Bulk phase degradation of Acid Red 14 by nanophotocatalysis using immobilized titanium(IV) oxide nanoparticles

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Abstract

Immobilized titanium(IV) oxide nanoparticles were used for the photocatalytic degradation of Acid Red 14 (AR 14). A simple and effective method was used for immobilization of titanium(IV) oxide nanoparticles. Photocatalytic degradation processes were performed using pilot scale (7 L) colored dye solutions. UV–vis and ion chromatography (IC) analyses were employed to obtain the details of the photocatalytic degradation of AR 14. It has been found that adsorption has a negligible effect on the aqueous dye concentration and the photocatalytic process occurred at solution bulk. The effects of operational parameters such as H_2O_2, dye concentration, anions (NO_3^-, Cl^-, SO_4^{2-}, HCO_3^- and CO_3^{2-}) and pH were investigated. Reaction rate was drastically inhibited by carbonate. Produced aromatic intermediates were not studied. Formate, acetate and oxalate anions were detected as dominant aliphatic intermediates where, they were further oxidized slowly to CO_2. Nitrate and sulfate anions were detected as the photocatalytic mineralization of AR 14. Kinetics analysis indicates that the photocatalytic decolorization rates can usually be approximated first-order model for AR 14. Results show that the employment of optimal operational parameters may lead to complete decolorization and mineralization of dye solutions.
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Keywords: Bulk phase; Nanophotocatalysis; Acid Red 14; Titanium(IV) oxide nanoparticle; Decolorization; Mineralization

1. Introduction

Azo dyes, which contain one or more azo bonds (−N=N−), are among the most widely used synthetic dyes and usually become major pollutants in textile wastewaters. About 50% among annually world produced dyes (700,000 t) are azo dyes. About 15% of the total world production of dyes is lost during textile dyeing which is released in textile effluents. The discharge of dye-bearing wastewater from textile industries into natural stream and rivers poses severe problems, because of toxicity of some dyes to the aquatic life and damaging to the aesthetic nature of the environment [1–3]. Thus, there is an urgent need for textile wastewater to develop effective methods of treatment.

Heterogeneous nanophotocatalysis constitute one of the emerging technologies for the degradation of organic pollutants. Several advantages of this process over competing processes are: (1) complete mineralization, (2) no waste-solids disposal prob-
lem and (3) only mild temperature and pressure conditions are necessary [1,3–6].

At heterogeneous nanophotocatalysis, semiconductor can act as sensitizer for light-reduced redox processes due to their electronic structure, which is characterized by filled valence band and an empty conduction band. When a photon with energy of $h\nu$ matches or exceeds the band gap energy, E_g, of the semiconductor, an electron, e_{cb}^-, is promoted from the valence band, VB, into the conduction band, CB, leaving a hole, h_{vb}^+ behind. Excited state conduction band electrons and valence band holes can recombine and dissipate the input energy as heat, get trapped in meta-stable surface states, or react with electron donors and electron acceptors adsorbed on the semiconductor surface. The h_{vb}^+ is a strong oxidant, which can either oxidize a compound directly, or react with electron donors like water or hydroxide ions to form hydroxyl radicals, which react with pollutants such as dyes. Hydroxyl radicals react with organic pollutants leading to the total mineralization of most of them [1,3,6–8].

Adsorption is a key factor in slurry photocatalytic system due to the large surface area of catalyst available for reaction. Thus, in a suspension system, the photocatalytic reactions are surface

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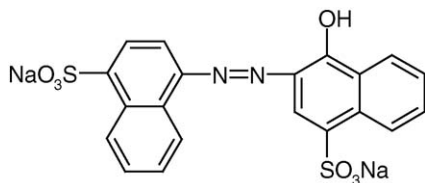*E-mail address:* nm_mahmoodi@yahoo.com (N.M. Mahmoodi).

Fig. 1. The chemical structure of AR 14.

