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Photocatalytic transformation of acid orange 20 and Cr(VI) in aqueous TiO_2 suspensions

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Abstract

The ultraviolet (UVA)-induced photocatalytic treatment of aqueous solutions containing the azodye acid orange 20 alone, hexavalent chromium alone as well as their mixture over TiO_2 anatase suspensions was investigated. Experiments were conducted at dye concentrations varying between 25 and 100 mg/L, catalyst loadings between 50 and 500 mg/L, Cr(VI) concentrations between 5 and 20 mg/L, solution pH values between 2.5 and 10 and in the presence of several water matrix components, while the photocatalytic activity was assessed in terms of color removal, chemical oxygen demand (COD) decrease and Cr(VI) reduction. Treatment efficiency for the binary dye/TiO_2 system generally increased with increasing catalyst loading, decreasing dye concentration and decreasing solution pH and it was also promoted in the presence of dissolved oxygen. The presence of sodium azide, sodium chloride or sodium sulfate in the reaction mixture at concentrations up to 5000 mg/L decreased decolorization due to the scavenging of radicals and other reactive moieties. Complete color and COD removal could be achieved after 120 or 240 min of treatment at 500 or 250 mg/L catalyst loading, respectively, at near-neutral pH.

Dark redox reactions between the dye and Cr(VI) occurred readily at acidic conditions but not at near-neutral conditions in the dye/Cr(VI)/TiO_2 ternary system. However, UVA irradiation accelerated significantly both dye and metal conversion regardless the working solution pH. Interestingly, the rates of dye degradation and metal reduction for the ternary system were generally lower than those for the respective binary systems and this was more pronounced at near-neutral conditions; this could, to some extent, be due to partial catalyst deactivation.

Keywords: Azodye; Chromium; Photocatalysis; TiO_2; Wastewater

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1. Introduction

Over the years, several studies have dealt with the heterogeneous photocatalytic treatment of synthetic solutions as well as of actual effluents containing various commercial dyes. Dyes are one of the most notorious contaminants in aquatic environments because of their large volumes of production from industries, slow biodegradation and decolorization and high toxicity. It is estimated that approximately 15% of the total production of colorants is lost during synthesis and processing and the main source of this loss is to be found in wastewaters due to incomplete exhaustion [1].

Particular emphasis has been given on azodyes since they are extensively used in dyeing processes. These molecules are chemically stable and hardly biodegradable aerobically [2]. Although they are easily reduced under anaerobic conditions, they produce potentially more hazardous aromatic amines [3]. The TiO_2-mediated degradation of various azodyes by means of ultraviolet (UVA), visible and solar irradiation has been reported in several publications which are summarized in a recent review article [4].

TiO_2 photocatalysis is an emerging treatment technology for the destruction of various organic pollutants found in industrial effluents with key advantages including no mass transfer limitations, operation at ambient conditions and the possible use of solar irradiation. The catalyst itself is inexpensive, commercially available in various crystalline forms and particle characteristics, non-toxic and photochemically stable [5,6].

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General description of heterogeneous photocatalysis under artificial or solar irradiation has been discussed previously [7,8]. However, a brief summary is presented here for the sake of completeness. Irradiation of an aqueous TiO_2 suspension with light energy greater than the band gap energy of the semiconductor ($h\nu > E_g = 3.2$ eV) yields conduction band electrons (e_{cb}^-) and valence band holes (h_{vb}^+), (Eq. (1)):

$$TiO_2 + h\nu \xrightarrow{\lambda<400\,\text{nm}} e_{cb}^- + h_{vb}^+ \quad (1)$$

The photogenerated valence band holes (h_{vb}^+) and conduction band electrons (e_{cb}^-) can either recombine to liberate heat, or make their separate ways to the surface of TiO_2, where they can react with species adsorbed on the catalyst surface. The photogenerated valence band holes can react with water (Eq. (2)) and the hydroxide ion (Eq. (3)) (i.e. under alkaline conditions) to generate hydroxyl radicals which are strong oxidizing agents as well as oxidize directly the dye (Eq. (4)) [9]:

$$h_{vb}^+ + H_2O \rightarrow HO^{\bullet} + H^+ \quad (2)$$

$$h_{vb}^+ + HO^- \rightarrow HO^{\bullet} \quad (3)$$

$$h_{vb}^+ + \text{dye} \rightarrow \text{oxidation products} \quad (4)$$

On the other hand, the photogenerated conduction band electrons react with adsorbed molecular oxygen on the Ti(III) sites, reducing it to superoxide radical anion (Eq. (5)) which, in turn, reacts with protons to form peroxide radicals (Eq. (6)). The substrate can then undergo oxidative degradation through its reaction with radicals (Eq. (7)):

$$e_{cb}^- + O_2 \rightarrow O_2^{\bullet -} \quad (5)$$

$$O_2^{\bullet -} + H^+ \rightarrow HO_2^{\bullet -} \quad (6)$$

$$\text{radicals}\,(HO^{\bullet},\ O_2^{\bullet -},\ HO_2^{\bullet -}) + \text{dye} \rightarrow \text{oxidation products} \quad (7)$$

In addition to its application for the treatment of organic-containing effluents, it has also been used for the conversion of metals from their toxic and hazardous ionic states to less toxic forms. For instance, several studies report the heterogeneous photocatalytic reduction of toxic and carcinogenic Cr(VI) to less hazardous and mobile Cr(III); these studies are summarized elsewhere [10].

