (6)$$

$$HO_2^- + H^+ \rightarrow H_2O_2 \quad (7)$$

Numerous studies have proposed that the addition of oxidants, such as H_2O_2, $S_2O_8^{2-}$, HSO_5^-, and BrO_3^-, eliminates the recombination process as the added oxidants rapidly react with conduction band electrons, generating extremely reactive oxidizing radicals, which increases the efficiency of TiO_2. UV light can excite $S_2O_8^{2-}$ to form sulfate radical ($SO_4^{-\cdot}$), a stronger oxidant ($E^0 = 2.60$ V) than $S_2O_8^{2-}$, to significantly enhance the oxidation of contaminants. Consequently, an electron acceptor ($S_2O_8^{2-}$) was used in this investigation to inhibit the recombination of electron/hole pairs and improve the photodegradation efficiency of UV/TiO_2 [6,8]. In this study, use of immobilized TiO_2 nanoparticles and peroxydisulfate for photodegradation of dye pollutions is truly studied. Peroxydisulfate concentration, dye concentration, and pH are investigated.

2. Materials and methods

2.1. Materials

Immobilized TiO_2 nanopowders (Fig. 1) [Degussa P-25 having 70% anatase and 30% rutile, BET; $50\,m^2\,g^{-1}$, particle size 21 nm, Degussa Co. (Germany, Rheinfelden)] on glass beads (0.5 cm diameter, Armfield Co. (England, Ringwood)) by a heat attachment method that prepared and reported previously [9] were used and the dye AR 14 (Table 1) was provided by Alvan Sabet Company (Iran, Tehran) and used without further purification. Ammonium peroxydisulfate was obtained from Merck (Germany, Darmstadt). Its solution was immediately prepared before the measurements to avoid the change of concentration due to self-decomposition. Other chemicals were of analytical reagent grade and were used without

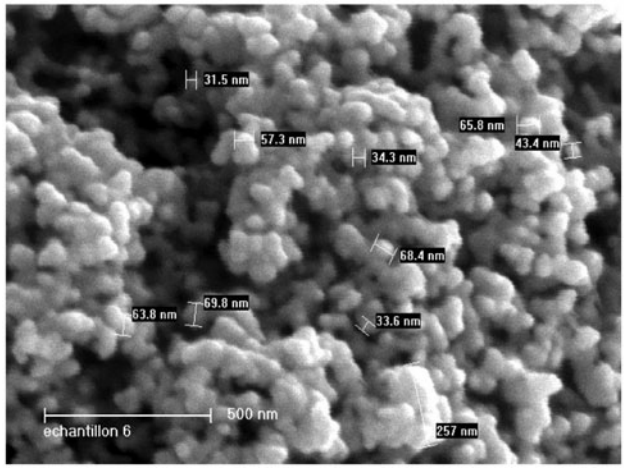
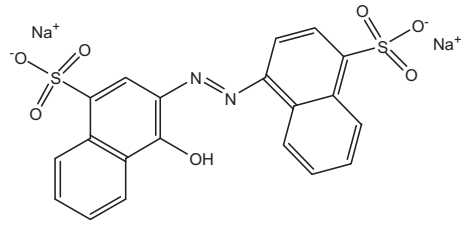


Fig. 1. SEM-TiO_2 Degussa P25.

Table 1
Properties of AR 14

Color index	AR 14
Azo group	One
Type	Anionic
Structure	
λ_{max} (nm)	514
Molecular weight (g/mol)	502.4

further purification, and all solutions were prepared in distilled water.

As for the UV/TiO_2 process, irradiation was performed in a batch photoreactor with a mercury lamp (Philips 30 W, Holland) (UV-C). There is a plate in the reactor where glass beads attach, allowing the reactor to agitate by a magnetic flea (Fig. 2).

