

Effective Photocatalytic Reduction of Cr(VI) by Carbon Modified (CM)-n-TiO₂ Nanoparticles under Solar Irradiation

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Received August 23, 2013; revised September 20, 2013; accepted September 27, 2013

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ABSTRACT

Photocatalytic reduction of toxic Cr(VI) was successfully achieved using carbon modified titanium oxide (CM-n-TiO₂) nanoparticles under natural sunlight illumination. Modification of titanium oxide by carbon significantly enhanced the photocatalytic reduction of Cr(VI) under natural sunlight irradiation. The effects of various experimental parameters such as catalyst dose, initial concentration of Cr(VI), and solution pH on the reduction rate of Cr(VI) were investigated. The highest reduction rate of Cr(VI) was obtained at the optimal conditions of pH 5 and 2.0 g·L⁻¹ of CM-n-TiO₂. Interestingly, in the presence of phenol, as a sacrificial electron donor, the rate of Cr(VI) reduction was nearly 1.7 times higher than in its absence. The solar photoreduction of Cr(VI) in aqueous solution using CM-n-TiO₂ obeyed a pseudo-first order kinetics according to the Langmuir-Hinshelwood model.

Keywords: Photocatalytic Reduction; Chromium; Titanium Oxide; Carbon Modification

1. Introduction

The discharge of toxic heavy metals into aquatic environment has been known to cause serious pollution problems. Among these pollutants, chromium possesses the most severe environmental concern due to its high toxicity, potential carcinogenicity, and high mobility in water [1,2]. The major sources of chromium pollution are electrochemical, steel manufacturing industries and leather tanning [3,4]. In aquatic environments, chromium exists in hexavalent (Cr(VI)) and trivalent (Cr(III)) forms, of which hexavalent form is more toxic than the trivalent one, and is known to be human carcinogen [5]. Different techniques have been reported for the treatments of Cr (VI), such as ion exchange [6], membrane separation [7], physical and biological adsorption [8-10], and electrocoagulation [11,12]. However, most of these techniques have several limitations and drawbacks, and they require either high energy or massive use of reducing agents.

Semiconductor photocatalysis has attracted considerable interest as an effective and economical technique for detoxification of polluted waters [13-22]. It can effectively reduce highly toxic Cr(VI) into the less harmful

Cr(III), which can then be precipitated as Cr(OH)₃ in neutral or alkaline solutions [23]. Titanium dioxide photocatalyst was considered as one of the most practical candidates due to its optical and electronic properties, low cost, high level of photocatalytic activity, chemical stability and non-toxicity. However, its wide band gap (3.0 - 3.2 eV) limits its photoresponse in the ultraviolet region which is only a small fraction (~5%). Therefore, much attention has been devoted to enhancing its catalytic efficiency or expanding its applicability under solar irradiation. Recently, carbon modification of n-TiO₂ has been proved to be an effective approach to enhance its catalytic efficiency [21,22,24-26].

Most of the studies on heterogeneous photocatalytic reduction of Cr(VI) using n-TiO₂ were performed under illumination of UV light. Therefore, in this study, visible light active carbon-modified (CM)-n-TiO₂ nanoparticles were prepared via sol-gel method. The photocatalytic performance of CM-n-TiO₂ was examined for the photoreduction of Cr(VI) in aqueous solution under illumination of natural sunlight. The photocatalytic activity of CM-n-TiO₂ was compared with regular n-TiO₂. The effects of various experimental parameters such as photo-

catalyst loading, Cr(VI) concentration, and pH on the photocatalytic removal rate of Cr(VI) were studied. Additionally, the effect of presence of phenol, as a sacrificial electron donor, on the photocatalytic reduction of Cr(VI) was also investigated.

2. Experimental

2.1. Synthesis and Characterization of n-TiO₂ and CM-n-TiO₂ Nanoparticles

Visible light active carbon modified titanium dioxide (CM-n-TiO₂) nanoparticles were synthesized by a sol-gel method using titanium butoxide (Ti[O(CH₂)₃CH₃]₄, Fluka, 97%), a carbon-containing precursor, as a molecular precursor of TiO₂ as well as a carbon source. Regular (unmodified) titanium dioxide (n-TiO₂) nanoparticles were synthesized by hydrolysis and oxidation of titanium trichloride (TiCl₃ 12% in hydrochloric acid (5% - 12%), Sigma-Aldrich) in an aqueous medium. Details on the procedures used for catalysts preparation and characterization can be found elsewhere [22].