The photocatalytic treatment of effluents containing various organic contaminants and the photocatalytic removal of metal ions are well documented in the literature. On the other hand, the simultaneous treatment of organics and metals in water by photocatalysis and, indeed other advanced oxidation processes, has received appreciably less attention [3,11]. Interestingly, the photocatalytic treatment of mixtures containing dyes and metals has merely been reported in the literature although both co-exist in actual effluents; for instance, chromium and dyes are commonly found in effluents from leather tanning [11,12]. Tanneries use compounds that contain chromium in its trivalent oxidation state [13]. In the natural environment, Cr(III) compounds can be oxidized to Cr(VI) compounds. Therefore, tannery effluents typically contain both trivalent and hexavalent chromium and their aggregate concentration may range from tenths to thousands mg/L [14,15]. Schrank et al. [11] studied the UVA/TiO_2 treatment of model solutions containing the dye luranzol S kong alone, Cr(VI) alone, as well as their mixture as a function of the substrate concentration and solution pH and reported that the rates of both dye oxidative degradation and Cr(VI) reduction in their mixture were faster than the respective rates in the single-component systems. In a recent work [16], the TiO_2-mediated treatment of solutions containing acid orange 7 or rhodamine B dye and Cr(VI) or silver under visible or UVA irradiation was investigated with emphasis on the elucidation of the synergistic and antagonistic effects occurring during the simultaneous treatment.

The aim of the present work was to investigate the photocatalytic degradation of acid orange 20, a model azodye, in aqueous TiO_2 suspensions under UVA irradiation regarding the effect of various operating conditions such as concentration of dye and catalyst, solution pH, aeration, water matrix, and catalyst reuse on the extent of decolorization and COD decrease. Furthermore, the photocatalytic behavior of Cr(VI)/dye mixtures under various operating conditions was also studied since they can both be found in various industrial effluents. To the best of our knowledge, the UVA/TiO_2 photocatalytic treatment of acid orange 20 either alone or in the presence of heavy metals has not been studied before.

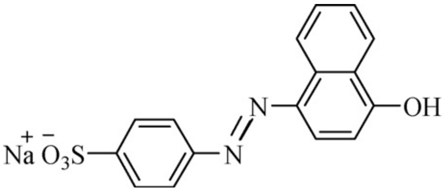
2. Experimental

2.1. Materials

Acid orange 20 (also referred to as Orange I), a mono-azo dye whose formula is shown in Scheme 1, and Cr(VI) in the form of sodium dichromate ($Na_2Cr_2O_7{\cdot}2H_2O$, >99.5% purity) were purchased from Fluka and used without further purification. TiO_2 anatase supplied by Kerr-McGee (USA) with a specific surface area of 90 m^2/g and mean particle size of 20 nm was used as the photocatalyst. Sodium chloride (>99.5% purity) was supplied by Merck, while sodium azide (>99% purity) and sodium sulfate (>99% purity) were supplied by Aldrich. They all were used as matrix components during photocatalytic experiments. Deionized water used for sample preparation was prepared on a water purification system (EASYpureRF) supplied by Barnstead/Thermolyne (USA).

2.2. Photocatalytic experiments

Photocatalytic experiments were conducted in a cylindrical vessel (55 mm i.d., 185 mm high) in the center of which was



Scheme 1. Molecular formula of acid orange 20 (Orange I).

placed a Pyrex cylindrical tube (40 mm o.d., 300 mm high) housing a 9 W UVA lamp (Radium Ralutec, 9 W/78, 350–400 nm). The vessel was covered with aluminum foil and immersed in a water bath, which was connected to a temperature control unit (Polystat, cc2 model, Huber), thus maintaining a constant liquid-phase temperature of 25 °C. In a typical run, 200 mL of an aqueous solution containing either the dye alone or the metal alone or a mixture of dye and dichromate were prepared daily, loaded in the vessel and slurried with the appropriate concentration of photocatalyst. The reactor contents were magnetically stirred, while (unless otherwise stated) air was continuously sparged in the liquid. The solution was left to equilibrate for 30 min in the dark before the lamp was switched on. In most cases, experiments were performed at ambient pH which was 6.5 and left uncontrolled during the reaction. In those cases where runs were carried out at basic or acidic conditions, the initial pH was adjusted adding the appropriate amount of 1 M NaOH or HCl as needed. Samples of about 5 mL periodically drawn from the vessel were centrifuged to remove solid particles and then analyzed with respect to dye conversion, COD decrease and (where appropriate) Cr(VI) reduction.

