Enhanced Solar Photocatalytic Reduction of Hexavalent Chromium in Seawater over Carbon Doped TiO₂ Nanoparticles

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Abstract. The photocatalytic removal of hexavalent chromium Cr(VI) from polluted seawater has been successfully investigated by using carbon doped titanium oxide (CTiO₂) nanoparticles under irradiation of natural sunlight. The photoactivity of CTiO₂ was comparatively evaluated with pure TiO₂ under the same experimental conditions. The effects of catalyst dose, initial Cr(VI) concentration and pH were studied and optimized. The highest removal rate was obtained at pH 3 and catalyst dose of 2.0 g L⁻¹. Furthermore, the existence of hole scavenger remarkably enhanced the reduction rate of Cr(VI). According to Langmuir–Hinshelwood model, the photocatalytic reduction of Cr(VI) using CTiO₂ obeyed the pseudo-first-order kinetics

Keywords: Photocatalytic reduction; Chromium; Titanium oxide; Nanoparticles; Carbon modification.

1. Introduction

The hexavalent chromium Cr(VI) is one of toxic heavy metals, which is frequently released into aquatic bodies from various industrial activities such as metallurgy, leather tanning, electroplating, printing, and dyeing. Beyond the permitted limit of 0.05 mg L⁻¹ in aqueous medium, Cr(VI) is considered as highly toxic pollutant (WHO, 2008). Due to its high toxicity, solubility and easy mobility, Cr(VI) is recognized as a potent carcinogenic and mutagenic to humans (Deng and Bai, 2004; Lee *et al.*, 2007). Most of the common technologies adopted for Cr(VI) remediation such as membrane separation (Guell *et al.*, 2008), ion exchange (Xing *et al.*, 2007), electrodialysis and adsorption (Mor *et al.*, 2007; Carmona *et al.*, 2005) are either expensive or their effectiveness is limited only for the removal of trace levels. Therefore, an

efficient and economic technology for the removal of Cr(VI) from polluted water is urgently desirable.

The reduction of Cr(VI) to less harmful species Cr(III), which subsequently can be precipitated as Cr(OH)₃, is one of the most favorable remediation strategies. Particularly, heterogeneous photocatalysis mediated by nano-sized semiconductors has been recognized as an environmentally friendly technology. It provides a green approach for detoxification of polluted water, due to the in situ generation of the strongly reducing electrons (e⁻) and strongly oxidizing hydroxyl radicals (·OH), which can, respectively, reduce and oxidize a broad range of pollutants that could be present in water and wastewaters. Among the existing semiconductors, titanium oxide (TiO₂) is believed to be an extraordinary photocatalyst for its non-toxicity, low cost, high photostability and

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excellent photocatalytic efficiency. However, with the wide band gap energy of 3.2 eV, the photocatalytic activity of TiO_2 is restricted to UV light irradiation ($\lambda < 388 \text{ nm}$), which only accounts for 4% of the solar spectrum. Therefore, the extension of its utilization over the main part (45%) of visible region in solar spectrum is of crucial importance. Many efforts have been devoted to reduce its optical band gap energy through different approaches such as doping with metals (Anpo *et al.*, 1997; Al-Azri *et al.*, 2015; Chen *et al.*, 2011), and non-metal ions (Asahi *et al.*, 2001; Khan *et al.*, 2002; Shaban *et al.*, 2013; Shaban *et al.*, 2016; Umebayashi *et al.*, 2002). In particular, modification of TiO_2 via carbon incorporation has been evidenced as an effective approach to enhance its photocatalytic performance under visible light (Fang *et al.*, 2016; Khan *et al.*, 2002; Liu, *et al.*, 2016; Shaban *et al.*, 2013; Shaban *et al.*, 2016).

