

Recovery of hexavalent chromium from water using photoactive TiO₂-montmorillonite under sunlight

Ridha Djellabi^{1,*}, Mohamed Fouzi Ghorab¹, Claudia Letizia Bianchi², Giuseppina Cerrato³ and Sara Morandi³

¹ Laboratory of Water Treatment and Valorization of Industrial Wastes, Chemistry department, Faculty of Sciences, Badji-Mokhtar University, BP12 2300, Annaba, Algeria

² Università degli Studi di Milano, Dip. Chimica & INSTM-UdR Milano, Milano, Italy

³ Università degli Studi di Torino, Dipartimento di Chimica & NIS Interdepartmental Centre & Consorzio INSTM-UdR Torino, Italy

Abstract: Hexavalent chromium was removed from water under sunlight using a synthesized TiO₂-montmorillonite (TiO₂-M) employing tartaric acid as a hole scavenger. Cr(VI) species was then reduced to Cr(III) species by electrons arising from TiO₂ particles. After that, the produced Cr(III) species was transferred to montmorillonite due to electrostatic attractions leading to set free TiO₂ particles for a further Cr(VI) species reduction. Furthermore, produced Cr(III), after Cr(VI) reduction, does not penetrate into the solution. The results indicate that no dark adsorption of Cr(VI) species on TiO₂-M is present, however, the reduction of Cr(VI) species under sunlight increased strongly as a function of tartaric acid concentration up to 60 ppm, for which the extent of reduction is maximum within 3 h. On the other hand, the reduction extent of Cr(VI) species is maximum with an initial concentration of Cr(VI) species lower than 30 ppm by the use of 0.2 g/L of TiO₂-M. Nevertheless, the increase of the Cr(VI) initial concentration led to increase the amount of Cr(VI) species reduced (capacity of reduction) until a Cr(VI) concentration of 75 and 100 ppm, for which it remained constant at around 221 mg/g. For comparison, the increase of Cr(VI) species concentration in the case of the commercial TiO₂ P25 under the same conditions exhibited its deactivation when the reduced amount decreased from 198.1 to 157.6 mg/g as the concentration increased from 75 to 100 ppm.

Keywords: TiO₂-montmorillonite; Deactivation; Hexavalent chromium; Reduction; Water; Sunlight.

Introduction

Chromium is a common heavy metal contaminant in manufacturing regions because of its environmental risk^{1,2}. It primarily exists in aqueous effluents both in the form of anion of Cr(VI) (chromate) and cation Cr(III) species. Cr(VI) species is very toxic to most organisms and has been classified as carcinogenic and mutagenic, whereas Cr(III) species is less toxic and readily precipitates as Cr(OH)₃^{3,4}. Furthermore, Cr(VI) species is far more mobile than Cr(III) species and more difficult to remove from water. For these reasons, the maximum concentration limit of Cr(VI) species allowed by the European Union for discharging into industrial and civil wastewaters is 0.2 mg/L⁵. The World Health Organization (WHO) prescribed 0.5 mg/L as a maximum level of Cr(VI) species for drinking water⁶. As, Cr(VI) species exhibits a higher toxicity and mobility than Cr(III), the remediation of chromium polluted wastewaters by its reduction from Cr(VI) to

Cr(III) species is an effective approach frequently chosen. Among the various reduction methods, such as chemical, microbial and electrochemical⁷, photocatalytic reduction of Cr(VI) species has been mainly used in recent years⁸⁻¹¹. This process consists of the irradiation with UV light of a semiconductor, like for instance TiO₂: it results in excited electron-hole pairs that can be applied as a redox system for the degradation/reduction of pollutants in water, including the possible use of solar irradiation and operation at ambient conditions^{12,13}. In the context of metal reduction, this reaction is highly dependent on the metal redox potentials relative to the TiO₂ conduction band (CB) edge. The energy of the semiconductor band gap must be more negative than the energy of the metallic couple (Mⁿ⁺/M⁽ⁿ⁻²⁾⁺)^{14,15}. Furthermore, in order to ensure the reduction of metals by the photogenerated electrons, the promotion by additives (A) as a holes scavenger, usually in the form of organic compounds, is required^{16,17}.