Table 1
Properties of AR 14

Parameter	AR 14
Commercial name	Basovit Red 440 E
C.I. number	14720
C.I. name	Acid Red 14
Class	Acid dye
Ionization	Acidic
Solvent	Water
Color	Bluish red
Empirical formula	$C_{20}H_{12}O_7N_2S_2Na_2$
Formula weight	502
Company	BASF

processes. The immobilization of TiO_2 nanoparticle decreases the effective surface of catalyst. There is still an ongoing debate whether photocatalytic oxidation reactions are surface or solution processes in an immobilized system. In this study, after adsorption experiment, the absorbance of both dyes does not decrease, indicating the negligible effect of the adsorption on the dye concentration. On the other hand, it was assumed that the reactive hydroxyl radicals and other oxidizing species can diffuse into the solution bulk to react with organic pollutants.

However, in the large scale applications, the use of suspensions requires the separation and recycling of the catalyst particles from the treated wastewater prior to the discharge and can be a time-consuming expensive process. In addition, the depth of penetration of UV light is limited because of strong absorptions by both catalyst particles and dissolved dyes [9]. Above problems can be avoided by immobilization of photocatalyst over suitable supports.

The aim of the present study is to investigate the pilot scale heterogeneous photocatalytic degradation of aqueous solution of Acid Red 14 (AR 14) using an immobilized TiO_2 nanoparticle photocatalytic reactor. The effects of operational parameters such as H_2O_2, dye concentration, anions (NO_3^-, Cl^-, SO_4^{2-}, HCO_3^- and CO_3^{2-}) and pH were investigated. These are the major variables governing the efficiency of the process. The produced dominant aliphatic intermediates and mineralization of AR 14 were studied. Furthermore, the kinetics of the photocatalytic decolorization of AR 14 was investigated. It has been found that adsorption has a negligible effect on the aqueous dye concentration and the photocatalytic process occurred at solution bulk.

2. Experimental

2.1. Reagents

AR 14 (95% ≤ purity) was obtained from BASF (Germany). The descriptions (name, color and molecular weight) of AR 14 and its chemical structure are shown in Table 1 and Fig. 1. HCO_2Na, H_3CCO_2Na, $Na_2C_2O_4$, Na_2SO_4 and $NaNO_3$, $NaHCO_3$, Na_2CO_3 and H_2O_2 were purchased from Merck. Titanium dioxide nanoparticle was utilized as a photocatalyst. Its main physical data are as follows: average primary particle size around 30 nm, purity above 97% and with 80:20 anatase to rutile.

2.2. Photocatalytic reactor

Experiments were carried out in a batch mode immersion rectangular immobilized TiO_2 nanoparticle photocatalytic reactor made of Pyrex glass (Fig. 2). The radiation source was
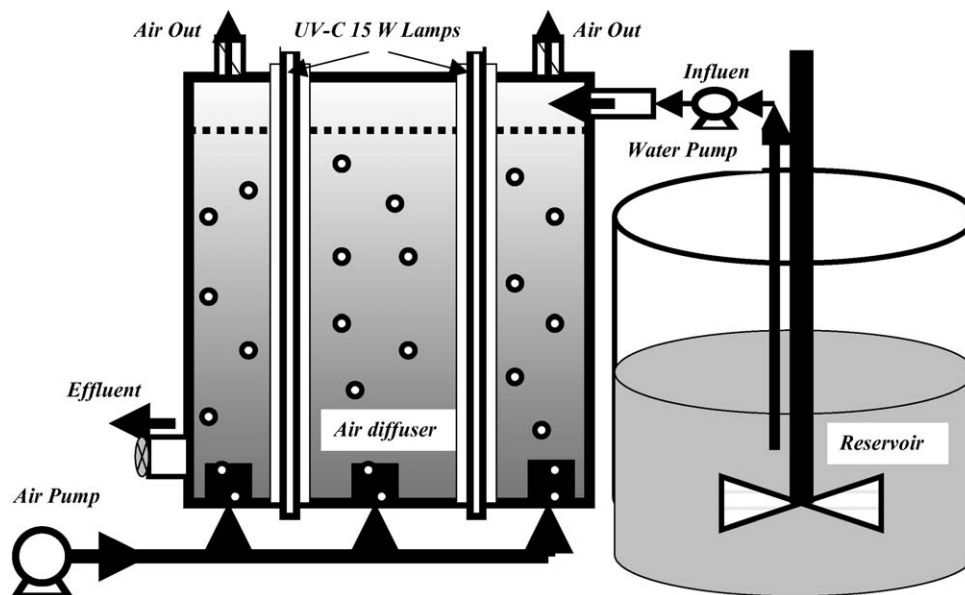

