Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.772077

51 (2013) 7194–7200
November

Taylor & Francis
Taylor & Francis Group

Enhancement of heterogeneous Cr(VI) reduction using clay minerals in the presence of organic carboxylic acids under UV irradiation

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Received 25 October 2012; Accepted 28 January 2013

ABSTRACT

Chromium is a well-known highly toxic metal, considered as a priority pollutant. In this study, a series of experiments were conducted to investigate the effect of the properties of clay minerals and organic carboxylic acids on the reduction of Cr(VI) in aqueous solution under UV illumination. Two common clay minerals (montmorillonite, kaolinite) and two typical organic carboxylic acids (oxalate and citrate) were utilized in our system. The experimental results confirmed that the existence of oxalate or citrate can markedly accelerate the Cr (VI) photoreduction reaction on the clay minerals in aqueous solution compared with clay minerals alone. This process of photo-reduction follows approximately zero-order kinetics. The effects of pH, dissolved oxygen, and initial Cr(VI) concentration, and clay minerals dose on removal ratio were also investigated. The photoreduction ratio of chromium was favorable under acidic pH than in the weakly alkaline pH. Furthermore, it was found that the dissolved oxygen exerted an inhibition effect on Cr(VI) removal.

Keywords: Hexavalent chromium; Montmorillonite; Kaolinite; Carboxylic acids

1. Introduction

Clay minerals are widespread layer type aluminosilicates in the environment, which are important constituents of soils, sediments and aquifer materials and have potential applications in pollution control and environmental protection [1–4]. The redox activity of clay minerals' surfaces also affects their oxidation state and consequently the speciation and chemical behavior of redox-sensitive metal ions in the surrounding solution [5]. Especially, iron-containing clay minerals are both potential reducing and binding agents for chromium [6]. They can promote Cr(VI) to Cr (III) reduction and bind chromium species by electrostatic interactions on the permanent-charged sites, by covalent binding with hydroxyl groups, and by cation exchange. Recently, photoreduction Cr(VI) has been recognized to be another major pathway for Cr (VI) reduction in the environment. Naturally occurring low molecular weight organic anions, such as oxalate and citrate, were also capable of reducing Cr(VI) in the presence of Fe(III) and under illumination [7].

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Organic carboxylic acids, which originate from both natural and anthropogenic sources, form an important class of ligands in soils and aquatic ecosystems [8]. Among the most important organic carboxylic acids in soil solution are oxalate, tartrate, and citrate. Because of their ability to form complexes in solution and at surfaces, the sorption of organic carboxylic acids significantly modifies the surface properties of clay minerals. Furthermore, under light illumination, in the presence of carboxylates as ligand/reductant, which is particularly effective at ligand-induced dissolving iron in the minerals both by complexation and by reduction [9,10].

Chromium is commonly found as a contaminant in water and soil as a result of extensive use in industry. Recently, as a friendly environmental treatment process, Cr(VI) photoreduction has been recognized to be another major pathway for Cr(VI) reduction in the environment [11]. Our research results showed that Cr (VI) could be effectively photoreduced in montmorillonite K series commercial acid activated clay suspensions, and the photoreduction of Cr(VI) was greatly enhanced in the presence of citrate. But, to our best knowledge, there is little report on the photoreduction of Cr(VI) in the system consisting of clay minerals and organic carboxylic acids [12].

In this work, the effect of oxalate and citrate on chromate (Cr(VI)) reduction at the interface of two different clay minerals (montmorillonite and kaolinite) aqueous solution was investigated. The objectives of this study were to investigate the effects of organic carboxylic acids (structure and concentration), pH value, the initial concentration of Cr(VI), dissolved oxygen, and clay mineral dose on the photoreduction of Cr(VI). Since this process can utilize natural matters (clay minerals and polycarboxylic acids) and solar energy for decontamination of pollutants in the environment, this work could provide a better understanding of the cycling of Cr(VI) in natural surface water, soils and sediments, or developing new practical, economic techniques for chromium site remediation.

