

Research Article

Photoreduction of Cr(VI) Ions in Aqueous Solutions by UV/TiO₂ Photocatalytic Processes

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This study discussed the photoreduction of Cr(VI) ions in aqueous solutions by UV/TiO₂ photocatalytic processes under various operational factors. Experimental results showed that the removal rate of Cr(VI) increased with decreasing solution pH values and with increasing dosages of organic compounds, indicating that the recombination rate of electrons and h⁺ can be retarded in the reaction systems by the addition of the scavenger, thus raising the reaction rate of Cr(VI). The relationship of the chemical reaction rate of Cr(VI), TiO₂ dosage, and changes of Cr(VI) concentration was expressed by the pseudo-first-order kinetic equation. Comparing the experimental results of two different doping metals in modified TiO₂ photoreduction systems, the removal rate of Cr(VI) by the Ag/TiO₂ process is larger, possibly because the electron transferring ability of Ag is superior to that of Cu. However, the photoreduction rates of Cr(VI) by modified UV/TiO₂ processes are worse than those by a nonmodified commercial UV/TiO₂ process.

1. Introduction

Chromium is a common toxic pollutant present in industrial effluents [1, 2]. Conventional methods used in the removal of Cr(VI) ions from wastewater include reducing following hydroxide precipitation, ion exchange, adsorption, electrochemical precipitation, foam separation, membrane separation, solvent extraction, and bacterial reduction [2–4]. In recent years, different semiconductors have been intensively studied as the photocatalysts for photoreduction reactions, as electron-hole pairs can be generated by the photoexcitation of the photoreduction process to remove and recycle heavy metals and to reduce heavy metal pollutants in aqueous solution [5–8]. The photocatalysts which are often used include TiO₂, CdS, and ZnO. TiO₂ has been extensively studied in regard to its application as the physical sunblock in sunscreens or other cosmetic products and in environmental remediation processes because of its high degree of photocatalytic activity, chemical stability, and nontoxicity [5–10].

In the reaction process of UV/TiO₂, an electron-hole pair is generated after TiO₂ has been exposed to ultraviolet light (UV) with a wavelength ($\lambda = 365$ nm) in the near visible

spectrum. The electrons then reduce the heavy metals; this is the reduction path. The hole generates the free radical through a series of reactions, and then organic matters are oxidized into carbon dioxide; this is the oxidation path. However, a shortcoming of this process is that the electron-hole pair may be bound again, thus decreasing the efficiency of the photoreduction. Hence, the addition of an organic hole scavenger enhances the photoreduction effect. Generally, organic holes scavengers comprise organic compounds such as methanol, ethanol, formic acid, and acetic acid [11].

Chromium is widely used in several industrial processes such as metal plating and paint making. Due to its acute toxicity and high mobility in water, Cr(VI) is in the list of priority pollutants of most countries [6]. On the other hand, Cr(III) is readily precipitated or adsorption onto solid phase. Cr(VI) has a toxicity one hundred times higher than that of Cr(III). Advanced oxidation processes have demonstrated their usefulness in cleaning of industrial wastewater [12–14]. After the photoreduction of Cr(VI), it can be separated from the suspension by several procedures. From the environmental point of view knowledge of chromium, photoreduction mechanism is essential not only for tracing Cr(VI) fate in

environment, but also for understanding its role in remediation of pollution by organic compounds [9].

The aim of this study was to use commercial TiO_2 and an organic hole scavenger together. Previous work has seldom probed into the doping metals (Ag and Cu) used in the TiO_2 photoreduction system; therefore, this study examined the impact of different calcination temperatures on the activity of modified photocatalysts with $\text{Ag}(\text{NO}_3)$ - and CuCl_2 -doped commercial TiO_2 . Further, the Cr(VI) removal under various operational factors, such as solution pH values, TiO_2 dosages, types, and dosages of organic compound, was explored, and a possible reaction kinetic equation has been proposed to simulate the kinetic behaviors of various species in the reaction.