2.2. Photocatalytic Experiments

All solar photocatalytic experiments were carried out at the Faculty of Marine sciences, Obhur, Jeddah, KSA, in the daytime between 11:00 am to 15:00 pm, during May-June, 2013. Experimental set up consisted of a magnetically stirred 500 mL glass photoreactor loaded with the aqueous solution containing different concentrations of Cr(VI) ranging from 1 to 10 ppm, then the synthesized photocatalyst (n-TiO₂ or CM-n-TiO₂) was added. The photocatalytic reactor was then directly exposed to natural sunlight. The average solar intensity was about 1200 W m⁻², measured by Field Scout Light Sensor Reader (Spectrum Technologies, Inc.) equipped with 3670i Silicon Pyranometer Sensor. Prior to analysis, aliquots of treated samples were regularly withdrawn from the reactor and centrifuged immediately to remove the catalyst. The Cr(VI) was determined colorimetrically at 540 nm using a Shimadzu UV-VIS Spectrophotometer (Model PharmaSpec UV-1700) according to the diphenylcarbazide colorimetric method [27].

3. Results and Discussion

3.1. Photocatalytic Activity of n-TiO₂ and CM-n-TiO₂

Figure 1 compares the photoreduction efficiency of 3.0 ppm of Cr(VI) under illumination of real sunlight in the presence of 2.0 g·L⁻¹ of CM-n-TiO₂ and n-TiO₂, respectively. It is clearly observed that the photocatalytic activity of CM-n-TiO₂ is higher than that of n-TiO₂ under sunlight irradiation. Complete photoreduction of 3.0 ppm of Cr(VI) was achieved after only 10 min using 2.0 g/L

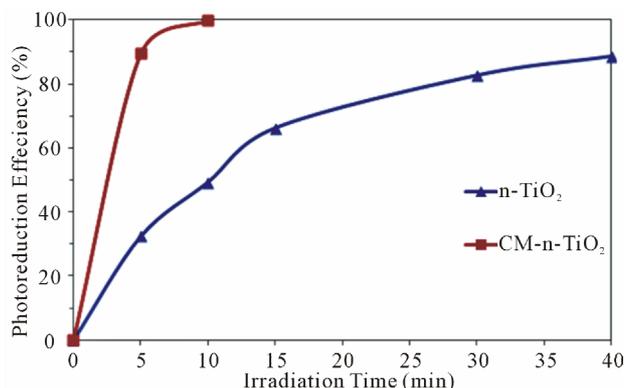


Figure 1. Photoreduction of 3 ppm of Cr(VI) in the presence of 2.0 g·L⁻¹ of CM-n-TiO₂ and n-TiO₂ under illumination of natural sunlight.

CM-n-TiO₂. After the same irradiation time, only 49.25% of the same concentration of Cr was removed using regular n-TiO₂ under the same experimental conditions. The observed enhanced photocatalytic activity of carbon modified CM-n-TiO₂ nanoparticles, can be attributed to carbon modification of TiO₂ during the synthesis process [21,22,24-26].

