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SORPTION OF TOXIC METALS ON GOETHITE: STUDY OF CADMIUM, LEAD AND CHROMIUM

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In this study the trapping capacity of synthetically prepared goethite (a-FeOOH) in the removal of Cr3+, Cd2+ and Pb2+ (10-4 M) in varying ionic strength conditions of the medium was determined. The adsorption study was carried out in the pH range of 4.0 to 10.0 and media ionic strengths of 0.1M, 0.01 M and 0.001 M KNO3. The metal ion adsorption on goethite is strongly pH-dependent and the adsorption edges of Cr3+, Cd2+ and Pb2+ on goethite show an S-shaped behavior. The highest adsorption medium observed was the 0.001 M KNO3. Furthermore, competitive adsorption of Cd2+, Cr3+ and Pb2+ on goethite showed the following adsorption capacity order Cr3+ > Pb2+ > Cd2+. The surface tiration data showed that the iso electric point of goethite was 9.2. KEYWORDS: Goethite, lead, cadmium, chromium, sorption.

INTRODUCTION

The release of metals from wastewater and metal-laden sludge into the soil as well as ground and surface water has a detrimental impact on these natural systems. The toxic effects of metals on aquatic and terrestrial life, are well documented.¹ The fate of metals in a particular environment depends on physical, chemical and biochemical interactions between the metals and the immediate environment. One of these processes which affect the metal concentration in an environment is its adsorption onto solid phases. There are various types of adsorbents present in the aquatic or soil environment. The hydrous oxides of iron and manganese adsorb trace metals more strongly than most other adsorbents.²

In the last decade, experimental and theoretical studies of adsorption of anions and cations at aqueous solution/hydrous oxide interfaces have been intensified in an attempt to understand the diverse phenomena which control the adsorptive behavior of trace metal ions and molecules at hydrous oxide surfaces.³ The present state of knowledge and understanding is such that a general framework can now be organized for interpretation of data on adsorptive removal of solutes in engineered systems.

The main objectives of this work are to determine, a) the trapping capacity of synthetically prepared goethite (α -FeOOH) in the removal of Cd²⁺, Cr³⁺, and Pb²⁺ in varying ionic strength conditions. b) the competitive ion adsorption on goethite. c) the effect of pH on metal adsorption.

EXPERIMENTAL

a) Preparation of Goethite

Goethite was prepared synthetically according to the procedure described by Djafer *et al.*⁴ The X-ray diffractometry and IR spectroscopy analysis confirmed the presence of

goethite (α -FeOOH) and no other iron oxides were found. The sample had a BET nitrogen surface area of 34 m²g⁻¹. The pH_{IEP} (iso electric point) at 25°C is 9.2.

b) Metal Adsorption on Goethite

Solutions of cadmium nitrate, lead nitrate, chromic chloride and potassium nitrate as supporting electrolytes were prepared just prior to use. Distilled/deionized water was used in all experiments.

The first set of adsorption runs involved a survey of the adsorption characteristics of metal ions (10^{-4} M) on goethite (0.45 g/l) at different ionic strength conditions $(10^{-3} \text{ M}, 10^{-2} \text{ M} \text{ and } 10^{-1} \text{ M} \text{ KNO}_3)$. The required solutions of goethite and metal ion concentration were added to the distilled + deionized water in 50 ml plastic vessels. The ionic strength was adjusted using KNO₃. The suspension pH was adjusted, adding micro amounts of acid (HNO₃) or base (KOH). The system was left to be continuously stirred overnight under an N₂ atmosphere. The following day, equilibrated pH of the system was measured and the suspensions, contained in the plastic tubes centrifuged.

The metallic cation concentration of the supernatant was determined in duplicate samples by atomic absorption spectrophotometry (Model: Shimadzu AA-670). Further, the effect of Cd^{2+} on Cr^{3+} adsorption and Cr^{3+} on Cd^{2+} adsorption were determined, at different metal concentrations. Finally, Cd^{2+} , Pb^{2+} and Cr^{3+} competitive ion adsorption on goethite was determined at equal (10^{-4} M) metal concentration levels.

c) Surface Titration Studies of Goethite

In this study, a goethite concentration of 1.9 g/l was prepared using KNO₃ as background medium. Here 0.2 M, 0.1 M, 0.05 M and 0.005 M KNO₃ media were prepared for goethite. Subsequently, 100 ml of each of these solutions were taken and first titrated to pH 10 adding standardized KOH (0.09N) and then to pH 5 adding standardized HNO₃ (0.09N), using an auto titrator (Model: METROHM 645 Multi-Dosimat/Dosigraph 625).

