Removal of Aqueous Cr(VI) by a Combination of Photocatalytic Reduction and Coprecipitation

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Semiconductor photocatalytic reduction is a relatively new technique for the removal of dissolved toxic metal ions from wastewater. In this paper, adsorption and photocatalytic reduction of Cr(VI) to Cr(III) in aqueous solutions by UV/TiO₂ photocatalysis has been investigated. It has been observed that the pH of the solution plays an important role in this reaction. An acidic medium is favorable for Cr(VI) photocatalytic reduction, where 94% of Cr(VI) was photoreduced within 1 h at pH 3 when 2 g/L of TiO₂ was used as the slurry. An adsorption study shows that the photocatalytic reduction mainly occurs on the surface of TiO₂. The presence of Fe(III) improved the photocatalytic reduction of Cr(VI) because it was observed that an additional reaction between Fe(II) and Cr(VI) takes place in the UV/TiO₂ reduction process. A new combination of photocatalytic reduction and metal ion coprecipitation using Fe(OH)₃ for complete removal of aqueous Cr [Cr(VI) as well as Cr(III)] was designed, which reduced the chromium concentration from 30 ppm to 17 ppb for a simulated wastewater. Thermodynamic analysis showed that TiO₂ cannot photoreduce Cr(III) to Cr(0), but reduction is possible with ZnS. When kinetic experiments were performed, it was observed that more than 86% of Cr(III) could be photoreduced to Cr(0) in 5 h with a ZnS catalyst.

Introduction

The interest in the application of semiconductor photocatalysis for wastewater treatment has grown exponentially over the past 10 years.¹ This technology is based on the reactive electrons and holes generated on the surface of a semiconductor when it is illuminated by light with energy greater than its band-gap energy. These electrons and holes either recombine or become involved in redox reactions. Any species with a reduction potential more positive than that of the conduction band of the semiconductor can consume electrons, while any species with an oxidation potential more negative than that of the valence band can consume the holes to complete the redox reaction cycle. Several metal oxide and sulfide semiconductors can be used to promote a wide range of chemical reactions because they have suitable band-gap energies, Eᵣ. They include TiO₂ (Eᵣ = 3.2 eV), ZnO (Eᵣ = 3.2 eV), and ZnS (Eᵣ = 3.6 eV). Among these semiconductors, TiO₂ is the most widely used photocatalyst because of its favorable chemical property, high stability, and low cost.² The band-gap energy of TiO₂ is 3.2 eV, equivalent to UV light of 380 nm, and therefore is photoexcited by near-UV illumination. The holes that are generated on TiO₂ are highly oxidizing, and there has been abundant literature on the utilization of TiO₂ in the oxidative degradation of organics. In addition to organics, the inorganic species with a reduction potential more positive than that of the conduction band of the semiconductor can consume the electrons and complete the redox reaction cycle. Recently, increasing attention has been paid to the photocatalytic reduction of inorganic contaminants. The application of the TiO₂ photocatalytic reduction process is reported to effectively remove various toxic metal ions, such as Hg(II),³ Ag(I),³ As(V)/As(III),⁵ and Cr(VI).⁶

Figure 1 illustrates the position of the conduction band of semiconductors¹⁶ and reduction potentials of relevant metal ions¹⁷ as a function of pH.

Besides TiO₂, the application of ZnO¹²–¹⁴ and CdS¹⁵ in the photocatalytic reduction of Cr(VI) to Cr(III) has also been reported.

Figure 1 illustrates the position of the conduction band of various semiconductors as a function of pH. The figure is generated using data from the literature.¹⁶,¹⁷ Comparing them with the reduction potentials of chromium in different forms, one can see that (a) Cr(VI) can be photocatalytically reduced to Cr(III) by most semiconductors, while only ZnS can photoreduce Cr(III) to Cr(0), (b) the reduction potential of Cr(VI) to Cr(III) is pH dependent, and the thermodynamic driving force for Cr(VI) reduction decreases with increasing pH, indicating that the photocatalytic reduction of Cr(VI) is favored at low pH, and (c) if Fe(III) or O₂ is present in the...
solution, they would compete with photoreduction of Cr(VI) because their reduction potentials are comparable. Although there are a number of studies on the photocatalytic reduction of Cr(VI) over semiconductor catalysts, little information is reported related to coreactants except oxygen. In this paper, a detailed investigation of the photocatalytic reduction of Cr(VI) in the presence of ferric ions and in the presence (and absence) of dissolved oxygen is presented.