2. Materials and Method

The materials of this experiment comprised laboratory methanol, ethanol, and isopropanol with different concentrations (0.29 mM, 0.74 mM, 1.47 mM, 2.94 mM, and 5.88 mM) to observe the dosage effect of organic hole scavengers, potassium dichromate (Katayama Chemical) to prepare 20 mg L^{-1} of aqueous solution, and the photocatalyst using Degussa P-25 (Union Chemical Ind.).

2.1. Wastewater Preparation. 0.1130 g potassium dichromate was weighed and then combined with 2 L RO water to prepare the aqueous solution with a Cr(VI) concentration of 20 mg L^{-1} .

2.2. Photocatalyst Modification. Via the incipient wetness method, Cu and Ag were calcined in a modified TiO_2 process. First, the critical moisture content of TiO_2 was measured by solvent, the fixed amount of metal precursor was dissolved in the deionized water with the critical moisture content, TiO_2 was slowly added to the metal-containing aqueous solution and well stirred, TiO_2 was calcined in a high-temperature furnace, and then the grains pulverized into powder once it had cooled to room temperature. The crystallization level morphology and the specific BET surface area of the photocatalyst were determined by a Siemens D-8 X-ray diffractometer (XRD) and a Micromeritics ASAP 2000 analyzer, respectively. Field emission scanning electron microscopy (FESEM, JEOL, JSM-6500F) was operated at 15 kV and used to measure the surface morphology of the prepared samples.

At the same Cr(VI) concentration, the samples were analyzed every half hour under different pH values, organic hole scavengers, dosages of organic hole scavenger, and dosages of photocatalyst over the four-hour reaction period. The optimum operational conditions thus attained were the optimum reaction conditions of modified TiO_2 . With different doping amounts of metal and at different calcination temperatures under the optimum operational conditions obtained, an analysis of the variations of Cr(VI) concentration was made every half hour. The samples were filtered and analyzed by an HITACHI U-2000 Spectrophotometer.

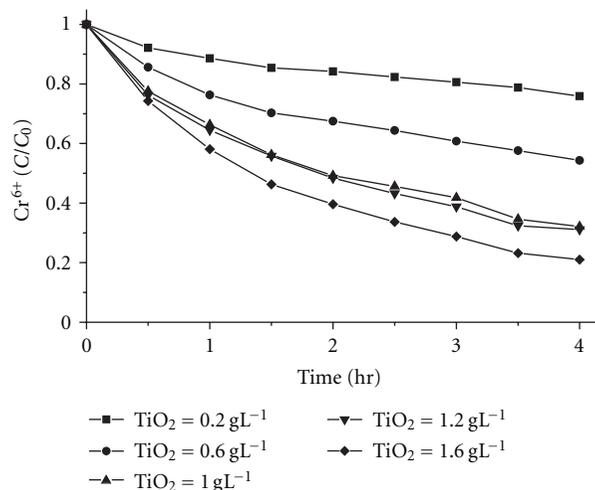


FIGURE 1: Effect of the TiO_2 dosage on the photocatalytic reduction.

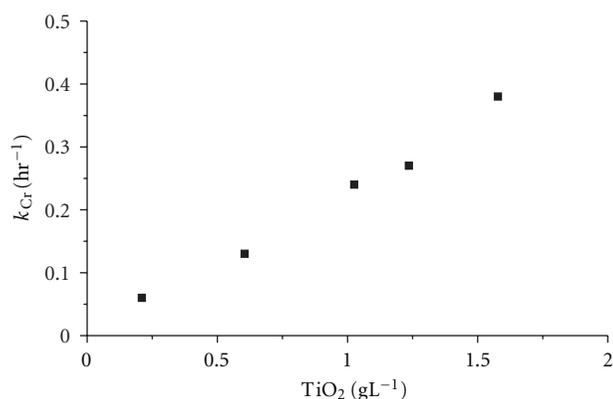


FIGURE 2: Relationship of the rate constant on the photocatalytic reduction.

3. Results and Discussion

This study utilized the UV/ TiO_2 process to treat Cr(VI) pollutants in aqueous solution. In this section, the experimental results of the photoreduction of Cr(VI) by a nonmodified TiO_2 system and modified TiO_2 are explained and discussed. In the experiment, the variations of Cr(VI) concentration over time were as shown in Figure 1; the removal rate of Cr(VI) was 24.1% when the TiO_2 dosage was 0.2 g L^{-1} , and 80% when the TiO_2 dosage was 1.6 g L^{-1} . Therefore, as the TiO_2 dosage increased, the removal rate increased.

