Removal of Cr(VI) and Cr(III) from Aqueous Solutions and Industrial Wastewaters by Natural Clino-pyrrhotite

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This paper introduced a simple method of treating Cr-(VI)-bearing toxic wastewaters using a natural mineral: clinopyrrhotite. Laboratory bench-scale mixing experiments were carried out in both Cr(VI)-bearing artificial solutions and industrial wastewaters under controlled conditions. The effects of solution pH, Cr(VI) concentration, mineral grain size, mineral/solution ratio, and reaction time on the Cr-(VI) removal were studied. Chromium was effectively removed from the solutions and wastewaters. After the treatment, the liquid was clean enough to be discharged directly into the natural environment. The Cr(VI) removal process involved sequentially the adsorption of Cr(VI), in the form of $Cr_2O_7^{2-}$ or CrO_4^{2-} , onto the mineral surface, the reduction of the adsorbed Cr(VI) to Cr(III), catalyzed at the vacant Fe sites of the mineral, and finally the precipitation of Cr(III) as Cr_2S_3 , Cr_2O_3 , and $Cr(OH)_3$ solid phases. Conditions such as a fine mineral grain size, an excessive quantity of clino-pyrrhotite and a weak acidic media. favored the removal process. For clino-pyrrhotite with a restricted grain size, the minimum required quantity of the mineral was proportional to the total quantity of Cr(VI) to be removed. Quantitatively, one cubic meter of industrial wastewater that contained ~ 1 mmol dm⁻³ of Cr(VI) and had a pH value between 1 and 10 would be effectively treated after it was in contact with 220 kg of 145 \pm 28 μ m clinopyrrhotite for an hour. Furthermore, the quantity of the final solid waste byproduct was small, and the solid residue of clino-pyrrhotite could be reused after a simple rinse with water. Compared to the previous Cr(VI)-bearing wastewater treatment schemes, this method was simple, effective, economical, and environmentally sound. It has great potential for use in industrial-scale applications.

Introduction

Chromium, because of its widespread industrial use, is a common heavy metal contaminant in industrial regions throughout the world. Many Cr(VI) species are known carcinogens. In the U.S., chromium is, after lead, the second most important inorganic contaminant in groundwater (*1*). The safe disposal of large quantities of Cr(VI)-bearing toxic industrial wastewaters is also one of the major environmental problems that China faces.

Environmental remediation of Cr(VI)-contaminated sites or industrial wastewaters usually involves the reduction of Cr(VI) to the less mobile and less toxic Cr(III) species (2, 3). Reduction of Cr(VI) to Cr(III) took place if a strong chemical reductant (e.g., sodium sulfite) was added and Cr(III) was then removed through precipitation (e.g., Cr(OH)₃) by adding sodium hydroxide or lime. This procedure usually required sophisticated equipment and expensive chemical reagents. It would therefore result in high operational costs and large quantities of toxic byproducts. Partial immobilization of aqueous Cr(VI) could be realized directly, without reduction to Cr(III), by the coprecipitation of the CrO₄²⁻ ions into Barite, where CrO₄²⁻ was substituted for SO₄²⁻ in the crystal structure (4, 5).

Treating industrial Cr(VI) wastes using natural materials such as iron sulfide minerals has shown some great potential and attracted the attention of the international scientific community (3, 5-21). Pyrite, in particular, has been proven to be effective in removing dissolved Cr(VI) from solutions (6). In this paper, we report another simple, effective, and economical alternative for treating Cr(VI)-bearing wastewaters using another natural iron sulfide mineral: clinopyrrhotite.