Fig. 2. Scheme of the photocatalytic reactor for photocatalytic degradation of AR 14.

two UV-C lamps (200–280 nm and 15 W, Philips). The apparatus employed in the photocatalytic experiments has been described in detail elsewhere [1,10].

A simple and effective method was used for immobilization of TiO_2 nanoparticles as follows: inner surfaces of reactor walls were cleaned with acetone and distilled water to remove any organic or inorganic material attached to or adsorbed on the surface and was dried in the air. A pre-measured mass of TiO_2 nanoparticle were attached on the inner surfaces of reactor walls using a thin layer of a UV resistant polymer. Immediately after preparation, the inner surface reactor wall–polymer–TiO_2 system was placed in the laboratory for at least 60 h for complete drying of the polymer.

2.3. Methods and analyses

Photocatalytic degradation processes were performed using a 7 L solution containing specified concentration of dye. The initial concentration of dye was 0.1 mM. The degradations were carried out at 298 K and natural pH value (5.6). Different optimal pHs (5.4–7) have also been reported for other dyes [11–13]. Samples were withdrawn from sample point at certain time intervals and analyzed for decolorization and degradation.

Decolorization of dye solutions were checked and controlled by measuring the absorbances of dye solutions at different time intervals by UV–vis CECIL 2021 spectrophotometer. The maximum absorbances of AR 14 in the visible region of UV–vis spectrum were 517 nm.

Ion chromatograph (METROHM 761 Compact IC) was used to assay the appearance and quantity of formate, acetate, oxalate, $SO_4{}^{2-}$ and $NO_3{}^-$ ions formed during the degradation and mineralization of AR 14 using an METROSEP anion dual 2, flow 0.8 mL/min, 2 mM $NaHCO_3$/1.3 mM Na_2CO_3 as eluent, temperature 20 °C, pressure 3.4 MPa and conductivity detector.

3. Results and discussions

3.1. Adsorption of AR 14 onto immobilized TiO_2 nanoparticles

Adsorption (dark) experiments were carried out for AR 14 dye under gentle air agitation in immobilized TiO_2 nanoparticles at the same experimental conditions (dye: 0.1 mM and H_2O_2: 6 mM and 60 min in the dark).

After adsorption experiment, the absorbance of AR 14 does not decrease, indicating the negligible effect of the adsorption on the dye concentration. On the other hand, other studies have concluded from their analyses that the photocatalytic process does not need not to occur at the catalyst surface, as here it was assumed that the reactive hydroxyl radicals and other oxidizing species can diffuse into the solution bulk to react with organic pollutants [14,15].

3.2. Effect of the H_2O_2 concentration

In photocatalysis, it has been found that the hydrogen peroxide concentration is a key parameter in the photocatalytic
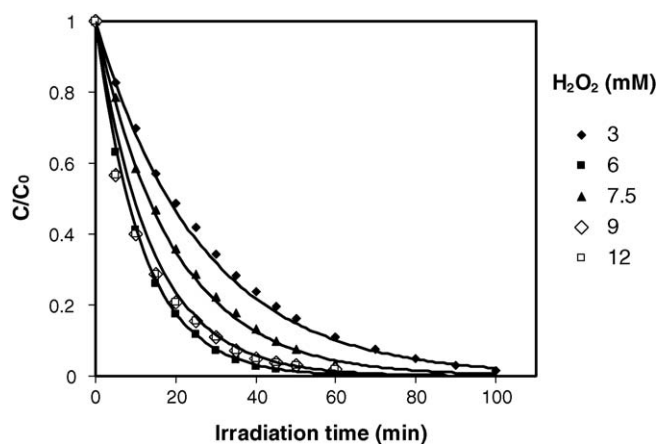