Most previous photocatalysis studies that focus on the elimination of Cr(VI) were carried out in simulated polluted water under artificial UV light. However, utilization of TiO_2 nanoparticles has not been reported for the elimination of Cr(VI) from real polluted seawater under natural sunlight illumination. In this study, CTiO_2 nanoparticles will be synthesized and employed to eliminate Cr(VI) from real polluted seawater samples under natural sunlight illumination. To attain the highest removal rate, catalyst dosage, initial concentration of Cr(VI), and solution pH will be optimized. Furthermore, the effect of the presence of holes scavenger on the photocatalytic reduction of Cr(VI) will be also investigated.

2. Experimental

2.1 Preparation and Characterization of the Catalysts

CTiO_2 nanoparticles were synthesized via a sol-gel method using titanium

isopropoxide as a molecular precursor of TiO_2 , whereas glycine was used as a carbon source. Pure titanium oxide (TiO_2) nanoparticles were synthesized by hydrolysis and oxidation of titanium trichloride (carbon free precursor) in an aqueous medium. Additionally, no glycine was added, to avoid any probability for carbon incorporation. Details on the preparation and characterization procedures have been described in our previous work (Shaban *et al.*, 2016).

2.2. Photocatalytic Removal Experiments

Clean and polluted seawater samples were collected from Sharm Obhur and Al-Arbacen Lagoon (Jeddah, KSA), respectively. Samples were passed through Whatman GFC in order to remove any solid particles. Clean seawater was used for optimizing the procedure of chromium removal using TiO_2 and CTiO_2 , whereas polluted seawater was used as a model to test the optimizing procedure. Clean seawater samples were spiked with different concentrations of Cr(VI) over the range from 1 to 50 ppm. A magnetically stirred 500-mL Pyrex glass reactor loaded with both contaminated samples and the photocatalyst was used to carry out all photocatalytic removal experiments. Prior to light illumination, the suspensions were kept in the dark for 30 min. Then, the photoreactor was directly exposed to natural sunlight in the daytime between 11:00 am to 14:30 pm. The average solar intensity was found to be 1140 Wm^{-2} , measured by Field Scout Light Sensor Reader (Spectrum Technologies, Inc.) equipped with 3670i Silicon Pyranometer Sensor.

Treated samples were regularly withdrawn from the reactor and centrifuged to eliminate the photocatalyst. The supernatant was immediately analyzed for Cr(VI) content by using a UV-Visible spectrophotometer (UV-1700 PharnaSpec, Shimadzu) at $\lambda = 540$

nm, according to the diphenylcarbazide colorimetric method (APHA, 1998). The Cr(VI) removal efficiency (E %) was calculated as follows:

$$E \% = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where C_0 and C_t represent the concentrations of Cr(VI) at zero and irradiation time (t), respectively.

3. Results and Discussion

3.1. Effect of Solution pH

The effect of pH on the photocatalytic reduction rate of 5 ppm of Cr(VI) in seawater in the presence of 2.0 g L⁻¹ of CTiO₂ under sunlight irradiation is shown in Fig. 1. It is clearly observed that, the highest removal efficiency of Cr(VI) in seawater was obtained at lower pH value (pH 3). After 10 min of sunlight irradiation, complete reduction of Cr(VI) was achieved at pH 3, whereas the removal efficiency significantly declined to 79% and 42% at pH 8 and pH 9, respectively. This observation can be explained on the basis of pH at point of zero charge (pH_{pzc}) of TiO₂, which is around 6.3 (Yang *et al.*, 2008). At low pH value, which is lower than pH_{pzc} of TiO₂, the surface of TiO₂ is dominated by the positively charged TiOH₂⁺ (Wang *et al.*, 2007), whereas Cr exists as chromate species (CrO₄²⁻ and/or HCrO₄⁻). Therefore, due to the electrostatic attraction between the oppositely charged species, Cr(VI) ions are strongly adsorbed onto TiO₂ surface, leading to an enhanced removal efficiency at pH 3. While at higher pH value, the photocatalytic reduction efficiency of Cr(VI) is low due to the dominance of the negatively charged TiO⁻ and Cr₂O₇²⁻, leading to unfavorable repulsion between the similarly charged species, which inhibits the adsorption of Cr(VI) on the catalyst surface. Additionally, the alkaline medium increases the precipitation of Cr(OH)₃ which covers the active sites on TiO₂ surface,

leading to a significant reduction of the photocatalytic activity. Based on these results, the favorable pH value for better photoreduction was found to be 3, which will be considered as an optimal value for the entire Cr(VI) photocatalytic reduction experiments.

