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Enhanced Removal of Lead(II) and Cadmium(II) from Water in Alum Coagulation by Ferrate(VI) Pretreatment

Yong-mei Liang^{1,2}, Ma Jun¹, Wei Liu^{1,2*}

ABSTRACT: A laboratory study demonstrated that ferrate pretreatment significantly enhanced lead and cadmium removal in alum coagulation, under the conditions of natural surface water. The enhancement of lead removal was approximately 21 to 37% by ferrate pretreatment at a dosage of 1 to 5 mg/L. The enhanced removal of cadmium by ferrate pretreatment at a dosage of 1 to 5 mg/L exceeded the removal by alum coagulation alone 2- to 12-fold. Cadmium is much more difficult to remove than lead in alum coagulation. The performance of ferrate in enhancing the removal of lead and cadmium in alum coagulation was better than that of ferric chloride. The removal of lead and cadmium was highly pH-dependent, following the general trend of higher pH being related to higher removal. Satisfactory removal of cadmium could be expected by ferrate pretreatment combined with adjusting the pH of the water. *Water Environ. Res.*, **79**, 2420 (2007).

KEYWORDS: ferrate, pretreatment, lead, cadmium, alum, coagulation, pH.
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Introduction

The heavy metal pollution status of surface water is becoming more severe in developing countries. In the case of China, for example, this is because of the increasing absolute amount of discharged untreated or insufficiently treated industrial wastewater containing heavy metals to natural aqueous environments, despite the fact that the country's overall wastewater treatment rate has been steadily increasing in recent years. Some industrial processes (i.e., metal smelting, metal plating, textile production, and microelectronics) discharge heavy metal wastewater to aqueous environments, which then pollutes water sources for drinking water. Heavy metals can also be released into rivers and lakes from the use of fertilizers and pesticides, causing large area pollution. According to the annual report on environmental quality, issued by the National Environmental Protection Agency of China (Beijing), heavy metals, such as lead (Pb), cadmium (Cd), and mercury, are present in almost all of China's large rivers at various levels. In some seriously contaminated areas, the annual average concentrations of heavy metals are much higher than the regulated levels of the national standards for surface water quality. In fact, in most of the polluted rivers in China, the water has been contaminated by a mixture of contaminants, including organics, which both complicate and

aggravate the deterioration of surface water quality. Such severe heavy metal pollution of surface water has aroused a growing awareness of the problems related to the safety of drinking water supplies using contaminated water sources.

Metals can be distinguished from other toxic pollutants because of their resistance to biodegradation and accumulation in living tissues. The presence of heavy metals in the environment can be detrimental to a variety of living species. Heavy metals can be readily absorbed by aquatic animals and directly transferred to the human food chain, thus exhibiting a high health risk to consumers. Some heavy metals (i.e., mercury, chromium, cadmium, copper, lead, and nickel) have harmful effects on human health, and many are listed in the U.S. Environmental Protection Agency (Washington, D.C.) priority pollutant list. The existence of heavy metals in water, even at rather low concentrations, has serious significance, with respect to the quality of water supplies.

Several physicochemical processes have been developed to remove heavy metals from industrial wastewater, including chemical precipitation, ion exchange, cementation electrolysis, reverse osmosis, and the membrane separation process (Grosse, 1986; Janson et al., 1982). However, these technologies seem both inadequate and expensive in the practical application of drinking water treatment processes. For example, chemical precipitation using lime, carbonate, sulfides, or organosulfides can lead to the unexpected softening of water and leave poisonous residuals in the resulting water. Ion exchange, on the other hand, has been proven to be effective in the selective removal of cadmium from surface water (Zhao et al., 2002). Nonetheless, because contaminated source water typically contains low levels of heavy metals that should be further lowered to meet water quality standards for drinking water, the high cost of the application of ion exchange, membrane processes, and cementation electrolysis is still not economically acceptable in developing countries. In addition, the existence of various organic pollutants in surface water will lead to the rapid contamination of ion exchange resins and membranes, resulting in even higher operating costs. The development of cost-effective and "easy-to-operate" approaches to removing heavy metals from drinking water are therefore essentially needed, to provide safe drinking water and curtail the hazards to human health caused by heavy metals.