RESULTS

a) Surface Titration of Goethite

Figure 1 shows the surface titration of goethite at various ionic strengths. Here, at about pH 9.2, intersection of titrated curves can be observed.

b) Effect of Media pH and Ionic Strength on Metal Removal

Initially, metal removal was investigated for 10^{-4} metal concentration at three ionic strengths, 0.001 M, 0.01 M and 0.1 M KNO₃ in the pH range of 4.0 to 10.0. Figure 2 (a, b, c) show the S-shaped adsorption edges for metal adsorption on goethite. The highest adsorption was observed for the lowest ionic strength, 0.001 M KNO₃. Metal removal is clearly affected by pH, the removal percentage increasing with increasing pH. Above pH 8, one hundred percent of metal is removed. An increase of ionic strength from 0.001 M to 0.1 M shifts the adsorption edge approximately 1.2 units to the right at pH_{50%} adsorption for Cd²⁺ and 0.5 pH unit to the right at pH_{50%} adsorption for Pb²⁺.





c) Cd^{2+} , Cr^{3+} and Pb^{2+} —Interaction on Goethite

Figure 3 shows the Cd^{2+} , Cr^{3+} and Pb^{2+} adsorption on goethite and follows the order Cr^{3+} > $Pb^{2+} > Cd^{2+}$. Figures 4(a, b) show the effect of Cd^{2+} on Cr^{3+} adsorption and Cr^{3+} on Cd^{2+}



FIGURE 2(b) Pb²⁺ adsorption on geothite: effect of media pH/ionic strength.



FIGURE 2(c) Cr³⁺ adsorption on geothite: effect of media pH/ionic strength.

adsorption. In both cases when one metal concentration is fixed and the other increases, reduction of metal adsorption on goethite is observed.

DISCUSSION

a) Surface Titration of Goethite

At the point of zero proton condition, the pH_{zpc} corresponds to the pH where the surface is uncharged and is, in the absence of specifically adsorbable ions other than H⁺ and OH⁻,



FIGURE 3 Cd^{2+} , Cr^{3+} and Pb^{2+} adsorption on geothite ($Cd^{2+:Cr^{3+}}$: $Pb^{2+} = 1:1:1$).



FIGURE 4(a) Effect of Cd²⁺ on Cr³⁺ adsorption on geothite.

identical with the iso electric point (iep). Figure 1 shows that pH_{zpc} of goethite in this study is about 9.2. Further, other authors had reported different pH_{zpc} values (e.g. Johnson,² 9.1; Djafer *et al.*,⁴ 8.5; Djafer *et al.*,⁵ 8.4; Balistrieri and Murray,⁶ 8.4).

At pH _{zpc}, neutral and positively charged hydroxyl groups predominate, resulting in low metal removal efficiency. Conversely, at pH > pH_{zpc}, the metal removal would be improved. Specifically adsorbed cations increase the pH of the iso electric point but lower the pH of the zero proton condition, while specifically adsorbed anions decrease the pH



FIGURE 4(b) Effect of Cr³⁺ on Cd²⁺ adsorption on geothite.

of the iso electric point.⁷ The pH_{zpc} is an important parameter in water treatment technology.

b) Effect of Media pH and Ionic Strength on Metal Removal

Site-binding models are formulated around the assumption that the oxide-water interface is populated by surface hydroxyl groups, which act both as adsorption sites and sources of surface charge development. For excellent reviews of oxide chemistry viewed from the site-binding modelling perspective, the reader is referred to Schindler,⁸ James and Parks⁹ or Sposito.¹⁰ Surface hydroxyl groups result from the hydrolysis of surface species that have unsatisfied coordination sites. These surface hydroxyl groups are amphoteric, that is they can act as either an acid or a base, by adsorbing or desorbing H⁺. These oxide surfaces acquire electrical charges which vary according to the pH of the solution. Important variable-charge constituents in the soil environment are the oxides of iron, aluminum, titanium and manganese. The term "oxide" is used here to include oxyhydroxides such as goethite (α -FeOOH) as well. Adsorption of metal ions to *ga-FeOOH is a surface complexation reaction between aqueous metal ions and hydroxyl-specific surface sites. The adsorption of metal ions onto goethite (α -FeOOH) in these experiments involves a number of equilibrium steps. When considering metal adsorption, account must be taken not only of bare cation, but also of the hydrolyzed species present at any specific pH.