2. Experimental

2.1. Reagents and materials

The Cr(VI) stock solution was prepared by using analytical grade potassium dichromate ($K_2Cr_2O_7$). Hydrochloric acid and sodium hydroxide were used to adjust the pH values of the solutions. All of the other reagents were analytical grade. Ultrapure water was treated with an ultrapure water system (Liyuan Electric Instrument Co. Beijng, China) and was used throughout the experiment.

Natural kaolinite and natural montmorillonite were purchased from Fluka, Alfa-Aesar, respectively. The main surface properties of two nature clay minerals were listed in Table 1. The major chemical compositions of natural kaolinite and montmorillonite summarized in Table 2 were determined on Philips PW1480 X-ray fluorescence (XRF) Spectrometer. The total irons expressed as terms of Fe_2O_3 content in nature kaolinite and montmorillonite were found to be 0.601 and 4.28%, respectively.

2.2. Dark adsorption of Cr(VI) on the clay minerals

Batch adsorption experiments were carried out in 250-mL Erlenmeyer flasks by mixing together 2-g/L clay minerals with different concentrations of Cr(VI) in the dark. The pH of the adsorptive solution was adjusted by the addition of 0.01 mol/L NaOH or 0.01-mol/L HCl as needed. The tests were performed in a shaker at 25℃ for 24 h at a reciprocal shaking speed of 120 rpm. The samples were taken and then centrifuged at 10,000 rpm for 20 min. The supernatant was then filtered through 0.22-μm filters, and the concentration of Cr(VI) was determined with 1,5-diphenylcarbazide (DPC)colorimetric method.

2.3. Photochemical experiment setup and procedure

All the experiments were carried out at constant temperature (25 ± 0.5℃) by using cylindrical Pyrex glass vessels, which was surrounded by a circulating water jacket. The light source was a 250 W metal halide lamp ($\lambda \geqslant 365$ nm, Chenguang Illumination Instrument, Jinzhou, China). The pH values of reaction solutions were adjusted using hydrochloric acid or sodium hydroxide. The dispersions in the 500 mL photoreactor were vigorously stirred with a magnetic stirrer throughout the photochemical experiments. Samples were collected at specific time intervals, centrifuged at 10,000 rpm for 20 min. The supernatant was then filtered through 0.22 μm filters. Aliquots of the samples were analyzed immediately in order to avoid further reaction.

2.4. Analyses

The concentration of Cr(VI) in supernatant solutions was determined at 540 nm by 1,5-DPC methods with a Shimadzu UV-1601 UV–vis spectrophotometer.

The concentrations of ferrous (Fe(II)) and total aqueous iron (TFe_{aq}) in the clay minerals suspensions were determined colorimetrically with 1, l0-o-phenanthroline by measuring the absorbance of the Fe(II)-phenanthroline

Table 1
Important physical and chemical characteristics of clay materials

Clay mineral	Layer structure	Particle size[a] (nm)	Surface area[b] (m^2/g)	pzc[c]	Layer pace[d] d001(Å)	pH[e]
Kaolinite	1:1	700	9.9	1.8	2.0	6.9
Montmorillonite	2:1	769	224	2.2	29.7	9.0

[a] Determined by the laser particle sizer.

[b] Determined from nitrogen adsorption isotherm.

[c] Point of zero charge (pzc) determined by the pH titration of clay minerals suspensions in various ionic strength media.

[d] Calculated from the X-ray (2θ).

[e] Measured in the 10 g/L clay mineral suspensions.

Table 2
Main chemical compositions of two clay minerals obtained by XRF (wt.%)

Clay mineral	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	K_2O	TiO_2	MnO	Na_2O
Kaolinite	56.1	39.1	0.601	0.154	0.111	1.89	0.375	0.0097	0.0412
Montmorillonite	66.4	21.8	4.28	2.44	1.24	0.522	0.166	0.0134	2.22

complex at 510 nm. And for the total aqueous iron determination, Fe(III) is reduced with excess ascorbic acid. Free iron in clay minerals was extracted with CBD and determined by the same method of the total aqueous iron [13].

All the measurements of Cr(VI) and Fe were carried out three times and the relative errors were all less than 5%.