Coagulation is the most traditional and most effective approach to removing contaminants from water. The process generally aims at the removal of minerals (i.e., clay, asbestos, and silica) and organic matters (i.e., algae and dissolved organic materials), and it does not control specifically for the removal of dissolved inorganic materials and, in particular, heavy metals. Currently, coagulation processes

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specifically designed to remove trace metals have not been well developed. One promising, cost-effective means for the removal of heavy metals from surface water is adsorption and/or co-precipitation combined with conventional coagulation processes. Various kinds of biomass materials have been used as adsorbents to remove or recover heavy metals from aqueous solutions (Prasad and Freitas, 2000). Iron oxide adsorption is capable of removing heavy metals from tap water or wastewater over a wide range of pH values (Benjamin and Leckie, 1981). However, solid-liquid separation is fairly difficult after the application of powdered adsorbents (i.e., iron oxide). Recently, iron-oxide-coated sand has been developed and tested for the adsorption of metals in synthetic or real water, to overcome the problems associated with the use of iron oxide powders (Benjamin et al., 1996). Considering the small amount of heavy metals in surface water, however, there still exist possibilities for the application of iron oxide adsorption with coagulation.

Ferrate (FeO_4^{2-}) has high oxidation potential ($E^\circ = 2.20 \text{ V}$), which makes it potentially useful in water purification. Ferrate(VI) has been studied as a disinfectant by many investigators, and it has been found that ferrate inactivates a wide variety of microorganisms in buffered water (Shrink and Waite, 1980) and in wastewater (Waite, 1979). Ferrate(VI) has also been shown to destroy several priority pollutants in stimulated soft water (Deluca et al., 1983b). The results of initial studies showed that ferrate preoxidation in alum coagulation can enhance the removal of algae concentration (Ma and Liu, 2002) and aid in the reduction of turbidity (Liu and Liang, 2004). In addition, another previous study found that ferrate treatment does not produce any remaining mutagenic byproducts during the treatment process (Deluca et al., 1983a). The ferric hydroxide gel generated after ferrate decomposition could perform the adsorption and co-precipitation of metal ions and radionuclides in synthetic water and wastewater (Murmman and Robinson, 1974; Potts and Churchwell, 1994). Because ferric hydroxide can be effectively removed from water by following coagulation and filtration processes, there should not be any residual problems in the application of ferrate pretreatment, even at high dosages (Liu and Liang, 2004). Ferrate is thus expected to be a potential and safe chemical for the removal of heavy metals in the treatment of drinking water, meaning that ferrate offers an extra advantage in addition to its usefulness in organic pollution removal and inactivation.

The objective of this paper is to investigate the effectiveness of ferrate pretreatment on heavy metals removal from surface water using alum coagulation. The study was conducted under batch conditions, and lead(II) and cadmium(II) were selected as the target heavy metal pollutants because of their wide presence in the surface water of China. The study variables included ferrate dosage, alum dosage, and pH. The effects of pH on species fraction and adsorption were also addressed.

Materials and Methods

Chemical Preparation and Water Collection. Potassium ferrate solid was prepared by the modification of the method of reaction between hypochlorite (OCl^-) and $\text{Fe}(\text{OH})_3$ in strong basic media and isolated from the saturated potassium hydroxide (KOH) solution (Goff and Murmann, 1971), then stored in a silica gel desiccator. The purity of ferrate solid was determined to be 95%. Potassium ferrate solution (0.3 g/L, in ferrate [K_2FeO_4]) was prepared by dissolving potassium ferrate solid in distilled water just before use, to minimize the loss of ferrate as a result of its rapid decomposition rate in solution. Alum working solution (10 g/L) was prepared by dissolving aluminium sulfate in double-distilled water.

All chemical reagents used in the tests were analytical reagents obtained from Tianjin Chemical Inc. (Tianjin, China).

Raw water from a river located in a northern plateau area of China was collected. The river serves as the principal drinking-water source for several surrounding large cities, and the main pollutants originate from industrial and domestic discharges upstream. In addition, during the winter season, the pollution becomes further aggravated, as a result of the relative low river flow and constant wastewater influent. The water was moderately polluted at the point of water sample collecting, and it contained substantial amounts of natural organic materials and trace amounts of synthetic organic pollutants. The raw river water was transferred to the laboratory in ice-cold containers and stored in a cooling room at 4°C. The water was brought back to an ambient temperature of 22°C immediately before the tests. The parameters of the tested water sample were as follows: 18 NTU turbidity, 32 CU color, 7.0 pH, 11.5 mg/L total organic carbon, and 96 and 64 mg/L as calcium carbonate for hardness and alkalinity, respectively.

