

The Influence of Metal Ions on the Adsorption of Phosphonates onto Goethite

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Mono- and polyphosphonates, which contain $R_3CP(O)(OH)_2$ functional groups, are used in an increasing variety of industrial and household applications including cooling water systems, oil production, textile production, and detergents. The main pathway of phosphonate removal in the environment is via adsorption onto surfaces. This study examines the effect of Ca, Cu, Zn, and Fe^{III} on the adsorption of six phosphonates onto the iron (hydr)oxide goethite. HEDP, NTMP, EDTMP, and DTPMP are commonly used, while AMP and IDMP have been identified as breakdown products of NTMP. When the molar concentration of Ca, Cu, Zn, and Fe^{III} is equal to the concentration of the phosphonate, the effects on phosphonate adsorption are either negligible or slight. This can be explained by dissociation of the metal–phosphonate complex and separate adsorption of the metal ion and phosphonate onto different surface sites. When Ca and Zn concentrations are added in excess of the phosphonate concentration, considerable increases in adsorption are observed, presumably through ternary surface complex formation and adsorption onto precipitated (hydr)oxides of Zn. Excess Ca concentrations can double the maximum surface coverage of NTMP. Phosphonate adsorption at low pH deposits negative charge on (hydr)oxide surfaces and hence increases Cu adsorption through favorable long-range electrostatic interactions. The results are discussed with respect to the removal of phosphonates in natural systems. The presence of di- and trivalent metals is not expected to diminish the removal of phosphonate during wastewater treatment or in natural waters contrary to aminocarboxylates such as EDTA where most metals result in a reduction of EDTA adsorption. Optimal phosphonate removal can be expected in waters containing mM Ca and employing addition of iron salts for flocculation or phosphate elimination.

Introduction

It is well-known that chelating agents affect the environmental behavior of metals in aquatic systems (1). In a reciprocal manner, chelating agents are themselves influenced by the presence of metals. Since chelating agent adsorption (2–6), photodegradation (7), thermal degradation (8), and biodegradation (9) are all modified by metal ion complexation, the presence of metals must always be taken into account in assessing the reactions and ultimate fate of chelating agents in the environment.

Phosphonate complexing agents, which contain one or more $R_3CP(O)(OH)_2$ Lewis acid groups, possess a number of qualities that make them attractive for use in industrial applications: high water solubility, high chemical stability, the ability to complex metal ions from very low to very high pH values, and the ability to adsorb strongly onto (hydr)oxides and other metal coatings (10). Phosphonates are used in oil production, in cooling water, boiler, and desalination systems to inhibit scale formation and corrosion, in the textile industry to stabilize peroxide-based bleaching agents, in industrial and household detergent formulations, and in nuclear medicine as bone-seeking carriers for radionuclides (10). Approximately 20 000 tons are used in the U.S. each year, corresponding to \$2.5 billion in revenues (11).

In some instances phosphonates are discharged into wastewater treatment plants, while in others they are discharged directly into natural waters. Complete microbial mineralization of phosphonates has been observed in pure bacterial cultures (12). However, phosphonates (13) are similar to EDTA (14) in that low or negligible biodegradation takes place during activated sludge treatment.

Under most treatment plant conditions, EDTA is not retained by solids (14). Phosphonates differ in this respect: strong sorption onto sewage sludge (13, 15, 16), clays (17), (hydr)oxides (18), sediments (16), and soils (16) has been observed. The equilibrium partitioning coefficient K_D was found to be 640–1830 for sediments (16) and 250–2400 for clays (17). It has been assumed, therefore, that phosphonates are only present at low concentrations in the effluent of wastewater treatment plants and in the environment (10). In a recent study (19) phosphonate concentrations in seven Swiss wastewater treatment plants have been measured. Phosphonates were present in the influent of most of the plants at concentrations between 0.05 and 2 μM . They were removed during water treatment by more than 80%. Effluent concentrations were found to be mostly below the detection limit of 0.05 μM . All seven treatment plants operated with chemical phosphate precipitation by iron salts. Facilities without such treatment will probably exhibit less efficient phosphonate removal.

Polyphosphonates are very strong chelating agents for transition and heavy metal ions, with log K values between 14 and 23 (20). Despite this fact, all adsorption studies so far have been conducted with uncomplexed phosphonates or in systems without control over aqueous phase speciation. Metal–ligand complexes may exhibit a completely different adsorption behavior than uncomplexed ligands. Carboxylate-based NTA and phosphonate-based NTMP otherwise possess the same structure; EDTA and EDTMP are also related in this way (Phosphonate names, abbreviations, and structures are shown in Table 1.). For this reason, prior studies of the adsorption of EDTA and NTA in the presence of metal ions are informative. The presence of divalent metal ions causes the adsorption of EDTA to shift toward lower pH values due to the formation of ternary surface–EDTA–metal ion complexes (2, 3). Complexation of EDTA by trivalent metal ions may either decrease (Fe^{III} , Co^{III}) or increase (La^{III} , Bi^{III}) EDTA adsorption to a great extent (3, 4). The presence of Co^{II} (5) or Pb^{II} (21) changes the adsorption behavior of NTA slightly.

