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Photoreduction of toxic chromium using TiO_2-immobilized under natural sunlight: effects of some hole scavengers and process parameters

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ABSTRACT

This work focuses on the photocatalytic reduction of Cr(VI)–Cr(III) using TiO_2-immobilized onto glass slides under natural sunlight. The commercial TiO_2 Degussa P25 was used as a photocatalyst in this work. The effects of some additives as hole scavengers for Cr(VI) reduction are studied. The results show that their presence enhances the reduction rate in the order: tartaric acid > oxalic acid > EDTA > ethanol > methanol > no-additive. The optimization of tartaric acid concentration is determined. The effect of process parameters such as Cr(VI) concentration, pH, and the presence of interfering substances such as inorganic anions (SO_4^{2-}, CO_3^{2-}, NO_3^-, Cl^- and PO_4^{3-}) and metallic cations (Fe^{3+}, Cu^{2+}, Zn^{2+}, and Mn^{2+}) is investigated. The results show that the removal rate is maximum at pH 1.5. On the other hand, the coexistence of interfering ions with Cr(VI) decreases the reduction rate except for the Fe^{3+}. Finally, the results show that the TiO_2-immobilized can be reused several times.

Keywords: Cr(VI); Photoreduction; TiO_2-immobilized; Hole scavenger; Sunlight

1. Introduction

The industrial effluents are the main causes of water pollution by heavy metals. Many of these metals are considered toxic, even carcinogenic especially in some of their valance states [1]. Consequently, there is a clear need to remove these metals from wastewaters prior to discharging them to avoid their accumulation in the environment. Traditionally, wastewater treatments are achieved by processes such as physicochemical and electrochemical [2–6]. However, these processes have some limitations, namely low removal rate, high cost, disability to remove some elements, and the production of secondary waste which needs further treatment. This can be overcome by the use of advanced oxidation processes (AOPs) which are considered to be low or even non-waste formation technologies.

The AOPs can be used both for the removal of organic [7,8], inorganic [6–9] compounds, or both [10–14]. The heterogeneous photocatalysis is one of the technologies of AOPs that has received much attention to treat wastewaters. It is based on the photonic excitation of a photocatalyst (semiconductor) by photons which have higher energy than the band gap of the semiconductor which leads to generation of electron–hole pairs [15]. These pairs are responsible for the reactions on the photocatalyst surface. The advantage of this method is its ability to oxidize and reduce a large number of organic and inorganic

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compounds. Furthermore, the sunlight can be used as a free source for UV photons. This clean process can be successfully used in Algeria where the average sunshine duration is about 2,500 h annually [16]. The photocatalytic reduction of metals is known to convert them into non-toxic or metallic states on the semiconductor surface (Fig. 1(a)). The photoreduction reaction is highly dependent on the metal cation redox potentials relative to the TiO_2 conduction band (CB) edge (Fig. 1(b)). The energy of the semiconductor band gap must be more negative than the energy of the metallic couple ($M^{n+}/M^{(n-z)+}$) [1,14]. To ensure the reduction of metals by the photogenerated electrons, the addition of additives (A) as hole scavenger, usually an organic compound, is required [17,18]. Hence, it is necessary to choose an appropriate sacrificial electron donor. A wide range of metal ions, including hexavalent chromium, have been investigated in photocatalytic reduction studies [13,15,19–22] using different semiconductors and various types of TiO_2 like TiO_2-suspension, TiO_2-supported, and TiO_2 slurry reactor.

In the present study, the photoreduction of Cr(VI) ions using TiO_2-immobilized onto glass slides under natural sunlight was carried out (at Annaba University during July 2013). The choice of additive as an optimal hole scavenger was studied. The Cr(VI) photoreduction reaction was investigated under different conditions such as hole scavenger concentration, Cr(VI) concentration, pH solution, and the presence of interfering substances. Finally, the reuse of TiO_2-immobilized was studied under the same conditions.