Materials and Methods

Materials. Pyrrhotite used in this study was obtained from the Dongshengmiao sulfide mineral deposit in the Inner Mongolia, Northern China. Hand-picked samples were crushed, washed with tap water, dried at room temperature, and then sieved. Pyrrhotite crystals were selected using a magnetic mineral separator. It was identified as monocline pyrrhotite with $a_0 = 1.1892$ nm, $b_0 = 0.6897$ nm, $c_0 = 2.2742$ nm, $\beta = 90^{\circ}11'$, and a super-crystal structure of 2A2B4C by X-ray diffraction. Its chemical composition was 60 wt % for Fe and 39% for S by electron-probe analysis. This gave a crystal formula of Fe_{0.88}S. The nonstoichiometric Fe to S ratio indicated vacancies at the Fe site in the crystal structure. The sum of the heavy metal (i.e., Mn, Cu, Pb, Zn, Cd, Co, and Ni) content of this mineral was less than 0.1 mmol g^{-3} , as determined by the flame atomic absorption spectrophotometric (AAS) analysis of the mineral after wet chemical digestion. Microscopic observation showed that the selected pyrrhotite particles fell into a restricted grain size range. Its reactive surface area was, therefore, proportional to its mass.

Solutions with different Cr (VI) concentrations were prepared from reagent grade $K_2Cr_2O_7$ and distilled water. Their pH values were adjusted to the predetermined values by adding small quantities of concentrated H_2SO_4 or NaOH solution and confirmed by pH measurements.

Two Cr(VI)-bearing industrial wastewater samples were collected from two electroplating plants, one in Beijing and the other in the Fujian Province, Southeast China. The wastewater from the Beijing plant had a Cr(VI) concentration of 600 μ mol dm⁻³ and a pH of 6.86, while that from the Fujian plant had a Cr(VI) concentration of 3400 μ mol dm⁻³ and a pH between 2 and 3.

Experiments. All Cr(VI)-clino-pyrrhotite interaction experiments were carried out in 200 mL glass beakers at room temperature (15–25 °C) and one atmospheric pressure. In general, a weighed amount of clino-pyrrhotite with restricted

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TABLE 1. Summary of the Effects of Initial Solution pH and Reaction Time on the Efficiency of Cr(VI) Removal

reaction time (h)									
0	рН	1.22	3.35	5.32	6.24	7.24	8.74	9.89	11.5
	Cr(VI) concentration (µmol dm ⁻³)	190	190	190	190	190	190	190	190
2.5	рН	1.00	3.56	3.89	4.08	5.48	5.30	5.73	10.0
	Cr(VI) concentration (µM)	7.5	6.3	6.9	4.4	4.4	15.1	8.2	104
	Cr(VI) removal efficiency %	96.1	96.7	96.4	97.7	97.7	92.2	95.8	45.8
0	pH	1.08	3.40	5.32	6.85	7.80	8.61	9.66	12.1
	Cr(VI) concentration (µmol dm ⁻³)	190	190	190	190	190	190	190	190
18	рН	1.14	3.61	3.84	3.77	4.23	3.98	4.47	8.95
	Cr(VI) concentration (µmol dm ⁻³)	9.4	1.3	1.9	1.3	0.6	0.6	0.6	76
	Cr(VI) removal efficiency %	95.1	99.4	99.0	99.4	99.7	99.7	99.7	60.5

grain size was first introduced into a known volume of the prepared Cr(VI) solution. The mixture was stirred by a glass rod and then left standing for a predetermined period of time. The pH of the solution was measured periodically during the experiment. At the end of the experiment, the mixture was filtered through a 1.0 micron paper filter. The pH of the supernatant was measured, and an aliquot was sampled for Cr(VI) determination.

Four series of experiments were carried out to determine the effects of solution pH, solid/solution ratio, mineral grain size, Cr(VI) solution concentration, and reaction time on the Cr(VI) removal from solution by clino-pyrrhotite. In the first series, 50.0 mL solutions of various initial pH and a Cr(VI) concentration of 10 mg dm⁻³ (or 190 μ mol dm⁻³) were used to react with 3.0 g of 80-120 mesh (i.e., $117-173 \mu$ m) clinopyrrhotite for up to 18 h. In the second series, clino-pyrrhotite of different grain sizes and quantities was added to 50.0 mL solutions of Cr(VI) concentration of 190 μ mol dm⁻³ and an initial pH of around 7.0 for 2.5 h. In the third series, 50.0 mL solutions of various Cr(VI) concentrations and an initial pH of 4.5 were mixed with different quantities of 80-120 mesh clino-pyrrhotite. In the last series, solutions of various volumes with a Cr(VI) concentration of 250 μ mol dm⁻³ and an initial pH of 4.5 were mixed with varied quantities of 80-120 mesh clino-pyrrhotite. In addition, clino-pyrrhotite residual from one experiment was washed with distilled water and reused in the next experimental run. This procedure was repeated s6ix times to determine the reusability of this mineral.