The aim of this study is to investigate the effect of Ca^{II} , Cu^{II} , Zn^{II} , and Fe^{III} on the adsorption of ligands possessing one to five phosphonate groups. HEDP, NTMP, EDTMP, and DTPMP are the most widely used phosphonates in industrial applications (10). Two degradation products of NTMP (15) are also included: the monophosphonate AMP and the diphosphonate IDMP. Goethite ($\alpha-FeOOH$), the (hydr)oxide

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TABLE 1. Names Abbreviations and Structures of the Phosphonates Used in This Study

Abbreviation	Name	Structure
AMP	Aminomethylphosphonic acid	$\text{H}_2\text{N}-\text{CH}_2-\text{PO}(\text{OH})_2$
IDMP	Iminodi- (methylenephosphonic acid)	$ \begin{array}{c} (\text{OH})_2\text{OP}-\text{CH}_2 \quad \diagdown \\ \quad \quad \quad \text{N} - \text{H} \\ (\text{OH})_2\text{OP}-\text{CH}_2 \quad \diagup \end{array} $
HEDP	1-Hydroxyethane- (1,1-diphosphonic acid)	$ \begin{array}{c} (\text{OH})_2\text{OP} \\ \\ \text{HO}-\text{C}-\text{CH}_3 \\ \\ (\text{OH})_2\text{OP} \end{array} $
NTMP	Nitrilotris- (methylenephosphonic acid)	$ \begin{array}{c} (\text{OH})_2\text{OP}-\text{CH}_2 \quad \diagdown \\ \quad \quad \quad \text{N} - \text{CH}_2-\text{PO}(\text{OH})_2 \\ (\text{OH})_2\text{OP}-\text{CH}_2 \quad \diagup \end{array} $
EDTMP	Ethylendinitrilotetrakis- (methylenephosphonic acid)	$ \begin{array}{c} (\text{OH})_2\text{OP}-\text{CH}_2 \quad \diagdown \quad \quad \quad \diagup \text{CH}_2-\text{PO}(\text{OH})_2 \\ \quad \quad \quad \text{N}-\text{CH}_2-\text{CH}_2-\text{N} \\ (\text{OH})_2\text{OP}-\text{CH}_2 \quad \diagup \quad \quad \quad \diagdown \text{CH}_2-\text{PO}(\text{OH})_2 \end{array} $
DTPMP	Diethyltrinitrilopentakis- (methylenephosphonic acid)	$ \begin{array}{c} (\text{OH})_2\text{OP}-\text{CH}_2 \quad \diagdown \quad \quad \quad \diagup \text{CH}_2-\text{PO}(\text{OH})_2 \\ \quad \quad \quad \text{N}-\text{CH}_2-\text{CH}_2-\text{N}-\text{CH}_2-\text{CH}_2-\text{N} \\ (\text{OH})_2\text{OP}-\text{CH}_2 \quad \diagup \quad \quad \quad \quad \quad \quad \diagdown \text{CH}_2-\text{PO}(\text{OH})_2 \\ \quad \quad \quad \quad \quad \quad \text{CH}_2 \\ \quad \quad \quad \quad \quad \quad \text{PO}(\text{OH})_2 \end{array} $

most commonly employed in surface chemical studies, serves as the representative surface.

Materials and Methods

Materials. The goethite used in this study was synthesized and characterized as described in ref 22 and was stored as a slurry containing 44 g/L goethite. The surface area was determined to be 47.6 m²/g (22). AMP, HEDP, IDMP, and NTMP were obtained in the acid form from Fluka with >97% purity, EDTMP (Dequest 2041, 95%), and DTPMP in the acid form were provided by Monsanto (St. Louis, U.S.A).

Metal ion solutions were prepared by dissolving the metal nitrate salts in water. Silica and Zn(hydr)oxide were used in two sets of experiments. Silica was obtained from Degussa (Aerosil 200). Particulate Zn(hydr)oxide was prepared by adding NaOH to a 10 mM $\text{Zn}(\text{NO}_3)_2$ solution until a pH of 10 was achieved.