Fig. 3. Photocatalytic decolorization of AR 14 with different concentration of hydrogen peroxide at different time intervals of irradiation (C_0 is the initial dye concentration and C is the dye concentration at time t).

dye decomposition, depending on its concentration and nature of reductants [16], since the H_2O_2 concentration is directly proportional to the number of hydroxyl radicals generated in the photocatalysis. Hydrogen peroxide increases the formation rate of hydroxyl radicals in two ways. Firstly, the reduction of H_2O_2 at the conduction band would produce hydroxyl radicals. Secondly, the self-decomposition by illumination would also produce hydroxyl radicals [16,17]. Generally, the degradation rate of dye increases as the H_2O_2 concentration increases until an optimal H_2O_2 concentration is achieved. However, at high concentration, H_2O_2 can also become a scavenger of valence bond holes and hydroxyl radicals [16,18,19].

Fig. 3 shows the AR 14 concentration as a function of the illumination time when different H_2O_2 concentrations were used. It is shown to be exponential to time at each concentration of H_2O_2. This means that the first-order kinetics relative to AR 14 is operative. The correlation coefficient (R^2) and degradation rate constants (k, min^{-1}) of AR 14 for the various H_2O_2 concentrations are shown in Table 2. Apparently, as H_2O_2 concentration increases from 0 to 6 mM, the decolorization rate is greatly enhanced because more hydroxyl radicals are formed at higher hydrogen peroxide concentrations in solution. However, when H_2O_2 concentration is larger than 6 mM, the decolorization rate of AR 14 slows down. This can be explained by the scavenging effect when using a higher H_2O_2 concentration on the further generation of hydroxyl radicals in aqueous solution.

Changes in the absorption spectrums (250 nm $\leq \lambda \leq$ 650 nm) of AR 14 with H_2O_2 (6 mM) in the presence of UV/TiO_2 at

Table 2
Parameters (k and R^2) for the effect of different H_2O_2 concentrations on the decolorization rate of AR 14

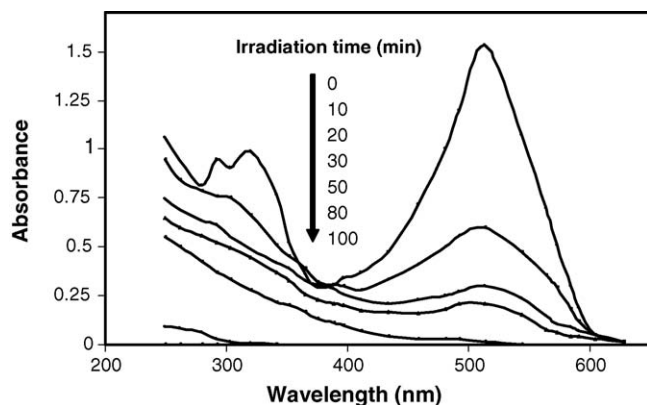| H_2O_2 (mM)	k (min^{-1})	R^2
3	0.0381	0.9933
6	0.0862	0.9908
7.5	0.0521	0.9936
9	0.0717	0.9831
12	0.0719	0.9840

Fig. 4. Changes in the absorption spectrums of AR 14 (0.1 mM) with H_2O_2 (6 mM)/TiO_2/UV at different time intervals of irradiation.

different time intervals of irradiation are shown in Fig. 4. With irradiation time elapse of 50 min, the maximum absorbance in visible region of UV–vis spectra decreased rapidly, which indicates that azo chromophore in AR 14 is the most active site for oxidation attack. Also, absorbance measurements of the samples at 260 nm were taken as an indication of the aromatic compounds content in the solution [20]. Degradation of the aromatic intermediates is shown in Fig. 5. The lack of any absorbance in 260 nm was indicative of the complete aromatic intermediates degradation.

