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Removal of Copper (VI) from Aqueous Solution by Ag/TiO_2 Photocatalysis

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Chromium (VI) is present in effluent waters of several different industries such as electro-plating, metallurgy and chemical engineering. It is hazardous because it affects human physiology, accumulates in the food chain and causes several ailments. The stricter environmental regulations related to the discharge of heavy metals make it necessary to develop processes for Cr^{6+} removal from wastewater. The preferred treatment of Cr^{6+} contamination is reduction of Cr^{6+} to the less harmful Cr^{3+}. Compared to the possible secondary pollution brought by the traditional Cr^{6+} wastewater treatment method, TiO_2 photocatalytic reduction treatment exhibited more attraction (Colón G, Hidalgo C, Navýo J A 2001; Young K, Jung I-L, 2001).

TiO_2 photocatalytic reduction process, however, has not been widely applied in wastewater treatment due to some limits. High electron-hole pairs recombination rate significantly limit the rate of metallic compounds photocatalytic reduction on TiO_2 surface. Therefore, improvement of the activity by optimizing the composition of TiO_2-based photocatalyst is one of the most important tasks for technical applications of heterogeneous photocatalysis in future (Hoffmann M R, Martin S T, Choi W, et al 1995; Linsebigler A L, Lu G Q, Yates J T 1995). Therefore, in recent years, many investigations on the basic principles of photocatalysis and enhancement of the photocatalytic activity have been undertaken (Liu H, Ma H T, Li XA et al., 2003). For example, in our previous work, modification of TiO_2 photocatalyst to form nanosize silver cluster on the TiO_2 surface by silver deposition, which was found to accelerate the electron transfer and inhibited recombination (Liu SX, Qu ZP, Han XW, et al 2004a). However, the effectiveness of Ag/TiO_2 photocatalysis for Cr^{6+} reduction is seldom investigated. In the present work, proton starvation and photo-generated electron-hole recombination effect on Cr^{6+} reduction process were minimized or deleted, and then the photocatalytic activities of Ag/TiO_2 and TiO_2 for Cr^{6+} reduction were comparatively studied. The feasibility of removal of Cr^{6+} from aqueous solution by Ag/TiO_2 photocatalysis was evaluated. The mechanism for the enhanced activity of silver modification for Cr^{6+} photocatalytic reduction on TiO_2 was also proposed.

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MATERIALS AND METHODS

Titanium dioxide (TiO_2) (anatase form 100%) in all experiments was obtained from Aldrich. Silver was deposited on TiO_2 surface by photochemical impregnation method (Liu SX, Qu ZP, Han XW, et al 2004b). The amount of silver loading was 1.0 wt% (mass ratio, determined by Philips X-ray Fluorescence). Cr^{6+} aqueous solution was prepared by dissolving analytical grade $K_2Cr_2O_7$ in deionized water. H_2SO_4 and NaOH solutions were used to adjust the pH and nitrogen was used as gas.

A cylindrical quartz photoreactor surrounded with water a jacket was used for Cr^{6+} photocatalytic reduction, an 8 W UV lamp with a maximum emission at 253.7 nm was positioned inside the quartz vessel (Liu SX, Qu ZP, Han XW, et al 2004b; Li XZ, Liu H, Cheng L F et al 2003). The reactor was maintained at 28 ±1℃ by a thermostat and the out layer of the reactor was wrapped with tinfoil to reduce the light energy loss. 0.25 g photocatalyst powder was added into 250 ml of aqueous reaction solution with model compound. Prior to photo-reduction, the suspension was magnetically stirred in a dark condition for 30 min in order to establish a Cr^{6+} adsorption/desorption equilibrium. During given time intervals, the analytical samples were withdrawn from the suspension and immediately centrifuged at 4000 r/min for 5 min. Then the supernatant was used for Cr^{6+} analysis.

The concentration of Cr^{6+} was determined spectrophotometrically by a Varian 50 UV-Vis spectroscopy at 290 nm. pH was determined by a digital pH meter. The specific surface area of photocatalyst was determined at 77 K using a micrometrics ASAP 2010 automatic apparatus on the basis of BET equation.