3.2. Effect of photocatalyst dose

Figure 2 shows the photoreduction efficiency of 5 ppm of Cr (VI) in seawater at the optimum pH 3 using various amounts of CTiO₂ under illumination of natural sunlight. It is clearly noted that the photocatalytic reduction efficiency enhanced with the increase of the catalyst dose from 0.5 to 2.0 g L⁻¹, due to the availability of more active sites and the growth of the total surface area for Cr(VI) adsorption. Subsequent increment in the catalyst dose to 2.5 g L⁻¹ resulted in a reduction of the photoremoval efficiency, which can be explained by the reduction in surface area available for light absorption due to the increase of particles aggregation as the catalyst loading exceeds the optimum amount (Wang *et al.*, 2009). Moreover, the reduction of light penetration due to the enhancement of light scattering; lead to the decrease of the number of activated sites on the TiO₂ surface and shrinking of the effective photoactivated volume of suspension (Chin *et al.*, 2004).

3.3. Effect of Initial Cr(VI) Concentration

The effect of initial Cr(VI) concentration on its photoreduction rate in seawater over the range of 1 to 50 ppm at the optimal conditions of pH 3 and 2.0 g L⁻¹ of CTiO₂ is shown in Fig. 3. With the elevation of the initial Cr(VI) concentration, a longer irradiation time is required for complete elimination. The increase in Cr(VI) concentration can lead to the saturation of the limited number of accessible active sites and/or deactivation of the active sites on the photocatalyst surface. Additionally, the path length of photons

entering into the reaction mixture decreases, and a fewer photons reach the catalyst surface, leading to a remarkable decline in the photoreduction rate of Cr(VI) (Chen *et al.*, 2011; Mekatel *et al.*, 2012).

3.4. Photocatalytic Reduction of Cr(VI) by TiO₂ and CTiO₂

To determine the photocatalytic performance of the TiO₂ and CTiO₂ catalysts, photoreduction experiments of 5.0 ppm of Cr(VI) were carried out at pH 3 in the presence of 2.0 g L⁻¹ of the photocatalyst under illumination of real sunlight (Fig. 4). Remarkably, higher photocatalytic activity was observed for CTiO₂ compared to that of pure TiO₂. Complete removal of 5.0 ppm of Cr(VI) was achieved after only 10 min using CTiO₂. Whereas after the same irradiation time, only 42.3 % of the same concentration of Cr(VI) was removed using pure TiO₂ under the same experimental conditions. The observed enhanced photocatalytic activity of CTiO₂ nanoparticles, can be attributed to carbon modification of TiO₂ (Khan *et al.*, 2002; Shaban *et al.*, 2013; Shaban *et al.*, 2016; Shaban and Khan, 2008; Xu *et al.*, 2006). The origin of visible-light response of carbon doped TiO₂ is due to the presence of the dopant carbons at the oxygen sites of TiO₂ and the formation of C 2p states above the valence band which can be mixed with the O 2p valence band, leading to a significant narrowing of the optical bandgap energy of CTiO₂ (Irie *et al.*, 2006).