The river water contained substantial levels of lead and cadmium, with concentrations of 32 and 12 $\mu\text{g/L}$, respectively. In China, the concentrations of lead and cadmium are currently regulated at 10 and 5 $\mu\text{g/L}$ in the national standards for drinking water quality. To simulate heavily polluted water, 220 $\mu\text{g/L}$ $\text{Pb}(\text{NO}_3)_2$ as Pb(II) or 40 $\mu\text{g/L}$ $\text{Cd}(\text{NO}_3)_2$ as Cd(II) were added to the river water, and then the water was well mixed and settled overnight before use. After overnight settling, the initial concentrations of lead and cadmium in the water were measured to be 245 and 50 $\mu\text{g/L}$, respectively—that is, approximately 10 times higher than the regulated levels. The pH values of some raw water samples were adjusted to 3, 4, 5, 6, 8, 9, 10, 11, and 12, with 0.1 N hydrochloric acid (HCl) or sodium hydroxide (NaOH).

Experimental Procedures. Standard jar tests were carried out with a six-unit stirrer apparatus, to study the enhanced removal of lead and cadmium by ferrate pretreatment. In the tests, a carefully calculated amount of ferrate solution was mixed with water samples in several 1-L beakers for a period of time before the addition of alum. Then, all of the water samples were subjected to coagulation with the addition of a specific dose of alum testing solution at 300 r/min for 1 minute. Subsequently, the samples were slowly stirred with the coagulant at 60 r/min for 10 minutes and settled quiescently for 30 minutes. Samples of supernatant were siphoned from 1 cm below the water surface and further filtered with a 0.45- μm cellulose acetate membrane filter.

Batch vibrating trials were also conducted to investigate the effects of dosage and pH. In these trials, a certain dosage of potassium ferrate solution was first injected to a series of plastic bottles (250 mL) containing 100-mL raw water samples, and then the bottles were vibrated at 275 times/min for 20 minutes. Afterward, 40 mg/L aluminium sulfate was added to the water samples, and the bottles were vibrated for an additional 5 minutes. The samples were then settled quiescently for 20 minutes, before filtration with a 0.45- μm membrane filter. The data shown in Figures 1 and 2 were obtained from the jar tests, while the other data were obtained from the batch vibrating tests.

Analytical Methods. The lead and cadmium concentrations in the filtered water samples were measured using an atomic absorption spectrophotometer (PE 703, HGA 400 graphite furnace, PerkinElmer Inc., Shelton, Connecticut). All the glassware used for the lead and cadmium analyses in this study were acid-soaked (1% nitric acid) overnight, rinsed with double-distilled water, and then dried at 110°C in an oven.

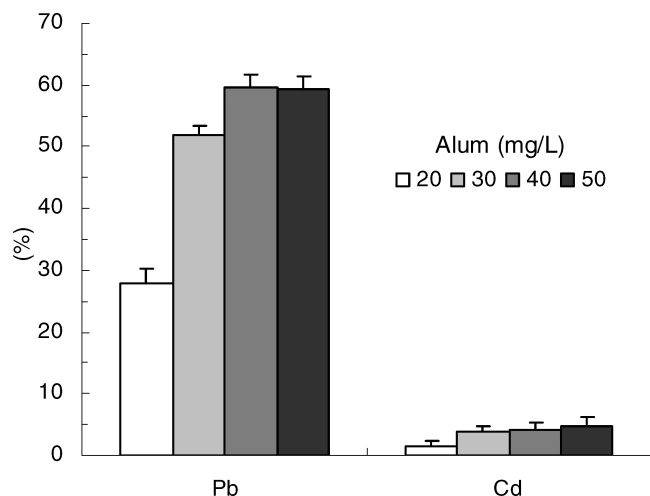


Figure 1—Lead and cadmium removal by alum coagulation (error bars show the range of three measurements).