2.2. Methods

For the photocatalytic decolorization of AR14, glass beads were placed on the plate, which was 1 cm above the bottom of batch reactor (Fig. 2). Then, 50 mL of the solution, containing a known concentration of dye and peroxydisulfate, was transferred to the Pyrex bottle. This amount of solution was enough to cover the glass beads. Then, the lamp was switched on to initiate the reaction (exposure time was 15 min for each one of experiments). The concentration of dye in each degraded sample was determined by a UV–Vis spectrophotometer (Shimadzu UV-160) at $\lambda_{max} = 514$ nm. The photocatalytic decolorization efficiency (X) is given by Eq. (8), where C_0 is the initial concentration value of AR 14 and, C_t is the concentration value of AR 14 at time t.

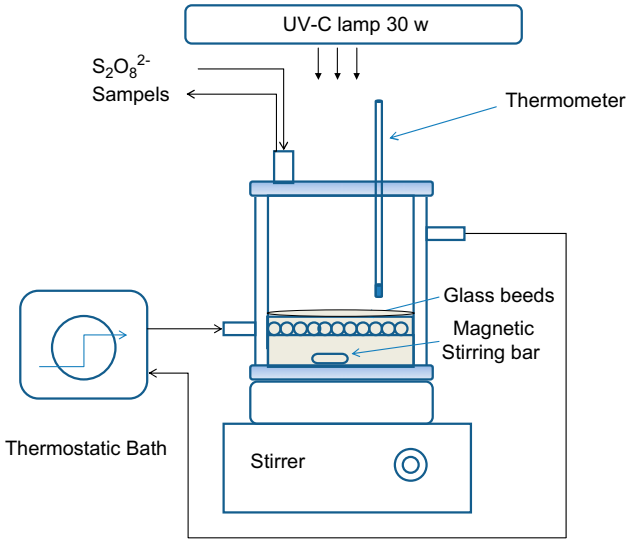


Fig. 2. Scheme of experimental setup.

$$X = \frac{C_t}{C_0} \tag{8}$$

3. Results and discussion

3.1. Photo-oxidation effect of UV/TiO_2/$S_2O_8^{2-}$ in comparison with that without either $S_2O_8^{2-}$, UV, or TiO_2 on AR14 degradation

Fig. 3 shows the photocatalytic degradation of AR14 vs. time for experiments carried out without either UV or TiO_2. There was no observable loss of the color when the UV or UV/TiO_2 was applied in the absence of $S_2O_8^{2-}$.The results reveal that a considerable decrease in the concentration of the dye occurs when the sample was photocatalytic degradaded by $S_2O_8^{2-}$.

3.2. Effect of initial peroxydisulfate concentration

The results from the photocatalytic degradation of the AR 14 (20 ppm) using different concentration of $S_2O_8^{2-}$ (0, 0.1, 0.5, 1, 1.5, 2, 3, 4, 5 mM) at 25°C and natural pH (6.7) were summarized in Fig. 4. The removal efficiency increased as the dosage of peroxydisulfate ions increased. Peroxydisulfate ions trap photogenerated electrons, preventing their recombination with positive holes, while simultaneously producing sulfate free radicals (Eq. (9)) which can react with water

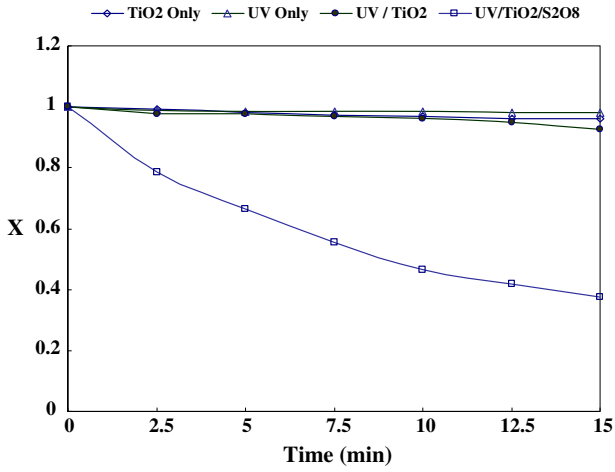


Fig. 3. Photo-oxidation effect of UV/TiO_2/$S_2O_8^{2-}$ in comparison with that without either $S_2O_8^{2-}$, UV, or TiO_2 on AR14 degradation. $[AR14]_0 = 20$ ppm, $[S_2O_8^{2-}]_0 = 4$ mM, [UV] = 30 W, pH_0 = natural (6.7), $T = 25$ °C.