Experiments were also carried out in Cr(VI)-bearing industrial wastewater samples collected from the two electroplating plants: 50.0 mL of wastewater from the Beijing plant was mixed with 7.0 g of clino-pyrrhotite for 10 min, and 50.0 mL of wastewater from the Fujian plant was allowed to react with 27.0 g of clino-pyrrhotite for 5 min.

Two additional experiments were conducted to determine the Cr(III) concentrations in the final solution and in the precipitate at the end of the Cr(VI) removal process. In one experiment, 1 g of 80–120 mesh clino-pyrrhotite was introduced into 100.0 mL of solution that contained an initial Cr(VI) concentration of 1920 μ mol dm⁻³ and a pH of 1.9 and was allowed to react for 1 h; while in the other, the initial solution concentration of Cr(VI) was reduced to 962 μ mol dm⁻³, the quantity of clino-pyrrhotite was increased to 13.0 g, and the reaction time was extended to 10 h.

Analysis. The pH of the solution was measured by a pH meter (Model PHS-3C, Shanghai High-Precision Scientific Instrument Inc., China) with a combined glass electrode. Two pH buffer solutions (pH = 4.00 and 9.18) were used to calibrate the pH meter prior to each measurement.

The concentration of Cr(VI) was determined by the 1,5diphenylcarbohydrazide spectrophotometric method (*22*). In an acidic medium, Cr(VI) would react with 1,5-diphenylcarbohydrazide, and the product could then be quantified at 540 nm with a spectrophotometer. The detection limit



reaction time (min)

FIGURE 1. pH fell into a narrow range of 3.5-4.5 after 20 min of Cr(VI) removal reactions, with two exceptions observed at extreme initial pH conditions (i.e., pH = 1.08 and 12.1).

and reproducibility of this method were estimated to be 0.1 $\mu g~dm^{-3}$ (or 0.0019 $\mu mol~dm^{-3}$) and 0.6%, respectively.

The concentrations of total Cr and other heavy metals (i.e., Cu, Pb, Zn, Co, Ni, Mn, and Cd) were determined by a flame atomic absorption spectrophotometer (AAS, Model GGX-2, Beijing Geo-Instrument Inc., China). It had a detection limit of 0.1 μ mol dm⁻³ and a precision of 5% for these elements.

X-ray photoelectron spectroscopy (XPS) is a surfacesensitive technique that provides semiquantitative information of chemical composition and the oxidation and binding state of the elements involved (23). XPS analyses of clinopyrrhotite and the solid products were carried out with a Model XSAM800 XPS (Kratos) under the experimental conditions of ALk α 1486.6 eV, 12 kV × 15 mA, high multiple and medium resolving power. The C_{1s} peak (E_b = 286.6 eV) was used as a reference point to eliminate the static charge effect. Spectral analysis was conducted using the XPS peak software package.

Results and Discussion

Effectiveness in Cr(VI) Removal. Table 1 presents the results that were obtained in solutions with different initial pH values. More than 90% of Cr(VI) was effectively removed within 2.5 h, if the two results from the runs with the initial pH of 11.5 and 12.1 were disregarded. The pH became steady within 20 min of the experimental runs and fell into a narrow range of 3.5-4.5, with the exception of experiments conducted at extreme initial pH conditions (i.e., pH = 1.08 and 12.1) (Figure 1).