Results and Discussion

Enhanced Removal of Lead and Cadmium. The removal of lead and cadmium solely by alum coagulation after sedimentation and filtration is illustrated in Figure 1. The removal efficiency of lead and cadmium is expressed as the ratio of the residual concentrations of heavy metals in the water samples after treatment to their initial concentrations in the raw water. Alum coagulation removed lead from the water, to some extent, with the percentage removal increasing with increased alum dosage. The removal of lead was 28% at the low alum dosage of 20 mg/L, while it was approximately 60% at the high alum dosage of 40 mg/L. With the increase of alum dosage from 40 to 50 mg/L, lead removal stayed in the plateau value of approximately 60%, with a residual concentration of 98 $\mu\text{g/L}$. This result indicates a limitation of lead removal using only alum coagulation. In the case of cadmium, on the other hand, the percentage removal was rather low, with the highest percentage being less than 10% at the largest alum dosage of 50 mg/L. The lowest residual cadmium after treatment was approximately 45 $\mu\text{g/L}$. Taken together, these results indicate that it was more difficult to remove cadmium than lead from water by alum coagulation alone, under natural surface water conditions. Though a relatively higher percentage removal of cadmium was achieved at higher alum dosages, there was no clear trend to indicate that cadmium removal increased with increased alum dosage, as the differences in percentage removal were not statistically significant. The basic mechanism of heavy metal removal by alum coagulation is the adsorption of heavy metals onto the hydrolysis species of aluminium(III) formed during coagulation and, eventually, solid-liquid separation through sedimentation and filtration. For the present study, the optimum alum dosage required to coagulate this river water was determined to be 40 mg/L, as higher alum dosages resulted in an increase of the residual turbidity of the settled water, and lower alum dosages only formed small and light floc in the water and consequent poor sedimentation. Considering the fact that the highest percentages of removal of lead and cadmium were also obtained at the relative optimum alum dosages for turbidity removal, these results also suggest that good coagulation and correspondingly adequate floc in the water may play important roles in removing heavy metals. Inadequate coagulation may therefore weaken the capability of water treatment processes to remove heavy

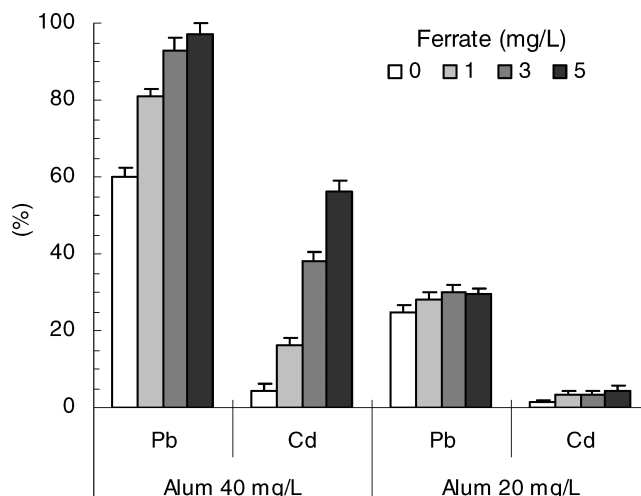
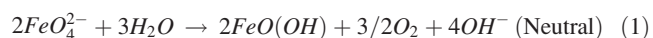


Figure 2—Enhanced removal of lead and cadmium by ferrate pretreatment (error bars show the range of three measurements).

metals. These findings also provide a possible explanation for the poor removal of lead and cadmium at low alum dosages.

Figure 2 shows the enhanced removal of lead and cadmium by ferrate pretreatment. Ferrate pretreatment significantly enhanced the removal of both lead and cadmium in alum coagulation at the 40 mg/L dosage. For both lead and cadmium, the enhancement further increased with the increase of ferrate dosage. Ferrate pretreatment at a dosage of 1 to 5 mg/L increased the removal of lead from 60% to approximately 81 to 97%, for an increased removal range of 21 to 37%, while ferrate pretreatment at 5 mg/L reduced the residual concentration of lead obtained by alum coagulation alone from 98 to approximately 7 $\mu\text{g/L}$, which is below the level of lead required by the national standard. The enhancement in cadmium removal by ferrate pretreatment, on the other hand, was much more significant than that of lead. The percentage removal of cadmium increased from 4% to approximately 16 to 56%, for an increased removal range of 12 to 52%, exceeding the removal by alum alone 2- to 12-fold. Even though a larger enhancement in the removal of cadmium than lead could be achieved by ferrate pretreatment, the overall percentage removal of cadmium was not high enough to meet the national standard under the test conditions. This is in agreement with the findings of Murmann and Robinson (1974), that lead is easier to be removed than cadmium from water by ferrate. In this study, ferrate pretreatment at 5 mg/L reduced the residual cadmium to approximately 24 $\mu\text{g/L}$, which was still higher than the regulated level of national standards.

The overall decomposition of ferrate in neutral aqueous solution can be expressed as follows:



Upon decomposition, ferric hydroxide, hydroxide ion, and molecular oxygen are generated. The enhancement of ferrate pretreatment on the removal of lead and cadmium was achieved primarily through the adsorption of heavy metal species onto ferric hydroxide (gel). This increase in the amount of adsorbent (i.e., ferric hydroxide) by the addition of ferrate before alum coagulation is thought to be the main explanation for the aforementioned enhancement. It is worth noting here that no significant enhancement could