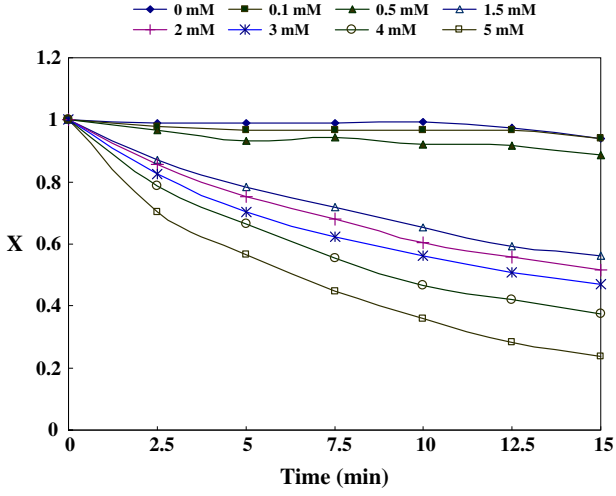


Fig. 4. Effect of initial peroxydisulfate concentration. $[AR14]_0 = 20$ ppm, [UV] = 30 W, pH_0 = natural (6.7), $T = 25$ °C.

molecules to generate hydroxyl radicals (Eq. (10)). Also, peroxydisulfate ions undergo photolysis under light irradiation, forming sulfate free radicals (Eq. (11)). According to Eqs. (9)–(11), increased amounts of peroxydisulfate ions generated additional sulfate free radicals and hydroxyl radicals which accelerated decolorization. Various studies have demonstrated that reactive radical intermediates, generated from peroxydisulfate ions reacting with photogenerated electrons, accelerate decolorization in the UV/TiO_2/$S_2O_8^{2-}$ system [10–12].

$$S_2O_8^{2-} + e_{CB-} \rightarrow SO_4^{2-} + SO_4^{-\cdot} \quad (9)$$

$$SO_4^{-\cdot} + H_2O \rightarrow SO_4^{2-} + H^+ + OH^{\cdot} \quad (10)$$

$$S_2O_8^{2-} + h\nu \rightarrow 2SO_4^{-\cdot} \quad (11)$$

3.3. Effect of initial dye concentration

From a practical point of view, it is important to study the dependence of removal efficiency on the initial concentration of dye. Fig. 5 shows the effect of initial dye concentration on dye photocatalytic degradation was determined by varying the initial dye concentration (5, 10, 15, 20, and 30 ppm) at natural pH (6.7). It can be seen that degradation efficiency decreased as initial dye concentration increased.

Several studies have obtained similar experimental findings for UV/TiO_2-based systems [1,6,9,13]. This phenomenon has three possible explanations.

(i) A significant quantity of UV light may be absorbed by the highly concentrated dye molecules rather than by the TiO_2 particles, thereby reducing decolorization efficiency; the dye therefore has a UV-screening effect insofar as, fewer photons reach the TiO_2 surface as dye concentration increase, slowing the formation of hydroxyl radicals. (ii) As the initial concentration of dye increased, the TiO_2 surfaces adsorbed additional dye molecules which inhibited direct contact between the dye molecules and photo generated holes and which also suppressed the generation of hydroxyl radicals at the TiO_2 surface as dye molecules covered active surface sites. (iii) Increased amounts of dye and reaction intermediates competed with both hydroxyl radicals and active reaction sites at the TiO_2 surface, as the initial dye concentration increased. Since the amount of TiO_2 remained