RESULTS AND DISCUSSION

Photocatalytic reaction mainly occurred on the surface of TiO_2, pre-adsorption of substrate can enhance the charge carrier transfer and capture. Adsorption of Cr^{6+} on TiO_2 surface is a crucial step for the subsequent reduction. The adsorption of Cr^{6+} on TiO_2 and Ag/TiO_2 under various pH conditions are shown in Figure1. It can be seen that the adsorption curves of TiO_2 and Ag/TiO_2 appeared the same tendency, and although the Cr^{6+} adsorption amount on the TiO_2 is a bit higher, the difference between the two samples is slight. Indicating that the Cr^{6+} adsorption behaviors on TiO_2 and Ag/TiO_2 are the same. Moreover, the BET surface area results showed that the surface area of unloaded TiO_2 was 10.47 m^2/g, while 9.59 m^2/g for silver loaded catalyst. The slight decrease of adsorption capacity may be attributed to the decrease in the Ag/TiO_2 surface area.

The influence of oxygen was a controversial subject for photocatalytic reduction process. For example, a detrimental effect has been reported (Muñoz J, Domènech X 1990). Since the molecular oxygen present in the reactor could work as a competitor for the photogenerated electrons. In contrast, no particular effect of oxygen has been observed in other cases (Iwata T, Ishikawa M, Ichino R, et al

2003), and even a beneficial effect has been found with TiO_2 or ZnO (Lin W Y, Wei C, Rajeshwar K 1993). Giménez et al proposed that the reduced form of oxygen could contribute to the reduction of chromate species to Cr^{3+}, oxygen only being an intermediate in the transfer of electrons (Sabaté J, Anderson M A, Gimenez J, March S C, et al 1992).

In this work, the Cr^{6+} photocatalytic reduction was performed in N_2 atmosphere in order to remove the possible effect of oxygen. Figure 2 shows the data of control experiment. It revealed that under UV irradiation with absence of photocatalyst, no Cr^{6+} reduction occurred, although Cr^{6+} exhibit strong light absorption in UV region.

The reduction of Cr^{6+} by electrons in acid aqueous solution occurs according to the following reactions (Liu SX, Qu ZP, Han XW, et al 2004b):

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O \qquad E^0 = 0.98 \text{ eV (SHE)} \qquad (1)$$

Under neutral medium as follows:

$$CrO_4^{2-} + 8H^+ + 3e^- \longrightarrow Cr^{3+} + 4H_2O \qquad E^0 = 0.56 \text{ eV (SHE)} \qquad (2)$$

And under basic medium:

$$CrO_4^{2-} + 4H_2O + 3e^- \longrightarrow Cr(OH)_3 + 5OH^- \qquad E^0 = 0.24 \text{ eV (SHE)} \qquad (3)$$

One of the most important parameters that determines the efficiency of reduction process is the standard redox potential of the involved metallic couple related to the conduction band and valence band of TiO_2. Only those species with reduction potentials much more positive than the conduction band can be photocatalytically reduced. According to the equations (1)-(3), with the increase of pH values, the redox potential of Cr^{6+} decreases, the thermodynamic driving force for Cr^{6+} photocatalytic reduction does become lower as the medium pH increases, and the reduction becomes more difficult. In addition, the Cr^{6+} photocatalytic reduction is favored at acidic or neutral condition because of its proton starvation nature, when one Cr^{6+} was reduced to Cr^{3+}, 7 and 8 protons were consumed respectively.

Proton supply is also crucial to the kinetic and dynamic of Cr^{6+} photocatalytic reduction. Is was reported that with the pH decrease the reaction kinetics shifted from the first-order to the zero-order reaction (Muñoz J, Domènech X 1990). In this work, the proton supply was controlled by adjusting the solution pH. As can be seen from Figure 3 and Figure 4, under higher pH, the Cr^{6+} decreased very slowly and 10% Cr^{6+} was removed after 120 min reaction. With the pH decrease, the Cr^{6+} reduction reaction proceeded more and more rapidly. At pH 2, 35% Cr^{6+} was removed after 120 illumination. The results indicated that Cr^{6+} reduction by UV-Ag/TiO_2 process was more effective than UV-TiO_2 process under the same conditions except for basic solution. Almost complete Cr^{6+} reduction could achieve within 400 mins for Ag/TiO_2, but 1200 mins for TiO_2. With the decrease of system pH, the activity of Ag/TiO_2 enhanced higher.