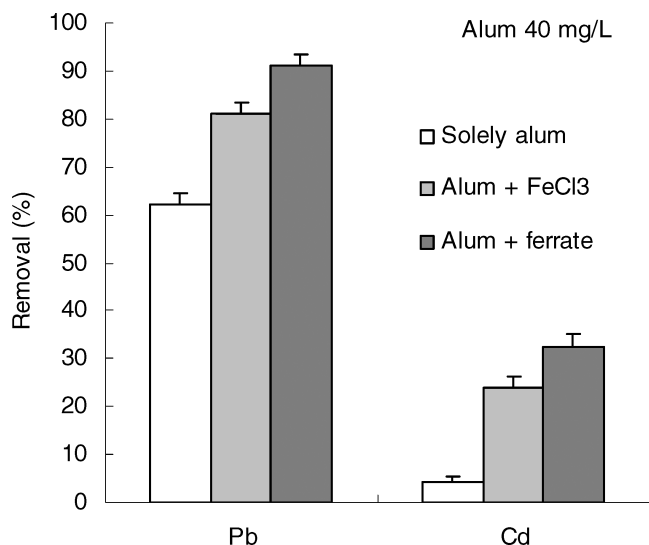


Figure 3—Enhanced removal of lead and cadmium by ferric chloride and ferrate pretreatment (error bars show the range of three measurements).

be identified in the removal of lead and cadmium by ferrate in alum coagulation at 20 mg/L. The percentage removal was less than 30% and 3% for lead and cadmium, respectively, for all samples, regardless of whether they had ferrate pretreatment. These results are consistent with the trend seen in the results of alum coagulation alone, shown in Figure 1, and they can also be attributable to the poor coagulation and consequent bad solid-liquid separation observed at low alum dosages. Again, these findings demonstrated the importance of coagulation efficiency in the removal of heavy metals in drinking-water-treatment processes.

Comparative results of the enhanced removal of lead and cadmium by ferric chloride (FeCl₃) and ferrate are shown in Figure 3. The results from alum coagulation alone are also presented, for comparison. The dosage of alum was selected to be 40 mg/L. The dosages of ferric chloride and ferrate were selected to be 1.64 and 2 mg/L, respectively, to obtain the same molar concentration of ferric hydroxide of that in the water. The addition of ferric chloride to the water samples was performed in the same manner as with the ferrate in the jar tests. Although it was very clear that the additional ferric chloride enhanced the removal of lead and cadmium, the enhancements were not as great as those obtained by ferrate. The observance of this phenomenon indicates that the increase in the amount of adsorbent (i.e., ferric hydroxide) could not be the only reason for the enhancement in the removal of lead and cadmium achieved by ferrate pretreatment. As discussed before, adequate coagulation results in a relatively high removal of lead and cadmium. We have observed that ferrate pretreatment can improve the coagulation of surface water and aid in the removal of turbidity (Liu and Liang, 2004). Thus, it can be inferred that ferrate pretreatment first improved the coagulation and then improved the removal of lead and cadmium, to some extent.

Effect of pH. The removal of lead and cadmium by alum coagulation, both with and without ferrate pretreatment, as a function of pH, is illustrated in Figure 4. In general, the percentage removal of lead and cadmium increased with the increasing pH of the water samples. The optimum removal pH range for lead by alum coagulation alone was pH > 6, where the

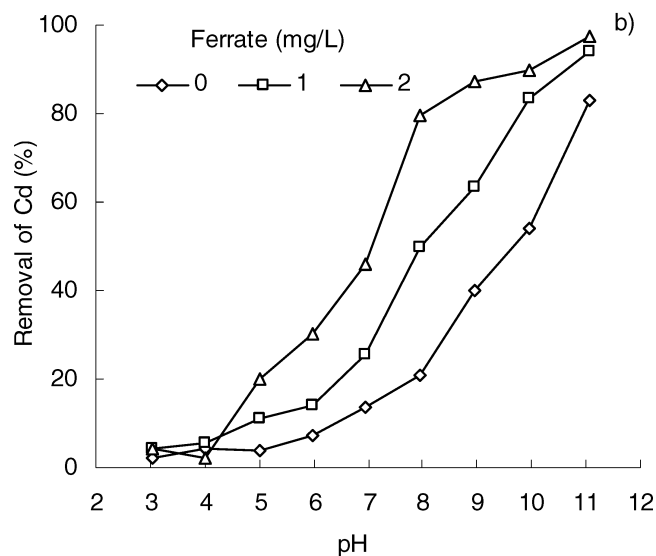
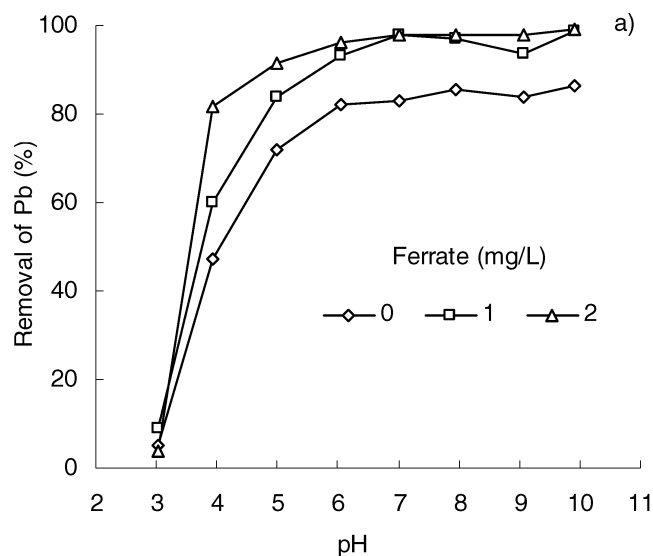