3.5. Kinetic Studies

The kinetics of photocatalytic reactions of aquatic reactant can be described by the Langmuir–Hinshelwood model (Petukhov, 1997; Bayarri *et al.*, 2005; Kusvuran *et al.*, 2005), which relates the degradation rate (r) of the reactant and its concentration (C) in water at time t , as follows:

$$r = -\frac{dc}{dt} = \frac{k_r K_{ad}}{1 + K_{ad} C} \quad (2)$$

where k_r and K_{ad} represent the constants of the rate and the adsorption equilibrium, respectively. When reactant concentration is low and/or the adsorption is relatively weak, Eq. (2) can be simplified to the pseudo-first order kinetics:

$$\ln\left(\frac{C_0}{C}\right) = k_r K_{ad} t = k_{app} t \quad (3)$$

where C_0 and k_{app} are the initial concentration and the apparent first-order rate constant, respectively. The kinetic analysis for the photoreduction of various concentrations of Cr(VI) ranging between 10 and 50 ppm in seawater at the optimal conditions of pH 3 and 2.0 g L⁻¹ of CTiO₂ under illumination of sunlight is shown in Fig. 5. The photocatalytic reduction of Cr(VI) was successfully described by pseudo-first order kinetic, as confirmed by the straight line obtained from the plot of $\ln(C_0/C)$ versus illumination time.

3.6. Effect of Addition of Hole Scavenger

Simply, when TiO₂ surface is illuminated with light, electron-hole (e^- - h^+) pairs are generated (Eq 4). These pairs are subsequently separated to the conduction (CB) and the valence (VB) bands, respectively. The holes (h_{vb}^+) may oxidize H₂O to generate O₂ (Eq 5), whereas Cr (VI) can be reduced by e_{cb}^- into Cr(III) (Eq 6). Shortly, the separated e_{cb}^- and h_{vb}^+ may be recombined again, in addition to the possible reversible oxidation of Cr(III) to Cr(VI) by the consumption of the produced $\cdot$ OH radical (Eq. (8)), causing a decline in the photocatalytic performance of the catalyst. To suppress this recombination step, a sacrificial reagent such as phenol, can be added to scavenge the generated positive holes (h_{vb}^+), and to consume the hydroxyl radicals (Bolton, 1996; Li, *et al.*, 2001). Accordingly, the

scavenged positive hole (h_{vb}^+) would oxidize either phenol directly (Eq. (9)) or indirectly through the generated $\cdot\text{OH}$ radical (Eq. (10)). A simplified diagram illustrating the photocatalytic reduction of Cr(VI) using CTiO₂ in the presence and absence of the hole scavenger is presented in Fig. 6.

The photocatalytic reduction of 50 ppm of Cr(VI) in absence and presence of 5 ppm of phenol is shown in Fig. 7. The existence of phenol as a hole scavenger remarkably enhanced the reduction rate of Cr(VI). As can be seen, the illumination time required for complete removal of Cr(VI) has been clearly shortened from 180 min to be only 20 min, as

a result of the suppression of electron–hole recombination process, due to the presence of the hole scavenger.

3.7. Photocatalytic Removal of Cr(VI) from Real polluted Seawater

The photocatalytic removal of 16.2 ppm of Cr(VI) from polluted seawater was investigated at the favorable conditions of pH 3 and photocatalyst (CTiO₂ and TiO₂) dosage of 2.0 g L⁻¹ under illumination of solar light (Fig. 8). It is worth pointing out that, even with possibility of the existence of different contaminants in polluted seawater samples, a complete elimination of Cr(VI) was successfully achieved after only 30 minutes of solar irradiation using CTiO₂. Notably, 50% decline in the removal efficiency was observed with the use of equivalent dosage of the pure catalyst (TiO₂) under identical experimental conditions. These results reflect the potentiality of CTiO₂ as an efficient photocatalyst which is capable for harvesting the maximum light photons in the visible region for the photocatalytic elimination of Cr(VI) from polluted seawater.

Fig. 1. Effect of pH on the photocatalytic reduction of 5 ppm of Cr(VI) in the presence of 2.0 g L⁻¹ of CTiO₂ under illumination of natural sunlight.

Fig. 2. Effect of CTiO₂ loading on the photocatalytic reduction of 5 ppm of Cr(VI) at pH 3 under illumination of natural sunlight.

Fig. 3. Effect of initial concentration of Cr(VI) on its photocatalytic reduction at optimal conditions of pH 3 and 2.0 g L⁻¹ CTiO₂ under natural sunlight.