3. Results and discussion

3.1. Dark adsorption of Cr(VI) on the clay minerals

The adsorptions of Cr(VI) onto 2.0 g/L clay minerals at pH 4.0 are shown in Table 3. The adsorption isotherms of Cr(VI) on kaolinite and montmorillonite were adequately treated with Langmuir model showing behavior characteristic of single-layer adsorption. The adsorption data agree well with Langmuir isotherm equation:

$$C_e/q_e = (1/bq_m) + (1/q_m)C_e$$

where b and q_m is the adsorption equilibrium constant and the monolayer capacity, respectively. C_e is the concentration of Cr(VI) at equilibrium. The lineal Langmuir plots are obtained by plotting C_e/q_e vs. C_e, from which the adsorption coefficients are evaluated (Table 3).

The predominant Cr(VI) species mainly exists in the monovalent $HCrO_4^-$ form from pH 2.0 to 6.5, as clay minerals are predominantly negatively charged, they have only a small capacity for taking-up anions because of the electrostatic repulsion. That is to say the chromate anions, $HCrO_4^-$ or $Cr_2O_7^{2-}$, could rarely adsorb on negatively charged clay surfaces. The adsorption capacity of montmorillonite is extremely exceeded on the kaolinite because of its large surface areas and layer paces.

3.2. Cr(VI) photoreduction at the interface of two different clay minerals

The results of previous studies suggested that Cr (VI) reduced by organic carboxylic acids and clay minerals is very slowly [14]. So direct reduction of Cr (VI) by oxalate, citrate, or natural montmorillonite, kaolinite in the absence of light within 60 min in our experiments is negligible. The rates of photochemical reduction of Cr(VI) in homogeneous and heterogeneous systems under a 250-W metal halide lamp ($\lambda \geqslant 365$ nm) irradiation are investigated. The results showed that more rapid decreases in Cr(VI) concentration were observed, the experimental data could be fit well with the zero-order equation, $d[Cr(VI)]/dt = k$. The Cr(VI) removal percentage within 20 min irradiation and the zero-order kinetic constants (k) in the two clay minerals-organic carboxylic acids systems are listed in Table 4. The Cr(VI) removals and k values were markedly enhanced in clay minerals suspensions in the presence of organic carboxylic acids. The results demonstrated that the carboxylic acids catalyzed the photoreduction of Cr(VI) in clay minerals suspension.

Under experimental conditions, the marked enhancement of Cr(VI) photoreduction is the consequence of combining the effects of both homogeneous

Table 3
Langmuir isotherm parameters for adsorption of Cr(VI) on kaolinite and montmorillonite

Clay mineral	Equation	Langmuir coefficients		
		R	q_m (μmol/g)	B (L mol^{-1})
Kaolinite	$1/q_e = 0.128 + 12.91/C_e$	0.996	7.81	9.91×10^3
Montmorillonite	$1/q_e = 0.0024 + 14.05/C_e$	0.997	416.6	1.70×10^6

Table 4
Comparison of Cr(VI) photoreduction at the interface of two different clay minerals in the presence of oxalate or citrate ([clay mineral] = 0.2 g/L, [Cr(VI)] = 20 μmol/L, [oxalate] = 100 μmol/L, [citrate] = 100 μmol/L, pH = 3.0)

System	Removal (%)	k (mol/(L min))	Correlation coefficient (R)
Oxalate	11.9	1.648×10^{-4}	0.9904
Citrate	14.13	1.748×10^{-4}	0.9958
Montmorillonite	4.0	3.153×10^{-5}	0.9372
Montmorillonite/oxalate	89.6	8.074×10^{-4}	0.9928
Montmorillonite/citrate	56.2	5.758×10^{-4}	0.9988
Kaolinite	2.1	4.48×10^{-6}	0.7022
Kaolinite/oxalate	37.3	3.406×10^{-4}	0.9974
Kaolinite/citrate	23.4	3.214×10^{-4}	0.9986