In a simulation of the Cr(VI) removal rate using the pseudo-first-order kinetic equation, the relationship of the removal rate and time was obtained, as shown in Figure 2. The photoreduction reaction rate sped up as the TiO_2 dosage increased, indicating that the increase of TiO_2 dosage facilitated the photocatalytic reaction. Similar results were obtained in the presence of other studies [11, 15, 16]. Therefore, it was estimated that before the optical screening appeared, and the TiO_2 dosage had a linear relationship with the pseudo-first-order removal rate.

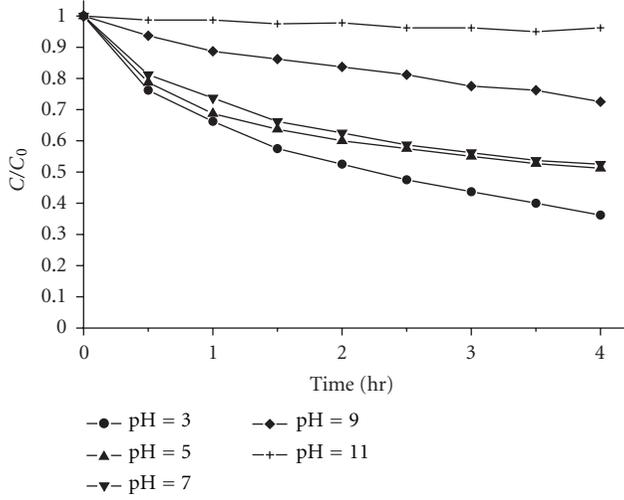


FIGURE 3: Effect of the pH on the photocatalytic reduction.

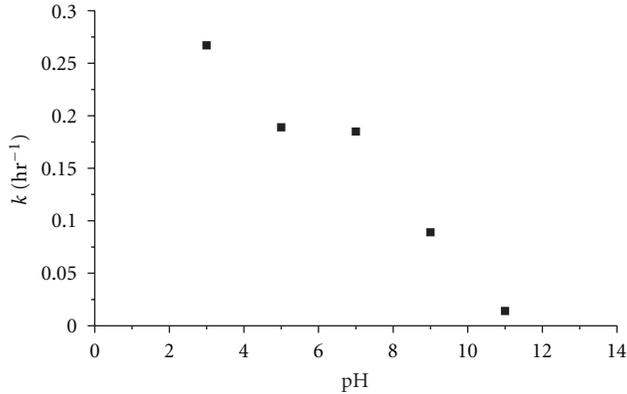


FIGURE 4: Relationship of the rate constant under different pH.

In order to clarify the relationship of the pseudo-first-order Cr(VI) removal rate, TiO₂ dosage, and changes of Cr(VI) concentration, it was assumed that three factors were present in the pseudo-first-order reaction kinetic equation as follows:

$$-r_a = \frac{d[C]}{dt} = k[C][\text{TiO}_2]^n = k_{Cr}[C], \quad (1)$$

where k_{Cr} is $k[\text{TiO}_2]^n$, k is Cr(VI) reduction rate, k_{Cr} is pseudo-first-order rate, $[C]$ is variations of Cr(VI) concentration over time, and $[\text{TiO}_2]$ is TiO₂ dosage.

With the logarithm of the equation above, we then have

$$\ln k_{Cr} = \ln k + n \ln[\text{TiO}_2], \quad (2)$$

by plotting $\ln k_{Cr}$ and $\ln[\text{TiO}_2]$, intercepting to get $\ln k = -1.4058$ and $k = 0.2344$; then from the slope we have $n = 0.87$. Thus, for the relationship of the pseudo-first-order