2. Materials and methods

2.1. Materials

P25 Titanium dioxide (Degussa AG Company) was used in this study. According to supplier, its polycrystalline structure is composed of approximately 80% anatase and 20% rutile. It has a BET surface area of $50\ m^2/g$ and is approximately 21 nm as primary particles. Acetone (Sigma–Aldrich, 99.99%) was used for fixing the P25 TiO_2 on the glass slides. Potassium dichromate (Sigma–Aldrich, ≥99.0%) solution was prepared using double-distilled water. Adjustment of the pH solution was achieved with H_2SO_4 (Sigma–Aldrich) and monitored by a pH meter (HANNA HI 9812-5). The additives used as hole scavengers were methanol (Sigma–Aldrich, ≥ 99.8% (GC)), ethanol (Sigma–Aldrich, ≥99.8% (GC)), EDTA (Sigma–Aldrich, BioUltra, anhydrous, ≥ 99% (titration)), oxalic acid (Sigma–Aldrich, puriss. p.a., anhydrous, ≥ 99.0% (RT)), and tartaric acid (Sigma–Aldrich, ACS reagent, ≥ 99.5%). Sodium salts of inorganic anions (SO_4^{2-}, $|CO_3^{2-}$,| NO_3^-, Cl^-, and PO_4^{3-}) and sulfate salts of metallic cations (Fe^{3+}, Cu^{2+}, Zn^{2+}, and Mn^{2+}) were used for the study of the effect of the interfering substances.

2.2. Preparation of TiO_2-immobilized

The P25 TiO_2-supported used in this study was prepared by depositing P25 TiO_2 on glass slides (2.6 cm × 7.6 cm) according to a slightly modified method used by Tusnelda and Fritz [23]. The method description was mentioned in our previous study [24].

2.3. Experimental procedure

The photocatalytic reduction of Cr(VI) experiments was performed using a static batch reactor consisting of 250 mL Pyrex beakers open to air under natural sunlight at sea level (in front of the Chemistry Department without any obstacle) at ambient temperature on sunny days (at Annaba University during July-2013) and were started at 10:00 am for a duration of 4 h (Fig. 2). The solution of the substrate (200 mL) in the presence of TiO_2 glass slide was exposed to natural sunlight under a constant stirring. For the study of the

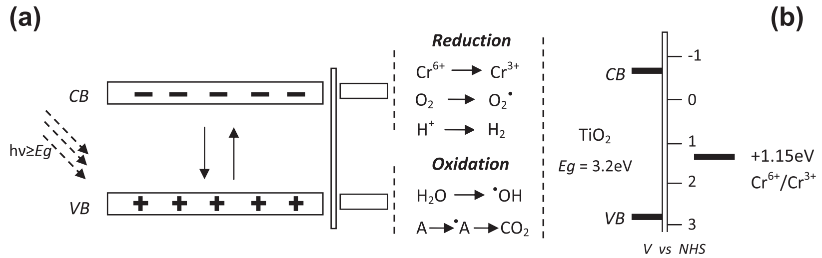

Fig. 1. (a) Scheme of the TiO_2-photoreduction process of metals (e.g. hexavalent chromium). (b) Schematic energy level diagram of TiO_2 semiconductor and the E_0(Cr(VI)/Cr(III) at pH 3.
Note: CB: conduction band; VB: valence band; A: additive; $A^{\bullet}$: additive radical.

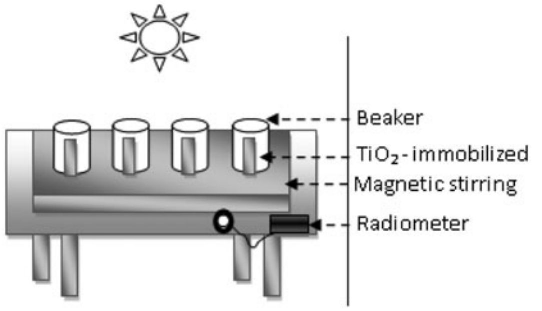

Fig. 2. Experimental setup used for the photoreduction of Cr(VI) under sunlight.

effect of interfering ions, the cation and anion salts were added separately to the Cr(VI) solution at concentration of 50 mg/L. The TiO_2 glass slide was kept in a slight inclination inside the beaker. During the experiments, samples (4 mL) were collected at selected time intervals. The residual concentration of Cr(VI) was determined at 350 nm using a UV–vis spectrophotometer (JENWAY 6405). The calibration curve for the determination of Cr(VI) gave a determination coefficient (R^2) ≥ 0.9998. The intensity of sunlight radiation at 365 nm was measured using a VLX-3 W radiometer (France) with a cell diameter of 1 cm. The radiation intensity in the working period was in the range 1.6–1.8 mW/cm^2. The extent of water evaporation during the experimentation was in average of 6.0% after 4 h of irradiation. Due to the inherent non-reproducibility of solar radiations and in order to minimize the experimental errors, the study of the effects of each parameter was performed simultaneously on a set of experiments. This is considered to be within experimental errors. In a separate trial, experiments were carried out in triplicate under the same experimental conditions in order to evaluate the error. All the results were reproducible within ± 10% variation.