and heterogeneous reactions. In homogeneous Cr(VI)/organic carboxylic acids systems, oxalate or citrate is a good electron donor; Cr(VI) is also easily reduced by PET (photoinduced electron transfer). Numerous researches indicated that Fe(II) could be an important reducing agent of Cr(VI) [15]. Both oxalate and citrate are powerful ligands for the complexation with iron, which suffer ligand-to-metal charge-transfer (LMCT) photolysis under irradiation with different quantum yields of Fe(II) formation (at 366 nm, $\Phi_{FeOx} = 1.26$ [16], $\Phi_{FeCit} = 0.3–0.4$ [17]. Oxalate or citrate can also complex with structural iron at the clay surface leads to a similar LMCT reaction. In the presence of oxalate or citrate as ligand/reductant, the removal of Cr(VI) is particularly effective due to the ligand-induced dissolving iron both by complexation and by reduction [18,19].

Natural clay minerals contain iron species with different chemical environments: structural iron in the octahedral lattice, free iron (Fe^{2+} and Fe^{3+}) complexed with hydroxyl groups at the edge sites and bound at cation-exchange sites on the basal surface. The different binding forms of reactive iron species are illustrated in Table 5. XRF analysis shows that total iron in montmorillonite and kaolinite are 4.28, 0.6%, respectively. The total free iron can be extracted with CBD process. The amounts are found to be 0.17 and 0.13%, respectively.

The leaching Fe amount under dark and irradiation was detected and shown in Fig. 1. The results showed that the dissolution rate of total iron was greatly enhanced under irradiation. By comparing the dissolution rate, we assume that the contribution of thermal dissolution in the dark to the overall dissolution in irradiation suspensions is negligible.

The formation of Fe(III) and organic carboxylic acid complexes facilitates Cr(VI) reduction and electron transfer proceeds through the Fe(III)/Fe(II) redox couple. So the Cr(VI) reduction reaction will be greatly enhanced in the presence of organic carboxylic acids.

In comparison with the rate of Cr(VI) reduction in the clay mineral/citrate system, the Cr(VI) reduction

Table 5
Iron species in clay minerals

Clay minerals	Iron (Fe_2O_3) (%)	CBD iron (Fe_2O_3) (%)	TFe_{aq} (μmol/L)	$Fe_{aq}{}^{2+}$ (μmol/L)
Kaolinite	0.60	0.13	ND*	ND
Montmorillonite	4.28	0.17	38.4	16.3

*ND-not determined.

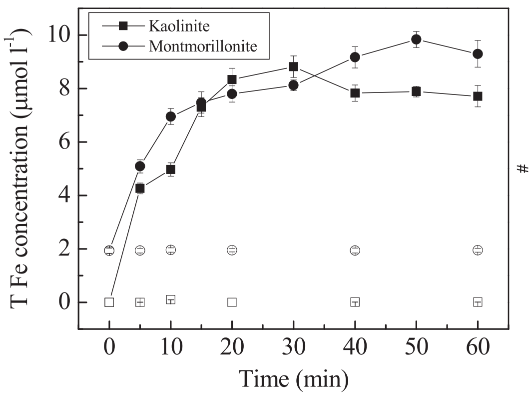

Fig. 1. The dissolution rate of total iron in the dark and in the irradiated experiments in the clay minerals suspensions in the presence of citrate. Results obtained in the dark (empty symbols) or under irradiation (filled symbols).

in the clay mineral/oxalate system is more efficient. For citrate, the main fraction was Fe citrate. For oxalate, Fe(III) was speciated as 1:2 and 1:3 complexes. (1) The rate coefficients increase with decreasing electron reduction potential of the Fe- (III) L-Fe(II) L redox couples. (2) Fe(III)-stabilizing ligands also accelerate the Cr(VI) reduction by Fe(II).

3.3. *Effect of the pH on the photochemical reduction of Cr(VI)*

This set of experiments employed 0.2 g/L kaolinite, and 0.2 g/L montmorillonite, 20 μmol/L Cr(VI), 100 μmol/L oxalate acids, and 100 μmol/L citrate. The pH was changed from 3.0 to 7.0. Under these conditions, the effects of pH on the photochemical reduction efficiency of Cr(VI) are shown in Table 6. Results indicate that Cr(VI) reduction ratios increase with decreasing pH.