3.2. Effect of Solution pH

pH of the solution plays a major role in the photocatalytic reaction as it is known to influence the surface charge of the semiconductor thereby affecting the interfacial electron transfer and the photoredox process [28]. The possible functional groups on TiO₂ surface in water are TiOH₂⁺, TiOH, and TiO⁻. The point of zero charge (pH_{pzc}) of TiO₂ is an important factor determining the distribution of the surface groups. The surface of TiO₂ is negatively charged with the species TiO⁻ when pH is higher than pH_{pzc}. On the contrary, it is positively charged with the species TiOH₂⁺. **Figure 2** depicts the effect of pH on the photocatalytic reduction rate of Cr(VI). It is worth noting that, the removal rate of Cr(VI) decreased with increasing the initial pH value from 5 to 9 (**Figure 2(b)**). The higher removal efficiency at pH 5, which is lower than the point of zero charge (pH_{pzc}) of TiO₂, can be attributed to the strong electrostatic attraction between the anionic chromate species (CrO₄²⁻ and/or HCrO₄⁻) and the positively charged TiOH₂⁺ surface [29]. On the other hand, at higher pH value the TiO₂ surface is negatively charged in a state of TiO⁻ and Cr₂O₇²⁻ becomes dominate species, which may be repelled away from the TiO₂ surface which subsequently leads to inhibited adsorption of Cr(VI). Furthermore, Cr(III) will be precipitated on the surface of TiO₂ as Cr(OH)₃ at increased solution pH, covering the activity sites of the catalyst [30]. As a result, Cr(VI) the photoreduction efficiency decreases in alkaline medium.

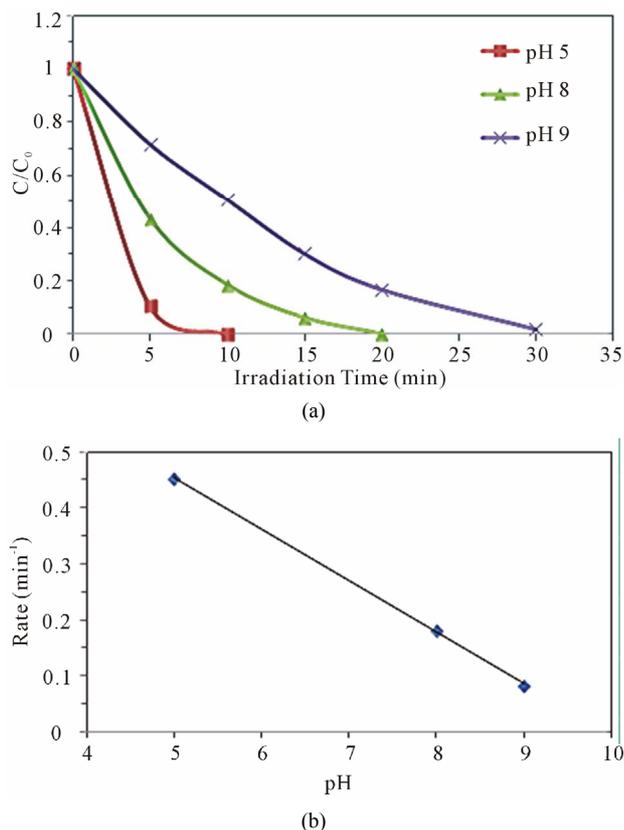


Figure 2. (a) Effect of pH on the photoreduction of 5 ppm of Cr(VI) in the presence of $2.0 \text{ g}\cdot\text{L}^{-1}$ of CM-n-TiO₂ under illumination of natural sunlight; (b) Rate of photoreduction of 5 ppm of Cr(VI) as a function of pH in the presence of $2.0 \text{ g}\cdot\text{L}^{-1}$ of CM-n-TiO₂.

3.3. Effect of Catalyst Loading

In a typical photocatalytic experiment, it is essential to determine the minimum amount of catalyst required to remove the maximum amount of pollutants. Therefore, the influence of CM-n-TiO₂ dose on photoreduction of Cr(VI) was investigated in order to attain the maximum absorption of efficient solar light photons as well as to avoid an ineffective excess amount of the photocatalyst.

Figure 3 shows the photoreduction rate of 3 ppm of Cr(VI) at the optimum pH 5 using various amounts of CM-n-TiO₂ under illumination of natural sunlight. The photocatalytic reduction rate of Cr(VI) increased with the increase in catalyst dose from 0.5 to $2.0 \text{ g}\cdot\text{L}^{-1}$. Further increment in catalyst loading to $2.5 \text{ g}\cdot\text{L}^{-1}$ leads to decrease in photoreduction efficiency. The observed increment in the photoreduction efficiency at the catalyst concentration of $2.0 \text{ g}\cdot\text{L}^{-1}$ is due to the increase of the total number of active sites on the photocatalyst surface thus causing an increase in the number of e^- which can take part in the photoreduction of Cr(VI). At catalyst loading beyond the optimum, the tendency toward particles aggregation increases, resulting in a reduction in