Adsorption Experiments. The adsorption experiments were carried out in 30 mL glass vials in a constant-temperature bath of $25 \pm 0.2^\circ\text{C}$. Carbon dioxide was excluded by purging the suspension with argon prior to the addition of the phosphonate. A 0.42 g/L loading was used in all goethite experiments, and a 1 g/L loading was used in all silica experiments. Particulate Zn (hydr)oxide suspensions were diluted until a loading of 1.0 mM Zn/L (about 0.1 g/L) was achieved.

A background concentration of 0.01 M NaNO₃ (Baker reagent) was used to maintain a constant ionic strength in all experiments. NaOH or HNO₃ were added to vary the pH. The concentration of phosphonate in the pH-adsorption edge experiments was 10 μM. Experiments at constant pH were conducted with 1 mM MOPS-buffer (4-morpholinepropane sulfonic acid, Aldrich) at pH 7.2. This buffer was selected because of its poor ability to complex metal ions (23). The

concentration of the phosphonate was varied from 0.2 to 50 μM in the constant pH experiments. The metal ion and the phosphonate were pre-equilibrated prior to addition to the goethite suspension. The metal-to-phosphonate ratio was 1 except when otherwise noted.

The suspension was stirred using a Teflon-coated stir bar for 1 h prior to pH measurement and sample collection. Suspension samples were filtered using 0.2 μm polycarbonate filters (Nuclepore Corp.) prior to analysis. Adsorption of uncomplexed phosphonates occurs within time scales of 1 min or less (19). Preliminary experiments also indicated that phosphonate adsorption in the presence of metals is complete within a few minutes for 10 μM Cu^{II} or Fe^{III} and 10 μM NTMP at pH 4.6 and 1 mM Ca and 10 μM NTMP at pH 11.2. Adsorbed Cu in the presence of NTMP also reached maximal values after 1 min (for 10 μM CuNTMP). The results are therefore valid for short equilibration times when dissolution reactions are not important (no dissolved iron was detected).

Dissolved HEDP, NTMP, EDTMP, and DTPMP concentrations in the filtered solutions were measured by forming the corresponding Fe^{III} complex, followed by HPLC (24). Dissolved IDMP and AMP were first converted into orthophosphate by peroxodisulfate digestion and then measured using the molybdenum blue colorimetric method (25). Dissolved Zn, Cu, and Fe^{III} concentrations in acidified samples (0.1% HNO_3) were measured using flame atomic absorption spectrophotometry.

Modeling Adsorption Data. Stability constants for phosphonate protonation and for metal–phosphonate complex formation were taken from the CRITICAL database (20) and calculated for an ionic strength of 0.01 M. Acid–base properties of free- and phosphonate-bound surface sites and electrostatic aspects of the (hydr)oxide–water interface were modeled using the 2-*pK* constant capacitance model (CCM).

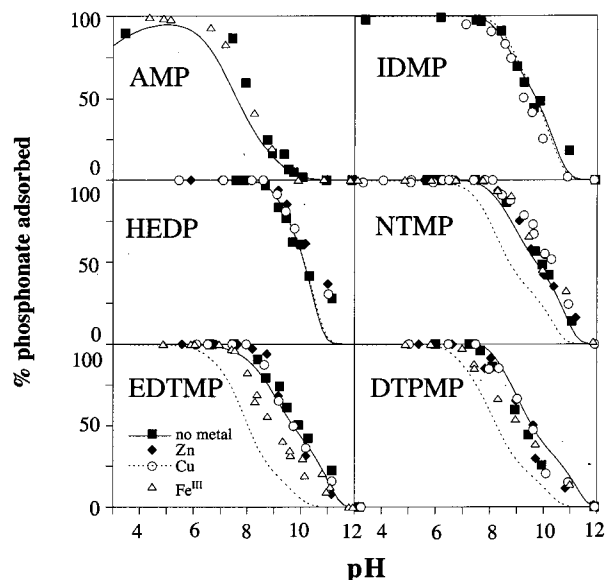
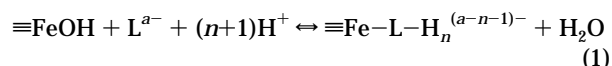


FIGURE 1. Adsorption of phosphonates onto goethite as a function of pH without metals and in the presence of equimolar concentrations of Zn, Cu, and Fe^{III}. Model calculations for adsorption of phosphonates in the absence of added metal ions, shown as continuous lines, are derived from ref 18. Model calculations for adsorption in the presence of equimolar Cu, shown as dashed lines, take Cu adsorption into account but ignore possible ternary complex formation. Conditions: 9.8 μ M phosphonate, 9.8 μ M Zn, Cu, or Fe^{III}, 0.42 g/L goethite, 0.01 M NaNO₃.