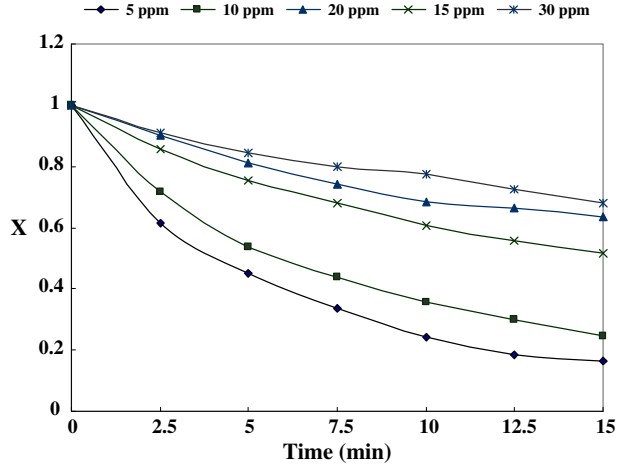


Fig. 5. Effect of initial dye concentration. $[S_2O_8^{2-}]_0 = 4$ mM, [UV] = 30 W, pH_0 = natural (6.7), $T = 25$ °C.

constant, the rate of formation of hydroxyl radicals at the TiO_2 surface was constant. Hence, the fraction of hydroxyl radicals that attacks the dye molecules and its reaction intermediates declined as the dye concentration increased [1,10,14].

3.4. Effect of temperature

The effect of temperature on AR 14 photocatalytic degradation process was studied by using 50 ml of solution with peroxydisulfate concentration of 4 mM and 20 ppm of dye at different temperatures. The results in Fig. 6 that shows the percent AR 14 photo degradation for the duration of 15 min at 10, 20, 30, 40, and 50˚C elucidate the temperature effect on the reactions of peroxydisulfate with dye. Comparison of the data reveals that the AR 14 photo degradation efficiency increased with increasing reaction temperature. In addition, the activation energy of the degradation reaction could be obtained based on the experimental data using the Arrhenius equation, $k = A \exp(-E_a/RT)$, where A is the frequency factor, E_a is the activation energy, R is the universal gas constant, and T is the temperature in Kelvin indicating that heat energy can activate peroxydisulfate to sulfate radicals more effectively [8,15].

3.5. Spectral changes of AR 14 solution during illumination in the UV/TiO_2/$S_2O_8^{2-}$ system

The changes in the absorption spectra of AR 14 solutions during the photocatalytic degradation process in concentration of 4 mM $S_2O_8^{2-}$ and 20 ppm of dye in natural pH (6.7) and 25˚C at different times are shown in Fig. 7. The color of an azo dye is the result of the interaction between an azo function (–N=N–) and two aromatic species: the dyes carry an acceptor group which is an aromatic nucleus frequently containing a chromophoric group, for example, $-SO_3^-$, and a donor group, for example, an aromatic nucleus containing an auxochromic group such as OH group [16]. The decrease in the absorption peak of AR 14 at 514 nm in Fig. 7 indicated a rapid decolorization of the dye. The decrease is also meaningful with respect to the nitrogen-to-nitrogen double bond (–N=N–) of the azo dye, as the most active site for oxidative attack. Decrease in absorption intensity of the band at λ_{max} during the irradiation also expresses the loss of conjugation, for example, especially the cleavage near the azo bond of the organic molecule. The weak band at 310–330 nm could be attributed to the π–π^* transition related to the aromatic ring attached to the –N=N– group in the dye molecule. Absorbance decrease at 310–330 nm indicates the degradation of aromatic part of the dye.

The degradation pathway of the AR 14 could be explained as follows: the fragile group in this dye is the NH group, which results from an equilibrium between two tautomeric forms where an H atom is exchanged between O and N as shown in Fig. 8. Indeed, the abstraction of H atom (carried by an oxygen atom in the azo form and by a nitrogen atom in the hydrazone form) by sulfate or hydroxyl radicals is the main degradation pathway of this dye [4].