The reduction rate of Cr(VI) was calculated using Eq. (1). The kinetics of the reduction process was investigated using a pseudo-first-order reaction according to a Langmuir–Hinshelwood kinetic model (Eq. (2)) [25].

$$R\,(\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \tag{1}$$

$$\ln \frac{C_t}{C_0} = -kt \tag{2}$$

where C_0 and C_t represent the Cr(VI) concentration (mg/L) before and after the treatment, t is the irradiation time (min), and k is the apparent rate constant.

3. Results and discussion

3.1. Effect of hole scavengers

During the photoreduction process of Cr(VI), some molecules as hole scavengers (A) were tested for the photoreduction using TiO_2-immobilized under natural solar light. The results show that their presence enhances the reduction rates in the following order: tartaric acid (83.9%) > oxalic acid (74.2%) > EDTA (63.4) > ethanol (36.8%) > methanol (28.4) > no-additive (15.3) (Fig. 3). Similar observation was reported by Wang et al. [26]. They found that tartaric acid has the most important reduction effect using TiO_2/visible light illumination system. These results confirm that the presence of additives is obligatory in order to ensure the photoreduction of Cr(VI). The presence of these additives can improve the photochemical quantum which facilitates the separation of the pair (electron/hole) by scavenging the photogenerated holes, thus decreasing the chance of charges (electron/hole) recombination [27,28]. The electrons librated from the conduction band of the TiO_2 (e^-_{CB}) participate directly in the reduction of Cr(VI) (Eq. (6)). Therefore, indirect reduction of adsorbed Cr(VI) ions is possible by getting the electrons from Ti^{3+} of TiO_2 surface (Eqs. (7) and (8)) [29]. The important efficiency of the first three additives (tartaric acid, oxalic acid, and EDTA) may be explained by the presence of carboxylic group in their structures which is able to form complexes with TiO_2 as an anchor species. These complexes may be excited by visible light ($\lambda > 420$ nm), where electrons could be injected from the excited state of the additive to the conduction band of the TiO_2 (Fig. 4) [30]. This charge-transfer complex TiO_2 leads to the reduction of Cr(VI) by electrons generated on the TiO_2 surface. On the

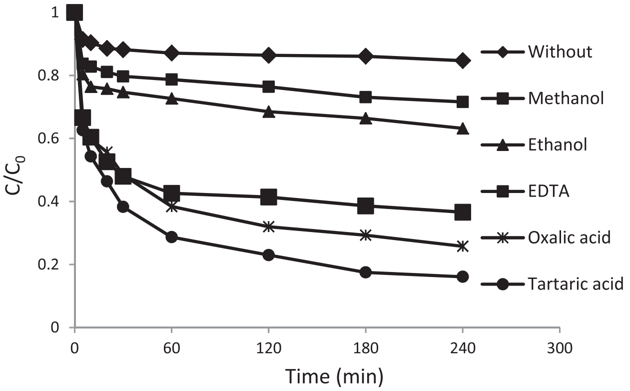

Fig. 3. Effect of different hole scavenger additives on the Cr(VI) photoreduction using TiO_2-immobilized under sunlight. Conditions: [Cr(VI)]: 30 mg/L, pH: 2.2, [hole scavenger]: 40 mg/L, one TiO_2 glass slide.

other hand, the oxidized additives can participate in the reduction of Cr(VI) ions (Eq. (5) and Fig. 4). Based on these results, tartaric acid was selected as a hole scavenger for the study of the following experiments.