Figure 4—Influence of pH on removal of lead and cadmium by ferrate pretreatment.

percentage removal reached the top plateau value of approximately 83%. However, no optimum pH range could be concluded from the removal curve of cadmium, because the removal of cadmium increased gradually with increasing pH. Ferrate pretreatment enhanced the removal of lead and cadmium in almost the whole range of pH adopted in the tests compared with alum coagulation alone. Considerable enhancement of the removal of lead was obtained at weak acid conditions of pH 4, 5, and 6 by ferrate pretreatment. The optimum pH range for lead removal by ferrate began from 5, which was broader than that for alum coagulation only. Similarly, the improvement of the removal of cadmium at pH 5 and 6 by ferrate was also found to become significant.

The general trend of removal curves observed for lead and cadmium as a function of pH may be attributable to the hydrolysis status of aluminium(III) in the water under various pH values. The principal ionic species of aluminum is the free metal ion Al³⁺ in

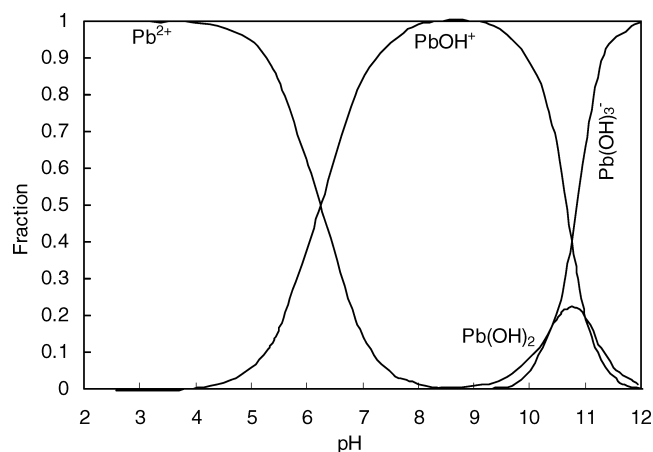


Figure 5—Distribution diagram for lead(II) hydroxide complexes at various pH values (Rickard and Nriagu, 1978).

dilute acid solutions below pH 4 (Hayden and Rubin, 1974). As the pH increases, hydrolyzed AlOH^{2+} forms, to a slight extent, while the soluble hydrolyzed species $\text{Al}_8(\text{OH})_{20}^{4+}$ is the largest fraction of aluminium present just before the precipitation of $\text{Al}(\text{OH})_3$. Correspondingly, in this study, relatively low removal of lead and cadmium was obtained at the weak acid condition $\text{pH} < 4$, with the removal efficiency gradually increasing with the increase of pH above 4 by alum coagulation alone. The removal curve for ferrate pretreatment also followed a similar trend, but at a higher value.

It should be noted here that there is a remarkable difference between the shapes of the removal curves of lead and cadmium. It can be inferred from this that the distribution of hydrolytic aluminium species in the water is not the only determining factor affecting the removal of lead and cadmium. The adsorption process also depends on the species of lead and cadmium and, in particular, the hydroxyl complexes. Heavy metals form various complexes (i.e., metal oxides, metal hydroxides, and metal carbonates) in aqueous systems, according to the pH and ionic environment. The complexes of heavy metals by a chelating-ligand typically respond to a function of pH and consequently affect the adsorption by adsorbents.