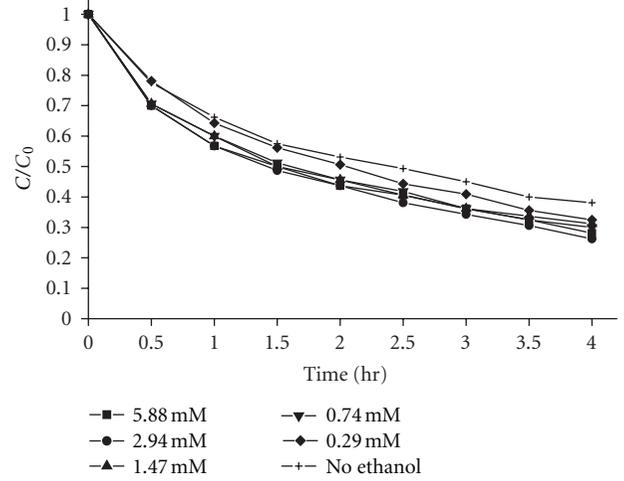


FIGURE 5: Effect of initial concentration on the photocatalytic reduction.

removal rate, TiO₂ dosage and variations of Cr(VI) concentration over time, the following equation was derived from the three equations above:

$$\begin{aligned} -r_a &= \frac{d[\text{Cr}^{6+}]}{dt} \\ &= 0.2344 [\text{Cr}^{6+}] [\text{TiO}_2]^{0.87} \quad (R^2 = 0.9887). \end{aligned} \quad (3)$$

The Cr(VI) reduction rate was in an 0.87th power relation with the TiO₂ dosage. The initial Cr(VI) concentration was fixed at 20 mg L⁻¹ for treatment of Cr(VI) in aqueous solution by UV/TiO₂. The changes of Cr(VI) over time under different values are shown in Figure 3, from which we could know that with the increase of pH value, the Cr(VI) removal rate gradually declined. At pH = 3, the removal rate was 63.5%, but, at pH = 11, the removal rate was just 5.1%.

As for the experimental results, the Cr(VI) removal rate was simulated by the pseudo-first-order kinetic equation to determine the removal rate and time, as shown in Figure 4. Similar results were obtained in the presence of other studies [11, 15, 16], who discussed the influence of different pH values of photocatalyst on the removal rate of Cr(VI) by photoreduction processes. As pointed out by Chen and Cao (2005) [16], as pH value increased, the reduction rate of dichromate ions gradually decreased because the increase of pH value reduced the adsorption of dichromate ions on the surface of the photocatalyst; also, at high pH value, Cr(OH)₃ covered the surface active position of TiO₂ so that the trivalent chromium deposits on TiO₂ depressed the photocatalytic activity. Consequently, for the photoreduction of Cr(VI) in aqueous solution by UV/TiO₂ process, a low pH value had the best reduction efficiency. The variations of Cr(VI) concentration over time in the experiment to discover the dosing effect of organic hole scavengers are shown in Figure 5. The Cr(VI) removal rate was the best, as high as 74% for a dosage of 2.94 mM, in the ethanol system.

Ethanol was used as the hole scavenger and at the optimum dosage of 2.94 mM, under different pH values and