(i) Amphoteric reaction at the goethite (α -FeOOH) surface

$$\text{FeOH}^+_{2(s)} \rightleftharpoons \text{FeOH}_{(s)} + \text{H}^+_{(aq)}$$
 (1)

$$FeOH_{(s)} \simeq FeOH_{(s)} + H^{+}_{(aq)}$$
 (2)

Where $\text{FeOH}_{(s)}$ represents a single protonated surface oxide site and $\text{FeO}_{(s)}^-$ and $\text{FeOH}_{(s)}^+$ refer to ionized, surface functional groups. In addition, the surface sites can enter into complexation reactions with other ions in solution:

$$FeOH_{(s)} + M^{n+}_{(aq)} + mH_2O_{(aq)} \rightleftharpoons FeO - M(OH)_m^{(n-m-1)}_{(s)} + (m+1)H^+_{(aq)}$$
 (3)

$$FeOH_{(s)} + A^{n-}_{(aq)} + mH^{+}_{(aq)} \qquad \rightleftharpoons FeOH_{m+1} - A^{m-n}_{(s)}$$
(4)

M and A represent cationic and anionic adsorbates, respectively, and $M(OH)_m^{n-m-1}$ refers to hydrolytic species of the metal.

Hence possible adsorption reactions include the following. Cadmium adsorption onto α -FeOOH

$$FeO^{-} + Cd^{2+} \rightleftharpoons FeOCd^{+}$$

$$FeO^{-} + Cd(OH)^{+} \rightleftharpoons FeOCd(OH)$$

$$FeO^{-} + Cd(OH)_{2} \rightleftharpoons FeOCd(OH)^{-}_{2}$$

$$FeOH + Cd^{2+} \rightleftharpoons FeOCd^{+} + H^{+}$$

$$FeOH + Cd(OH)^{+} \rightleftharpoons FeOCd(OH) + H$$

Lead adsorption on goethite follows the cadmium reactions. In this case $Pb_3(OH)_4^{2+}$ ion is also involved in the reaction.

(ii) Chromium adsorption onto α -FeOOH

When compared to Cr³⁺, Cd²⁺ and Pb²⁺, the K⁺ and NO³⁻ surface-ion complexes that are formed during these procedures are highly unstable.¹¹

(iii) α -FeOOH interaction with electrolyte ions

 $FeO^- + K^+ \qquad \rightleftarrows \qquad FeOK$ FeOH₂ + NO₃⁻ $\iff \qquad FeOH_2^+NO_3^-$

According to Figs. 2 (a, b, c), metal adsorption on goethite is strongly pH dependent. However all ions (Cr^{3+} , Cd^{2+} , and PB^{2+}) behave similarly, even though they show different valencies. It can also be suggested that metal adsorption is favoured if the adsorbent is negatively charged at high pH. According to the surface complexation model described earlier, negatively charged FeO⁻ goethite sites play a major role in metal adsorption, because negatively charged FeO⁻ sites and positively charged metal ions or species can form surface complexes. However, at low pH levels metal adsorption can also be observed. The reasons for this may be that at low pH levels less FeO⁻ sites and more FeOH sites in the solution can form surface complexes with metal ions or species in solution. Sorption of cations on oxides is characteristically low at low pH, increasing only slightly with increasing pH up to an "adsorption edge" where sorption increases markedly over a narrow pH range.¹² This behavior is usually thought to represent

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adsorption reactions producing surface complexes in which the adsorbing cation either retains its inner hydration sphere (forming outer-sphere complexes) or lose part of this sheath and bonds directly to surface oxygen atoms, forming inner-sphere complexes.¹³ Johnson² reported that Cd²⁺ can form a precipitate in the solution above pH 9. Therefore, not only surface complexation, but also precipitation, is involved in the adsorption of cations onto metal oxides.

According to the X-ray adsorption spectroscopy (XAS) study of Pb^{2+} partitioned at the goethite-water interface, Roe *et al.*¹² demonstrated that the controlling sorption process depends on the relative and absolute concentrations of sorbate and sorbent. The XAS results suggest that Pb forms inner-sphere surface complexes at low coverages. The formation of surface polymers of Pb is suggested at high coverages. Roe *et al.*¹² had found no evidence to suggest that there was any formation of a surface precipitation at high coverage.