Chromium is a typical component in many wastewaters, and there have been many studies to determine the effectiveness of water treatment processes in removing aqueous chromium ions. In these studies, the first step is always the conversion of Cr(VI) to Cr(III) by reducing agents, followed by the removal of Cr(III). Lime softening, alum coagulation, and iron coagulation (using ferric sulfate) have been found to be capable of removing Cr(III). Recently, the research focus has shifted to overcoming the limitations of the conventional pump-and-treat approach. Photocatalytic reduction of Cr(VI) is a relatively new technology. However, the UV/TiO₂ photocatalysis can only reduce Cr(VI) to Cr(III), which is still toxic to humans. Hence, to achieve a nearly complete removal of chromium from water, a new combination of photocatalytic reduction and metal ion coprecipitation is proposed in this study. In this paper, we also report the photocatalytic reduction of Cr(III) using ZnS because Figure 1 clearly indicates that the reduction of Cr(III) to the elemental form is thermodynamically possible by ZnS.

**Experimental Methods**

TiO₂ Degussa P25 was used as the photocatalyst in most experiments. Some experiments were carried out using other semiconductors, such as ZnO (Aldrich Chemicals) and ZnS (Riedel-de Haen Chemicals). The Brunauer–Emmett–Teller specific surface areas of TiO₂, ZnO, and ZnS, measured by nitrogen adsorption at −196 °C, were found to be 43.8, 5.9, and 6.4 m²/g, respectively. The following chemicals (all reagent grade) were prepared in ultrapure water. X-ray photoelectron spectroscopy (BDH Chemicals), and formic acid and Zn(NO₃)₂ (Merck Inc.).

Experiments were carried out in a 200-mL cylindrical Teflon reactor at room temperature (295 ± 2 K). A 150-mL reaction mixture inside the reactor was maintained in suspension by a magnetic stirrer. The pH adjustments were made using dilute HNO₃ and NaOH. Irradiation was provided by a 450-W Xe arc lamp (Oriel model 6266) with a UV–vis band-pass filter (Oriel model 59450) placed on the top of the reactor. The light emission is above the wavelength of 290 nm, and the light intensity at the level of the reactor bottom was found to be about 22.0 W/m² between 290 and 400 nm measured using a UVItec RX-003 radiometer. This light was employed as incident light in most experiments. In the experiment of lower light intensity, a neutral density filter (Oriel model 59680) was mounted on the band-pass filter. It can attenuate ~58% of the incident light intensity. The experimental setup is shown in Figure 2, and a more detailed description can be found elsewhere. In all of the photocatalysis experiments described below, formic acid is used to remove photogenerated holes in order to allow the redox reaction to continue. The concentration of formic acid in the reaction mixture was 20 mM in all experiments reported in this work because above this concentration no significant improvement in rate was observed. The suspensions are initially maintained under agitation in the dark for 60 min to allow for adsorption—desorption equilibrium to be established. During the irradiation, aliquots of the reaction solution were withdrawn intermittently.

All samples were filtered through a 0.45-μm Whatman Autovial poly(tetrafluoroethylene) filter before analysis. Inductively coupled plasma (ICP; Perkin-Elmer Optima 3000DV) was used for measuring the total iron and chromium concentrations. The concentrations of Cr(VI) and Fe(II) were analyzed colorimetrically using a Shimadzu 1240 UV–vis spectrophotometer. Cr(VI) was analyzed using the 1,5-diphenylcarbazide method, and Fe(II) was analyzed using the Ferrozine method. The ferrion concentration was obtained by subtracting the ferrous ion concentration from the total iron concentration measured by ICP. The Cr(III) concentration was obtained by subtracting the Cr(VI) concentration from the total chromium concentration. The pl of the TiO₂ particles in water was determined using a Brookhaven ZetaPlus ζ potential analyzer. Experimental TiO₂ suspensions for ζ potential analysis were prepared in ultrapure water. X-ray photoelectron spectroscopy (XPS) was performed on the AXIS-His spectrometer (Kratos Analytical Ltd., Manchester, England) using a monochromatic Al Kα X-ray source (1486.6-eV photons) at a constant dwell time of 100 ms and a pass energy of 40 eV.