The acid–base and surface site density properties (in 0.1 M NaNO₃) for the goethite preparation were taken from the literature (26). The capacitance at 0.01 and 0.1 M NaNO₃ was found to be nearly identical (27). Therefore, it is assumed that the same values also apply to our goethite preparation in 0.01 M NaNO₃.

The adsorption of phosphonates was calculated using the surface complexation model of Nowack and Stone (18). According to this model, phosphonates are adsorbed as mononuclear complexes with two or more distinct protonation levels. The following generalized reaction represents adsorption stoichiometries:



AMP adsorption required three protonation levels (the least), while DTPMP adsorption required 10 protonation levels (the most). The number of protonation levels is analogous to the number of protonation levels observed for dissolved species.

Results and Discussion

Adsorption of Phosphonates in the Presence of 10 μ M Cu, Zn, and Fe^{III}. This section examines phosphonate adsorption in the presence and absence of Cu, Zn, and Fe^{III}. Concentrations of transition metal ions in wastewaters and natural waters are typically low, but the 10 μ M concentrations employed here are within an order of magnitude of metal concentrations found in wastewater.

In the absence of metal ions, phosphonate adsorption decreases as the pH is increased (Figure 1, filled squares). The experiments employed an excess of surface sites and hence yielded 100% adsorption below pH 8. The solid line in this figure represents the model fit for phosphonate adsorption in the absence of dissolved metal ions (18).

For five of the six phosphonates examined, the presence of equimolar concentrations of Cu, Zn, or Fe^{III} had no

TABLE 2. Complex Formation Constants of the Phosphonates with Ca and Cu from Ref 20^a

phosphonate	log K_{Ca}	log K_{Cu}
AMP	1.71	8.12
IDMP	3.84	12.84
HEDP	6.0	11.84
NTMP	7.6	17.2
EDTMP	9.36	23.21
DTPMP	7.1	19.5

^a $I = 0.1$ M. Log K values correspond to the reaction $\text{Cu}^{2+} + \text{L}^{n-} = \text{CuL}^{(n-2)-}$.

discernible effect on phosphonate adsorption. This observation holds for phosphonates with weak abilities to complex metal ions (AMP, HEDP, and IDMP) and for phosphonates with strong abilities to complex metal ions (NTMP and DTPMP) (see Table 2 for comparison of log K values for Cu complexation).

For EDTMP and also a little bit for DTPMP, the presence of Fe^{III} causes a discernible decrease in the amount adsorbed; the decrease in adsorption with increasing pH begins approximately 1 pH unit lower than in the absence of Fe^{III}.

To assist in the interpretation of these results, adsorption calculations were performed for each phosphonate in the presence (dashed lines in Figure 1) and absence (full lines) of equimolar Cu. The assumption was made that the metal–phosphonate complexes do not adsorb and that dissociation takes place before separate adsorption of metal ion and phosphonate onto different surface sites takes place; ternary surface complex formation is therefore not part of the model. The stability constants of the surface complexes for Cu were taken from ref 28 and for the uncomplexed phosphonates from ref 18.

As Figure 1 indicates, the adsorption model fully accounts for AMP, IDMP, and HEDP adsorption in the presence and absence of Cu. Log K values of Cu complexation in solution are not large enough to significantly perturb phosphonate adsorption, and Cu adsorption is not high enough to compete with phosphonates for available sites.

With NTMP, EDTMP, and DTPMP, the adsorption model predicts significant decreases in phosphonate adsorption above pH 6 in the presence of Cu. As with the mono- and diphosphonates discussed in the preceding paragraph, the model predicts that competition between free Cu²⁺ and free phosphonate for adsorption sites is not important. Most of the decrease in phosphonate adsorption comes from Cu–phosphonate complex formation in solution, which draws phosphonate molecules away from the surface.

Because experimental data collected in the presence and absence of Cu are nearly indistinguishable, the adsorption model is not accurately capturing some important aspects of the system. It is interesting to note that most competitive adsorption studies examine cation–cation competition (29) or anion–anion competition (30, 31); only Venema et al. (32) examined cation–anion competition and successfully modeled the adsorption results using the CD-Music model (33). In their compilation of adsorption experiments with hydrous ferric oxide, Dzombak and Morel (34) postulate two types of surface sites for cation adsorption but one type of site for anion adsorption. Our simple model does not invoke such a small fraction of very strong Cu sites.