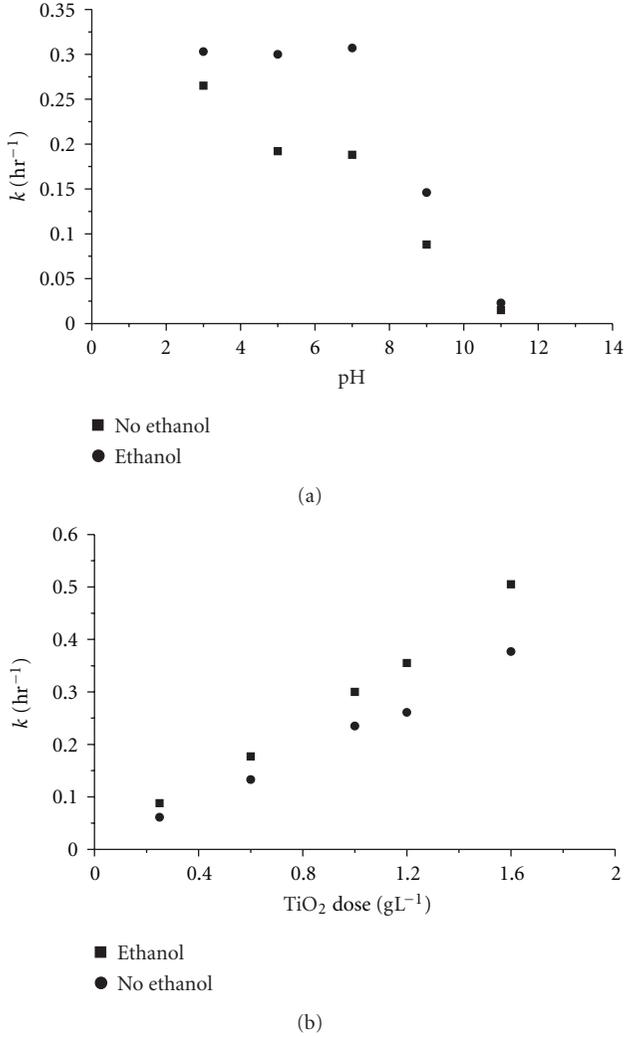


FIGURE 6: Relationship of the rate constant under different pH values and different TiO₂ dose.

different TiO₂ dose, and the influence of adding ethanol as the hole scavenger on the Cr(VI) removal rate was determined. The results are presented in Figure 6.

Adding ethanol facilitated the photoreduction of Cr(VI), but, at high pH values, the addition of ethanol did not achieve this result; when TiO₂ was added, ethanol promoted the Cr(VI) removal rate. Plotting $\ln[\text{TiO}_2]$ and $\ln k$ after adding ethanol and using the pseudo-first-order removal rate, the relationship of TiO₂ dosage and variations of Cr(VI) concentration could be determined as follows:

$$-r_E = \frac{d[\text{Cr}^{6+}]}{dt} = 0.3132[\text{Cr}^{6+}][\text{TiO}_2]^{0.81} \quad (R^2 = 0.9789). \quad (4)$$

When ethanol was added as the hole scavenger, the pseudo-first-order Cr(VI) removal rate was higher than before the addition.

The Cr(VI) removal rate was examined under nonreduced and reduced modified TiO₂ systems at the fixed pH = 3, with a 2.94 mM dose of ethanol as the organic hole

TABLE 1: The rate constant of reduction and nonreduction on the Cr(VI) concentration after the doping of metallic ions.

	Reduced			Nonreduced		
	0.5%	2.0%	5.0%	0.5%	2.0%	5.0%
Cu	0.110	0.101	0.129	0.111	0.097	0.104
Ag	0.131	0.129	0.156	0.107	0.123	0.136

TABLE 2: Surface area of P-25 TiO₂, 5% Ag/TiO₂ and 5% Cu/TiO₂.

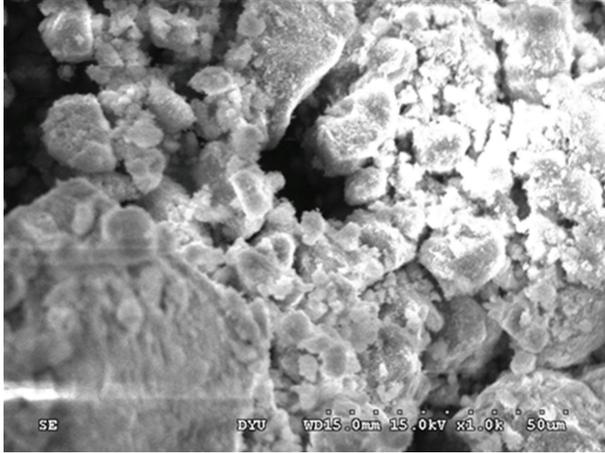
Material	Metals added (wt%)	Surface area (m ² g ⁻¹)
TiO ₂ (P-25)	—	53.61
	0.5	57.82
	5.0	59.38
Ag/TiO ₂	0.5	57.03
	2.0	58.42
	5.0	58.79

scavenger; the Cr(VI) removal reaction behaviors under various operational factors were solved by the pseudo-first-order reaction kinetic equation.