**Results and Discussion**

**Effect of the pH on the Photocatalytic Reduction of Cr(VI).** A series of experiments were conducted at different pH values ranging from 2.5 to 9, containing 600 μM Cr(VI) and 2 g/L of catalysts (TiO₂ or ZnO) in order to investigate photocatalytic reactions of Cr(VI). Under illumination with the UV lamp, the Cr(VI) solution gradually lost its original yellow color, while the originally white TiO₂ and ZnO turned pale green. According to the preliminary thermodynamic analysis (Figure 1), the product of the TiO₂ (or ZnO) photocatalytic reduction of Cr(VI) should be Cr(III). Figure 3 shows the temporal profiles of Cr(VI) reduction by UV/TiO₂ (and UV/ZnO) at different pH values. The figure shows the change of concentration for the photocatalytic reduction only (i.e., the results shown are obtained after it was ascertained that an adsorption equilibrium has been attained and the lamp was turned on) and indicates that reduction rates increase with decreasing pH. Because Cr₂O₇²⁻ ions are the predominant species at medium to low pH values, the reduction of Cr(VI) by...
photogenerated electrons can be described as follows:

\[
\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \quad (1)
\]

On the basis of the trends in Figure 1, the reduction potential of the \(\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}\) couple shifts 138 mV per pH unit to more cathodic potentials, whereas the conduction band of the semiconductor shifts 59 mV per pH. Consequently, the thermodynamic driving force for the reduction of \(\text{Cr}(\text{VI})\) decreases by 79 mV with an increase of pH by one unit. The decreasing reaction rate may also be attributed to the deposition of \(\text{Cr(OH)}_3\) on the catalyst surface at pH values above 5. It has also been reported that TiO2 may deactivate at pH > 4.5.

The kinetic experiments were conducted at different pH media to study the adsorption behavior of \(\text{Cr(VI)}\) on TiO2 particles as well as on ZnO particles. The experimental results shown in Table 1 indicate that the adsorptivity of \(\text{Cr(VI)}\) decreases with increasing pH. The trend is consistent with that reported by Prairie et al.3

Because the initial concentration of \(\text{Cr}(\text{VI})\) involved in this study was low, the adsorption kinetics can be described by a simplified first-order rate equation:

\[
-\frac{d[\text{Cr(VI)}]}{dt} = k_{\text{ads}}C \quad (2)
\]

\[
\ln(C_{A0}/C_A) = k_{\text{ads}}t \quad (3)
\]

where \(k_{\text{ads}}\) is the adsorption constant and \(C_{A0}\) and \(C_A\) are the \(\text{Cr(VI)}\) concentrations at the initial time and time \(t\). The \(k_{\text{ads}}\) values are listed in Table 1. Generally, the kinetics of the photocatalytic reaction follow a Langmuir-Hinshelwood mechanism in heterogeneous media, with the initial rate, \(r\), being

\[
r = k_{\text{rxn}} \frac{KC}{1 + KC} \quad (4)
\]

where \(K\) is taken to represent the Langmuir adsorption constant, \(k\) is a “reactivity constant”, providing a measure of the reactivity of the catalyst surface with the substrate, and \(C\) is the initial concentration of the substrate. For dilute solutions, such as 6 \(\times\) \(10^{-4}\) M in this study, the reaction could be reduced to first order, with \(k/K\) being the rate constant:

\[
\ln(C_{A0}/C_A) = k_{\text{rxn}}t \quad (5)
\]

The \(k_{\text{rxn}}\) values of the \(\text{Cr(VI)}\) reduction with \(r^2\) of linear regression at different pH media are listed in Table 2. The pH effect on the photocatalytic reduction of \(\text{Cr(VI)}\) is somewhat similar to the adsorption of \(\text{Cr(VI)}\) on TiO2 particles. Furthermore, the comparable rate constants for photocatalytic reduction and adsorption of \(\text{Cr(VI)}\) indicate that adsorption of \(\text{Cr(VI)}\) is the rate-determining step.