For those experiments where catalyst recovery and reuse was attempted, the catalyst was collected at the end of each experiment by centrifugation and used in the following experiment without any treatment.

2.3. Analytical measurements

Changes in the concentration of dye color were observed from its characteristic absorption band using a UV–vis spectrophotometer (Shimadzu, model 1240). Since a linear dependence between the initial concentration of the dye and the absorption at 480 nm was observed, the photodecomposition occurring throughout the experiment was monitored spectrophotometrically at this wavelength. Chemical oxygen demand is a widely used parameter to characterize the organic content of an industrial effluent. It is an aggregate measure of the organic compounds that can be oxidized to inorganic (mineral) end-products and, therefore, it was used to assess the degree of mineralization that had occurred during the photocatalytic process. COD was determined according to the dichromate digester colorimetric method at 620 nm, while Cr(VI) was determined according to the diphenyl carbazide colorimetric method at 540 nm, with both analyses occurring on a Hach DR/2010 spectrophotometer; more details can be found elsewhere [17].

3. Results and discussion

3.1. Effect of dye and catalyst concentration

Preliminary blank experiments were conducted to assess whether the dye could be removed through adsorption on the catalyst surface in the dark; in view of this, mixtures containing the dye at a concentration of 50 mg/L and the catalyst at concentrations of 125 and 250 mg/L were prepared and left in the dark at pH 6.5 and 3 for 240 and 1440 min. In all cases, adsorption alone even for prolonged time resulted in insignificant dye removal (i.e. <4%) at near-neutral or acidic conditions. An additional blank experiment was carried out where a 50 mg/L dye solution was irradiated for 120 min without catalyst leading to only about 9% color removal, thus showing that the dye is rather photostable under UVA irradiation.

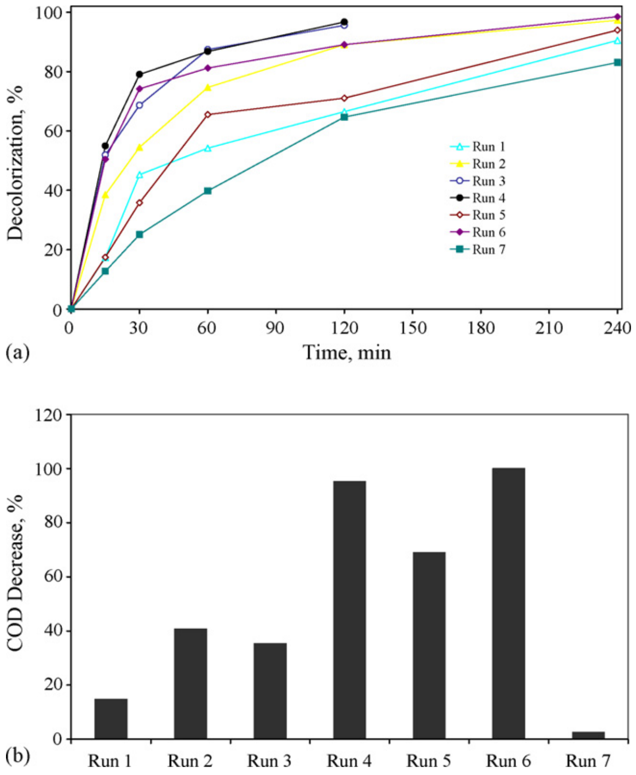


Fig. 1. Effect of dye and catalyst concentration on: (a) decolorization and (b) final COD decrease at initial solution pH 6.5. Run 1: [TiO_2] = 50 mg/L, [dye] = 50 mg/L; Run 2: [TiO_2] = 125 mg/L, [dye] = 50 mg/L; Run 3: [TiO_2] = 250 mg/L, [dye] = 50 mg/L; Run 4: [TiO_2] = 500 mg/L, [dye] = 50 mg/L; Run 5: [TiO_2] = 250 mg/L, [dye] = 100 mg/L; Run 6: [TiO_2] = 250 mg/L, [dye] = 25 mg/L; Run 7: [TiO_2] = 125 mg/L, [dye] = 100 mg/L. In Runs 3 and 4 irradiation time was 120 min, while in all other runs it was 240 min.

Fig. 1 shows decolorization-time profiles of acid orange 20 solutions as well as the corresponding final COD removal during the photocatalytic degradation at ambient solution pH 6.5 and various catalyst and dye concentrations. Increasing catalyst loading from 50 to 125 to 250 mg/L at 50 mg/L dye concentration (Fig. 1a, Runs 1–3) increased the extent of decolorization, while further increase to 500 mg/L (Fig. 1a, Run 4) had practically no significant effect on decolorization. For instance, the extent of decolorization after 120 min of reaction was 96% at 500 and 250 mg/L catalyst loading and decreased to 89 and 66%, respectively, at 125 and 50 mg/L.