The pH of the solutions plays an important role in the whole process. The redox reactions occurred on mineral surfaces involve adsorption and electron transfer [20]. (1) pH affects the surface charge of clay minerals, thereby affecting electrostatic interaction between clay minerals and Cr(VI), clay minerals and organic carboxylic acids; (2) pH affects the species distribution of metal ions. At pH of 2.0–6.5, the predominant Cr(VI) species mainly exists in the monovalent $HCrO_4^-$ form, which is then gradually converted to the divalent CrO_4^{2-} form as pH increases. Low pH benefits anion adsorption and, probably, its related redox reaction. It is also related to the iron ligands since Fe(III) will hydrolyze, and mixed Fe(III)-Cr (III) hydroxide solid solutions where the solubility of the

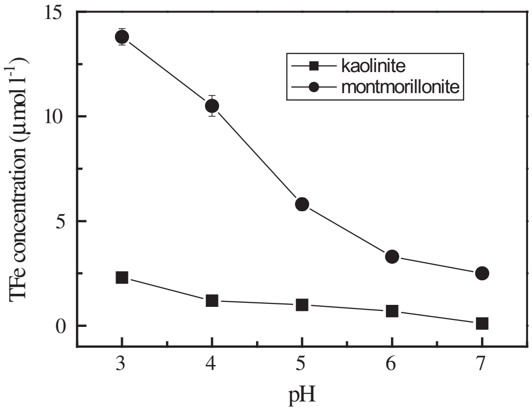

Fig. 2. Effect of pH on the photo-induced dissolution of total iron in clay mineral suspension.

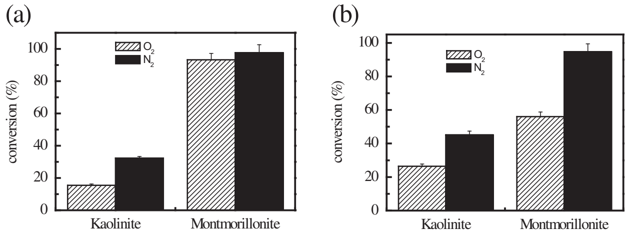

Fig. 3. Effect of dissolved oxygen on photo-reduction of Cr (VI) in 0.2 g/L, clay mineral solutions: Cr(VI) = 20 μmol/L, oxalate = citrate = 100 μmol/L, pH = 3.0, irradiation time = 20 min.

Table 6
Effects of the pH on the photochemical reduction of Cr(VI) (irradiation time 20 min)

pH	Cr(VI) removal (%)			
	Kaolinite/oxalate	Kaolinite/citrate	Montmorillonite/oxalate	Montmorillonite/citrate
3.0	21.8	11.4	89.6	56.2
4.0	6.8	10.7	47.4	54.7
5.0	4.8	7.5	7.6	22.1
6.0	1.6	1.5	0.8	0.8
7.0	0.008	0.005	1.3	5.0

Table 7
Effects of Cr(VI), organic carboxylic acids and clay mineral concentration on removal Cr(VI)

Concentration		Cr(VI) removal (%)			
		Kaolinite/ oxalate	Kaolinite/ citrate	Montmorillonite/ oxalate	Montmorillonite/ citrate
Clay mineral (g/L)	0.05	10.8	10.1	36.1	26.0
	0.1	28.2	11.3	48.3	35.1
	0.2	33.6	21.8	89.6	56.0
	0.4	61.5	34.7	98.8	87.1
Carboxylic acid (μmol/L)	50	10.3	9.7	73.5	44.1
	100	13.7	10.7	87.6	66.0
	200	15.3	11.0	89.6	75.8
	500	22.2	11.2	98.5	92.2
	1,000	50.4	12.5	98.7	98.2
Cr(VI) (μmol/L)	10.0	27.0	9.0	80.1	70.1
	20.0	28.2	10.1	89.6	56.2
	40.0	30.5	11.2	85.0	60.0
	80.0	24.5	9.5	87.2	71.0