*Corresponding author : Ridha Djellabi
Email address : ridha.djellabi@yahoo.com
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Hence, it is necessary to choose an appropriate sacrificial electron donor. In our previous work¹⁸, we studied the effect of a wide kind of hole scavenger molecules on the photoreduction of Cr(VI) using TiO₂ under sunlight.

TiO₂ is usually used in photocatalytic reduction of Cr(VI) species due to its excellent chemical and optical properties¹⁹⁻²¹. The efficiency rate of the photocatalytic reduction of Cr(VI) species by TiO₂ depends on Cr(VI) species concentration in the TiO₂ vicinity, as well as both the number of electrons produced and the role played by the organic additive as holes/radicals scavenger. By assuming a constant surface area of pure TiO₂ and using an efficient holes scavenger molecule with a sufficient concentration, the amount of Cr(III) species produced and deposited on the TiO₂ surface increases with the increase of the initial concentration of Cr(VI) species up to a maximum. In this condition, the TiO₂ surface is totally covered by Cr(III) species which will be inactive to reduce more Cr(VI) species. Furthermore, a large amount of Cr(III) species could be set free from the TiO₂ surface after saturation of the solution. Because Cr(III) species also represents a high hazard for both environment and human health at a certain concentration and also can be oxidized to Cr(VI) species in wastewaters, it must be removed by another treatment, like for instance ion-exchange, membrane filtration or by simple chemical precipitation, all these processes leading to increase the global treatment costs. Recently, in the context of a better and environmental-friendly chromium removal, a combination of supported materials containing TiO₂ particles has been demonstrated the feasibility of Cr(VI) species reduction with the subsequent adsorption of Cr(III) species on the supported material. Wen Liu *et al.* have studied the synergy of photocatalysis and adsorption for simultaneous removal of both Cr(VI) and Cr(III) species with TiO₂ and titanate nanotubes (TNTs)²². The nanotubes play two important roles: (i) the decrease of electron/hole pairs recombination and (ii) the transfer of the Cr(III) species produced from the TiO₂ surface to the nanotubes material. In this work, we used the TiO₂-montmorillonite composite for the reduction of chromium species.

Montmorillonite, a natural clay silicate, possesses a 2:1 layer structure: the negative charge between layers, caused by substitution, is neutralized by different hydrated cations adsorbed to the sheets surface. A characteristic feature of montmorillonite clay is the extensive surface for the adsorption of water and cations; therefore its cation-exchange capacity is very high.

These proprieties give to TiO₂-pillared montmorillonite material a very special advantage for the removal of chromium species from water by photocatalysis if compared to commercial TiO₂ materials. After the reduction of Cr(VI) species by the TiO₂ particles fixed on the montmorillonite support, the Cr(III) species produced is directly

attracted and adsorbed by the negative charges of the montmorillonite itself, thus leading to: (i) set free TiO₂ sites for a further Cr(VI) species reduction; (ii) avoid the penetration of Cr(III) species into the solution.

The present work demonstrates the efficiency of the TiO₂-montmorillonite system for the reduction and recovery of Cr(VI) species under natural sunlight.

Materials and methods

Materials

The montmorillonite used in this study is a natural sodium-exchanged bentonite (Na-M) from the Roussel deposit in Maghnia (Algeria) and was used without any further treatment or purification. Its cation-exchange capacity was determined by the methylene blue method and is 89.30 mmol/100 g. Potassium dichromate (Sigma-Aldrich, ≥99.0%) solution was prepared using double-distilled water. Adjustment of the pH solution was achieved with H₂SO₄ (Sigma-Aldrich) and monitored by a pH meter (HANNA HI 9812-5). Tartaric acid (Sigma-Aldrich, ACS reagent, ≥ 99.5%) was used as a holes scavenger.

Synthesis and characterization of of titania-montmorillonite

Titania-montmorillonite (TiO₂-M) was prepared by impregnation Na-M with TiCl₄ (Aldrich, 99.99%). The weight ratio of Ti/montmorillonite during the preparation was 10% (g/g). The experimental synthesis procedure and the characterization of the materials by different methods (FTIR, TG-TDA, BET, XRD and SEM-EDX) are reported in our previous paper²³. In the present paper, we added the results of TiO₂-M XPS analysis performed using M-probe Apparatus (Surface Science Instruments) equipped with a monochromatic source of Al K α (1486.6 eV).