3.3. Effect of the initial dye concentration

To study the effect of dye concentration on the rate of decolorization, the AR 14 concentration was varied 0.1–0.2 mM while the other variables were kept constant (H_2O_2: 6 mM, natural pH). Fig. 6 shows the time dependence of unconverted fraction of dye (C/C_0, C_0 is the initial dye concentration and C is the dye concentration at time t) for the various initial concentrations (0.1, 0.15 and 0.2 mM). It is shown to be exponential to time at each concentration of dye. This means that the first-order kinetics relative to AR 14 is operative. The correlation coefficient (R^2) and degradation rate constants (k, min^{-1}) of AR 14
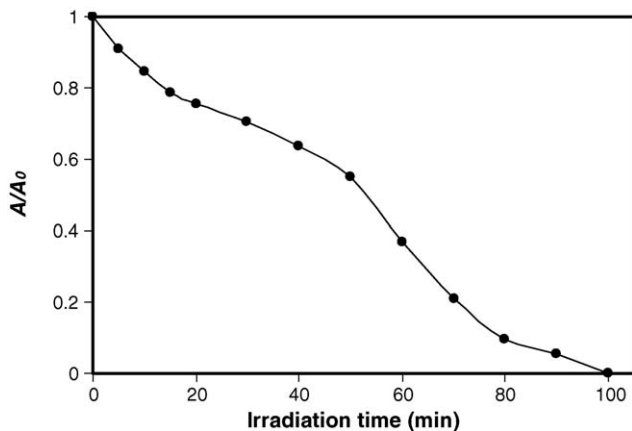

Fig. 5. Degradation of the aromatic intermediates during the photocatalytic degradation of AR 14 at 260 nm (A_0 and A are initial and final absorbance, respectively; dye: 0.1 mM and H_2O_2: 6 mM).
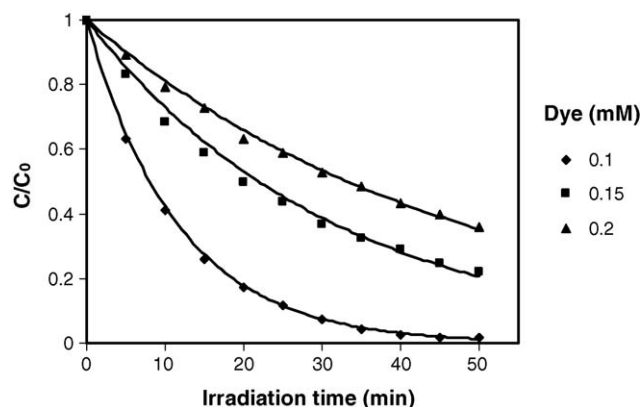

Fig. 6. The effect of dye concentration on the photocatalytic decolorization rate constants of AR 14 (C_0 is the initial dye concentration and C is the dye concentration at time t; H_2O_2: 6 mM).

for the various H_2O_2 concentrations are shown in Table 3. However, the apparent decolorization rate constant depends on the initial concentration of dye. As expected by increasing the dye concentration, the decolorization rate constant (k) is decreased (Table 3).

With the increase in the dye concentration, the possible cause is the interference from intermediates formed upon degradation of the parental dye molecules. Such suppression would be more pronounced in the presence of an elevated level of degradation intermediates formed upon an increased initial dye concentration [16].

3.4. Effect of the inorganic anions

The occurrence of dissolved inorganic ions is rather common in dye-containing industrial wastewater. These substances may compete for the active sites on the TiO_2 surface or deactivate the photocatalyst and, subsequently, decrease the degradation rate of the target dyes [3]. A major drawback resulting from the high reactivity and non-selectivity of OH$^\bullet$ is that it also reacts with non-target compounds present in the background water matrix, i.e. dye auxiliaries present in the exhausted reactive dye bath. This results in a higher OH$^\bullet$ demand to accomplish the desired degree of degradation, or complete inhibition of advanced oxidation rate and efficiency [4].