Figure 2 showed the minimum time required for reaching maximum Cr(VI) removal. With the exception of the initial pH of 7.63 experiment, maximum Cr(VI) removal was reached within 40 min, when 3.0 g of 80–120 mesh clino-pyrrhotite was used to treat 50.0 mL of 190 μ mol dm⁻³ Cr(VI) solution.

TABLE 2. Effects of the Quantity and Grain Size of Clino-pyrrhotite on Cr(VI) Removal

grain size (mesh)	40-80	80-120	80-120	80-120	80-120	80-120	80-120	120-160
mineral quantity (gram)	3	1	2	3	4	8	16	3
initial pH	7.51	7.89	7.06	7.38	7.78	7.23	7.35	7.34
final pH	5.89	6.40	5.63	4.77	4.31	3.13	3.26	3.98
initial Cr(VI) concentration (μ mol dm ⁻³)	190	190	190	190	190	190	190	190
final Cr(VI) concentration (µmoldm ⁻³)	67	120	65	24	5.0	3.8	1.3	5.0
Cr(VI) removal efficiency %	65.4	38.9	66.3	87.6	97.4	98.0	99.4	97.4

TABLE 3. Results of Cr(VI) Removal Using Recycled Clino-pyrrhotite

cycle initial pH	1 1.04	2 1.04	3 1.01	4 1.03	5 3.19	6 5.83
initial Cr(VI) concentration (μ mol dm ⁻³)	190	190	190	190	190	190
final pH	1.08	1.08	1.04	1.01	1.98	3.82
final Cr(VI) concentration (μ mol dm ⁻³)	1.3	6.3	< 0.0019	< 0.0019	1.9	< 0.0019
Cr(VI) removal efficiency (%)	99.4	96.8	100	100	99.0	100



FIGURE 2. Reaction time required to reach maximum Cr(VI) removal in solutions of different initial solution pH values.

The effects of the quantity and the grain size of clinopyrrhotite on Cr(VI) removal were summarized in Table 2. The quantity of the Cr(VI) removal was related positively to the amount of clino-pyrrhotite used and negatively to its grain size. Under our experimental conditions, Cr(VI) was effectively removed if more than 3.0 g of 80–120 mesh clinopyrrhotite was added to 50.0 mL of experimental solution that contained 190 μ mol dm⁻³ Cr(VI).

The minimum quantity of clino-pyrrhotite required for the effective removal of Cr(VI) was proportional to the Cr(VI) concentration and the volume of wastewater to be treated (i.e., the total quantity of Cr(VI) to be removed). If 80–120 mesh of clino-pyrrhotite was used to treat 1 L of wastewater, the relationship between the quantity of the solid (*G*, g) and the Cr(VI) concentration (*C*, μ mol dm⁻³) was *G* = 0.212*C* (Figure 3a), while for a wastewater with an initial Cr(VI) concentration of 250 μ mol dm⁻³, the minimum solid-tosolution ratio was 55 g dm⁻³ (Figure 3b). To effectively remove every μ mol of Cr(VI) from solution, therefore, a minimum of 0.22 g or 2.7 mmol of 80–120 mesh clino-pyrrhotite was required.

Three grams of 80–120 mesh clino-pyrrhotite was used and then reused in six consecutive experimental runs under the following conditions: an initial Cr(VI) concentration of 190 μ mol dm⁻³, 50.0 mL of solution, and 20 min reaction time (Table 3). The effectiveness of Cr(VI) removal was maintained in all the runs.

Table 4 provided the results of seven parallel Cr(VI) removal experiments in wastewater collected from the Beijing electroplate plant. The wastewater had a pH of 6.86 and a Cr(VI) concentration of 600 μ mol dm⁻³. Although the final pH was much higher than those observed from our previous



FIGURE 3. (a) Linear relationship between the minimum quantity of clino-pyrrhotite required (*G*, g) to effectively treat 1 L of Cr(VI)bearing solutions and the Cr(VI) concentration (*C*, μ mol dm⁻³) of the Cr(VI)-bearing solutions. (b) Linear relationship between the minimum quantity of clino-pyrrhotite required (*G*, g) to effectively treat a Cr(VI)-bearing solution ([Cr(VI)] = 250 μ mol dm⁻³) and the volume of the solution (*V*, mL).

experiments conducted in artificial Cr(VI)-bearing solutions, Cr(VI) was effectively removed (i.e., removal efficiency > 98%). Experiments conducted in wastewater from the Fujian plant yielded similar results.