From infra-red studies of the goethite surface, it has been shown that the surface hydroxyl groups can coordinate with one, two, or three iron atoms, providing sites with very different reactivities.² Because of surface roughness on an atomic scale, there will also be differences in reactivity between sites with the same coordination. Together, these effects should generate a surface with a wide range of adsorption energies. Metal (Cd²⁺, Cr^{3+} and Pb^{2+}) adsorption onto goethite surface sites, therefore, may not be uniform. Thus bonding energies for metal ions vary within the goethite surface. These bonding properties are important where desorption studies are concerned. The chemical separation of heavy metal species becomes even more complicated because specific adsorption is not only restricted to surface sites of minerals, but also takes place within the surface layer or inside the structure of the minerals. It has been shown that a slow diffusion of heavy metals onto the goethite structure is possible. The pathways along which metal ions diffuse into the goethite particles are very complex. It is very likely that diffusion takes place in micropores or at positions with defects or dislocations in the goethite structure. Thus, adsorption of heavy metals by goethite takes place at three different steps: a) surface adsorption b) diffusion into the goethite particles and c) adsorption and fixation at positions inside the particles.¹⁴ Figures 2 (a, b, c) show that metal adsorption onto the goethite surface is strongly dependent on ionic strength. A larger ionic strength of the medium (KNO₃) decreases the adsorption of metal ions.

This may be due to the lowering of the activity of the metal, a reduction in coulombic attraction for metal species on solid surface, and/or, to the presence of competing ions in the solution. Further, at high ionic strengths, it is possible to form solid Cd (NO₂) and KNO₃ in the solution.

c) Interaction of Goethite with Cd^{2+} , Cr^{3+} and Pb^{2+}

A comparison of the pH—dependent adsorption of Cd²⁺, Cr³⁺ and Pb²⁺ onto α -FeOOH at total metal concentration (10⁻⁴M) is given in Figure 3. As solution pH increases, the metal is adsorbed in the following order: Cr³⁺ > Pb²⁺ > Cd²⁺.

A generally accepted view is that the specific adsorption of heavy metals by goethite is mainly related to metal-ion hydrolysis.¹⁵ Generally, with the increasing ability of the metals to form hydroxy complexes, the specific adsorption of the metals also increases.¹⁶ Thus the pK (hydrolysis constant) values of the reaction,

$$M^{2+} + H_2O \rightleftharpoons MOH^+ + H^+$$

characterizes the general adsorption behavior of the different metals. This sequence of removal corresponds well with the decreasing magnitude of the first hydrolysis constant of these metals.⁵ Hence according to the above explanation more hydroxy complexes (eg.

 $CrOH_2^+$) are formed by Cr^{3+} ions than by Pb^{2+} and Cd^{2+} ions. More Cr^{3+} hydroxy ions can therefore bind to the FeOH sites than to those of other metal hydroxy (eg. $Cd(OH)^+$, $Pb(OH)^+$) ions. Bonding characteristics of metal ions to goethite surface also follows the $Cr^{3+} > Pb^{2+} > Cd^{2+}$ order. The relatively low pH of adsorption (pH 4–5), compared to other cations studied under similar concentration conditions, reflects a relatively strong bonding interaction between Cr^{3+} and oxide surface.

Generally speaking, cations which bond to oxides at pH values that are below the zero point of charge (pH_{zpc}), must do so by some chemical coordinative bonding interaction, since the surface charge becomes more positive with increasing pH. Stronger chemical interactions are postulated for cations such Cr³⁺, which get adsorbed at lower pH values. Figures 4(a, b) show the effect of Cd²⁺ on Cr³⁺ adsorption and Cr³⁺ on Cd²⁺ adsorption on goethite.

Competitive adsorption was studied by comparing the adsorption of 10^{-3} M Cr³⁺ onto α -FeOOH in the presence of 0, 10^{-3} and 5×10^{-4} M Cd²⁺. As shown in Figure 4(a), the pH-adsorption edge for Cr³⁺ shifts to the right when a competing metal is added to the solution. Addition of Cd²⁺ to the system somewhat decreases, the Cr³⁺ adsorption on each solid. When Cr³⁺ and Cd²⁺ are present in solution for adsorption on goethite, more Cr³⁺ ions than Cd²⁺ are adsorbed to goethite sites, as discussed in the earlier part of this paper.

Further, when Cr^{3+} and goethite concentrations are fixed, while Cd^{2+} concentration increases in the solution, the larger concentration Cd^{2+} ions may reduce adsorption sites for Cr^{3+} . These two types of metals can also bind to different groups of surface sites in goethite. Benjamin and Leckie¹⁷ studied the competitive ion adsorption (Cd^{2+} , Pb^{2+} , Zn^{2+} and Cu^{2+}) on amorphous iron oxide and obtained the same results.