$$\mathrm{TiO_2} \xrightarrow{\text{UVphotons}} \mathrm{e^-_{CB}} + \mathrm{h^+_{VB}} \tag{3}$$

$$\mathrm{h^+_{VB}} + \mathrm{A} \rightarrow \mathrm{A^{\bullet}} + \mathrm{H^+} \tag{4}$$

$$\mathrm{Cr_2O_7^{2-}} + \mathrm{A^{\bullet}} \rightarrow 2\mathrm{Cr^{+3}} + \text{product(s)} \tag{5}$$

$$\mathrm{Cr_2O_7^{2-}} + 14\mathrm{H^+} + 6\mathrm{e^-_{CB}} \rightarrow 2\mathrm{Cr^{+3}} + 7\mathrm{H_2O} \tag{6}$$

$$\mathrm{Ti^{4+}} + \mathrm{e^-} \rightarrow \mathrm{Ti^{3+}} \tag{7}$$

$$\mathrm{Cr_2O_7^{2-}} + \mathrm{Ti^{3+}} \rightarrow 2\mathrm{Cr^{+3}} + \mathrm{Ti^{4+}} \tag{8}$$

3.2. Effect of tartaric acid concentration

The [hole scavenger]/[TiO_2] ratio determination is important in the chemical doses optimization. For this reason, the optimization of tartaric acid concentration was determined. The results show that the rates of the photoreduction are more significant when the tartaric acid concentration increases up to 40 mg/L (Fig. 5). Then the photoreduction rate slightly decreases at 50 mg/L. The enhancement observed demonstrates the effect of the hole scavenger concentration on the reduction process. The slight decrease found at 50 mg/L may be accounted for by the competitive adsorption between tartaric acid molecules and Cr(VI) ions on the photocatalyst surface.

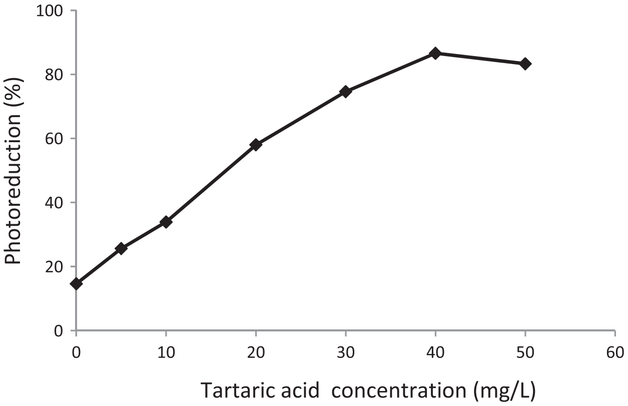

Fig. 5. Effect of tartaric acid concentration on the Cr(VI) photoreduction using TiO_2-immobilized/sunlight. Conditions: [Cr(VI)]: 30 mg/L, pH: 2.2, one TiO_2 glass slide.

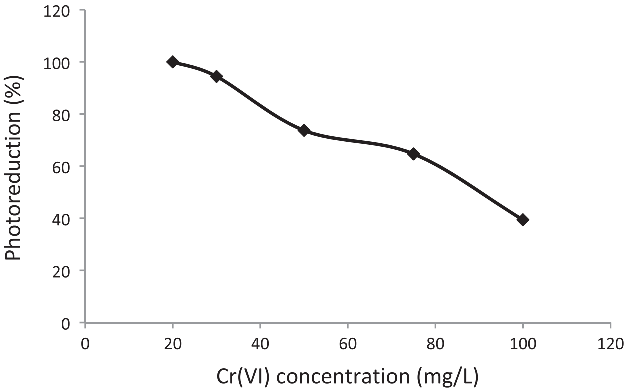

Fig. 6. Effect of Cr(VI) concentration on the photocatalytic reduction process. Conditions: pH: 2.2, [tartaric acid]: 40 mg/L, one TiO_2 glass slide, time: 4 h.

3.3. Effect of Cr(VI) concentration

The effect of Cr(VI) concentration was investigated in the range 20–100 mg/L (Fig. 6). The photoreduction rates were 100% ($k = 0.0136\ \mathrm{min^{-1}}$); 94.4% ($k = 0.0120\ \mathrm{min^{-1}}$); 73.7% ($k = 0.0055\ \mathrm{min^{-1}}$); 64.7% ($k = 0.0052\ \mathrm{min^{-1}}$); and 39.4% ($k = 0.0020\ \mathrm{min^{-1}}$) for 20, 30, 50, 75, and 100 mg/L of Cr(VI), respectively. This decrease may be attributed to the insufficient amount of electrons produced by the photocatalyst to reduce all Cr(VI) ions present in the solution at high concentration, as their production is constant for a given amount of the photocatalyst and selected irradiation time. Therefore, the screen effect could take place to inhibit the Cr(VI) photoreduction at high concentration, where the dichromate molecules intercept the sunlight photons before reaching the surface of photocatalyst thereby decreasing its photoactivity [31].