Solid Phases After Cr(VI) Removal. At the end of the experiments, the liquid settled into two distinctive layers: a clear supernatant layer and a cloudy yellowish lower layer. The concentrations of Cr(VI) and total Cr, Cu, Pb, Zn, Cd, and Fe in both layers were determined. They were much higher in the lower layer than in the supernatant. In the supernatant, the Cr(VI) concentration was at $0.77 \,\mu$ mol dm⁻³, which was below the Cr(VI) industrial wastewater discharge standard in China. Its total Cr concentration, however, was at 920 μ mol dm⁻³, which exceeded the discharge standard. In the traditional methods, this problem was resolved by adding Ca(OH)₂ or NaOH to initiate the precipitation of Cr-(OH)₃. In this research, the content of total Cr in the supernatant liquid was effectively reduced to a level that was



FIGURE 4. (a) XPS scan of clino-pyrrhotite after the reaction. (b) XPS analysis of Cr-bearing phases precipitated at the clino-pyrrhotite surface in acidic solution. (c) XPS analysis of Cr-bearing phases at the clino-pyrrhotite surface in basic solution.

below the discharge standard simply by adding an excessive quantity of clino-pyrrhotite. Desirable results of the contents of Cu, Pb, Zn, Cd, and Fe in the supernatant were also obtained when the reaction was extended to 10 h. In addition, when the reaction time was extended from 1 to 10 h, the content of Cr(VI) was decreased from 5.8 to $1.2 \,\mu$ mol dm⁻³, which was much lower than the discharge standard of industrial wastewater (i.e., 1.5 mg dm⁻³ or 29 μ mol dm⁻³) and slightly above the standard of potable water (i.e., 0.05 mg dm⁻³ or 0.95 μ mol dm⁻³). It was apparent that Cr(VI) in solution was effectively removed, resulting in the yellowish precipitates.

To determine the chemical compositions, the oxidation states, and the binding states of the solid products, two parallel experiments were conducted to generate relatively large quantities of solid precipitates by adding 5.0 g of 140–160 mesh (96–107 μ m) clino-pyrrhotite to 100.0 mL of 3850 μ mol dm⁻³ Cr(VI) solutions with the initial pH of 1.87 and 11.6, respectively, and then letting the mixtures react for 40 h. The final pH values of 2.56 and 9.18 were obtained, and 95.7 and 44.6% of Cr(VI) were removed, respectively. Results of XPS spectra of the precipitates, which were collected from

the cloudy yellowish lower layer, were given in Figure 4. The following Cr-bearing phases were positively identified using published standard Cr $2p_{3/2}$ binding energy (24): Cr₂S₃ (574.80 eV) and Cr₂O₃/CrOOH mixture (577.55 eV in Figure 4b or 577.30 eV in Figure 4c).

Chromium sulfides are rare in nature. Brezinaite (Cr_3S_4) has been found in meteorites (25). When the mixtures of Cr and S of different proportions were heated to 1000 °C and then cooled to room temperature, a series of chromium sulfides, such as α -Cr, CrS, Cr₇S₈, Cr₅S₆, Cr₃S₄, Cr₂S₃, etc., would be crystallized (13). To the best of our knowledge, this was the first time that a Cr₂S₃ phase was identified in an aqueous system. Further studies are needed to obtain the mineralogical and chemical properties of this phase.

Process of Cr(VI) Removal. The experimental data were fitted to the Langmuir isotherm

$$G = 4.58C_{\rm eq}/(1.20 + C_{\rm eq})$$

where C_{eq} (µmol dm⁻³) is the equilibrium solution concentration of Cr(VI), and *G* (µmol g⁻¹) is the corresponding

quantity of Cr(VI) adsorbed onto the surface of a unit mass of clino-pyrrhotite.