CONCLUSIONS

Results of these experiments showed that, almost 99% of cadmium and lead could be removed by using goethite when the pH of the medium is 7 or above. Here, initial metal concentrations are equal (10^{-4} M) and the goethite concentration is 0.48 g/l. The KNO₃ dominated ionic strength is 0.01 M. The competitive adsorption of cadmium, chromium and lead on goethite showed the adsorption capacity order of $Cr^{3+} > Pb^{2+} > Cd^{2+}$. The highest adsorption was observed for the lowest ionic strength media of 0.001 M KNO₃. Evidence from metal adsorption studies on goethite indicates that goethite can be successfully used to remove toxic trace elements from polluted water. However, the efficiency of metal removal will depend on the ionic strength of other elements in the background, and also the pH of the medium.

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REFERENCES

- 1. M. Sittig, "Toxic metals pollution control and worker protection" *Noyes Data Co.* (Park Ridge, USA, 1976, NJ).
- B. B. Johnson, "Effect of pH, temperature and concentration on the adsorption of cadmium on goethite" Environmental Science and Technology 24(01), 112–118 (1990).

- J. O. Leckie, D. T. Merrill and W. Chow, "Trace element removal from power plant waterstreams by adsorption/co-precipitation with amorphous iron oxyhydroxide" *AlChE Symposium Series* 81(243), 28–42 (1985).
- 4. M. Djafer, I. Lamy and M. Terce, "Interaction of metallic cations with hydrous goethite (α-FeOOH) surface" Progress in Colloid Polymer Science 79, 150-154 (1989).
- 5. M. Djafer, R. K. Khandal and M. Terce, "Interaction between different anions and the goethite surface as seen by different methods" *Colloid and Surfaces* 54, 209-218 (1991).
- 6. L. S. Balistrieri and T. W. Murray, "The adsorption of Cu, Pb, Zn and Cd on goethite from major ion seawater" *Geochimica et Cosmochimca Acta* 46, 1253-1265 (1982).
- 7. W. Stumm, and J. J. Morgan, Aquatic Chemistry, 2nd edition (John Wiley, N.Y., 1981).
- P. Schindler, "Surface complexes at oxide-water interface" In: Adsorption of Inorganics at Solid/Liquid Interface (M. A. Anderson and A. J. Rubin Eds.) (Ann Arbor Science Publications, Ann. Arbor, MI, 1981) pp. 1–49.
- 9. R. O. James and G. Parks, "Characterization of aqueous colloids by their electrical double-layer and intrinsic surface chemical properties" Surface and Colloid Science 12, 119–216 (1982).
- 10. G. Sposito, The Surface Chemistry of Soils (Oxford University Press, N.Y., 1984).
- C. Papelies and J. O. Leckie, "Adsorption of trace elements from coal-fired power plant effluents on iron oxyhydroxide: experimental and modelling studies" Department of Civil Engineering, Stanford University, EPRIRP-910-1, Technical Report No. 307 (Dept. of Civil Engineering, Stanford University, Palo Alto, California, 1988).
- A. L. Roe, K. F. Hayes, C. Chisholm-Brause, G. E. Brown, G. A. Parks, K. O. Hodgson and J. O. Leckie, "In situ X-ray absorption study of lead ion surface complexes at the goethitewater interface" *Langmuir* 7(02), 367–373 (1991).
- C. E. Cowan, J. M. Zachara and C. T. Resch, "Cadmium adsorption on iron oxides in the presence of alkaline earth element", *Environmental Science and Technology* 25(03), 437–446 (1991).
- G. W. Brummer, "Heavy metal species, mobility and availability in soils" In: *The Importance of Chemical Speciation in Environmental Processes*, (M. Bernhard., F. F. Brinckman and P. J. Sadler, eds.), (Springer-Verlag, Berlin, 1986) pp. 169–192.
- E. A. Forbes, A. M. Posner and G. Brummer, "The specific adsorption of divalent Cd, Co, Cu, Pb and Zn on goethite" J. Soil Science 27, 154–166 (1976).
- K. G. Tiller, J. Gerth and G. Brummer, "The relative affinities of Cd, Ni and Zn for different soil clay fractions and goethite" *Geoderma* 34, 17-36 (1984).
- M. M. Benjamin and J. O. Leckie, "Adsorption of metals at oxide interface: effect of the concentrations of adsorbate and competing metals In: Contaminants and Sediments, vol. 2, analysis, chemistry and biology (ed. R.A. Barker) (Ann Arbor Science, MI, 1980) pp. 305-