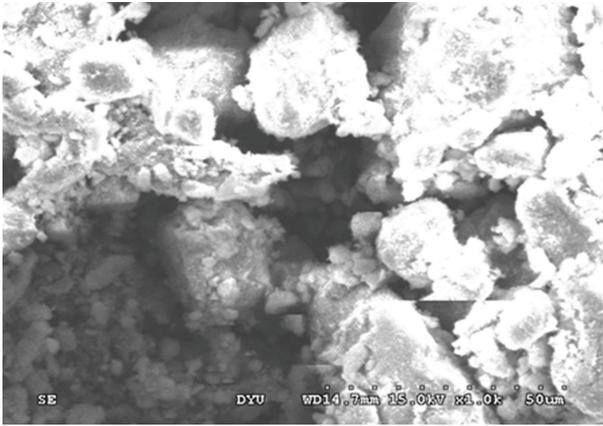
This section discusses the effects of reduction and nonreduction on the Cr(VI) concentration after the doping of metallic ions. The experimental results were as shown in Table 1. The Cr(VI) removal rate of reduced 5 wt% Cu/TiO₂ was 0.1298 hr⁻¹, which was 1.24 times that of the nonreduced. In the Ag-doped system, the Cr(VI) removal rates of the triple doping after reduction were higher than those of the nonreduced. The Cr(VI) removal rate of reduced 5 wt% Ag/TiO₂ was 0.156 hr⁻¹, 1.14 times higher than that of nonreduced 5 wt% Ag/TiO₂. Furthermore, the surface area of Ag/TiO₂ and Cu/TiO₂ from the BET surface area measurements was only slightly increased, as shown in Table 2. Figure 7 presents the surface structure and morphology of 5% Ag/TiO₂ before and after photocatalysis. It was clearly observed from SEM images that surface of catalyst was no difference between them.

For the experiment results of the two kinds of modified TiO₂, the removal rate simulated by the pseudo-first-order kinetic equation and the doped percent were plotted, as shown in Figure 8, to explore the relationship of two kinds of modified TiO₂ under the condition of reduced or nonreduced. As the figure clearly shows, reduced or not, the Cr(VI) removal rate of Ag(NO₃)₃-modified TiO₂ was higher than that of CuCl₂-modified TiO₂. These results were consistent with other studies [17, 18] discussion on the modified TiO₂ and TiO₂ reduction reaction. Ag had a higher electron capture, and Ag ions doped on TiO₂ played the role of an electron storage system to improve photocatalytic activity so as to quickly transfer electrons.

The Cr(VI) removal rates in the two systems with the initial Cr(VI) concentration of 20.0 mg L⁻¹, pH = 3, [M/TiO₂] = 1.0 g L⁻¹, and ethanol concentration of 2.94 mM are shown in Figure 9. The modified photocatalyst had a lower Cr(VI) removal rate than that of the nonmodified photocatalyst, with 5 wt% Ag/TiO₂ having the best Cr(VI)



(a)

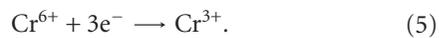


(b)