To consider how the presence of dissolved inorganic anions on the photocatalytic decolorization rate of AR 14, we have chosen the NaCl, NaNO$_3$, Na$_2$CO$_3$, NaHCO$_3$ and Na$_2$SO$_4$ salts. The same amount (2.5 mM) of these salts was used (H_2O_2: 6 mM, natural pH). Fig. 7 shows the effects of anions on the photocatalytic decolorization rate of AR 14. The parameters k

Table 3
Parameters (k and R^2) for the effect of different dye concentrations on the decolorization rate of AR 14

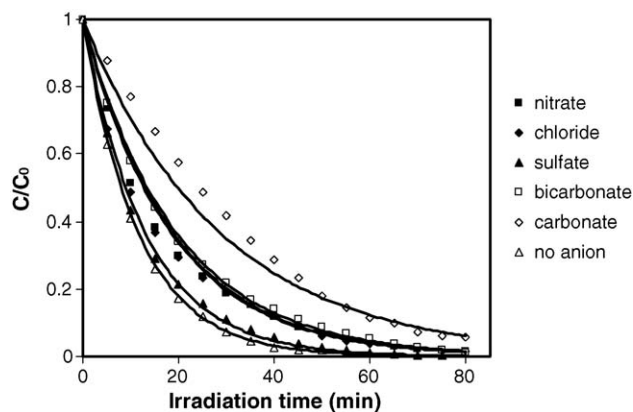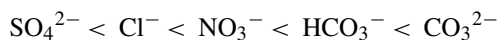| Dye (mM)	k (min^{-1})	R^2
0.1	0.0862	0.9908
0.15	0.0316	0.9909
0.2	0.0209	0.9974

Fig. 7. The effect of anions on the photocatalytic decolorization rate constants of AR 14 (C_0 is the initial dye concentration and C is the dye concentration at time t; dye: 0.1 mM, H_2O_2: 6 mM and anion: 2.5 mM).
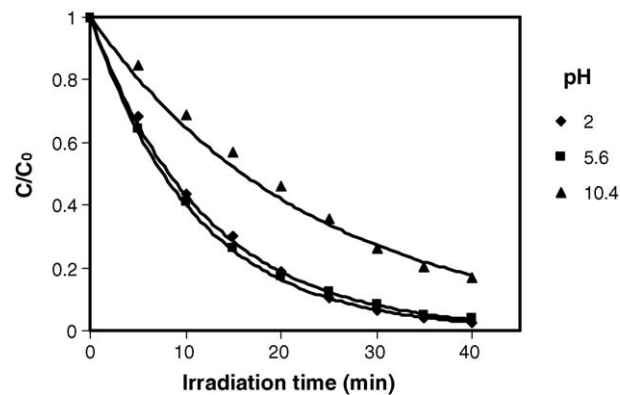

Fig. 8. The effect of pH on the photocatalytic decolorization rate constants of AR 14 (C_0 is the initial dye concentration and C is the dye concentration at time t; dye: 0.1 mM and H_2O_2: 6 mM).

(rate constant) and R^2 (correlation coefficient) of decolorization process are shown in Table 4. Of the anionic species studied (NaCl, NaNO$_3$, Na$_2$SO$_4$, NaHCO$_3$ and Na$_2$CO$_3$), Na$_2$CO$_3$ exhibited the strongest inhibition effect followed by NaHCO$_3$. The observed detrimental effect on the photocatalytic decolorization of AR 14 obeyed the following order:

$$SO_4^{2-} < Cl^- < NO_3^- < HCO_3^- < CO_3^{2-}$$

Inhibition effects of anions can be explained as the reaction of positive holes and hydroxyl radical with anions, that behaved as h_{vb}^+ and $OH^\bullet$ scavengers resulting prolonged color removal [3,4].

3.5. Effect of the solution pH

Since dyes to degrade can be at different pHs in colored effluents, comparative experiments were performed at three pH values: one reasonably acidic, one reasonably basic and natural pH. The studies in this report were carried out at pH range of 2–10.4. The results of blank studies indicated that the initial pH of dye solutions has negligible effect on the chemistry of AR 14. Also, the pH of solution is an important parameter in reaction taking place on semiconductor particle surfaces, since it influences the surface charge properties of the photocatalyst. The point of zero charge (pzc) is at pH$_{pzc}$ 6.8 for the TiO$_2$ particles [21]. The TiO$_2$ surface is positively charged in acidic media (pH < 6.8). Therefore, an electrostatic attraction exists between the positively charged surface of the TiO$_2$ and anionic dyes. As the pH of the system increases, the number of negatively charged sites increased. A negatively charged surface site on the TiO$_2$ does not favor the adsorption of dye anions due to the electrostatic repulsion. Also, lower adsorption of AR 14 at alkaline pH is due to the presence of excess OH$^-$ ions competing with the dye anions for the adsorption sites. However, the interpretation of pH effects on the efficiency of the photocatalytic decolorization process is a difficult task, because the different reaction mechanisms such as hydroxyl radical attack, direct oxidation by positive hole and direct reduction by the electron in the conducting band can contribute to dye degradation. The importance of each one depends on the substrate nature and pH [22,23].