Photocatalytic tests

The photocatalytic reduction of Cr(VI) species was performed using a static batch reactor, consisting of Pyrex beakers open to air under natural sunlight at sea level (in front of the Chemistry Department without any obstacle) on sunny days (at Annaba University) and were started at 10:00 am for a duration of 4 h. The Cr(VI) solution (250 mL) in the presence of the photocatalyst and tartaric acid was exposed to natural sunlight under a constant stirring. In this study, we used a pH value of 2.2 based in the results of our previous study¹⁸. The reduction of Cr(VI) needs an acidic medium in order to ensure a high difference between the energy level of the conduction band (ECB) of TiO₂ and the redox Cr(VI) potential (E_0 Cr(VI)/Cr(III)). The use of tartaric acid as a hole scavenger does not change the pH of the solution since the working pH was fixed after adding of tartaric acid and the solution pH was controlled and was keeping at 2.2 along the experiments by adding dropping of NaOH or H₂SO₄ if it changed. During the experiments, samples (4

mL) were collected at selected time intervals. The photocatalyst was removed by filtration (0.45 μm , Whatman) and the residual concentration of Cr(VI) species was determined at a wavelength of 540 nm via the 1,5-diphenylcarbazide (DPC) method²⁵. The intensity of sunlight radiation at 365 nm was measured using a VLX-3W radiometer (Vilber Loumart, France) with a cell diameter of 1 cm^2 : it always was in the 16 to 18 W/m^2 range during the experimental period. The extent of water evaporation during the solar photocatalysis experimental was in average of 6.0% in volume after 4 h of irradiation and was considered to be within the experimental errors. 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 parallel experiments.

The extent of Cr(VI) reduction species was calculated using Eq.(1). The kinetics of the reduction process was investigated using a pseudo-first-order reaction Eq.(2). The amount of Cr(VI) species removed (mg/g) from the solution was estimated using Eq. (3).

$$\text{Extent of reduction} = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (1)$$

$$\ln \frac{C}{C_0} = -k \cdot t \quad (2)$$

$$Q_{\text{removed}} = \frac{(C_0 - C_t) \times V}{m \times 1000} \quad (3)$$

Where C_0 and C_t represent the Cr(VI) concentrations (mg/L) before and after the treatment, t is the irradiation time (min); k is the apparent rate constant; V is the solution volume (mL); m is the mass of the photocatalyst (g).

Results and discussion

Characterization of the material

As reported in our previous papers^{23, 24}, the main results of material characterization can be summarized in the following points:

- FTIR spectra in the 4000-1200 cm^{-1} range, for both sample (Na-M and TiO_2 -M) showed different bands like that of OH groups, SiO_2 -like matrix and water. However, Na-M exhibits a sharp and complex spectral component at 1490 cm^{-1} which is totally absent in TiO_2 -M.

- The specific surface area has been changed after the introduction of TiO_2 from 49 m^2/g of the starting material (Na-M) to 51 m^2/g of TiO_2 -M. The change of the pore volume is more evident (from 0.107 to 0.144 cm^3/g): for Na-M and TiO_2 -M samples, respectively.

- TG/DTA curves of Na-M and TiO_2 -M samples in the 25-500 $^\circ\text{C}$ temperature range reported a similar weight loss for both materials, most likely due to the evaporation of physisorbed/adsorbed water.

- XRD pattern of TiO_2 -M exhibits the crystalline features of titania, in which only the anatase polymorph is evidenced. The average crystallite size of anatase was estimated of 15-20 nm.

- SEM image of TiO_2 -M composite showed a clear change of the montmorillonite morphology, compared to that of Na-M, by the addition of TiO_2 species.

- EDX results showed that the content of Ti element in TiO_2 -M is 48.6 wt%.

Fig.1 presents the XPS survey spectra of TiO_2 -M sample. The chemical composition derived from XPS analysis is shown in **Table 1**. Sample depicts mainly Ti and O elements and C at 284.8 eV as well. Adventitious C is always present and is explained by the environmental contamination. High resolution Ti2p and O1s is reported in **Fig.2**. One single Ti species is present due to Ti(IV)²⁶. On the contrary, O1s spectrum can be fitted with three different peaks attributed to lattice oxygen in TiO_2 at lower BE, OH species and O-C band in montmorillonite at higher BE.