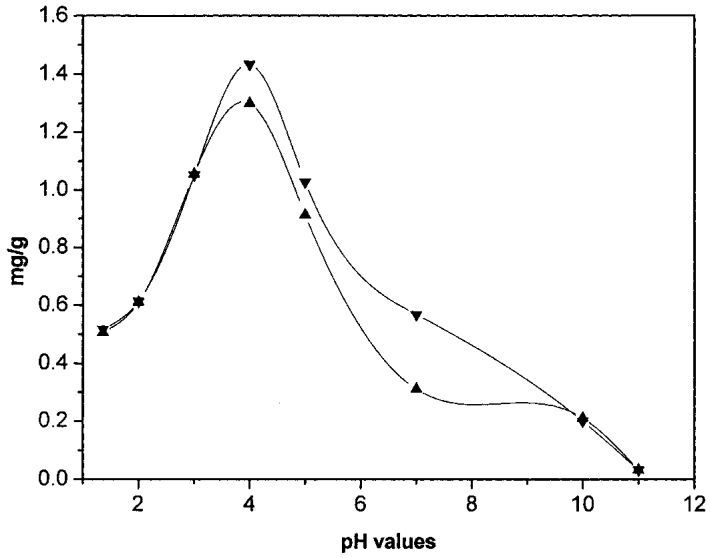

Figure 1. Adsorption of Cr^{6+} under various pH conditions.
▼-TiO_2; ▲-Ag/TiO_2.

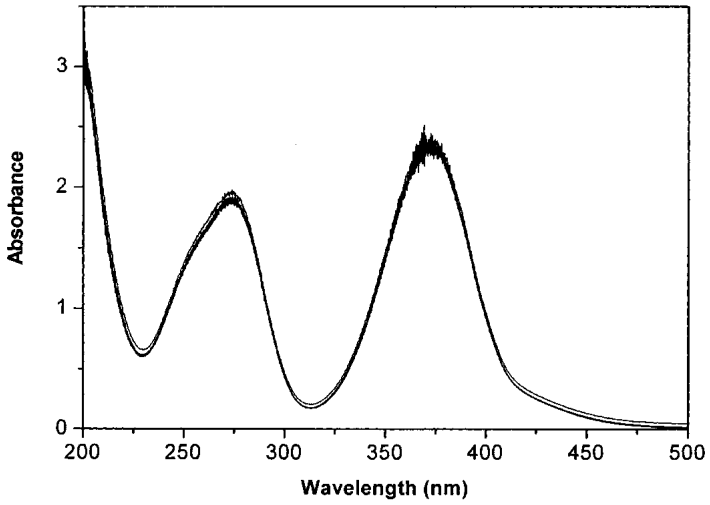

Figure 2. Direct photolysis of Cr^{6+} aqueous solution.
From top to bottom were 0, 20, 40, 60, 80, 100, 120 min respectively.