As shown in Fig. 7 and Table 4, the sulfate anion has negligible effect on the decolorization rate. Thus, H$_2$SO$_4$ and NaOH were used for pH adjustment of dye solutions. The effect of pH on the decolorization of AR 14 is shown in Fig. 8. The parameters k (rate constant) and R^2 (correlation coefficient) of decolorization process are shown in Table 5. As shown in Table 5, the order of rate constants was pH$_{natural}$ > pH$_{acidic}$ > pH$_{alkaline}$. In this study, natural pHs were found to be the optimal pH under the given experimental conditions (dye: 0.1 mM and H$_2O_2$: 6 mM). A similar trend (different optimal pHs 5.4–7) was observed for the decolorization of other dyes [1,11–13].

3.6. Degradation of AR 14

During the photocatalytic degradation of AR 14, various organic intermediates were produced. Consequently, destruction of the dye should be evaluated as an overall degradation process, involving the degradation of both the parent dye and its intermediates.

Table 4
Parameters (k and R^2) for the effect of different anions on the decolorization rate of AR 14

Anion	k (min^{-1})	R^2
No anion	0.0862	0.9908
Sulfate	0.0768	0.9858
Chloride	0.0543	0.9946
Nitrate	0.0534	0.9951
Bicarbonate	0.0513	0.9927
Carbonate	0.0350	0.9854

Table 5
Parameters (k and R^2) for the effect of different pH on the decolorization rate of AR 14

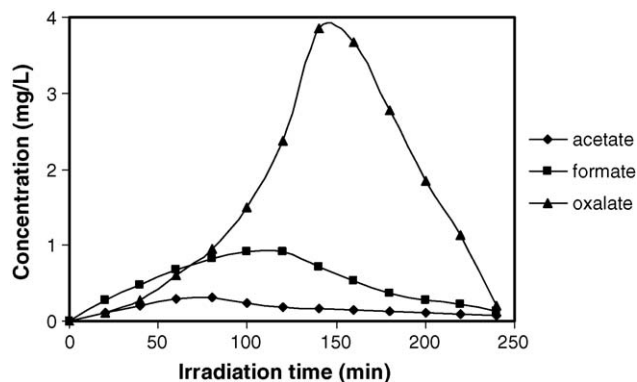| pH	k (min^{-1})	R^2
2	0.0839	0.9973
5.6	0.0910	0.9945
10.4	0.0434	0.9896

Fig. 9. Formation and disappearance of aliphatic carboxylic acids in the solution during the photocatalytic degradation of AR 14 (dye: 0.1 mM and H_2O_2: 6 mM).

Further hydroxylation of aromatic intermediates leads to the cleavage of the aromatic ring resulting in the formation of oxygen-containing aliphatic compounds [24]. In this research, only aliphatic carboxylic acid intermediates were investigated. The aliphatic carboxylic acid intermediates generated during the degradation process were analyzed by ion chromatography (IC) and identified by comparison with commercial standards. Formate, acetate and oxalate were detected as important aliphatic carboxylic acid intermediates during the degradation of AR 14 (Fig. 9). The formation of oxalate initially increased with the illumination time, and then sharply dropped. Carboxylic acids can react directly with holes generating CO_2 according to the "*photo-Kolbe*" reaction:

$$R\text{-}COO^- + TiO_2(h_{vb}{}^+) \rightarrow TiO_2 + R^{\bullet} + CO_2$$
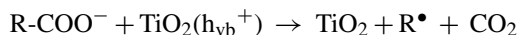
Also, the photocatalytic mineralization of AR 14 implies the appearance of inorganic products, mainly anions, since heteroatoms are generally converted into anions in which they are at their highest oxidation degree.