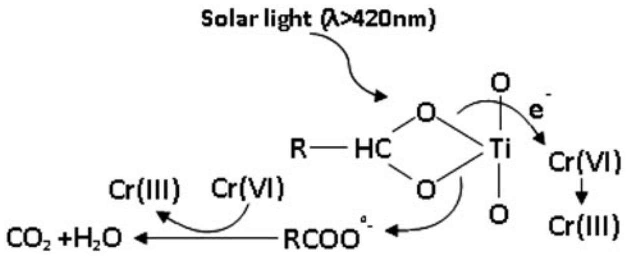

Fig. 4. Cr(VI) photoreduction via a R-carboxyl-TiO_2 complex under visible irradiation.

3.4. Effect of pH

The pH solution is one of the most important controlling parameters on the photoreduction reaction. Table 1 shows the effect of pH on the photoreduction

Table 1
Effect of pH on the Cr(VI) photoreduction using TiO_2-immobilized/sunlight

	Cr(VI) photoreduction rate (%)			
Time (min)	pH 1.5	pH 2.2	pH 3	pH 4.5
30	51.00	43.90	21.40	18.00
60	62.40	56.20	42.20	21.40
120	84.60	67.20	45.90	30.50
180	100	78.40	56.70	37.30
240	100	89.40	68.20	41.30
k (min^{-1})	0.0155	0.0093	0.0047	0.0021

Note: Conditions: [Cr(VI)]: 30 mg/L, [tartaric acid]: 40 mg/L, one TiO_2 glass slide.

process. These results demonstrate that the photoreduction rates are more considerable at lower pH values. The kinetics of the Cr(VI) photoreduction, described by a pseudo-first-order reaction, is presented in Fig. 7. At pH 1.5, the reduction rate reaches 100% after 3 h with a relatively high apparent rate constant ($k = 0.0155\ min^{-1}$). Then the photoreduction efficiency of Cr(VI) decreases with increasing pH solution. This result may be due to several reasons. (1) both the energy level of the conduction band (ECB) of the TiO_2 and the redox Cr(VI) potential (E_0 Cr(VI)/Cr(III)) depend on the pH values. It is known that the (ECB) of TiO_2 changes from −0.11 V to −0.46 V as pH varies from 1 to 7 [32]. This behavior leads to the reduction in the difference between E_0 Cr(VI)/Cr(III) and ECB of the TiO_2 resulting in lower photoreduction with increasing pH [10,32]. (2) the TiO_2 surface ionization state changes with increasing pH solution which decreases the electrostatic attraction of Cr(VI) on the surface [33]. (3) furthermore, in an acidic solution, the protons adsorbed onto the photocatalyst surface can capture the photogenerated electrons in the conduction band to form $H^{\cdot}_{ads}$, which are able to reduce Cr(VI) ions [34]. At pH 6.5, no Cr(VI) reduction was observed since Cr(VI) cannot be photocatalytically reduced. This is due to the change of potentials, ionization, and absence of H^+, which makes the Cr(VI) reduction reaction impractical.

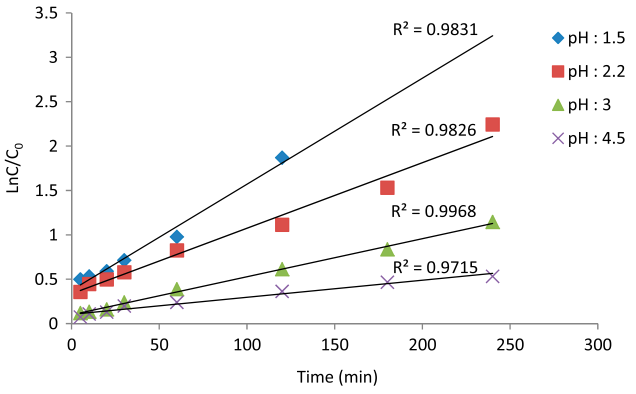

Fig. 7. Pseudo-first-order equation assumption as a function the pH solution.