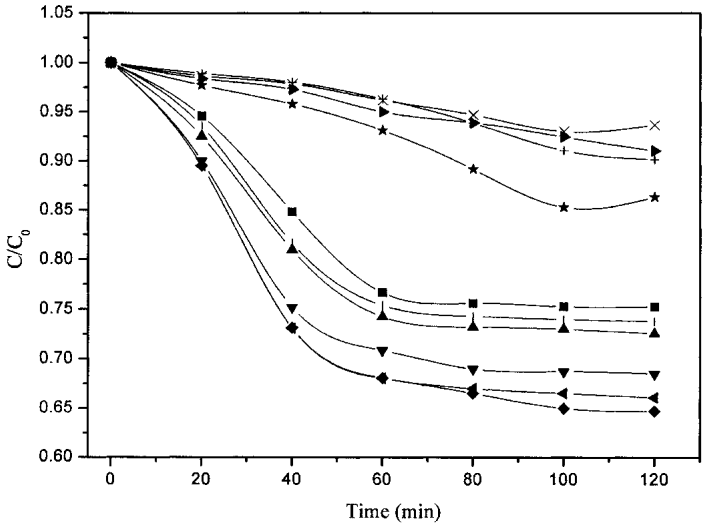

Figure 3. Effect of pH on Cr^{6+} photocatalytic reduction.
×pH=10, TiO_2; ▶ pH=10, Ag/TiO_2; +pH=7, TiO_2; ★pH=2, TiO_2;
■pH=7, Ag/TiO_2; | pH=5, Ag/TiO_2; ▲pH=4, Ag/TiO_2;
▼pH=3, Ag/TiO_2; ◀ pH=1.4, Ag/TiO_2; ◆pH=2, Ag/TiO_2.

The Cr^{6+} adsorption equilibrium results revealed that the amount of Cr^{6+} adsorbed on the surface of Ag/TiO_2 almost the same that on TiO_2 surface. So, the higher reduction activity of Ag/TiO_2 photocatalyst was caused by the higher number of free electrons or electron –supply centers.

Judging from the trend from Figure 1 and 3, the pH effect on the photocatalytic reduction of Cr^{6+} is somewhat different from the adsorption studies discussed in the previous section. In which the optimum solution pH for the adsorption of Cr^{6+} on TiO_2 particles was about pH 4 (Figure.1), but the highest reduction efficiency was obtained at pH 2 (Figure.3). This result indicated that Cr^{6+} adsorption itself appeared to be a less critical factor than the proton supply at the surface, and the rate-determining step (RDS) for the photocatalytic reduction of Cr^{6+} is the surface reaction step after Cr^{6+} was adsorbed on TiO_2 particles, therefore, the pH effect on the adsorption step was not echoed very clearly in the following surface-reaction step. Moreover, it suggested that the most effective means to accelerate the Cr^{6+} reduction should be focused on the surface-reaction step, but not the adsorption step (Liu H, Li, X Z., Leng Y J, et al, 2004).

Recombination of photogenerated carriers is a negative factor for Cr^{6+} photocatalytic reduction. If photogenerated holes are rapidly scavenged at the TiO_2 particles surface, more electrons are available for reduction of the target oxidant. In Cr^{6+} photocatalytic transformed to Cr^{3+} reaction, two conjugate

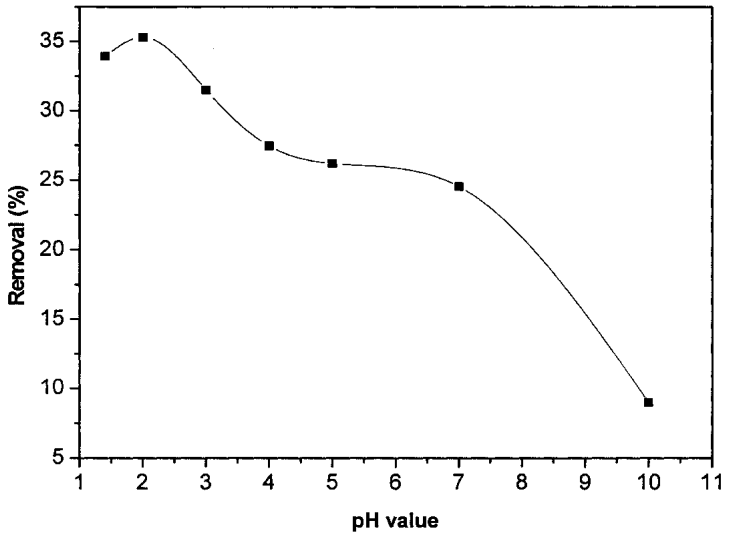

Figure 4. Cr^{6+} photocatalytic reduction efficiency under different pH conditions on Ag/TiO_2.