Figure 5 (Rickard and Nriagu, 1978) shows the variation of the fractions of hydrolyzed lead(II) species with pH, under conditions in which no other complexing agents are present. As the concentration of lead in natural waters is low ($< 10^{-6}$ M), significant amounts of polynuclear hydrolyzed complexes [i.e., $\text{Pb}_3(\text{OH})_4^{2+}$, $\text{Pb}_4(\text{OH})_4^{4+}$, and $\text{Pb}_6(\text{OH})_8^{4+}$] are unlikely present in water. The predominant species under acidic conditions is Pb^{2+} , while PbOH^+ dominates in the typical pH range ($\text{pH} > 6$) of natural aquatic systems. As can be seen in Figure 3, a large increase in the removal curve at the range pH 4 to 6 was identified. Hence, it can be concluded that, compared with Pb^{2+} ions, $\text{Pb}(\text{OH})^+$ more easily takes part in the bridging processes and consequent adsorption onto hydrolyzed aluminium species.

The distribution of the hydroxide cadmium(II) species [i.e., Cd^{2+} , CdOH^+ , $\text{Cd}(\text{OH})_2(\text{aq})$, HCdO_2^- , and CdO_2^{2-}], as a function of pH, is shown in Figure 6 (Weber and Posselt, 1974). The Cd^{2+} is the only species dominant from the acid pH range up to pH 10. Hydrolysis becomes significant in solutions above pH 7, and mononuclear hydrolysis products appear above pH 8. After pH 8,

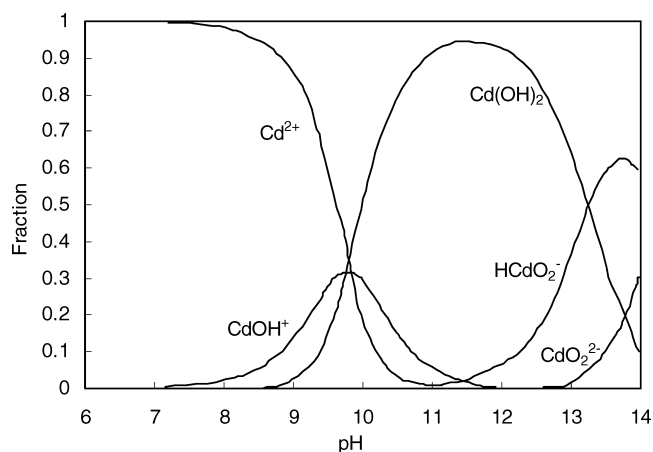
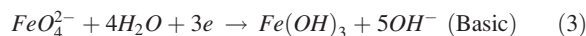
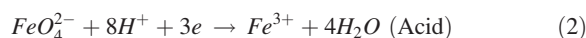


Figure 6—Distribution diagram for cadmium(II) hydroxide complexes at various pH values (Walter et al., 1974).

CdOH^+ and $\text{Cd}(\text{OH})_2$ start to form, although the fractions of these species are very small, until pH 10. In the range pH 8 to 10, the removal of cadmium by alum coagulation increases gradually with increasing pH (see Figure 3). Subsequently, better removal of cadmium by alum coagulation was achieved under basic conditions of $\text{pH} > 10$, where $\text{Cd}(\text{OH})_2$ species prevailed in the solution.

These phenomena strongly demonstrate that hydrolyzed heavy metal species have high affinity to adsorbents compared with heavy metal ions. Removal curves exhibited a remarkable increase in adsorption around the pH where the hydrolysis of metal ions occurs. These results are consistent with previous findings that metals are easily adsorbed onto inorganic adsorbent at high pH conditions (Bell and Saunders, 2005; Donat et al., 2005), and they also suggest that the hydroxide ligand plays a specific role in adsorption processes. Further, the presence of the hydroxyl ($-\text{OH}$) group on metal ion hydrolysis products may allow hydrogen bonding to occur between the hydrolysis species and the substrate surface and result in further adsorption.

The final pH of the water samples in the batch tests were measured, but no detectable changes were observed compared with the initial pH. This finding indicates that the enhancement seen in the removal of lead and cadmium by ferrate pretreatment is a result of the additional adsorbents and not changes in pH, although the removal was highly pH-dependent. The decomposition of ferrate in acid and basic solutions can be described by the following:



In acid solution, ferric ions generated upon the decomposition of ferrate. However, the ferric ion has a much higher tendency to hydrolyze than does the aluminium ion (Leckie and James, 1974). A large proportion of several mononuclear and polynuclear hydrolyzed species of ferric, such as $\text{Fe}(\text{OH})^{2+}$, $\text{Fe}_2(\text{OH})_2^{4+}$, $\text{Fe}(\text{OH})_2^+$, and $\text{Fe}_2(\text{OH})_4^{2+}$, coexists with Fe^{3+} under acidic conditions ($\text{pH} < 2$). Most of the hydrolyzed species convert to $\text{Fe}(\text{OH})_3$ when $\text{pH} > 3$. Compared with aluminium hydroxide, $\text{Fe}(\text{OH})_3$ is present in water at relatively lower pH conditions. This can explain the present results that ferrate pretreatment enhanced the removal of lead and cadmium in a wider pH range, while the small or no enhancement observed at pH 3 for lead and pH 4 and 5 for cadmium by ferrate pretreatment was likely the result of poor coagulation.