Ternary surface complex formation, presently ignored in the model, would counteract cation–anion competition for available surface sites. Ternary complex formation in these systems is, however, much less significant in comparison to the previously studied metal–EDTA–goethite system (3). Cu and Zn shift the EDTA adsorption edge 1.5 pH units to the more acidic side, while Fe^{III} causes EDTA adsorption to

TABLE 3. Maximum Surface Coverage of Phosphonates at pH 7.2 in the Absence of Metals and in the Presence of Equimolar Cu and Fe^{III} and of 1 mM Ca^a

phosphonate	metal free suspension	max. surf coverage ($\mu\text{mol/g}$)		excess Ca 1 mM Ca
		equimolar (1:1 metal ion/phosphonate)		
		Cu ^{II}	Fe ^{III}	
AMP	63			63
IDMP	47		51	65
HEDP	39		40	68
NTMP	31	31	29	57
EDTMP	28	29	30	50
DTPMP	24	26	19	44

^a The maximum surface coverage of the phosphonates was determined by a Langmuir plot.

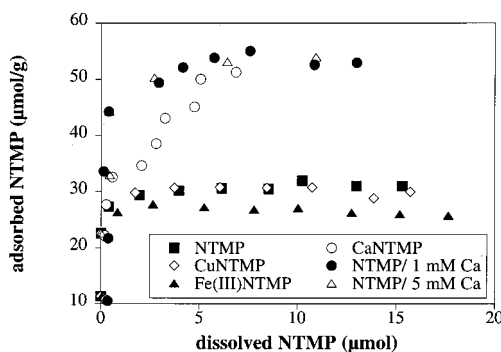


FIGURE 2. Adsorption isotherms of NTMP onto goethite in the presence of equimolar Cu, Fe^{III}, and Ca and in excess Ca (1 and 5 mM) at pH 7.2. Conditions: CuNTMP, Fe^{III}NTMP and CaNTMP as 1:1 complex, uncomplexed phosphonates and 1 or 5 mM Ca(NO₃)₂ for the Ca experiments, 0.42 g/L goethite, 1 mM MOPS buffer, 0.01 M NaNO₃.

decrease significantly at pH < 7 and to increase significantly at pH > 7. The ternary surface complexes that were evoked to explain these observations with EDTA (3) are apparently much less significant with the corresponding phosphonate EDTMP.

Adsorption isotherms at pH 7.2 were measured for the six phosphonates in the presence and absence of equimolar concentrations of Cu and Fe^{III}. All phosphonates and their metal complexes exhibit strong adsorption at low phosphonate concentrations and a distinct plateau at higher concentrations. Table 3 gives values for the maximum surface coverage (determined by a Langmuir plot) in the absence and presence of Cu and Fe^{III}. The maximum phosphonate adsorption is not altered significantly by the presence of equimolar concentrations of Cu or Fe^{III}. Figure 2 shows some isotherms for NTMP in the absence and presence of Cu and Fe^{III}. It can be clearly seen that the data points for uncomplexed NTMP and CuNTMP cannot be distinguished. The influence of Ca will be discussed in a later part of this manuscript.

Adsorption of 10 μM Cu in the Presence of Phosphonates. Dissolved Cu measurements also were made as part of the experiments described in the preceding section, allowing us to explore the effects of phosphonates on Cu adsorption. Figure 3 shows the extent of Cu adsorption as a function of pH in the presence and absence of six phosphonates. pH regions below and above the Cu adsorption edge (centered at approximately pH 5.3) respond to the presence of phosphonates differently and are hence treated differently. Cu adsorption in the absence of phosphonates was satisfactorily modeled using the log *K* values from ref 28.

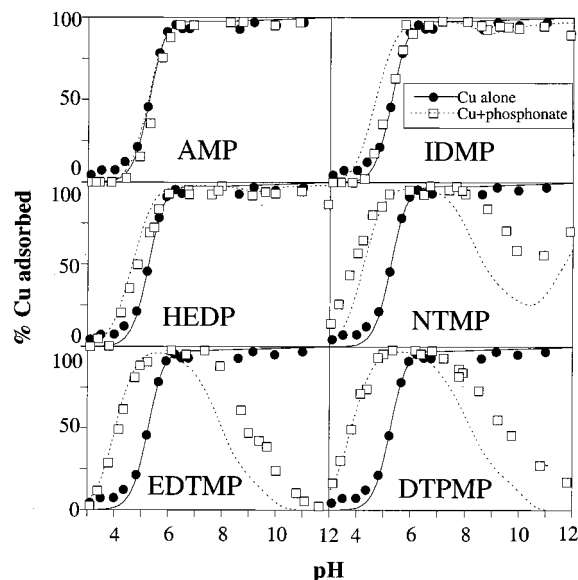


FIGURE 3. Influence of phosphonates on Cu adsorption as a function of pH. Phosphonates and Cu were present at equal concentrations of 9.8 μM. The lines are calculated based on a model which considers Cu-only (26) and phosphonate-only surface complexes (18) but no ternary Cu-phosphonate-surface complexes. Suspensions contained 0.42 g/L goethite and 0.01 M NaNO₃.