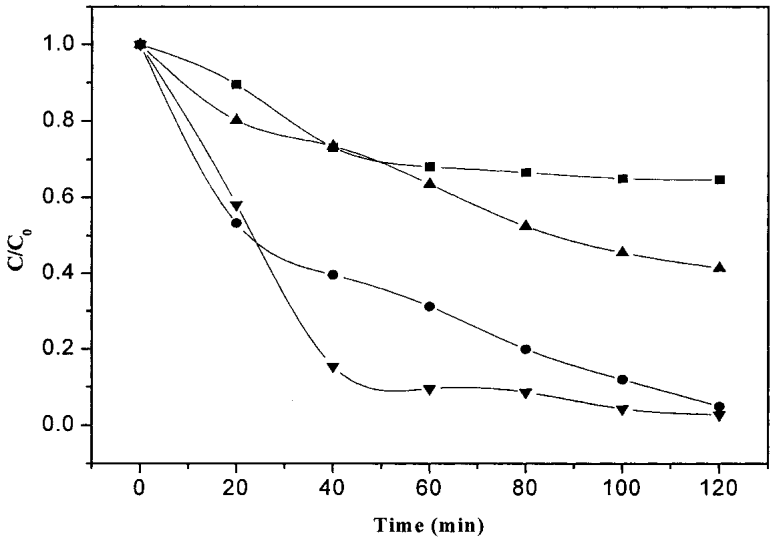

Figure 5. Effect of sacrificial hole capture additives on the photocatalytic reduction of Cr^{6+}.
■—TiO_2;●—Ag/TiO_2;▲—TiO_2 + citric acid;▼—Ag/TiO_2 + citric acid

reactions are present: oxidation induced by holes and reduction induced by electrons. For the successive one-electron reduction of Cr^{6+} (equation 4), the reaction is very slow in the absence of hole scavengers because the anodic reaction is the oxidation of water by holes (equation 5), which is kinetically sluggish (Chenthamarakshan C R, Rajeshwar K 2000).

$$Cr^{6+} \xrightarrow{e^-} Cr^{5+} \xrightarrow{e^-} Cr^{4+} \xrightarrow{e^-} Cr^{3+} \quad (4)$$

$$1/2H_2O + h^+ \longrightarrow 1/4O_2 + H^+ \quad (5)$$

Some studies have found that the addition of organic acids can enhance the photocatalytic reduction rate of Cr^{6+} (Chenthamarakshan C R, Rajeshwar K 2000; Colón G, Hidalgo C, Navýo J A 2001). In the present work, citric was also added as hole scavengers to enhance the conjugate reaction rate, and minimize or eliminate the hole-electron recombination negative effect on the photocatalytic reduction of Cr^{6+}. Figure 5 shows the Cr^{6+} reduction efficiency under various amount of citric addition at pH 2. It can be seen that the citric acid enhances the Cr^{6+} photocatalytic reduction both on TiO_2 and Ag/TiO_2.

When citric acid was added into the reduction system, the possibility of electron capture by Cr^{6+} was promoted because holes were scavenged by the additive, and the photocatalytic reduction rate of Cr^{6+} was subsequently increased both for UV-TiO_2 and UV-Ag/TiO_2 system. But the enhanced degree for UV-Ag/TiO_2 was more significant than UV-TiO_2 system under the same condition. This result revealed that after photogenerated holes were effectively captured, the number of free electrons or electron-supple center existing on the surface of Ag/TiO_2 were higher than that of TiO_2. In addition, the higher efficiency of UV-Ag/TiO_2 process revealed that Ag/TiO_2 photocatalysis is an advantageous method for Cr^{6+} removal.

Cr^{6+} photocatalytic reduction by directly capturing photo-generated electrons is possible, but mainly reduced indirectly by getting electrons from surface Ti^{3+} of TiO_2 photocatalyst, the reactions were as following (Colón G, Hidalgo C, Navýo J A 2001):

$$Cr^{6+}_{suspension} \longrightarrow Cr^{6+}_{adsorbed} \quad (6)$$

$$TiO_2 \xrightarrow{h\nu} e^- + h^+ \quad (7)$$

$$Ti^{4+} + e^- \longrightarrow Ti^{3+} \quad (8)$$

$$Ti^{3+} + Cr^{6+}_{adsorbed} \longrightarrow Cr^{3+}_{adsorbed} + Ti^{4+} \quad (9)$$