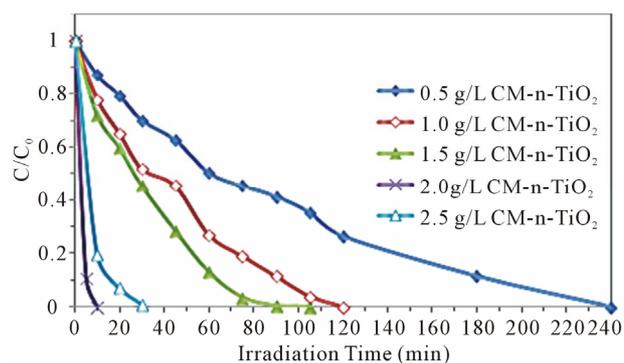


Figure 3. Effect of CM-n-TiO₂ loading on photoreduction of 3 ppm of Cr(VI) under illumination of natural sunlight.

surface area available for light absorption and hence a drop in photocatalytic degradation rate [31]. Furthermore, the increase of the turbidity of the suspension reduces light penetration due to the enhancement of light scattering; the result is the decrease of the number of activated sites on the TiO₂ surface and shrinking of the effective photoactivated volume of suspension. The interaction of these two processes resulted in a reduced performance of photocatalytic performance with the overloaded catalyst [32].

3.4. Effect of Initial Cr(VI) Concentration

The effect of initial Cr(VI) concentration on its photoreduction rate was investigated over the range of 1 to 10 ppm at the optimal conditions of pH 5 and $2.0 \text{ g}\cdot\text{L}^{-1}$ of CM-n-TiO₂ (**Figure 4**). It is clearly noted that the irradiation time required for complete removal of Cr(VI) under natural sunlight was extended as the initial Cr(VI) concentration increased. This can be rationalized according to Beer-Lambert's law, as Cr(VI) concentration increases, the path length of photons entering into the reaction mixture decreases, and a fewer photons reach the catalyst surface. As the incident intensity, catalyst amount and irradiation time are constant, therefore, the availability of active sites will be reduced. Consequently, the photoreduction rate of Cr(VI) decreases as the concentration increases [33,34]. Moreover, an increase in Cr(VI) concentration can lead to the saturation of the limited number of accessible active sites on the photocatalyst surface and/or deactivation of the active sites of the catalyst, resulting in a reduction in the photoreduction rate.

3.5. Kinetic Studies

Typically, the Langmuir-Hinshelwood (L-H) model is usually used to describe the photocatalytic removal of inorganic and organic pollutants [35-38]. It basically relates the degradation rate (r) and reactant concentration in water at time t (C), which is expressed as follows:

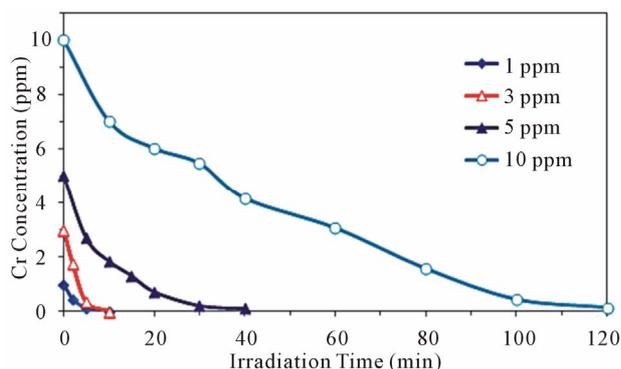


Figure 4. Effect of initial concentration of Cr(VI) on its photoreduction at optimal conditions of pH 5 and $2.0 \text{ g}\cdot\text{L}^{-1}$ CM-n-TiO₂ under natural sunlight.