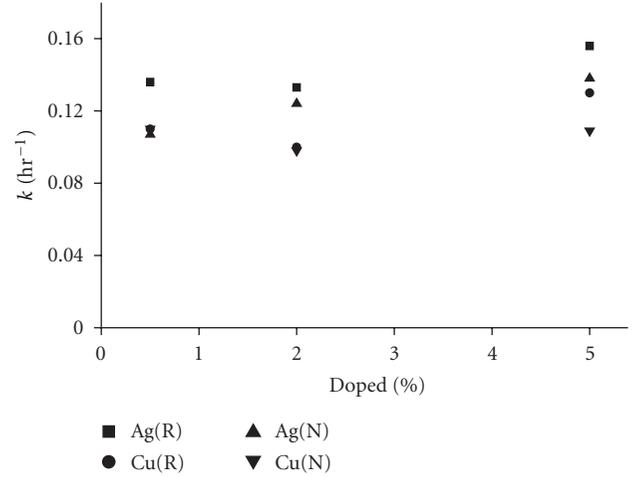
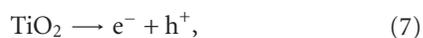
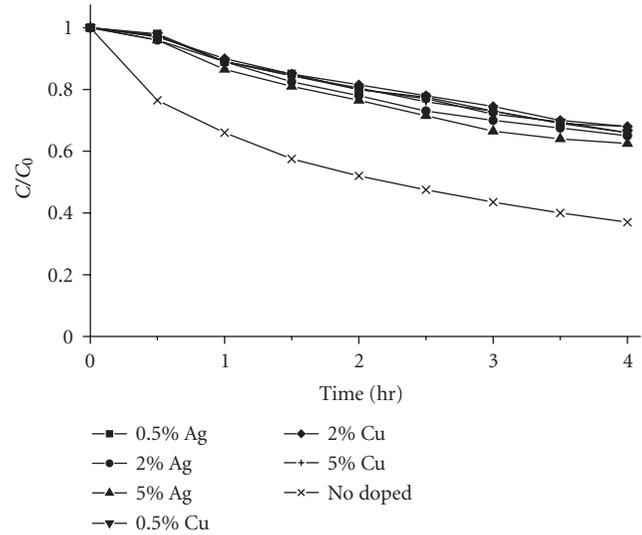
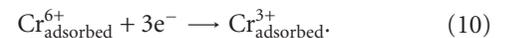
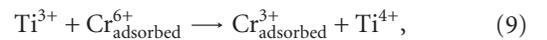
 FIGURE 7: SEM images of 5% Ag/TiO₂ (a) before photoreduction and (b) after photoreduction.

reduction rate of the modified photocatalysts, but a removal rate of less than 50%; the Cr(VI) removal rate of the nonmodified photocatalyst reached 64%. The experimental results were consistent with the results of the modified TiO₂ prepared by the other study [14, 15], and the Cr(VI) reduction rate after being modified was lower than that of the nonmodified.

The reduction of Cr(VI) by electrons in aqueous solution basically follows the following reactions:



Liu et al. [18] reported that Cr(VI) photocatalytic reduction by directly capturing photogenerated electrons is possible, but is mainly realized indirectly by getting electrons from surface Ti³⁺ of TiO₂ photocatalyst. The reactions were as follows [18]:


 FIGURE 8: Relationship of the rate constant on the photocatalytic reduction by modified TiO₂.

 FIGURE 9: Relationship of the Cr(VI) removal rates on the photocatalytic reduction by modified TiO₂.


During the photoreduction of Cr(VI) ions in aqueous solutions by UV/TiO₂ photocatalytic processes, the TiO₂ surface changed from the original white to light yellow after adsorption, and light green after the reaction. This meant that, after photoreduction, Cr(VI) deposited on the TiO₂ surface in the form of Cr(III). Comparing with the experimental results reported by previous researcher [11], chromium on the surface of TiO₂ particles was identified to be Cr(III), while no indication of the presence of Cr(VI) was observed.