The fact that our experimental data fitted well to the Langmuir isotherm suggested that the adsorption of $Cr_2O_7^{2-}$ or CrO_4^{2-} ions onto the surface of clino-pyrrhotite was an important step in Cr(VI) removal from solution. Reduction of Cr(VI) to Cr(III) and the consequent Cr(III) precipitation probably happened at the solution–mineral interface. This process could be expressed by the following reactions.

Dissolution of clino-pyrrhotite

$$FeS(s) + 2H^+ \rightarrow Fe^{2+} + H_2S(aq)$$
(1)

Reduction of $\mbox{Cr(VI)}$ to $\mbox{Cr(III)}$ and precipitation of $\mbox{Cr(III)}$ in acid solutions

$$4Cr_{2}O_{7}^{2-} + 15H_{2}S(aq) + 2H^{+} = 4Cr_{2}S_{3}(s) + 3SO_{4}^{2-} + 16H_{2}O (2)$$

$$\operatorname{Cr}_{2}\operatorname{O}_{7}^{2^{-}} + 4\operatorname{H}_{2}\operatorname{S}(\operatorname{aq}) = \operatorname{Cr}_{2}\operatorname{S}_{3}(\operatorname{s}) + \operatorname{SO}_{3}^{2^{-}} + 4\operatorname{H}_{2}\operatorname{O}$$
 (3)

$$\operatorname{Cr}_{2}O_{7}^{2-} + 6\operatorname{Fe}^{2+} + 8\operatorname{H}^{+} = \operatorname{Cr}_{2}O_{3}(s) + 6\operatorname{Fe}^{3+} + 4\operatorname{H}_{2}O$$
 (4)

Reduction of Cr(VI) to Cr(III) and precipitation of Cr(III) in basic solutions

$$CrO_4^{2-} + 3Fe^{2+} + 4OH^- + 4H_2O =$$

 $Cr(OH)_3(s) + 3Fe(OH)_3(s)$ (5)

$$4\text{CrO}_4^{2^-} + 9\text{Fe}^{2^+} + 6\text{HS}^{2^-} + 0\text{H}^- + 10\text{H}_2\text{O} = 2\text{Cr}_2\text{S}_3(s) + 9\text{Fe}(O\text{H})_3(s)$$
 (6)

As the solubility of clino-pyrrhotite was extremely low, the previous reactions occurred most likely at or near the solution-mineral interface. Similar reactions were reported during acid mine drainage formation (3, 9).

The nonstoichiometry (i.e., $Fe_{0.88}S$) of clino-pyrrhotite was attributed to the existence of vacancies of the Fe sites, rather than an excess of sulfur ions, in the mineral crystal structure. Charge balance was maintained by the existence of Fe^{3+} ions in the crystal structure (i.e., $(Fe^{2+}, Fe^{3+})S)$, as proposed by Vaughan and Craig (*26*). Hydrogen sulfide and a hydroxyl radical interacted with clino-pyrrhotite at the vacant Fe sites on the surface (*27, 28*). Such types of interactions were cited as the classical Lewis base/acid-type reactions, with HS⁻ and OH⁻ acting as base by donating a pair of electrons to a vacant Fe site (*28*).

It was most likely that the vacant Fe sites in clinopyrrhotite acted as surface reactive sites for Cr(VI) reduction. Similar to HS⁻ and OH⁻, Cr(VI), in the form of Cr₂O₇²⁻ or CrO₄²⁻, was attracted to the vacant Fe sites of clino-pyrrhotite. The Cr₂O₇²⁻ or CrO₄²⁻ ion had sufficient electron affinity to remove the trapped electrons from the vacant Fe sites, and consequently, its Cr(VI) was reduced to Cr(III).

Potential Industrial Application. This laboratory benchscale experimental study showed that natural clino-pyrrhotite mineral could be used in the effective removal of Cr(VI) from aqueous solutions and industrial wastewaters. It would have a great potential in the industrial-scale treatment of Cr(VI)bearing toxic wastewaters.