3.5. Effect of interfering ions

In general, the presence of interfering ions with Cr(VI) in wastewaters is unavoidable. In order to investigate their effect on the Cr(VI) photoreduction, the effect of some ions frequently present in wastewaters was studied. The results of the effect of inorganic anions and metallic cations are shown in Figs. 8 and 9, respectively. The numeric results are summarized in Table 2.

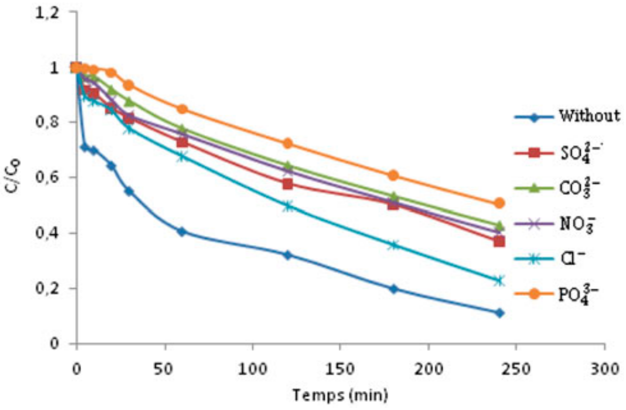

Fig. 8. Effect of inorganic anions on the Cr(VI) photoreduction using TiO_2-immobilized under sunlight. Conditions: [Cr(VI)]: 30 mg/L, pH: 2.2, [tartaric acid]: 40 mg/L, [anion]: 50 mg/L, one TiO_2 glass slide, time: 4 h.

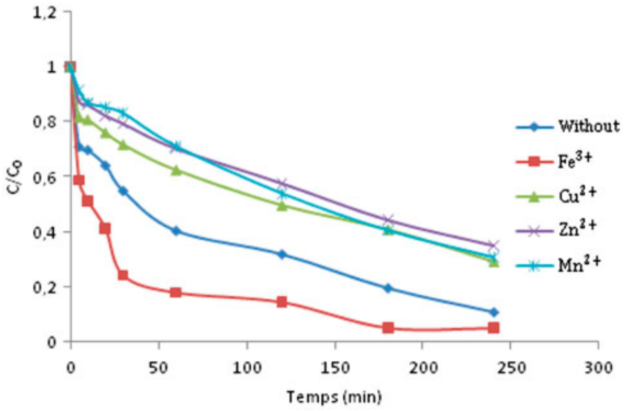

Fig. 9. Effect of metallic cations on the Cr(VI) photoreduction using TiO_2-immobilized under sunlight. Conditions: [Cr(VI)]: 30 mg/L, pH: 2.2, [tartaric acid]: 40 mg/L, [cation]: 50 mg/L, one TiO_2 glass slide, time: 4 h.

Table 2
Effect of interfering ions on the photoreduction rate of Cr(VI)

Ion	Without	SO_4^{2-}	CO_3^{2-}	NO_3^-	Cl^-	PO_4^{3-}	Fe^{3+}	Cu^{2+}	Zn^{2+}	Mn^{2+}
R (%)	89	63	57.3	60	77.5	49.6	94.9	70.3	64.8	69

From these results, it can be noticed that, except Fe^{3+}, both cations and anions inhibit the photocatalytic process by different degrees in the range 11.5–39.4%. The negative effect of inorganic anions can be explained by the ability of inorganic photo-oxidizing species such as $Cl^{\bullet}$, $SO_4^{\bullet -}$, $NO_3^{\bullet}$, $CO_3^{\bullet -}$, and $PO_4^{\bullet 2-}$ to oxidize tartaric acid molecules. As consequence, the positive effect of the latter as a hole scavenger decreases. These radicals can be produced by the reactions of anions with the positives holes of TiO_2 or by reactions with $^{\bullet}OH$ radicals. Furthermore, this decrease of photoactivity may be attributed to the competitive adsorption on the photocatalyst surface and light screening effect [35,36]. The phosphate anions had the most negative effect which is due to its strong adsorption on the TiO_2 surface. In the case of metallic cations, their effect may be due to their competitive adsorption, their ability to capture the photogenerated electrons on the photocatalyst surface and the screen effect caused by the complexes formed from these metals [37,38]. The increase in the Cr(VI) reduction rate observed in the presence of Fe^{3+} can be explained by the reduction in Cr(VI) by Fe^{2+} (Eq. (10)), as it is known that Fe^{2+} is capable of reducing Cr(VI) to Cr(III) in acidic medium [39,40]. The Fe^{2+} ions can be formed during the solar photolysis of Fe(III)-OH^{2+} (Eq. (9)) where $^{\bullet}OH$ radicals are generated and Fe^{3+} is reduced to Fe^{2+} [38,41]. These two reactions (Eqs. (9) and 10) make a cycle as a homogeneous photocatalysis, which plays a determinant role for Cr(VI) reduction. Furthermore, the Fe^{2+} can be also produced by the photoreduction of Fe^{3+} by the photogenerated electrons on the conduction band of TiO_2 (Eq. (11)).