On the other hand, the extent of COD decrease was affected by the catalyst concentration over the whole range of loadings studied. As seen in Fig. 1b, increasing catalyst loading from 250 to 500 mg/L at 50 mg/L dye concentration increased considerably COD removal from 35 to 95% (Runs 3 and 4, respectively), thus yielding complete mineralization. It should be pointed out that the final COD decrease at 125 mg/L catalyst loading and 50 mg/L dye concentration (Fig. 1b, Run 2) appears to be higher than that at 250 mg/L catalyst loading and 50 mg/L dye concentration (Fig. 1b, Run 3) but this is so simply because the former experiment lasted twice as long as the latter. As seen from Fig. 1, increasing dye concentration at a constant catalyst loading suppressed both color and COD removal. At a catalyst loading of 125 mg/L for example, the final color and COD decrease was 97 and 41%, respectively, at 50 mg/L dye concentration (Run 2) and became 83 and 3%, respectively, at 100 mg/L dye concentration (Run 7). In general, at the conditions employed in this study degradation increased with increasing the catalyst to dye mass concentration ratio and this was more pronounced for COD rather than dye degradation.

TiO_2 loading in slurry photocatalytic processes is an important factor that can influence strongly treatment performance. The catalyst concentration above which conversion levels off depends on several factors (e.g. reactor geometry, nature of substrate, wavelength and intensity of light source) and corresponds to the point where all catalyst particles, i.e. all the surface exposed, are fully illuminated [18,19]. At higher concentrations, a screening effect of excess particles occurs, thus masking part of the photosensitive surface and consequently hindering light penetration [7]; this usually results in conversion reaching a plateau, while at excessive catalyst concentrations conversion may also decrease due to increased light reflectance onto the catalyst surface.

Dye degradation occurs through the oxidative cleavage of the chromophore N=N bond leading to the formation of primary reaction by-products [20,21] which are subsequently oxidized and eventually yield carbon dioxide and water. As seen from Fig. 1, fast decolorization was accompanied by low to moderate levels of COD removal, thus implying that the organic carbon originally present in the azodye had been converted to oxidation intermediates that were relatively refractory to mineralization and accumulated in the reaction mixture.

3.2. Effect of solution pH

Fig. 2 shows decolorization-time profiles as well as the final COD removal during the photocatalytic degradation of a 50 mg/L dye solution at 125 and 250 mg/L catalyst concentration under acidic and alkaline conditions. As seen from Figs. 1 and 2, degradation was strongly dependent on the solution pH and was substantially hindered at alkaline conditions. At either catalyst concentration, the extent of decolorization remained practically unchanged decreasing the starting solution pH from its ambient value of 6.5 to 3; however, acidic conditions favored COD removal, e.g. at 125 mg/L catalyst loading the final COD decrease was 41 and 64% at pH 6.5 and 3, respectively. Reaction at pH 10 impeded both dye and COD conversion; after 240 min of reaction at 250 mg/L catalyst loading, the COD reduction was as low as 30% with this value being even lower than that achieved after 120 min of reaction at ambient pH.

The effect of pH on degradation is a complex issue closely related to the pathways of dye degradation, the amphoteric behavior of TiO_2, as well as the lowering of the oxidative power of the photogenerated holes by increasing the pH value. Solution pH influences the ionization state of the TiO_2 surface according to the following reactions:

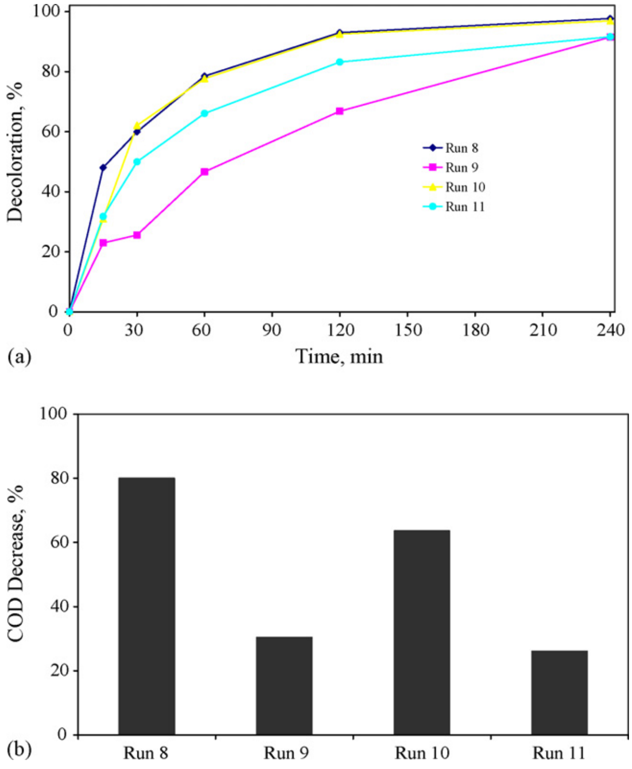


Fig. 2. Effect of solution pH and aeration on: (a) decolorization and (b) final COD decrease at 50 mg/L initial dye concentration. Run 8: $[TiO_2] = 250$ mg/L, pH 3; Run 9: $[TiO_2] = 250$ mg/L, pH 10; Run 10: $[TiO_2] = 125$ mg/L, pH 3; Run 11: $[TiO_2] = 250$ mg/L, pH 3, no aeration.

$$>\mathrm{Ti{-}OH} + \mathrm{H^+} \rightleftharpoons\ >\mathrm{Ti{-}OH_2^+} \qquad (8)$$

$$>\mathrm{Ti{-}OH} + \mathrm{HO^-} \rightleftharpoons\ >\mathrm{Ti{-}O^-} + \mathrm{H_2O} \qquad (9)$$

In Eqs. (8) and (9) $>\mathrm{Ti{-}OH}$ represents the primary hydrated surface functionality of TiO_2 [22]. At pH values greater than about 5.9 (this value corresponds to the point of zero charge for TiO_2 [23]) the catalyst surface becomes negatively charged, thus preventing the negatively charged dye as well as the hydroxide anion from adsorbing onto the surface; this would explain the reduced degree of degradation recorded at alkaline conditions. Conversely, acidic conditions would favor the electrostatic attraction between the positively charged surface and the dye both of which would result in increased degradation.

To evaluate the effect of air sparging on degradation, an additional experiment was conducted where the solution was not aerated and the results are also shown in Fig. 2. Lack of oxygen expectedly retarded both dye and COD conversion since the reactions of oxygen with conduction band electrons that would eventually yield reactive peroxide radicals (i.e. Eqs. (5) and (6)) as well as prevent e^-/h^+ recombination (a major cause of low TiO_2 photocatalytic quantum yield) do not occur to an appreciable extent.

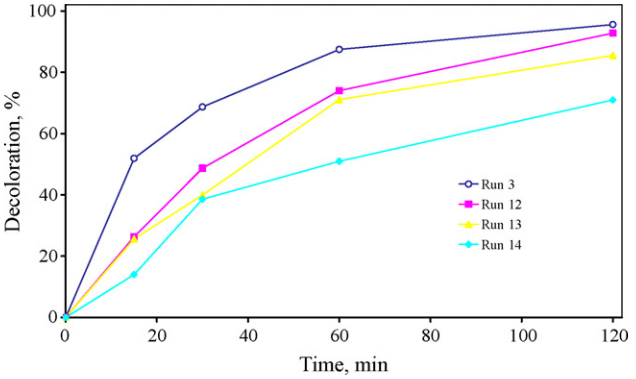


Fig. 3. Effect of water matrix on decolorization at 250 mg/L TiO_2 concentration, 50 mg/L initial dye concentration and initial solution pH 6.5. Run 3: no matrix; Run 12: [NaCl] = 5 g/L; Run 13: [Na_2SO_4] = 5 g/L; Run 14: [NaN_3] = 0.5 g/L.

3.3. Effect of water matrix

In further experiments, the effect of water matrix on decolorization was studied and the results are shown in Fig. 3. The presence of 5 g/L sodium chloride or sodium sulfate led to decreased decolorization and this can be explained as a result of trapping the photogenerated valence band holes and the hydroxyl radicals by the respective anions (Eqs. (10)–(13)):

$$Cl^- + h_{vb}{}^+ \rightarrow Cl^\bullet \tag{10}$$

$$Cl^- + OH^\bullet \rightarrow OH^- + Cl^\bullet \tag{11}$$

$$SO_4{}^{2-} + h_{vb}{}^+ \rightarrow SO_4{}^{\bullet -} \tag{12}$$

$$SO_4{}^{2-} + OH^\bullet \rightarrow OH^- + SO_4{}^{\bullet -} \tag{13}$$

Although chloride and sulfate radicals are also capable of oxidizing organic compounds, their reduction potential is lower than that of hydroxyl radicals, i.e. the respective values are 1.36, 2.6 and 2.8 V (versus NHE) [24]. The detrimental effect of increased salt concentration on degradation should be carefully considered bearing in mind that industrial effluents containing dyes also contain salts at concentrations of several grams per liter [3]. Decolorization also decreased in the presence of 0.5 g/L sodium azide which is a scavenger of both oxygen and hydroxyl radicals [25].