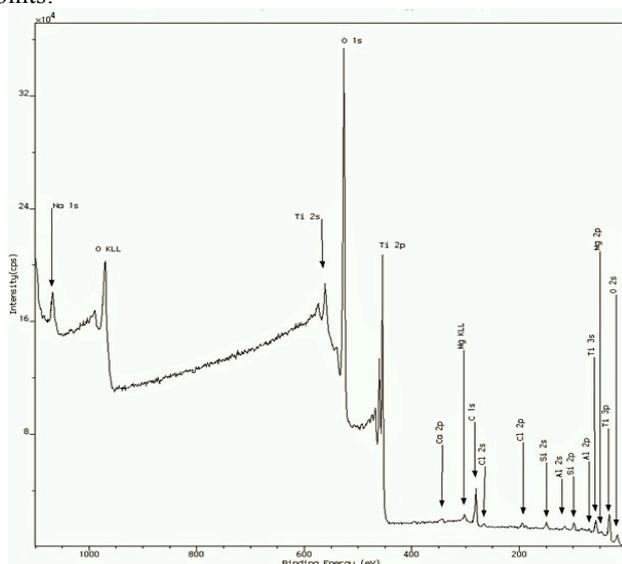


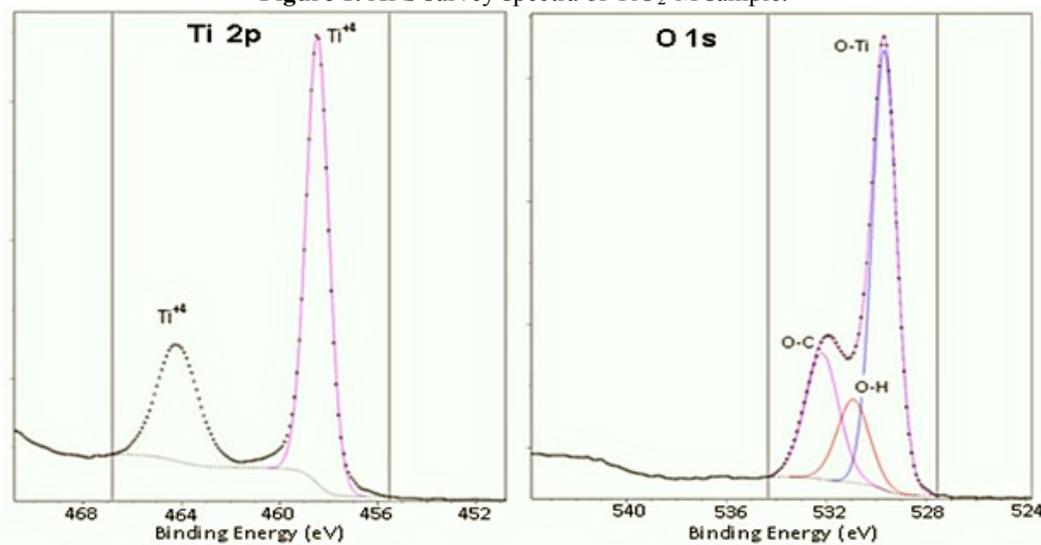
Figure 1. XPS survey spectra of TiO₂-M sample.

Figure 2. High resolution XPS core level spectra of Ti 2p and O 1s.

Table 1. Measured mass ratios of TiO₂-M sample.

Element	Na 1s	O 1s	Ti 2p	N 1s	Ca 2p	C 1s	Cl 2p	Si 2p	Al 2p	Mg 2p
Mass ratio (%)	2.05	39.78	37.22	0.24	0.53	9.41	1.30	3.74	2.47	3.25

Effect of tartaric acid concentration on Cr(VI) adsorption and reduction

One of the most important keys to reduce metal cations by photocatalysis is the presence of an efficient holes scavenger molecule. In this work, we used tartaric acid as scavenger molecule based on the results of our previous study¹⁸, in which it was demonstrated to be the most efficient agent for the reduction of Cr(VI) species among the various tested molecules. In order to show the photocatalytic reduction of hexavalent chromium, the effect of tartaric acid concentration on the adsorption and reduction of the Cr(VI) at 30 ppm under sunlight has been studied at the 0-120 ppm range. The results of Cr adsorption and photoreduction are reported in Figs 3 and 4, respectively. The direct photolysis of Cr(VI) species both in the absence and in the