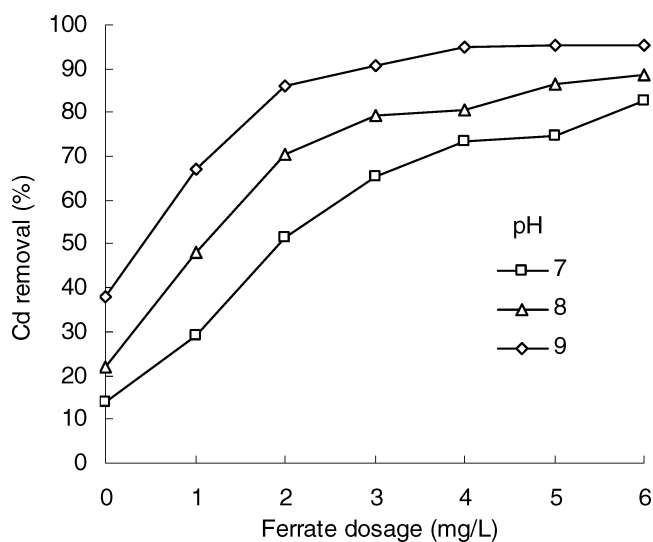


Figure 7—Effects of pH on enhance removal of cadmium by ferrate, with respect to dosage.

Under natural water conditions, it was very difficult to remove cadmium in alum coagulation to the level required by the water standards, even when the water samples were pretreated by ferrate. Considering the fact that the removal of cadmium was highly pH-dependent, trials on the enhanced removal of lead and cadmium by ferrate, with respect to dosage under weak basic conditions, were conducted, and the results are shown in Figure 7. The pH of the water samples was adjusted to pH 7, 8, and 9, and the dosage of alum was 40 mg/L. The percentage removal of cadmium continuously increased with the increase of ferrate dosages up to 6 mg/L under the three pH conditions. It is interesting to note that the removal of cadmium increased more rapidly with ferrate dosages at higher pH values than that at a relatively lower pH. The significance of the influence of pH on this increasing rate was in the order of pH 9 > pH 8 > pH 7. This phenomenon is very meaningful in practice, as the residual cadmium can be reduced to a lower level to comply with the regulated standard level, by adjusting the pH of the water. For example, ferrate pretreatment at 3 mg/L could reduce the residual concentration of cadmium to a level of slightly less than 5 µg/L at pH 9, while a dosage of ferrate higher than 6 mg/L would be needed to achieve the same removal at pH 7. Thus, ferrate pretreatment combined with pH adjustment could be a cost-effective way of removing heavy metals, such as cadmium, that are difficult to removed at neutral conditions in alum coagulation. Considering the multiple functions of ferrate on the removal of pollutants from water, the application of ferrate pretreatment could offer a better choice for water utility enterprises that encounter problems of heavy metal pollution in source water and, in particular, those related to seasonal deterioration. Therefore, the application of ferrate pretreatment in the treatment of drinking water could be performed by the simple addition of ferrate at small dosage (i.e., 1 to 5 mg/L), which adds an additional cost of less than 3 cents/ton (in USD).

Conclusions

In this study, the enhanced removal of lead and cadmium from natural surface water by ferrate pretreatment in alum coagulation

was studied. Significant enhancement in the removal of lead and cadmium was obtained by ferrate pretreatment under the conditions of natural surface water. Cadmium was more difficult to remove than lead in alum coagulation, both with and without ferrate pretreatment. The performance of ferrate in enhancing the removal of lead and cadmium in alum coagulation was better than that of ferric chloride. The removal of lead and cadmium in alum coagulation and with ferrate pretreatment was found to be highly pH-dependent. Taken together, these results indicate that hydrolyzed heavy metal species are more easily removed than heavy metal ions by the adsorption of hydrolyzed aluminium or ferric hydroxide generated from the decomposition of ferrate. Therefore, the satisfactory removal of cadmium can be expected by ferrate pretreatment combined with the adjustment of pH of the water.

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