The acidic condition that was generally associated with most industrial wastewaters would in fact favor the removal of Cr(VI) by clino-pyrrhotite. In an acidic medium, the proton was a reactant in both clino-pyrrhotite dissolution and Cr-(VI) reduction reactions (e.g., see reactions 1, 2 and 4). Proton consumption would result in a reduction of the acidity of the waste solution. If an excessive amount of clino-pyrrhotite was added to the acidic waste solution, the acid in the waste would be partially neutralized, and the waste solution could be discharged directly without the addition of any basic chemical reagent.

Sodium sulfite (Na₂SO₃) used in the traditional methods for treating Cr(VI) wastewaters was in fact produced from natural pyrrhotite (FeS) or pyrite (FeS₂). While one molecule of Na₂SO₃ provided only two electrons for the reduction of Cr(VI) to Cr(III), where SO₃²⁻ was oxidized to SO₄²⁻, one molecule of pyrrhotite (FeS) would provide eight electrons for the Cr(VI) to Cr(III) reduction, as S²⁻ was oxidized to SO₄²⁻. Pyrrhotite was therefore 4 times as effective as sodium sulfite. In addition, the ferrous iron in pyrrhotite would also contribute one electron for the Cr(VI) reduction when it was oxidized to ferric iron. From an industrial standpoint, it implied that our method would have the potential of being much more cost efficient than the traditional methods.

The grain size and the quantity of clino-pyrrhotite were two of the most important factors in the removal of Cr(VI). In general, a small grain size and a large quantity of clinopyrrhotite and a weak acidic media favored the removal. Optimal Cr(VI) removal was found with a clino-pyrrhotite grain size of 80–120 mesh or $145 \pm 28 \,\mu$ m, and the pH values were between 1 and 10. Under such conditions, the minimum quantity of clino-pyrrhotite required for the effective removal of Cr(VI) was proportional to the Cr(VI) concentration and the volume of the wastewater, or in other words, to the total quantity of Cr(VI) to be treated. Our laboratory bench-scale experimental results indicated that only 220 g or 2.7 mol of clino-pyrrhotite with a grain size of 145 \pm 28 μ m was needed to remove effectively 1 mmol of Cr(VI) within 1 h from wastewater that had a pH between 1 and 10. From an industrial wastewater treatment perspective, one cubic meter of wastewater that contained $\sim\!\!1\,mmol\,dm^{-3}\,of\,Cr(VI)$ would be effectively treated within an hour if 220 kg of $145 \pm 28 \,\mu m$ clino-pyrrhotite was added to the wastewater.

Our method offered several important advantages over the traditional two-step methods (i.e., reduction of Cr(VI) to Cr(III) in an acidic medium + Cr(III) precipitation in a basic medium). The treatment process was a simple addition of clino-pyrrhotite to the wastewater. Both Cr(VI) reduction and consequent Cr(III) precipitation occurred when clinopyrrhotite was mixed with the Cr(VI)-bearing wastewater. No special equipments, costly chemicals, or complex operations were required. Chromium was precipitated out as solids and removed completely from the liquid phase. The treated wastewater was clean enough to be discharged directly into the natural environment. Furthermore, the solid residue of clino-pyrrhotite could be reused after a simple rinse with water. As a result, the quantity of the solid waste generated in this method was much smaller than that produced by any of the previously reported treatment methods. The problem of the production of large quantities of solid toxic wastes that was usually associated with other methods was avoided. In addition, the total Cr content in the resultant solid wastes might be high enough for economic Cr recovery. In particular, our method offered two additional important advantages over the method proposed by Zouboulis (6) using fine grain size pyrite: that a much coarser mineral grain size was used in our method (i.e., 145 \pm 28 μ m vs 12 μ m) and that clinopyrrhotite could be effectively reused in the treatment scheme, which, from an industrial standpoint, would further reduce the operational difficulty and cost.

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