3.4. Reactions of the Cr(VI)/TiO_2 binary system

To assess whether Cr(VI) anions can be adsorbed onto the catalyst surface, additional dark experiments were performed with solutions containing 10 mg/L Cr(VI) and 250 mg/L TiO_2 (i.e. without dye) for 240 min. No change in the metal concentration was recorded at pH 6.5 in the dark. At these conditions the catalyst surface consists of negatively charged and neutral groups as shown in Eq. (9). On the other hand in aqueous solutions, dichromate anions, $Cr_2O_7{}^{2-}$, participate in the following equilibrium (Eq. (14)) [26]:

$$Cr_2O_7{}^{2-} + H_2O \rightleftharpoons 2HCrO_4{}^- \rightleftharpoons 2CrO_4{}^{2-} + 2H^+ \tag{14}$$

In Eq. (14) the concentration of various anions depends on the solution pH [27]. In particular, at pH values around 2.5 the predominant species are the hydrogen chromate anion $HCrO_4{}^-$ and the dichromate anion $Cr_2O_7{}^{2-}$, while at pH values around 6.5 the predominant species are the hydrogen chromate anion $HCrO_4{}^-$ and the chromate anion $CrO_4{}^{2-}$ [27]. Therefore, at pH 6.5 the catalyst surface repels or shows no electrostatic affinity for the hydrogen chromate and the chromate anion. Conversely, about 12% metal conversion was recorded at pH 2.5 in the dark and this can be attributed to hydrogen chromate and dichromate anions adsorption onto the positively charged catalyst surface. The above findings are in agreement with previous literature reports stating that adsorption of Cr(VI) anions onto TiO_2 surface occurs mainly at acidic pH, while at near-neutral conditions adsorption was almost negligible [26,27].

The Cr(VI)/TiO_2 samples were also irradiated for 240 min after which the extent of Cr(VI) reduction was 29 and 36% at pH values of 6.5 and 2.5, respectively. This is in agreement with results reported elsewhere [26,28–31] concerning the beneficial effect of decreasing solution pH on Cr(VI) photocatalytic reduction. At acidic conditions, Cr(VI) anions capture the photogenerated conduction band electrons and their reduction occurs as follows:

$$HCrO_4{}^- + 7H^+ + 3e_{cb}{}^- \rightarrow Cr^{3+} + 4H_2O \tag{15}$$

$$Cr_2O_7{}^{2-} + 14H^+ + 6e_{cb}{}^- \rightarrow 2Cr^{3+} + 7H_2O \tag{16}$$

while at neutral or alkaline conditions:

$$CrO_4{}^{2-} + 4H_2O + 3e_{cb}{}^- \rightarrow Cr(OH)_3 + 5HO^- \tag{17}$$

In the absence of other reducing agents, water is oxidized by the photogenerated valence band holes, thus completing the redox cycle:

$$2H_2O + 4h_{vb}{}^+ \rightarrow O_2 + 4H^+ \tag{18}$$

The standard reduction potential at pH 0 for Eq. (15) is 1.35 V, for Eq. (16) is 1.232 V, while for Eq. (17) is −0.13 V (versus NHE) [32]. The pH dependence of the reduction potentials of Eqs. (15) and (16) can be calculated −0.138 V/pH unit at 25 °C by applying the Nernst equation [33]. Therefore, the reduction potential of the hydrogen chromate anion and the dichromate anion at pH 2.5 can be estimated 1.005 and 0.887 V, respectively. On the other hand, the reduction potential at pH 0 of the electrons in the conduction band of anatase TiO_2 is ∼−0.23 V (versus NHE) [34] and with a pH dependence of −0.059 V/pH unit at 25 °C the reduction potential at pH 2.5 can be estimated ∼−0.377 V (versus NHE). Since the reduction potentials at pH 2.5 of hydrogen chromate and dichromate anions are more positive than the reduction potential of the conduction band of anatase TiO_2, the photocatalytic reduction of Cr(VI) anions onto TiO_2 surface is thermodynamically favorable [34].

An additional run was carried out where 10 mg/L Cr(VI) was irradiated in the absence of catalyst yielding negligible (i.e. about 3%) metal conversion.

3.5. Reactions of the dye/Cr(VI)/TiO_2 ternary system

In further experiments, the effect of Cr(VI) on the photocatalytic degradation of the azodye was studied at various