Although the photocatalytic reduction of \(\text{Cr(VI)}\) in TiO2 suspensions is favored at low pH, the case for ZnO is different from that for TiO2. Because ZnO, unlike TiO2, can partially dissolve in an acidic solution and be photodecomposed to \(\text{Zn(II)}\):

\[
\text{ZnO} + 2\text{h}^+ \rightarrow \text{Zn(II)} + \frac{1}{2}\text{O}_2 \quad (6)
\]

experiments involving ZnO were carried out in a basic solution. As shown in Figure 1, at high pH values, the thermodynamic driving force for the reduction of \(\text{Cr(VI)}\) by ZnO is much smaller than that by TiO2 and the \(\text{Cr(VI)}\) adsorption on ZnO (shown in Table 1) was less than that on TiO2. Thus, the rate of \(\text{Cr(VI)}\) photoreduction in a ZnO suspension being lower than that in a TiO2 suspension (Figure 3) can be ascribed to the pH value. Moreover, it has been observed that \(\text{Zn}^{2+}\) is produced at pH 7.3 as a result of ZnO photocorrosion.

The results reported in Figure 3 were found to follow first-order rate dependence. The first-order reaction rate constant, \(k_{\text{rxn}}\) (\(\text{min}^{-1}\)), were determined for each pH by
least-squares regression, and the results are shown in Figure 4. It was observed that the reaction rate constant decreases linearly with an increase of the pH, and the pH dependence is given by

$$k \text{ (min}^{-1}) = 0.0442 - 0.00433 \text{pH}$$  \hspace{0.5cm} (7)

**Effect of HCOOH on the Photocatalytic Reduction of Cr(VI).** Previous studies5,23,24 on the influence of organic additives on metal ion reduction in UV-irradiated TiO2 suspensions reveal that the photoreduction of metal ions can occur by two pathways: One is a direct pathway where metal ions are reduced by reaction with the conduction band electrons on the TiO2 surface; another is an indirect pathway where metal ions are reduced by aqueous radical species. The following steps create these radicals:

$$\text{TiO}_2 \xrightarrow{\text{hv}} h^+ + e^-$$  \hspace{0.5cm} (8)

$$h^+ + RH \rightarrow ^*R + H^+$$  \hspace{0.5cm} (9)

$$h^+ + H_2O \rightarrow ^*OH + H^+$$  \hspace{0.5cm} (10)

$$^*OH + RH \rightarrow ^*R + H_2O$$  \hspace{0.5cm} (11)

where $h^+$ is the hole generated on the TiO2 surface. Organic radicals, such as $^*R$, are normally highly reducing.23 For example, the reduction potential of HCOO$^-$/CO2 is $-1.7 \text{ V vs SHE}$,24 which is negative enough to reduce Cr(VI).

Generally, the adsorption is mainly attributed to the surface properties of the substrate. TiO2 Degussa P25 has been reported as a nonporous mixture of anatase and rutile with a mass ratio25 of 70:30. The zeta potential of Degussa P25 in an aqueous solution as a function of pH are presented in Figure 5. The isoelectric point, pl, was $\approx 7.2$. This is in agreement with the value of the point of zero charge (around pH 6.7–7.5).8,25 Consequently, it can be assumed that the amount of positive charges on the TiO2 surface decreases with increasing pH until reaching zero at pH 7.2. For solution pH greater than 6, the groups with negative charges on the TiO2 surface are assumed to increase gradually; hence, both Cr(VI) oxyanions and COO$^-$ (pKa[HCOO$^-$/ COO$^-$] = 1.4) are repelled, and the adsorption is reduced at higher pH values. The high pH has a negative effect on the Cr(VI) reduction through direct electron transfer on the surface of TiO2 due to the electrostatic repulsion between TiO2 particles and Cr(VI) oxyanions. On the contrary, the rate of Cr(VI) reduction by free radicals increases as a result of more free COO$^-$ repulsed by TiO2 particles in the bulk solution. Figure 3 shows the reduction rate of Cr(VI) decreasing by increasing pH regardless of the increase of COO$^-$ in the bulk solution. Thus, the influence of pH on Cr(VI) photocatalytic reduction suggests that photocatalytic reduction of Cr(VI) is mainly through direct electron transfer on the surface of TiO2.