presence of tartaric acid was negligible: as reported in Fig.3, it is clear that the Cr(VI) species adsorption onto the TiO₂-M surface is negligible. Natural clays, such as montmorillonite, are not usually efficient to adsorb anions because of their intrinsic negative charge. However, a few anionic Cr(VI) species can result on the montmorillonite surface through either physical sorption or electrostatic binding mechanisms. It is worth to note that the presence of tartaric acid increases slightly the adsorption of chromate ions, may be due to the chelating effect caused by tartaric acid molecules that can fix Cr(VI) ions on the montmorillonite surface. However, the photo-reduction of Cr(VI) species increases strongly with the increase of tartaric acid concentration (Fig.4) up to a concentration of 60 ppm where the reduction extent is maximum within 3 h.

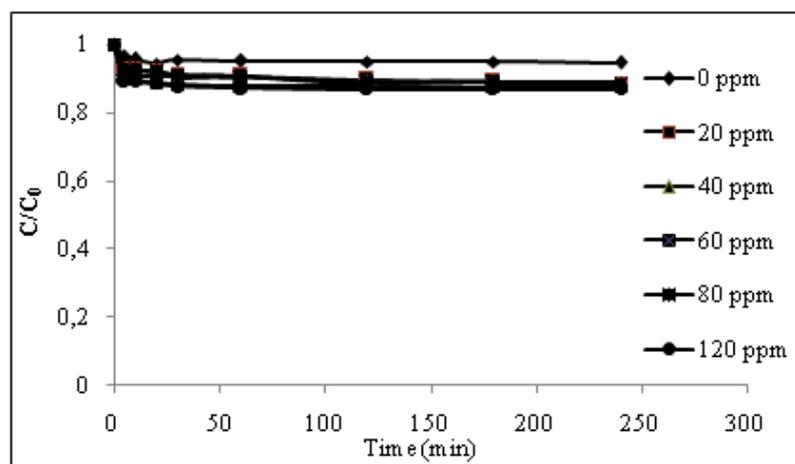


Figure 3. Effect of tartaric acid concentration on the dark adsorption of Cr(VI) on TiO₂-M. Conditions: [Cr(VI)] : 30 ppm, [TiO₂-M] : 0.2 g/L, pH : 2.2.

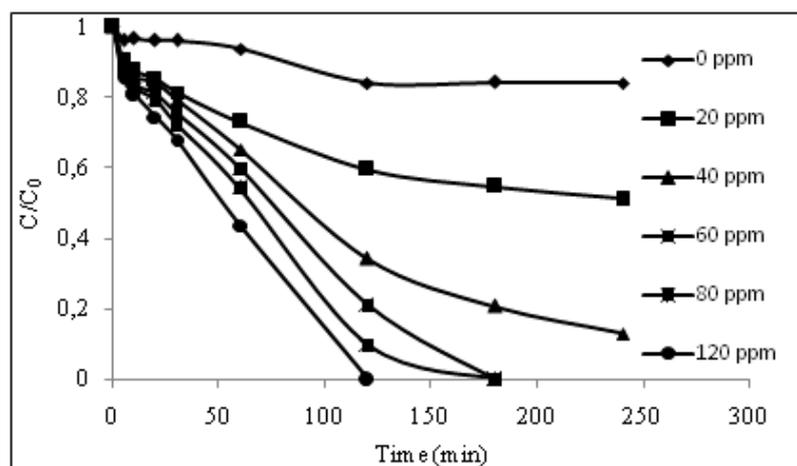
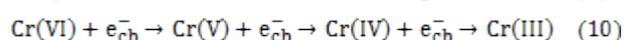
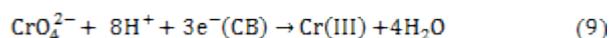
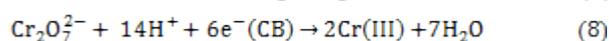
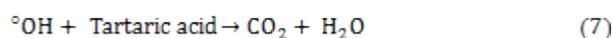
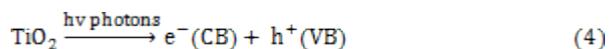


Figure 4. Effect of tartaric acid concentration on reduction of Cr(VI) using TiO₂-M under sunlight. Conditions: [Cr(VI)] : 30 ppm, [TiO₂-M] : 0.2 g/L, pH : 2.2.