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

where k_r is the rate constant and K_{ad} is the adsorption equilibrium constant. When the adsorption is relatively weak and/or the reactant concentration is low, Equation (1) can be simplified to the pseudo-first order kinetics with an apparent first-order rate constant k_{app} :

$$\ln\left(\frac{C_o}{C}\right) = k_r K_{ad} t = k_{app} t \quad (2)$$

where C_o denotes the initial concentration. Plotting $\ln(C_o/C)$ versus illumination time (t) yields a straight line, and the slope is the apparent rate constant k_{app} . The kinetic experiments for the photoreduction of various concentrations of Cr(VI) ranging between 1 and 10 ppm were conducted at the optimal conditions of pH 5 and $2.0 \text{ g}\cdot\text{L}^{-1}$ of CM-n-TiO₂ under illumination of sunlight. The photocatalytic reduction of Cr(VI) was successfully fitted using L-H model, and can be described by the pseudo-first order kinetic, as confirmed by the obtained straight line (Figure 5). Similar observation was reported for the photoreduction of Cr(VI) by Ku and Jung [39].

3.6. Effect of Phenol

Figure 6 shows the kinetic analysis of Cr(VI) reduction in the absence and presence of phenol. Interestingly, the presence of phenol (1 ppm) significantly promoted the reduction rate of 5 ppm of Cr(VI) by nearly 1.75 times higher than in its absence. This synergism is based on the photogenerated electrons and holes on the surface of n-TiO₂ semiconductor. Illumination of TiO₂ by light with energy ($h\nu$) greater than or equal to the bandgap energy (E_g) of TiO₂ elevates electron in the valence band (VB) to the conduction band (CB), and a positive hole is formed in the valence band (Equation (3)). At the external TiO₂ surface, the positive hole and the excited electron either recombine or become involved in redox reactions with ad-

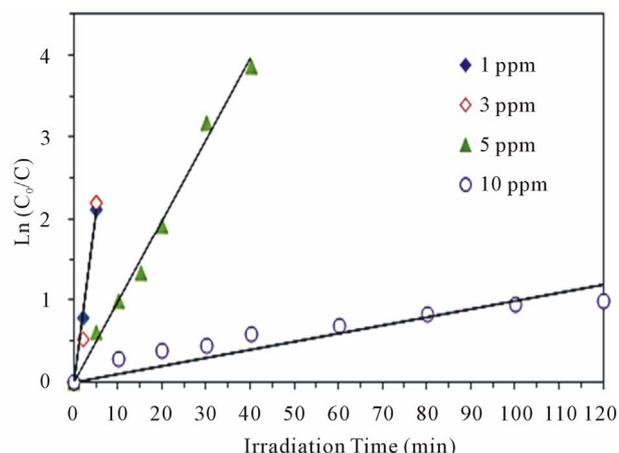


Figure 5. Plot of $\ln(C_o/C)$ versus illumination time for the photoreduction of Cr(VI) at optimal conditions of pH 5 and $2.0 \text{ g}\cdot\text{L}^{-1}$ CM-n-TiO₂ under natural sunlight.

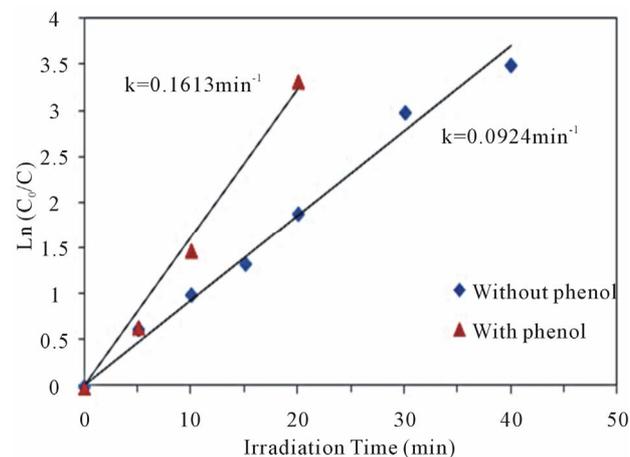
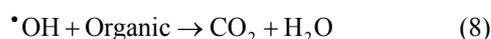
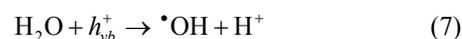
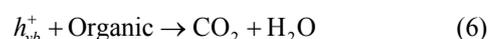
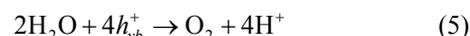
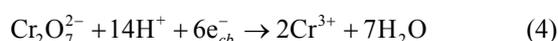
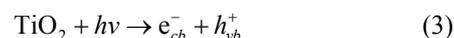