**Effect of Ferric Ion on Cr(VI) Reduction.** Figure 6 shows the Cr(VI) reduction profiles at pH 2.5 with 0.4 g/L of TiO2 in the absence and in the presence of Fe(III). The rather dramatic effect of ferric ions on the Cr(VI) reduction profile can be seen. Similar results were reported for the reduction of Cr(VI) by the UV/TiO2 process for solution pH between 4 and 8 by Munoz and Domenech.25 They assumed that the higher yield obtained for the Cr(VI) photoreduction was due to the iron(III) and chromium(III) hydroxides, which can maintain the pH during the whole process. However, the formation of hydroxides can be ruled out because the aqueous solution in our experiments was maintained at pH 2.5. Previous authors4 have reported that a ferrous ion generated by a photocatalytic reduction of Fe(III) had a promoting effect on the reduction of Hg(II) in illuminated TiO2 systems. To further prove that this mechanism is operative here, the reduction of Fe(III) in the Cr(VI)/TiO2 photocatalysis system was measured (Figure 7). As the Cr(VI) concentration decreased toward zero upon UV irradiation, the ferric ion level remained almost constant initially and then decreased when the Cr(VI) concentration was very low. The reduction of Fe(III) in this system is somewhat different from photocatalytic reduction of Fe(III) in the absence of Cr(VI) (Figure 7). Table 3 summarizes Fe(III) removal
by adsorption only. This demonstrates that TiO₂ has very high adsorption capacities for Fe(III) (compared to Cr(VI) shown in Table 1) and an adsorption equilibrium could be established within a few minutes. Therefore, when both Cr(VI) and Fe(III) are present in the solution, Fe(III) is preferably adsorbed on TiO₂ and, subsequently, photoreduced to Fe(II) on the surface of the catalyst. However, what made the Fe(III) concentration constant in the Cr(VI)/UV−TiO₂ system? Figures 6 and 7 indicate that Fe(II) generated by photocatalytic reduction of Fe(III) on the surface of TiO₂ may be consumed by the thermal reduction of Cr(VI) in the bulk solution. In the presence of Fe(III), Cr(VI) is reduced via two pathways: (a) by surface reaction (1) as mentioned before and (b) by the following redox reactions:

\[
\text{Fe(III)} + e^- + \text{TiO}_2 \text{,hv} \rightarrow \text{Fe(II)}
\]

(12)

\[
3\text{Fe(II)} + \text{Cr(VI)} \rightarrow 3\text{Fe(III)} + \text{Cr(III)}
\]

(13)

Reactions (12) and (13) were supported by the experiment considered in Figure 8. A photocatalysis experiment was carried out at pH 2.5 with initial concentrations of 600 μM Fe(III) and 600 μM Cr(VI); after 70 min of UV irradiation, the light was cut off. The behavior of Fe(II) was completely different from the case under the UV irradiation for 3 h, which is illustrated in Figure 8. The homogeneous reaction between Fe(II) and Cr(VI) under UV illumination demonstrated that the Cr(VI) concentration decreased with illumination time. Without UV irradiation, the concentration of Fe(II) decreased slowly, because it was oxidized by the residual Cr(VI). For the case when the system was still under UV irradiation after 70 min, it increased fast. When the temporal profiles of Cr(VI) reduction are compared in Figure 6, it is observed that the rates of Cr(VI) reduction during the first 10 min were almost the same. This indicates that reaction (13) took place only after an appreciable amount of Fe(II) was formed (i.e., after ~10 min).

Figure 9 shows the Cr(VI) reduction profiles at pH 2.5 with 2 g/L of TiO₂ in the absence and in the presence of Fe(III). Unlike the earlier experiments in Figure 6 where the dosage of TiO₂ was 0.4 g/L, the influence of Fe(III) on the reduction of Cr(VI) was found to be insignificant. It was observed that the rate of Cr(VI) photocatalytic reduction is affected by the dosage of the TiO₂ catalyst. In this case with a relatively large surface area of catalyst available for adsorption, both Fe(III) and Cr(VI) are adsorbed. Because the reduction potentials of both Fe(III)/Fe(II) and Cr(VI)/Cr(III) couples are of comparable value at pH 3, both Fe(III) and Cr(VI) are photoreduced at the same time. Moreover, the profiles of Cr(VI) reduction in the absence of Fe(III) in Figures 6 and 9 show that the reduction rate of Cr(VI) is much higher with 2 g/L of TiO₂ than with 0.4 g/L. It has been previously reported that an optimum TiO₂ dosage was ~2 g/L, while it was 5 g/L for CdS. The pseudo-first-order reduction rate constant of Cr(VI) with 2 g/L of TiO₂ at pH 2.5 was reported as 0.0048 min⁻¹ which is much larger than that of Cr(VI) reduction by a ferrous ion, which was reported as 0.0017 min⁻¹, when the concentration of the ferrous ion was 100 μM. Therefore, the positive effect from the ferrous ion is very small and negligible when the TiO₂ dose is near the optimum value of 2 g/L.