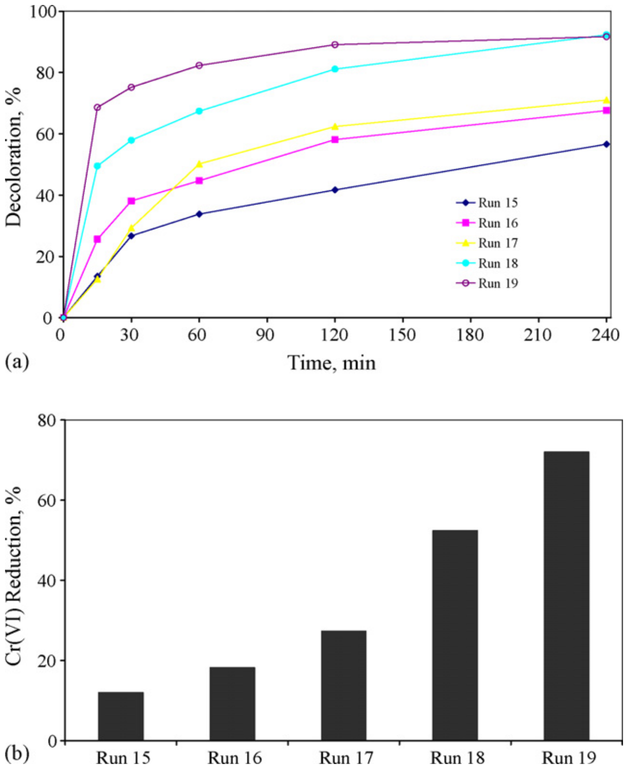


Fig. 4. Effect of catalyst concentration and solution pH on: (a) decolorization and (b) final Cr(VI) reduction at 50 mg/L initial dye concentration and 10 mg/L initial Cr(VI) concentration. Run 15: $[TiO_2] = 125$ mg/L, pH 6.5; Run 16: $[TiO_2] = 250$ mg/L, pH 6.5; Run 17: $[TiO_2] = 500$ mg/L, pH 6.5; Run 18: $[TiO_2] = 250$ mg/L, pH 2.5; Run 19: $[TiO_2] = 500$ mg/L, pH 2.5.

experimental conditions. In preliminary dark experiments, mixing 50 mg/L dye with 10 mg/L Cr(VI) in the presence of 250 mg/L TiO_2 at pH 6.5 led to neither decolorization nor metal reduction after 240 min. However, when exactly the same experiment was conducted at pH 2.5 the extent of decolorization and Cr(VI) reduction was 49 and 19%, respectively, after 240 min and these values increased to 86 and 37% after 1440 min. This can be explained in terms of adsorption of Cr(VI) species and dye molecule onto TiO_2 surface, as well as oxidation of dye by Cr(VI) species at acidic conditions.

Fig. 4 shows the decolorization-time profiles as well as final Cr(VI) reduction during the irradiation of the dye/Cr(VI)/TiO_2 ternary system at various solution pH values and catalyst concentrations. As clearly seen, UVA irradiation accelerated the conversion of both Cr(VI) and the dye compared to the respective dark runs since the UVA-induced excitation of TiO_2 generates conduction band electrons and valence band holes.

From Figs. 1, 2 and 4, it is interesting to note that for the binary dye/TiO_2 system decolorization always proceeded faster than that of the respective ternary dye/Cr(VI)/TiO_2 system regardless the solution pH and catalyst loading. This was more pronounced for the experiments conducted at near-neutral conditions, e.g. the extent of color removal after 120 min of irradiation at pH 6.5 and 250 mg/L catalyst was 96 and 58% for the binary and ternary systems, respectively, with the corresponding values at acidic conditions being 93 and 81%. Likewise, the extent of metal conversion for the binary Cr(VI)/TiO_2 system was greater than that for the ternary dye/Cr(VI)/TiO_2 one at near-neutral conditions (i.e. 29 and 18%, respectively, after 240 min). Nonetheless, the opposite was observed at acidic conditions with the extent of metal conversion being 36 and 52% after 240 min for the binary and ternary systems, respectively.

The reason for the decreased photocatalytic activity of the ternary system may be two-fold: (i) both dye and dichromate anions compete for the same catalyst active sites and, therefore, they have fewer chances to adsorb onto the catalyst surface and undergo photocatalytic reactions than in the respective binary systems, and (ii) the catalyst may, to some extent, become deactivated due to the formation of stable precipitates that block the active sites of the catalyst. For instance, Cr^{3+} is likely to precipitate as $Cr(OH)_3$ at pH values over 4–5 [27,28] thus covering the catalyst surface; this is consistent with the fact that the reduction in photocatalytic activity was more pronounced at near-neutral rather than acidic conditions.

Moreover, dye degradation by-products and chromic species may form complexes that also contribute to catalyst deactivation [16]. Given that: (i) acidic conditions are likely to prevent chromium precipitation and consequently confine catalyst deactivation, (ii) chromium seems to have a greater affinity for the catalyst surface than the dye at acidic conditions and (iii) Cr(VI) is readily reduced by the dye even in the dark could possibly explain the fact that Cr(VI) reduction in the ternary system was faster than that in the binary at acidic conditions. Kyung et al. [16] recently showed that, although the UVA-mediated TiO_2 photocatalytic reduction of Cr(VI) at pH 3 was enhanced in the presence of acid orange 7, the rate of dye mineralization in the ternary system was retarded compared to the respective binary system; the authors hypothesized that some kind of catalyst deactivation had occurred. Colon et al. [35] who studied the simultaneous photocatalytic treatment of salicylic acid and Cr(VI) over various TiO_2 suspensions at pH 2 reported that the conversion of both substrates in the ternary system was substantially lower than that in the respective binary systems and this was due to catalyst deactivation as a result of chromium deposition on the active sites.