$$\mathrm{Fe(III)} - \mathrm{OH}^{2+} \xrightarrow{hv\ \mathrm{photons}} \mathrm{Fe(II)} + {}^{\bullet}OH \quad (9)$$

$$\mathrm{Fe(II)} + \mathrm{Cr(VI)} \rightarrow \mathrm{Fe(III)} + \mathrm{Cr(III)} \quad (10)$$

$$\mathrm{Fe(III)} + e_{CB}^{-} \rightarrow \mathrm{Fe(II)} \quad (11)$$

3.6. *TiO_2-immobilized reuse*

The reuse of TiO_2 immobilized can have important economical repercussions. To investigate this aspect, the reuse of the photocatalyst was tested under the same working conditions several times. Prior to its reuse, the slide of the TiO_2-immobilized was washed with double distilled water and then dried for 2 h at 110˚C. Fig. 10 shows that the TiO_2-immobilized can be used several times with a relatively small decrease in the Cr(VI) reduction rate reaching 67.1% after the fifth use. This decrease of the removal rate can be accounted for by the saturation of photocatalyst surface by the Cr(III) ions photodeposited during the reduction reaction.

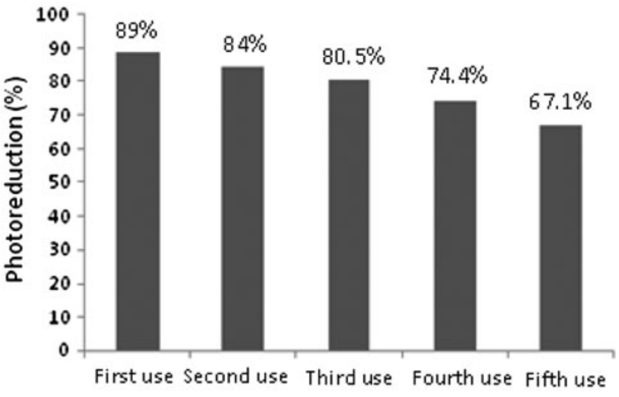

Fig. 10. Reuse of TiO_2-immobilized for the Cr(VI) reduction under sunlight. Conditions: [Cr(VI)]: 30 mg/L, pH: 2.2, [tartaric acid]: 40 mg/L, [ion]: 50 mg/L, one TiO_2 glass slide, time: 4 h.

4. Conclusion

The objective of the present work was to determine the effect of some parameters to reduce the Cr(VI) to Cr(III) using TiO_2-immobilized under natural sunlight. The results show that the presence of hole scavengers is necessary to ensure the Cr(VI) reduction. Tartaric acid was the most efficient among the additives tested. Under the present working conditions, the optimum concentration of the tartaric acid as a hole scavenger was 40 mg/L. The increase of the Cr(VI) concentration leads to a decrease in the reduction rate, from 100 to 39.4% when the Cr(VI) concentration increases from 20 to 100 mg/L. The acidification of the solution enhances the photoreduction of Cr(VI), where the removal rate increases from 41.30 to 100% when the pH solution decreases from 4.5 to 1.5. However, no photoreduction reaction was observed at pH 6.5. Except for Fe^{3+}, the co-presence of interfering ions with the Cr(VI) inhibits the photocatalytic reduction. Finally, the reuse of TiO_2-immobilized illustrates a relatively good stability of the TiO_2 particles onto the glass slide using a simple deposition method. Overall, the results of this work are a further evidence for the photocatalytic reduction of toxic chromium by the use of an economical process (TiO_2-immobilized/sunlight).

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