This observed enhancement confirms the importance of the presence of a hole scavenger molecule that can improve the photochemical quantum which, in turn, facilitates the separation of pairs (electron/hole) by scavenging the photogenerated holes (Eq.6), thus (i) decreasing the chance of charges (electron/hole) recombination and (ii) setting free more electrons in the conduction band available to reduce Cr(VI) ions (Eq.8). Since experiments were achieved at low pH, only Cr₂O₇²⁻ and CrO₄²⁻ species can exist. The net reaction of both species is a three electron-reduction of Cr(VI) to Cr(III) which are shown in Eqs. (8) and (9), respectively. Assuming that one electron transfer step could be occurred in Cr(VI)reduction process, Cr(V) and Cr(IV) species could be formed as intermediates in the first and second stages Eq. (10). Furthermore, the reaction between tartaric acid molecules and ^oOH which possess a high oxidizing potential (Eq.7), limits the oxidation of the produced Cr(III) species to Cr(VI) species (Eq.11). As discussed before, in the present case, the removal of chromium from water by the TiO₂-montmorillonite composite passes through two important steps: (i) negatively charged species (Cr₂O₇²⁻, HCrO₄⁻), which exhibit a very low adsorption behavior on the composite surface, is reduced to a positive species (Cr(III)) by electrons coming from the conduction band of TiO₂ particles deposited on the montmorillonite material. It is worth noting that binding between Cr(VI) and TiO₂ could take place. It is worth noting that the TiO₂ particles fixed on the montmorillonite can exhibit a positive charge at low pH which increases the attraction of chromium negatively charged species (Cr₂O₇²⁻, CrO₄²⁻). In general, if a pure commercial TiO₂ is employed, the produced Cr(III) ions still deposited on the TiO₂ surface lead to its deactivation. Hence after saturation, Cr(VI) ions cannot reach the TiO₂

surface. Furthermore, the desorption of Cr(III) species from the surface to the solution in the case of pure TiO₂ is strongly possible. (ii) The second important step caused by the montmorillonite support is the transfer of Cr(III) cations from the TiO₂ particles to the negative inter-layer pores where binding can take place between Cr(III) and the negative charge of montmorillonite sheets. The fixation of Cr(III) on the montmorillonite takes place through ion exchange, physical and in some cases chemical adsorption mechanisms. On the other hand, a part of Cr(III) could be immobilized onto TiO₂ particles fixed on the montmorillonite surface directly after Cr(VI) reduction through physical adsorption. This positive effect avoids the penetration of Cr(III) species in the solution and ensures a continuous contact of Cr(VI) species with photocatalytic TiO₂ sites. It is important to note that, for a high concentration of tartaric acid, the reduction rate of Cr(VI) species was not depleted, due to the high adsorption capacity of this material. The main steps of the effect of tartaric acid on the reduction of Cr(VI) are reported in the following reactions and described in Fig.5.