solid phase decreases as the fraction of Cr (III) decreases at higher pH values. Fe (oxalate)$^+$ or Fe (citrate) is the predominant photoreactive species in the aqueous solutions at pH 3–4, which will photoreduced to Fe(II), and is in favor of Cr(VI) reduction; (3) The reduction potential of Cr(VI) to Cr (III) is pH dependent. The oxidation potential of $HCrO_4^-$ is higher than that of CrO_4^{2-}; (4) The pH influences the amount of the iron species (Fe(III) or Fe(II)) leached from the clay minerals into the solutions as shown in Fig. 2. Any ferrous iron produced by dissolution will quickly reduce Cr(VI) as long as the pH is less than 3.0 [21]. The concentration of dissolved total iron decreased with the increase in pH. The results show that pH dependence of Cr(VI) reduction is closely related to the iron dissolution of clay minerals.

Thus, effect of the pH play a key role in the photoreduction of Cr(VI), and the net effects on the Cr(VI) photo-reduction were more significant at lower pH.

3.4. Effect of dissolved oxygen (DO) on photoreduction of Cr(VI)

The effect of DO concentration on Cr(VI) photoreduction with the initial concentration of 20 μmol/L at initial pH 3.0 was investigated by purging with N_2 or air, respectively. Fig. 3 clear shows that O_2 retards the reduction of Cr(VI) in clay minerals suspension. As previously reported, the intermediate radicals formed during the oxidation of oxalic acid are involved in Cr (VI) reduction, in the presence of oxygen, the reaction of $\cdot CO_2^-$ with dissolved molecular oxygen or its oxidation to CO_2 via reaction (1,2). So DO that serves to compete with Cr(VI) for the oxidation of carboxyl anion radical, and on the other hand, dissolved oxygen may serve to interfere in the reaction between Cr (VI) and Fe(II) by its own ability to oxidize Fe(II).

$$\mathrm{Cr(VI)} + {}^{\cdot}\mathrm{CO}_2^- \rightarrow \mathrm{Cr(V)} + \mathrm{CO}_2 \qquad (1)$$

$$^{\cdot}\mathrm{CO}_2^- + \mathrm{O}_2 \rightarrow \mathrm{CO}_2 + \mathrm{O}_2^{\cdot-} \qquad (2)$$

3.5. Effects of Cr(VI), organic carboxylic acids and clay mineral concentration on removal Cr(VI)

Table 7 shows results of Cr(VI) removal ratio at various initial Cr(VI) concentrations (e.g., 10–80 μmol/L), organic carboxylic acids concentration (50–1,000 μmol/L) and clay mineral concentrations (0.05–0.4 g/L) at pH 4.0 with reaction time up to 20 min. As indicated above, the rate of Cr(VI) reduction was fast during the first minutes, which fits well with the zero-order equation, the reaction order indicated that the overall reaction rate was independent of Cr(VI) concentration.

4. Conclusions

Experiments were conducted to investigate the Cr (VI) reduction in clay minerals suspended aqueous solution by photochemical process. The experimental results indicated that the Cr(VI) photoreduction rate could be greatly accelerated in the presence of low–molecular–weight organic acid. The adsorption of Cr (VI) on clay surfaces is weak and the isotherms were adequately treated with Langmuir model, the amount of adsorption on montmorillonite ≫ kaolinite. The Cr (VI) removal is more effective in acidic solution. The photoreduction ratio of Cr(VI) was found to increase with concentrations of organic carboxylic acids and clay minerals, while independent of Cr(VI) concentration. Since clay minerals and organic carboxylic acids are important constituents of soils, sediments and aquifer materials, heterogeneous Cr(VI) photoreduction in clay minerals-organic carboxylic acids system is significant for understanding the cycling of Cr(VI) in natural surface water, soils and sediments. So it is meaningful to investigate the photochemical reaction in the clay minerals–organic carboxylic acids system for understanding the Cr(VI) reduction and speciation in surface environments, which will probably becoming a new practical, economic technique for in situ chromium site remediation.

Acknowledgments

This study was financed by the Natural Science Foundation of P.R. China (No. 20811120557) and the Natural Science Foundation of Hubei, China (No. 2009CDB159). The authors thank the anonymous reviewers for their comments.

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