Figure 6. Kinetics of photocatalytic reduction of Cr(VI) in absence and presence of phenol at optimal conditions of pH 5 and $2.0 \text{ g}\cdot\text{L}^{-1}$ CM-n-TiO₂ under natural sunlight.

sorbed groups.



The conduction band electrons (e_{cb}^-) can reduce Cr(VI) to Cr(III) (Equation (4)) [40,41], and the valence band hole (h_{vb}^+) can oxidize water to generate O₂ (Equation (5)). Therefore, the net photocatalytic reaction is the three-electron-reduction of Cr(VI) to Cr(III) with oxidation of water to oxygen, which is a kinetically slow four-

electron process [40,42]. Accordingly, the photocatalytic reduction of Cr(VI) alone is quite slow. Furthermore, the photo-generated electrons and holes can recombine in bulk or on surface of the semiconductor within a very short time, resulting in a reduction in the photocatalytic efficiency. Therefore, adding electron donors (sacrificial reagents or hole scavengers) to react irreversibly with the photo-generated VB holes (h_{vb}^+), thereby suppressing the electron-hole recombination [43,44]. If this sacrificial agent is an organic pollutant present in water or wastewater, the positive hole (h_{vb}^+) would oxidize either pollutant directly (Equation (6)) or water to produce hydroxyl radicals ($\cdot\text{OH}$) which are strong oxidizing agents (Equation (7)). Therefore, in the presence of phenol, as a sacrificial electron donor, the photogenerated holes are rapidly scavenged from the TiO_2 particles, suppressing electron-hole recombination on CM-n- TiO_2 and accelerating the reduction of Cr(VI) by photogenerated electron [45]. It has been reported that the presence of organic species as sacrificial electron donor can accelerate the photocatalytic reduction of Cr(VI) [4,46,47]. A simplified diagram illustrating the simultaneous photocatalytic reduction of Cr(VI) and degradation of phenol using CM-n- TiO_2 under illumination of sunlight is presented in Figure 7.

4. Conclusion

The photocatalytic reduction of Cr(VI) in aqueous solution was successfully achieved using carbon-modified (CM)-n- TiO_2 nanoparticles under irradiation of natural sunlight. CM-n- TiO_2 nanoparticles exhibited significantly enhanced photocatalytic efficiency compared to unmodified n- TiO_2 . This observed enhancement in the photoactivity can be attributed to the carbon modification. The photoreduction of Cr(VI) was favorable at pH 5 and optimal catalyst dose of $2.0 \text{ g}\cdot\text{L}^{-1}$. The presence of phenol significantly promoted the reduction rate of Cr(VI) by nearly 1.75 times higher than in its absence. The solar photocatalytic removal of Cr(VI) in aqueous solution

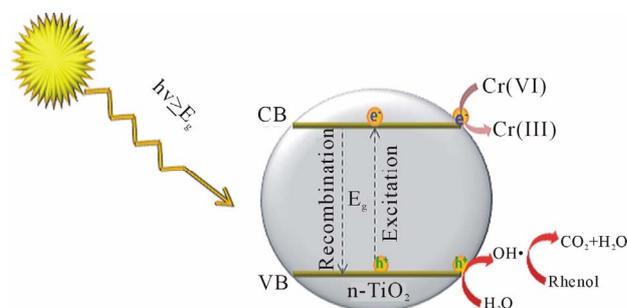


Figure 7. Simultaneous photocatalytic reduction of Cr(VI) and degradation of phenol using CM-n- TiO_2 under illumination of sunlight.

using CM-n- TiO_2 obeyed a pseudo-first order kinetics according to the Langmuir-Hinshelwood model.

5. Acknowledgements

The author is thankful to Mr. Mousa Al Zobidi for his valuable help in the experimental analysis.

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