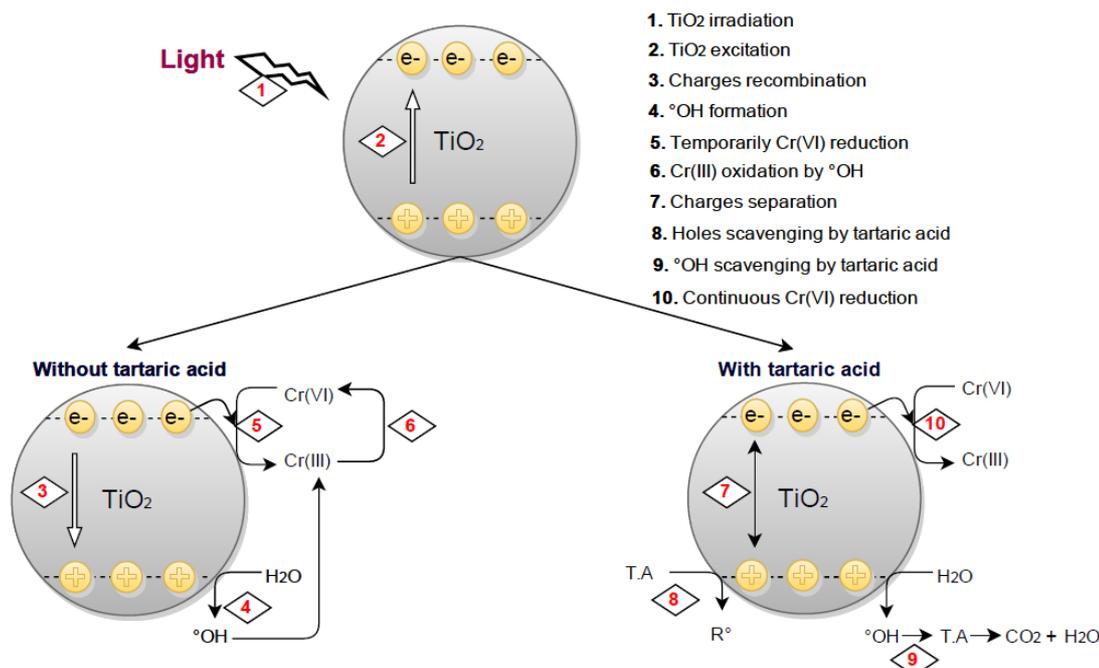


Figure 5. Scheme reporting the main steps of tartaric acid effects on the photoreduction of Cr(VI) species.

Effect of Cr(VI) concentration on the photoreduction efficiency

As it is known, there is a relationship between the amount of reduced ions and the amount of the used photocatalyst. For a fixed amount of photocatalyst, the amount of reduced ions increases proportionally to the increase of the initial concentration of ions in the solution up to a

maximum. If we evaluate the efficiency of the photocatalyst by using the amount of reduced ions, it is important to show the effect of initial concentration of Cr(VI) on the reduced amount. **Table 2** shows the effect of Cr(VI) species concentration on both the extent of reduction and the amount of Cr(VI) species reduced using a TiO₂-M mass of 0.2 g/L.

Table 2. Effect of Cr(VI) concentration on the photoreduction efficiency. [TiO₂-M]: 0.2 g/L, pH: 2.2, [tartaric acid]: 60 mg/L

Cr(VI) concentration	20 ppm	30 ppm	50 ppm	75 ppm	100 ppm
Extent of reduction (%)	100	100	73.7	58.9	44.2
Q removed (mg/g)	100	150	184.25	220.75	221
k_{app} (min ⁻¹)	0.0188	0.0109	0.0052	0.0345	0.0021

The data indicate that the reduction extent of Cr(VI) species is maximum with an initial concentration Cr(VI) species lower than 30 ppm, whereas for higher values, the extent of reduction decreases. This feature may be attributed to an insufficient number of electrons produced by the photocatalyst and able to reduce all Cr(VI) ions present in the solution at high concentration, as their production is constant for a given amount of both photocatalyst and a selected irradiation time. However, the amount of reduced Cr(VI) species increases proportionally with the increase of Cr(VI) species concentration up to 75 ppm. For higher values, it remains constant at the value found for 75 ppm. When concentration of Cr(VI) species increases in the solution, more Cr(VI) ions will be in contact with the photocatalyst surface leading to the reduction of a larger amount of Cr(VI) species. For values higher than 75 ppm, the reduced amount remains constant (~ 220 mg/g) because of two

possible reasons: (i) the activated surface of TiO₂-M mass (0.2 g/L) is unable to reduce more Cr(VI) species (a saturation step has been reached); (ii) the amount of tartaric acid molecules used (60 ppm) is consumed and this leads to a stop of the reduction process. In both cases, the amount of both reduced Cr(VI) species by this material is relatively high. On the other hand, as the reduced amount is still regular after saturation, we can state that the photocatalyst deactivation at concentration of 100 mg/L is not observed.

For comparison purposes, the results of the effect of Cr(VI) species initial concentration on the reduced amount of Cr(VI) species by a pure commercial TiO₂ (P25 by Evonik) under the same conditions are presented in **Fig.6**.

It is clear that the reduced amount increases with the increase of the initial concentration up to 198.1 mg/g at 75 ppm. Nevertheless, it strongly decreases to 157.6 mg/g at 100 ppm. This decrease, not

observed with TiO₂-M, may be explained by the deactivation of TiO₂ particles at high concentration. The Cr(III) species produced from the reduction of

Cr(VI) species still deposited on the TiO₂ surface limit the access of more Cr(VI) ions to the surface.