**Effect of Oxygen on Cr(VI) Reduction.** Table 4 contains data from two photocatalysis experiments at pH 2.5, where N₂ and air were used as the purge gas. Experiments were carried out under identical conditions for the 1-h adsorption and the 3-h photocatalytic reduction. Initial concentrations of Cr(VI) and Fe(III) were 600 μM. The TiO₂ dosage was 0.4 g/L, while formic acid at 20 mM was used as the hole scavenger.
followed by coprecipitation.

Table 5. Cr(VI) Removal by Photocatalytic Reduction Followed by Coprecipitation

<table>
<thead>
<tr>
<th>treatment details</th>
<th>total Cr (ppm)</th>
<th>total Zn (ppm)</th>
<th>total Fe (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial concentration</td>
<td>31.2</td>
<td>83.8</td>
<td>33.5</td>
</tr>
<tr>
<td>photocatalytic reduction at pH 2.5 for 50 mina</td>
<td>10.7</td>
<td>62.2</td>
<td>18.9</td>
</tr>
<tr>
<td>coprecipitation at pH 7.26</td>
<td>0.017</td>
<td>32.4</td>
<td>0.058</td>
</tr>
<tr>
<td>Zn removal at pH 10.08</td>
<td>0.012</td>
<td>0.038</td>
<td>0.037</td>
</tr>
</tbody>
</table>

a [TiO₂] = 2 g/L.

The amount of Fe(III) and Cr(VI) photoreduced in an air-equilibrated system and a N₂-purged system indicates that the reaction is not significantly influenced by oxygen. Opposite results of Cr(VI) photocatalytic reduction at pH 10 were reported by Wei et al.29 This may be explained by the fact that the thermodynamic driving forces for the reduction of Cr(VI) and O₂ depend on pH. It is clearly shown in Figure 1 that the thermodynamic driving forces are similar for the reduction of Cr(VI) and O₂ at pH 2.5. However, at pH 10, the thermodynamic driving force for O₂ is much higher than that for Cr(VI) and consequently oxygen competes with Cr(VI) for the photogenerated electrons. In the case of Fe(III), significant adsorption of Fe(II) on TiO₂ helps it to be reduced by conduction band electrons, e⁻.

Removal of Cr(VI) from Simulated Leather Tanning Waste. On the basis of a literature survey regarding heavy-metal adsorption by ferric hydroxide,30 a combination of photocatalytic reduction and metal ion coprecipitation was used to remove aqueous Cr(VI) from the simulated leather tanning industry. The sample that simulated waste from the leather tanning industry contained ~30 ppm of Cr(VI), 80 ppm of Zn(II), and 30 ppm of Fe(III). Following the photocatalytic reduction in TiO₂ suspensions at pH 2.5, the pH of the solution was adjusted to approximately 7 and the sample was allowed to settle following 1 h of flocculation. The supernatant samples were tested, with the results shown in Table 5. To achieve the complete removal of Zn as well as Cr, the pH of the supernatant samples was then raised to ~10.

As can be seen, the chromium concentration was reduced below the water quality criteria established by the U.S. EPA.31 Actually, it is comparable to the most widely used method using iron to reduce chromium to the trivalent state.32 33 The advantage of the combination of photocatalytic reduction and metal ion coprecipitation over other treatment methods is that it only took ~2 h for the entire process to remove 30 ppm of chromium with the same dose of iron. The amount of ferrous ions added to the Cr(VI)-contaminated water was kept in excess of the stoichiometric ratio of 3.2 lb of iron/lb of chromium in the treatment reported by El-Shoubary et al.32 Although Blowes et al.33 described in situ permeable reactive barriers containing Fe₀ to remove dissolved Cr(VI) from groundwater, the ferric oxyhydroxide precipitation during the process limited the available surface area of the reactive barrier, which would inhibit Cr(VI) reduction.

Figure 10. Photocatalytic reduction of Cr(III) in ZnS suspensions. Experimental conditions: [ZnS] = 8 g/L, [Cr(III)₀] = 8.5 ppm, [HCOOH] = 20 mM, pH 5.2. Inset: adsorption of Cr(III) on ZnS in the dark.