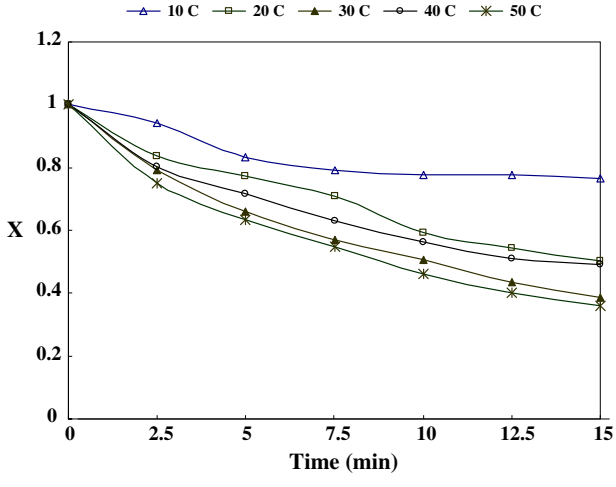


Fig. 6. Effect of temperature. $[S_2O_8^{2-}]_0 = 4$ mM, $[AR14]_0 = 20$ ppm, [UV] = 30 W, pH_0 = natural (6.7).

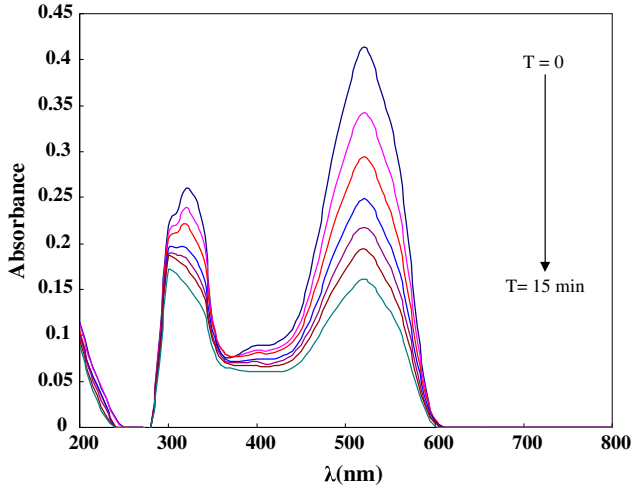


Fig. 7. Spectral changes of AR 14 solution during illumination in the UV/TiO_2/$S_2O_8^{2-}$ system. $[S_2O_8^{2-}]_0 = 4$ mM, $[AR14]_0 = 20$ ppm, [UV] = 30 W, pH_0 = natural (6.7), $T = 25$˚C.

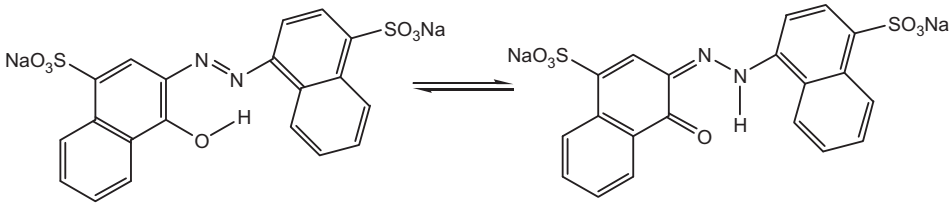


Fig. 8. Equilibrium between the two tautomeric forms in C. I. AR 14.

4. Conclusion

The results presented in this paper showed that UV/TiO_2/$S_2O_8^{2-}$ process could be efficiently used to degrade the AR14. Also, the results indicated that degrees of degradation of AR 14 were obviously affected by initial concentration of $S_2O_8^{2-}$, dye, and temperature. In the large-scale applications, the use of immobilized TiO_2 nanopowder on glass beads photocatalysts instead of suspended powder is gaining importance in the elimination of pollutants from wastewaters because have need of separation and recycling prior to the discharge and can be a time-consuming and expensive process. It is believable that UV/$S_2O_8^{2-}$ is applicable to the existing drinking water or wastewater treatment plants, especially for those equipped with UV systems as disinfection. With the advantages of the high reactivity of UV/$S_2O_8^{2-}$ process and the high solubility of peroxydisulfate, it is practically possible to dose the chemical solution at the upstream of wastewater to remove recalcitrant organic compounds effectively.

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