In a final set of experiments, the effect of changing Cr(VI) concentration on the photocatalytic activity was studied at acidic

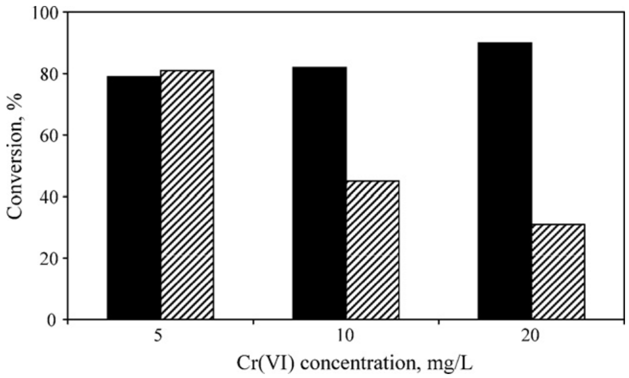


Fig. 5. Effect of Cr(VI) initial concentration on decolorization (black bars) and final Cr(VI) reduction (hatched bars) at 50 mg/L initial dye concentration, 250 mg/L catalyst concentration and initial solution pH 2.5 after 120 min irradiation.

conditions. As seen in Fig. 5, increasing Cr(VI) concentration to 20 mg/L had a positive effect on decolorization reaching 90% after 120 min of reaction; the respective value for the runs performed at 5 or 10 mg/L was about 80%. Metal conversion was found to decrease with increasing initial concentration from 5 to 10 and eventually to 20 mg/L. Nevertheless, it should be borne in mind that, in terms of amount of Cr(VI) removed rather than conversion, treatment performance improved with increasing metal concentration; for instance, increasing initial concentration from 5 to 20 mg/L increased the concentration of Cr(VI) removed by about 35%.

3.6. Catalyst reuse

To assess the stability of the catalyst on repeated use, the same TiO_2 catalyst was used in consecutive photocatalytic experiments with the dye/TiO_2 and dye/Cr(VI)/TiO_2 systems. At the end of each run, the catalyst was separated by centrifugation and used in the following run, while no pre-conditioning of the used catalyst was undertaken between consecutive runs. For the dye/TiO_2 system, four consecutive experiments were executed at 50 mg/L initial dye concentration, solution pH 6.5 and a fresh catalyst concentration of 500 mg/L. For all four runs, the extent of decolorization was $69 \pm 3\%$ after 30 min of reaction and increased to $97 \pm 1\%$ after 120 min, implying that the catalyst retained fully its activity.

Similarly, three consecutive experiments were executed for the dye/Cr(VI)/TiO_2 system at 50 mg/L initial dye concentration, 10 mg/L initial Cr(VI) concentration, solution pH 2 and a fresh catalyst concentration of 250 mg/L. For all three runs, the extent of decolorization was $56 \pm 2\%$ after 30 min of reaction and increased to $80 \pm 2\%$ after 120 min, implying that the catalyst retained fully its activity for color removal. Nonetheless, the extent of final (i.e. after 120 min) Cr(VI) reduction decreased by about 13% (i.e. from 45 to 32%) between the first and last use.

4. Conclusions

The conclusions drawn from this study can be summarized as follows:

(1) TiO_2-mediated photocatalysis is capable of oxidizing the azodye acid orange 20 in synthetic aqueous solutions. The extent of conversion depends on the operating conditions employed such as concentration of catalyst and the dye, solution pH, dissolved oxygen and the water matrix. Treatment efficiency was generally promoted with increasing catalyst loading, decreasing dye concentration and decreasing solution pH. The presence of matrix water components acting as hydroxyl radicals or photogenerated holes scavengers, such as sodium chloride, sodium sulfate and sodium azide, led to decreased decoloration.

(2) Decolorization for the binary dye/TiO_2 system always proceeded faster than that of the respective ternary dye/Cr(VI)/TiO_2 system regardless the solution pH and catalyst loading and this was more pronounced at near-neutral conditions. Likewise, the extent of metal conversion for the binary Cr(VI)/TiO_2 system was greater than that for the ternary dye/Cr(VI)/TiO_2 one at near-neutral conditions but the opposite was observed at acidic conditions.

(3) For the binary dye/TiO_2 system, the catalyst retained fully its activity in terms of color removal when used in consecutive runs at near-neutral conditions. For the ternary dye/Cr(VI)/TiO_2 system the catalyst retained fully its activity in terms of color removal but lost some of its catalytic activity in terms of Cr(VI) reduction when used in consecutive runs at acidic conditions.

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