At pH values below the adsorption edge, AMP and IDMP had very little effect on Cu adsorption. A slight decrease is observed at pH < 5. The other four phosphonates increased Cu adsorption, with this increase growing as the number of phosphonate groups is increased: HEDP < NTMP < EDTMP < DTPMP. To interpret these observations, the model discussed in the previous section was used to calculate the extent of Cu adsorption (dashed lines in Figure 3). Separate adsorption of the metal ion and phosphonate onto different surface sites was assumed; ternary complex formation is again not invoked. The model successfully predicts the effects of AMP, HEDP, NTMP, EDTMP, and DTPMP on Cu adsorption. The model predicts a slight increase in Cu adsorption in the presence of IDMP at low pH, although no increase was experimentally observed. In low pH, phosphonate-free systems, the goethite surface has a net positive charge; unfavorable long-range electrostatic interactions lessen Cu adsorption. According to the model employed here, negative charge deposition on the surface, which accompanies phosphonate adsorption, diminishes this positive surface charge and hence increases Cu adsorption. Venema et al. (32) postulated a similar influence of orthophosphate on cadmium adsorption under low pH conditions.

At pH values above the adsorption edge, AMP, IDMP, and HEDP have little effect on Cu adsorption, while NTMP, EDTMP, and DTPMP substantially decrease Cu adsorption (Figure 3). Again, the model assuming separate adsorption of metal ion and phosphonate onto different surface sites can be used to interpret the experimental data. The decrease in Cu adsorption at pH values above the adsorption edge is clearly linked to Cu-phosphonate complex formation in solution; the decrease in Cu adsorption is greatest with phosphonates which exhibit the largest log *K* values. AMP, IDMP, and HEDP are not effective chelating agents for Cu under alkaline pH conditions and hence do not appreciably lessen Cu adsorption.

The model, however, predicts less Cu adsorption in the presence of NTMP, EDTMP, and DTPMP above the Cu adsorption edge than observed experimentally. Discrepancies between experimental and model results for the adsorption of phosphonates in the presence of Cu discussed earlier

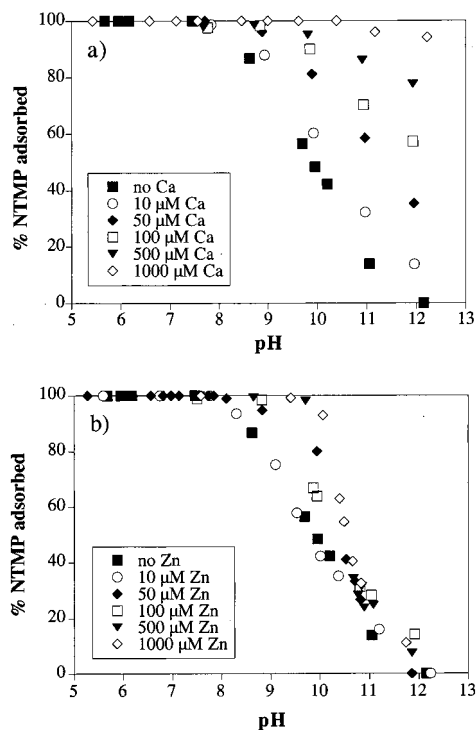


FIGURE 4. Influence of calcium and Zn on phosphonate adsorption onto goethite. (a) Adsorption of NTMP at Ca concentration from 0 to 1000 μM . (b) Adsorption of NTMP at Zn concentrations from 0 to 1000 μM . Conditions: 9.8 μM NTMP 0.42 g/L goethite, 0.01 M NaNO_3 .

(Figure 1) are comparable in magnitude. It is likely that the same phenomenon of ternary complex formation is responsible for both sets of observations.

An unambiguous answer to the question whether metal and phosphonate are adsorbed as ternary complex or as separate ions could be obtained by using spectroscopic methods such as FTIR or EXAFS. The complexes $\equiv\text{Fe}-\text{O}-\text{Cu}$ and $\equiv\text{Fe}$ -phosphonate should be distinguishable from a $\equiv\text{Fe}-\text{O}-\text{Cu}$ -phosphonate complex.

Adsorption of Phosphonates in the Presence of 10 μM – 5 mM Ca. Ca concentrations in excess of 1.0 mM are commonly observed in surface waters, and hence experiments exploring the effects of a wide range of Ca concentrations are appropriate.