Fig. 4. Photocatalytic reduction of 5.0 ppm of Cr(VI) at pH 3 in the presence of 2.0 g L⁻¹ of the photocatalyst (TiO₂ and CTiO₂) under natural sunlight.

Fig. 5. Plot of $\ln(C_0/C)$ versus illumination time for the photocatalytic reduction of various concentrations of Cr(VI) at optimal conditions of pH 3 and 2.0 g L⁻¹ CTiO₂ under natural sunlight.

Fig. 6. Schematic diagram for the photocatalytic reduction of Cr(VI) in the presence and absence of holes scavenger (phenol) under illumination of light.

Fig. 7. Photocatalytic reduction of 50 ppm of Cr(VI) in absence and presence of 5 ppm of phenol under natural sunlight.

Fig. 8. Photocatalytic reduction of Cr(VI) in polluted seawater at pH 3 in the presence of 2.0 g L^{-1} of the photocatalyst (TiO_2 and CTiO_2) under natural sunlight.

4. Conclusion

In the present study, the photocatalytic removal of hexavalent chromium Cr(VI) from polluted seawater has been successfully investigated by using carbon doped titanium oxide (CTiO_2) nanoparticles under irradiation of natural sunlight. The photocatalytic activity of CTiO_2 showed remarkably enhanced photoactivity towards the photocatalytic reduction of Cr(VI) compared to pure TiO_2 under the same experimental conditions. The highest removal rate was obtained at pH 3 and catalyst dose of 2.0 g L^{-1} . The existence of a hole scavenger remarkably enhanced the reduction rate Cr(VI). The photocatalytic reduction of Cr(VI) in seawater using CTiO_2 under real sunlight obeyed a pseudo-first-order kinetics.

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تعزير الاختزال الضوئي الحفزي بأشعة الشمس لأيون الكروم السداسي في ماء البحر باستخدام جسيمات أكسيد التيتانيوم النانوية المعدلة كربونياً

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المستخلص. تمت دراسة إزالة الكروم السداسي (Cr (VI) من مياه البحر الملوثة باستخدام التحفيز الضوئي في وجود جسيمات أكسيد التيتانيوم نانوية الحجم المعدلة كربونياً (CTiO₂) تحت إضاءة أشعة الشمس الطبيعية. تم استخدام أكسيد التيتانيوم النقي غير المعدل (TiO₂) وذلك لعمل المقارنات اللازمة في دراسة التحفيز الضوئي. وتمت دراسة تأثير كل من الأس الهيدروجيني (PH) للوسط والتركيزات الابتدائية لأيون الكروم، كذلك الجرعات المختلفة من المحفز الضوئي (CTiO₂) على الاختزال الضوئي الحفزي لأيون الكروم السداسي (Cr (VI) وكذلك بهدف الوصول للظروف المثالية لعملية الإزالة. ودلت التجارب العملية على أن أفضل معدل لعملية إزالة الكروم السداسي كانت في الظروف المثلى، وهي ٢ جرام/لتر من المادة المحفزة وعند الأس الهيدروجيني للمحلول ٣ (PH3). كما لوحظ أنه في حالة وجود الفينول فإنه يعمل كمانح للإلكترونات، مما يعزز وبشكل ملحوظ عملية اختزال الكروم السداسي. ولقد أثبتت الدراسة أن الاختزال الضوئي الحفزي لأيون الكروم السداسي (Cr (VI) باستخدام جسيمات أكسيد التيتانيوم نانوية الحجم المعدلة كربونياً (CTiO₂) تتبع معادلة طاقة حركية من الدرجة الأولى غير حقيقية هو تفاعل من الدرجة الأولى غير الحقيقية وفقاً لنموذج لانجمير-هنشلوود.

كلمات مفتاحية: الاختزال الضوئي الحفزي، أيون الكروم السداسي، أكسيد التيتانيوم، جسيمات نانوية، التعديل الكربوني.