Table 6. Conditions for Cr(III) Removala

<table>
<thead>
<tr>
<th>formic acid</th>
<th>UV irradiation</th>
<th>ZnS</th>
<th>%Cr(III) removed</th>
</tr>
</thead>
<tbody>
<tr>
<td>✓</td>
<td>✓</td>
<td>×</td>
<td>0</td>
</tr>
<tr>
<td>✓</td>
<td>×</td>
<td>✓</td>
<td>21</td>
</tr>
<tr>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>71</td>
</tr>
<tr>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>86</td>
</tr>
</tbody>
</table>

a Conditions: [Cr(III)] (210 µM), formic acid (20 mM), and ZnS (8 g/L): ✓ indicates the presence of the component; × indicates the absence of the component. After 5 h of irradiation.

Photocatalytic Reduction of Cr(III). Preliminary thermodynamic analysis (see Figure 1) reveals that photogenerated electrons in ZnS are capable of reducing Cr(III). Considering that Cr(III) is positively charged and that adsorption on the ZnS surface is favored in basic aqueous solutions, the experiments were conducted at pH ~5. Figure 10 shows the Cr(III) temporal profile in a solution containing 11 ppm of Cr(III). The rate of Cr(III) concentration decrease was found to be low in an open system (O₂ saturated); however, the rate was greatly enhanced in the N₂-purged system. This increase in rate indicates that Cr(III) photoreduction is inhibited in the presence of oxygen. This is because oxygen, whose reduction potential (E₀ = 1.0 V at pH 5) is much higher than that of Cr(III) (E₀ = −0.79 V at pH 5), competes with Cr(III) ions for the photogenerated electrons.

Interestingly, the data in the N₂-purged system exhibit zero-order kinetics, which is different from the reduction reaction of Cr(VI) by a TiO₂ photocatalyst. Because the inset in Figure 10 shows that adsorption of Cr(III) on ZnS is fast, Cr(III) adsorption on ZnS was allowed to reach an equilibrium in 1 h before the photocatalytic reaction. Meanwhile, electron transfer from ZnS to Cr(III) is more difficult than electron transfer from TiO₂ to Cr(VI) because of the small difference between the ZnS conduction band edge and the reduction potential of Cr(III). Therefore, the rate-determining step here may be the electron transfer from ZnS to Cr(III), not the adsorption of Cr(III).

The appearance of black particles in the suspension reveals that they were presumably metallic Cr. To ensure that Cr(VI) was not formed, chromium adsorbed on ZnS was desorbed at alkaline conditions after UV
To further identify the photoreduction of Cr(III) on the surface of ZnS, the ZnS powders after photocatalysis were investigated by XPS. A wide scan of the ZnS powder is shown in Figure 11. High-resolution scans of Cr 2p peaks are shown in Figure 12. In Figure 12a, a single peak after 30 min of dark reaction is located at 575.6 eV, which is assigned to Cr(III). After 5 h of dark reaction (Figure 12b), there are overlapping peaks of two different chromium species, one of which is in the peak position of Cr(III) and the other of which shifts to 573.8 eV, which is expected to be elemental Cr. Parts c and d of Figure 12 show the same system as in those in parts a and b of Figure 12 but after different periods of UV irradiation. The peak width at half-maximum and the peak height for Cr(0) appear narrower and sharper, respectively, with the longer period of UV irradiation, indicating that Cr(III) on the ZnS surface is increasingly reduced to Cr(0).

Conclusions. Both the thermodynamic and kinetic analyses show that the photocatalytic reduction of Cr(VI) under UV-A irradiation depends largely on pH. The reaction occurs on the surface of TiO₂ by directly capturing photogenerated electrons. Ferric ions are shown to exert a dramatic accelerating influence on Cr(VI) reduction, which can be accomplished within 90 min when the TiO₂ dose was as low as 0.4 g/L. However, the presence of oxygen does not affect the reduction of Cr(VI) and Fe(III) in acidic solutions because of the high reduction potential of Cr(VI) and a significant adsorption of Fe(III) onto TiO₂. Because TiO₂ can only photoreduce Cr(VI) to Cr(III), a new process for removing aqueous Cr(VI) using photocatalytic reduction followed by coprecipitation with ferric ions proved successful. Finally, it was found out that ZnS can be used as a photocatalyst for further reduction of Cr(III) to Cr(0).

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