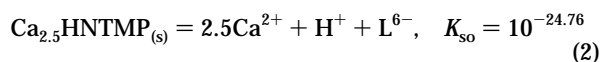
In the absence of added metal ions, 10 μM NTMP adsorption onto 0.42 g/L goethite is nearly complete below pH 8.0 but decreases to negligible levels as the pH is increased to 12.0 (18). As shown in Figure 4a, increasing Ca concentrations (10–1000 μM) shift NTMP adsorption edge toward increasing pH values. Ca (1 mM) is able to increase the adsorption of 10 μM NTMP from 40 to 100% at pH 10.0 and from 0 to 95% at pH 12.0.

Ca also has an effect on the maximum surface coverage of NTMP. Even low, equimolar Ca concentrations cause a remarkable increase in adsorbed NTMP, with a maximum surface coverage (in $\mu\text{mol/g}$) that is about twice as high as without Ca (Table 3). Ca at a 1 mM concentration causes even stronger NTMP adsorption, while the increase to 5 mM Ca does not result in a further change (Figure 2). As noted earlier, AMP yields a maximum surface coverage in the absence of added metal ions that is significantly higher than for the other five phosphonates. Table 3 indicates that 1 mM Ca enables IDMP and HEDP to adsorb to the same extent as AMP. NTMP reaches a maximum surface coverage in the presence of 1 mM Ca that is 91% of the value observed with AMP. EDTMP reaches a coverage that is 79%, and DTPMP reaches a coverage that is 70% the value observed with AMP.

The log K values for Ca complexation increase in the order $\text{AMP} < \text{IDMP} < \text{HEDP}$ (Table 2). This is the same sequence that we observe in the adsorption experiments. NTMP, EDTMP, and DTPMP have similar high log K values for Ca complexation; adsorption of all three is greatly affected by the presence of 1 mM Ca.

Whereas in the presence of low Cu and Zn ion concentrations, formation of ternary surface complexes is unimportant, the effect of Ca could be explained by formation of ternary surface–phosphonate–Ca complexes. Ca is also different from Cu and Zn with respect to solution chemistry of phosphonates because its complexes are much less soluble than the Cu and Zn complexes (35).

The fact, however, that we observe the same plateau for NTMP at 1 and 5 mM Ca demonstrates that the phenomenon responsible for the enhanced NTMP adsorption is not due to the formation of CaNTMP precipitates. A calcium hydrogen NTMP solid phase has been described by Gerbino (35), which corresponds to the following dissolution reaction (at 70 °C and 1 M ionic strength):



A value of K_{so} appropriate for 25 °C conditions can be readily calculated using ΔH° given in ref 35. Obtaining a value of K_{so} appropriate for our ionic strength (0.01 M) cannot be done precisely, since the Davies equation is valid only up to an ionic strength of 0.55 M (1). Provisional application of the Davies equation, along with the temperature correction, yields a value of $10^{-26.61}$ for K_{so} . At a Ca concentration of 1 mM and at pH 7.2, an equilibrium NTMP concentration of 740 μM is calculated, which is much higher than the actually measured dissolved concentration of 10–20 μM NTMP. At 50 μM Ca (adsorption isotherm in Figure 2), the equilibrium NTMP concentration is 1030 μM compared to the used concentration of 20 μM . If precipitation reactions play a role, we would expect to see a difference in NTMP adsorption in the presence of 1 or 5 mM Ca. As this is not the case, we can rule out the formation of CaNTMP precipitates.

Adsorption of NTMP in the Presence of 10 μM – 1.0 mM Zn. High metal ion concentrations other than Ca may be found in industrial wastewaters containing both phosphonates and metals. Metals such as Cu or Zn are different from Ca in that they form less soluble (hydr)oxides at neutral to high pH.

The experiments presented in Figure 4b were performed in the same manner as those presented in Figure 4a, except that Zn is used as the added metal ion. Below pH 10.5, both figures show an increase in NTMP adsorption as the concentration of added +II metal ion is increased. Above pH 10.5, however, increases in NTMP adsorption caused by Zn addition are much less than increases caused by Ca addition.

Thermodynamic calculations indicate that 1000 μM Zn solutions become saturated with respect to $\text{Zn}(\text{OH})_2(\text{am})$ at pH 7.8, while 1000 μM Ca solutions are soluble with respect to $\text{Ca}(\text{OH})_2(\text{s})$ at pH values below 12. It is therefore likely that $\text{Zn}(\text{OH})_2(\text{s})$ formed in the experiments presented in Figure 4b, either as a distinct phase or as a coating on the goethite surface.

To explore this possibility, Zn (hydr)oxide particles were added to solutions containing NTMP. As Figure 5a indicates, Zn (hydr)oxides at loadings comparable to those that might form in the Figure 4b experiments provided a suitable surface for the adsorption of NTMP. Adsorption decreases substantially at pH values greater than 9.0.