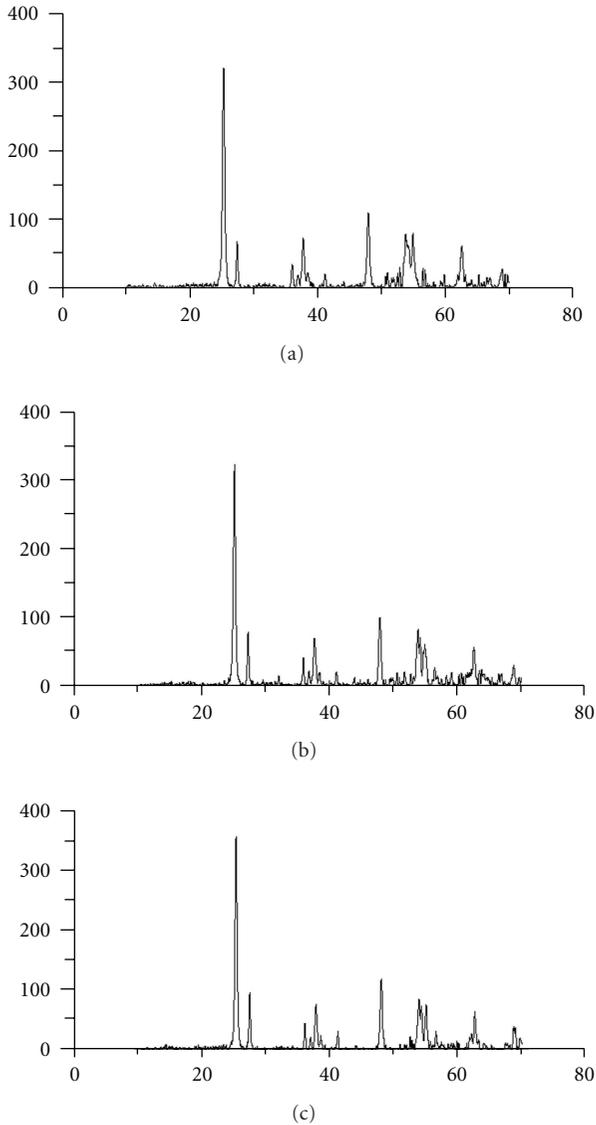


FIGURE 10: X-ray diffraction patterns of catalysts: (a) TiO_2 (P25), (b) 5% Ag/TiO_2 , and (c) 5% Cu/TiO_2 .

The impact of Cr(III) deposition on TiO_2 surface properties and structure after photoreduction was determined by XRD. The results are presented in Figure 10. For the XRD measurement, the crystal type analysis of doped 5% nonreduced Cu- and 5% nonreduced Ag-modified TiO_2 after reaction was made. The wave peaks appeared at the same angle, so it was concluded that Cr(III) deposition after reaction had no influence on the crystal type of TiO_2 .

4. Conclusions

The photoreduction reaction rate of Cr(VI) by UV/ TiO_2 photocatalytic process increased with the increasing TiO_2 dosage in the solution; from the pseudo-first-order model and Cr(VI) removal experiments, it was found that the

relationship of the pseudo-first-order Cr(VI) removal rate, TiO_2 dosage, and variations of Cr(VI) concentration was

$$-r_a = \frac{d[\text{Cr}^{6+}]}{dt} = 0.2344[\text{Cr}^{6+}][\text{TiO}_2]^{0.87}. \quad (11)$$

The Cr(VI) reduction rate was in a 0.87th power relation with the TiO_2 dosage. When ethanol was added as the organic hole scavenger, the relationship of the pseudo-first-order Cr(VI) removal rate, TiO_2 dosage, and variations of Cr(VI) concentration was

$$-r_E = \frac{d[\text{Cr}^{6+}]}{dt} = 0.3132[\text{Cr}^{6+}][\text{TiO}_2]^{0.81}. \quad (12)$$

The added ethanol facilitated the Cr(VI) reduction rate and resulted in a better reduction effect than when ethanol was not added. The photoreduction reaction rate of Cr(VI) by the UV/ TiO_2 photocatalytic process decreased with the increasing pH values of the solution. We found from the Cr(VI) removal experiment that as pH value increased, the reduction rate of dichromate ions gradually decreased because the increase in pH value reduced the adsorption of dichromate ions on the surface of the photocatalyst; also, at high pH value, $\text{Cr}(\text{OH})_3$ covered the surface active position of TiO_2 so that the trivalent chromium deposited on TiO_2 depressed the photocatalytic activity.

With the solutions at pH = 3, methanol, ethanol, and isopropanol were added as organic hole scavengers. Methanol and ethanol had the largest Cr(VI) removal rates of 0.3029 and 0.3066 hr^{-1} , respectively, at a concentration of 2.94 mM. With the increasing isopropanol concentration, the Cr(VI) removal rate gradually rose and reached 0.2848 hr^{-1} at 5.88 mM. In the photocatalytic reduction experiment of Cr(VI) by CuCl_2 and $\text{Ag}(\text{NO}_3)$ -doped TiO_2 , the $\text{Ag}(\text{NO}_3)$ -doped TiO_2 process had the better removal rate of Cr(VI), with the optimum removal rate of 38.1%, which was 1.04 times the 36.6% removal rate of the CuCl_2 -doped TiO_2 process. However, the removal rates of modified TiO_2 were lower than those of nonmodified TiO_2 .

Acknowledgments

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