The dye degradation leads to the conversion of organic carbon into harmless gaseous CO_2 and that of N and S heteroatoms into inorganic ions, such as nitrate and sulfate ions, respectively [8]. Mineralization of AR 14 is reported for an irradiation period of 240 min. The formation of NO_3^- and $SO_4{}^{2-}$ from AR 14 mineralization is shown in Fig. 10.

However, the quantity of sulfate ions released (12 mg/L) is lower than that expected from stoichiometry (19 mg/L). This could be first explained by a loss of sulfur-containing volatile compounds such as H_2S and/or SO_2. However, this is not probable since both gases are very soluble in water and known as readily oxidizable into sulfate by photocatalysis. The more probable explanation for the quantity of $SO_4{}^{2-}$ obtained smaller than that expected from stoichiometry is given by the partially irreversible adsorption of some $SO_4{}^{2-}$ ions at the surface of titania as already observed. However, this partial adsorption of $SO_4{}^{2-}$ ions does not inhibit the photocatalytic degradation of pollutants [8].

Also, the quantity of nitrate ions released (6 mg/L) is lower than that expected from stoichiometry (12 mg/L) indicating that N-containing species remain adsorbed in the photocatalyst surface or most probably, that significant quantities of N_2 and/or
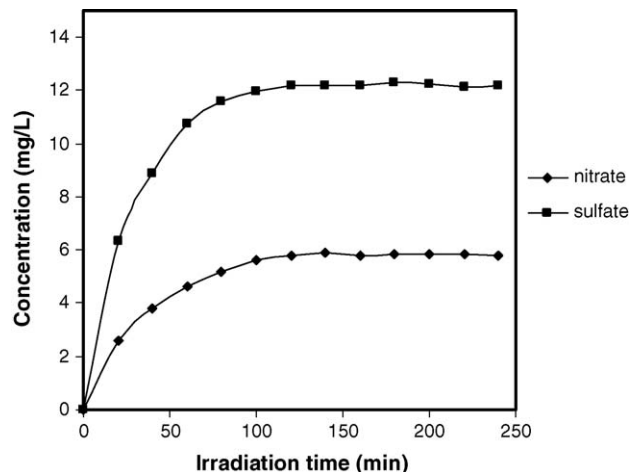

Fig. 10. Evolution of sulfate and nitrate ions during the photocatalytic degradation of AR 14 (dye: 0.1 mM and H_2O_2: 6 mM).

NH_3 have been produced and transferred to the gas phase. In the azo bonds each nitrogen atom is in its +1 oxidation degree. This oxidation degree favors the evolution of gaseous dinitrogen by the two-step reduction process expressed previously. N_2 evolution constitutes the ideal case for a decontamination reaction involving totally innocuous nitrogen-containing final product [3].

4. Conclusions

AR 14 could be successfully decolorized and mineralized by nanophotocatalysis in an immobilized TiO_2 nanoparticle photocatalytic reactor. It has been found that adsorption has a negligible effect on the dye concentration and the photocatalytic process occurred at solution bulk. The effects of operational parameters such as H_2O_2, dye concentration, anions (NO_3^-, Cl^-, $SO_4{}^{2-}$, HCO_3^- and $CO_3{}^{2-}$) and pH were investigated. Na_2CO_3 exhibited the strongest inhibition effect followed by $NaHCO_3$. The decolorization rate for AR 14 goes through a maximum when the concentration of the hydrogen peroxide increases from 0 to 6 mM and then it do not appreciable change. The photocatalytic decolorization kinetics follows a pseudo-first-order model for AR 14. Thin-film coating of photocatalyst may resolve the problem of suspension system of decolorization. Hence, this technique may be a viable one for treatment of large volume of aqueous colored dye solutions. Nanophotocatalysis appears a sub-division of heterogeneous catalysis, which is able to decolorize the colored textile wastewater without using high pressure of oxygen or heating.

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