A final set of experiments involved adding increasing amounts of Zn to suspensions containing 1.0 g/L silica and 10 μM NTMP (Figure 5b). Because no NTMP adsorption is observed in metal ion-free silica suspensions, an increase in

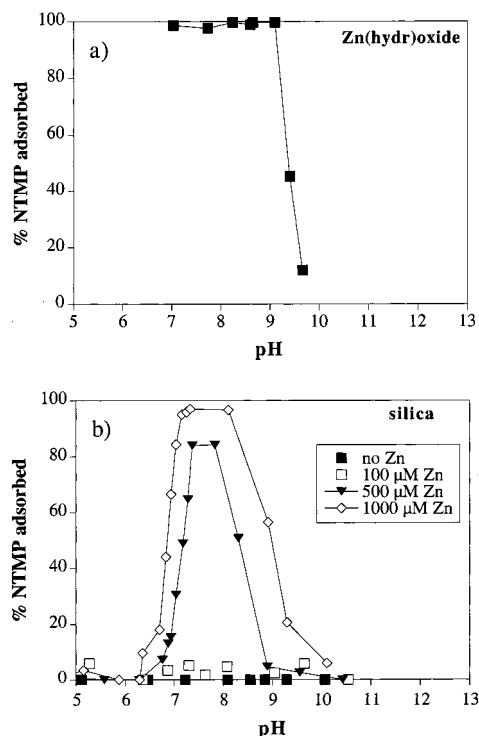


FIGURE 5. NTMP adsorption in (a) 1 mM (0.1 g/L) Zn (hydr)oxide suspensions and (b) 1.0 g/L silica suspensions containing 0–1000 μM Zn. Conditions: 9.8 μM NTMP, 0.01 M NaNO_3 .

NTMP adsorption in the presence of Zn would indicate the presence of metal-like ternary surface complexes ($\equiv\text{Si}-\text{Zn}-\text{NTMP}$) or adsorption onto precipitated zinc (hydr)oxide. In the presence of 500 μM Zn, NTMP adsorption rises dramatically within a narrow plateau centered near neutral pH. Increasing the Zn concentration to 1000 μM causes nearly complete NTMP adsorption within this narrow plateau. Examining this plateau more carefully, adsorption becomes significant when the pH is high enough ($6 < \text{pH} < 7$) for Zn adsorption and (hydr)oxide precipitation to occur and begins to diminish within the pH range ($8 < \text{pH} < 9.5$) where adsorption in the (NTMP + $\text{Zn}(\text{OH})_2$) system begins to diminish. Adsorption of NTMP is therefore clearly related to the adsorption and/or precipitation of zinc on the silica surface. It is, however, not possible at this time to distinguish between adsorption of free NTMP molecules onto the Zn (hydr)oxide surfaces versus formation of ternary surface complexes of the type $\equiv\text{Si}-\text{O}-\text{Zn}-\text{phosphonate}$.

Environmental Implications

The 10 μM concentrations of phosphonates and of Cu and Fe^{III} employed in our experiments are within an order-of-magnitude of concentrations found in municipal wastewaters (19). These amounts were found to be high enough to bring about significant Cu desorption from goethite surfaces when (i) the log K for Cu-phosphonate complex formation in solution is high, such as with NTMP, EDTMP, and DTPMP, and (ii) the pH is within the slightly alkaline to alkaline range. Fe^{III} (hydr)oxides are used as flocculating agents to remove orthophosphate during tertiary wastewater treatment (36); settling Fe^{III} (hydr)oxide particles have been found to remove Cu and other +II metal ions from lakes and other surface waters (37). These are desired processes that help decrease the dissolved fraction of metals in natural waters. It is therefore possible that synthetic phosphonates interfere with the removal of Cu and other +II metal ions under some circumstances and increase the dissolved fraction of a metal.

Of the metals used in this study, Cu and Fe^{III} had only a slight effect on the adsorption of the six representative phosphonates onto goethite. Although ternary surface complex formation may play a role in some of our experiments, it is less important than has been observed in experiments with carboxylate-based chelating agents (3). The Fe^{III} -based flocculation process mentioned in the preceding paragraph is effective at eliminating phosphonates from municipal wastewaters to a great extent (19). Based upon our findings, it is unlikely that Cu and Fe^{III} will interfere with this removal.

Dissolved Ca concentrations in municipal wastewaters and receiving waters often exceed 1 mM. Our results indicate that Ca concentrations in the mM range can have a dramatic effect on phosphonate adsorption. At pH 7, for example, the presence of 1 mM Ca resulted in removal of twice as much removal of the six representative phosphonates via adsorption onto goethite in comparison to metal-free suspensions. Thus, natural Ca concentrations could aid in the removal of phosphonates by Fe^{III} (hydr)oxides and other mineral surfaces.

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