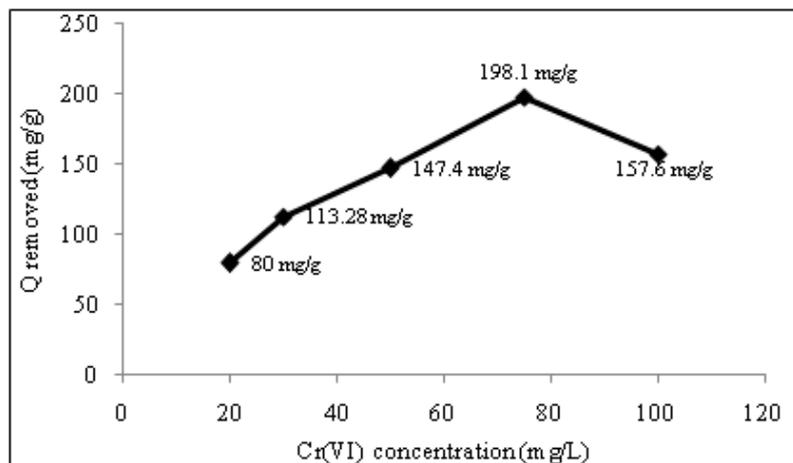


Figure 6. Effect of Cr(VI) concentration on the reduced Cr(VI) amount using commercial TiO₂P25 under sunlight. Conditions: [tartaric acid]: 60 ppm, [TiO₂P25]: 0.2 g/L, pH: 2.2.

The pathways of Cr(VI) photoreduction by

commercial TiO₂ and TiO₂-M can be summarized in **Fig. 7.**

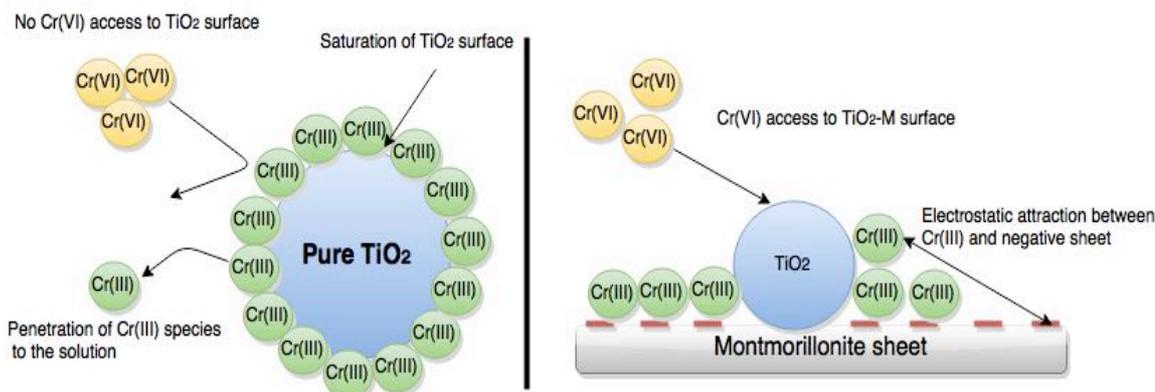


Figure 7. Pathways of Cr(VI) photoreduction by commercial TiO₂ and TiO₂-M under sunlight.

Conclusions

In the present study, we reported the high efficiency of the synthesized TiO₂-montmorillonite composite under sunlight for reducing and recovering chromium from water. Firstly, the characterization of this material by XPS analysis demonstrates the presence of only TiO₂ oxide in the Ti(IV) form in TiO₂-M. The use of tartaric acid as a hole scavenger shows high efficient for reducing Cr(VI) where the reduction process is proportional with the increase of its concentration. For a constant TiO₂-M mass, the amount of reduced Cr(VI) increases with the raise of the initial concentration of chromium until a constant value at about 220 mg/g at 75 and 100 ppm of initial Cr(VI). The non-deactivation of TiO₂-M at high Cr(VI) concentration can be explained by the special behavior of this composite where the produced Cr(III) is transferred from the TiO₂ surface to the negative interlayer of the montmorillonite support. Otherwise, with a pure

TiO₂ sample, like the commercial P25, a high Cr(VI) concentration leads to decrease the quantity of reduced Cr(VI) because of its saturation by Cr(III) deposited into the surface.

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