$$Cr^{6+}_{adsorbed} + 3\,e^- \longrightarrow Cr^{3+}_{adsorbed} \quad (10)$$

For UV irradiated TiO_2, there are two kinds of Ti^{3+} produced: inner Ti^{3+} and surface Ti^{3+}. The inner Ti^{3+} usually acts as recombination center which is detrimental to photocatalytic activity. Surface Ti^{3+} is the most reactive center for photocatalytic process (Liu H, Ma H T, Li XZ, et al, 2003). It provides unique site

for oxygen chemically adsorption (Sun B; Alexandre V V; Panagiotis G S (2003). Also, since the transfer of electrons to adsorbed Cr^{6+} was the rate determining step (surface-reaction step), so the reactive species for Cr^{6+} reduction should be surface Ti^{3+}.

Because the Fermi level of TiO_2 is higher than that of loaded silver catalyst, silver deposits behave as sites where electrons accumulate which resulted in photogenerated electrons transfer from TiO_2 to silver, better separation of electrons and holes would be achieved. These electrons could react with surface Ti^{4+} to form Ti^{3+} that is reactive center on the TiO_2 surface. Meanwhile the amount of recombination center of inner Ti^{3+} decreased. In addition, the loaded silver particle can transfer one electron to the TiO_2 surface Ti^{4+} to form surface Ti^{3+}. This suggested that the recombination was slowed and the generation of surface Ti^{3+} were accelerated (Liu SX, Qu ZP, Han XW, et al 2004a).

More surface Ti^{3+} involved in the Cr^{6+} photocatalytic reduction was the main cause for the higher activity of Ag/TiO_2. The strong mobility of electrons

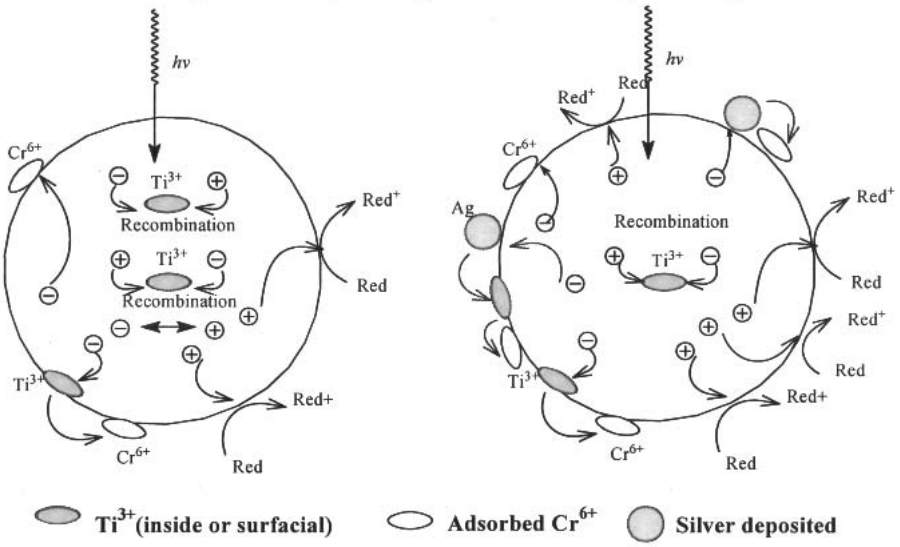

Figure 6. Mechanism for the enhanced activity of Ag/TiO_2.

accumulated on the surface of loaded silver also plays a certain positive role.

Because the high separation efficiency of charge carriers were achieved for Ag/TiO_2 catalyst, once the rate limited factors: proton starvation hole-electron recombination were minimized or deleted, the number of effective free electrons or electron supply center was higher for Ag/TiO_2 than TiO_2.The mechanism for the enhanced activity was schematically illustrated in Figure 6.

In the present work, UV-Ag/TiO_2 photocatalytic system exhibited high efficiency for Cr^{6+} transformation into Cr^{3+}. Thus UV-Ag/TiO_2 photocatalysis is an

advantageous alternative for Cr^{6+} removal from aqueous effluent. The higher reduction activity of Ag/TiO_2 photocatalyst was mainly attributed to the higher number of surface Ti^{3+}. The strong mobility of electrons accumulated on silver also plays positive role to a certain extent.

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