

Surface Complexation Modeling of Phosphate Adsorption by Water Treatment Residual

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ABSTRACT

Use of water treatment plant residuals (WTR), as a soil amendment is a promising alternative to landfill disposal. Unfortunately, WTR has a propensity to bind with phosphate, which is an important plant nutrient. Phosphate may be added to WTR prior to soil application. This type of pretreatment may convert WTR from a phosphate consumer to a phosphate supplier. The binding of phosphate to WTR is typically attributed to surface complexation with metal oxides. However, attenuated total reflectance Fourier transform infrared (ATR-FTIR) data and phosphate-WTR adsorption equilibrium data indicate that phosphate also binds to a cationic polyelectrolyte that is added during water treatment processes. Using the FITEQL optimization program, equilibrium constants and total number of surface sites were determined for the polymer. Results from the FITEQL optimization were used to model binding of phosphate by cationic polymer. Binding of phosphate by hydrous ferric oxide was modeled using a diffuse double layer model, which included surface precipitation (MICROQL). The model was validated through the use of phosphate equilibrium partitioning data at pH values of 6 and 8. The model predicted that a significant fraction of phosphate adsorbed onto WTR is associated with the cationic polymer.

THE water treatment industry generates large quantities of solid residual annually. In the past, landfilling of WTR has been the preferred method of disposal. The current emphasis on pollution prevention and limitations in landfill space have encouraged water treatment plant operators to seek beneficial reuse alternatives for WTR. Use of WTR, as a soil amendment is one such alternative. This option is desirable because little or no residue treatment is required prior to application. The primary constituents of WTR residuals, iron and aluminum, are found in relatively large concentrations in the lithosphere, are less toxic than most other metals, and are not considered hazardous by the U.S. Environmental Protection Agency (USEPA). Over the past two decades, research has been conducted to determine the environmental impact of land-applied aluminum and iron residues (Elliot et al., 1990; Novak et al., 1995). Benefits associated with use of WTR as a soil amendment include improved soil structure (El-Swaify and Emerson, 1975), increased moisture-holding capacity (Bugbee and Frink, 1985, p. 1-7) and increased availability of nutrients for various plants (Heil and Barbarick, 1989). Soil properties govern the significance of each of these benefits. For example, Heil and Barbarick (1989) reported that addition of ferric hydroxide resi-

due, at low application rates to an iron deficient soil, could improve plant growth until available phosphate becomes limited.

The most significant shortcoming associated with using WTR, as a soil amendment is the reaction that occurs with phosphate (Elliot et al., 1990). A strong reaction between oxides, which make up a significant fraction of WTR, and phosphate (Novak et al., 1995) results in a decrease in the quantity of plant available phosphate (Parfitt, 1979; Heil and Barbarick, 1989). However, these reports have not identified and quantified the various components of WTR, which have an impact on WTR-phosphate complexation. The chemistry of WTR generated at water treatment plants that treat surface waters, is a function of (i) the type and purity of metal salts added, (ii) the quantity and type of organic polyelectrolytes added, (iii) disinfection agents added, (iv) sand from drying lagoons (which may be combined with WTR during dewatering operations), and (v) raw water characteristics. These characteristics may significantly impact the complexation of phosphate.

The liability associated with WTR-phosphate complexation may be overcome by amending WTR with phosphate prior to land application. Moreover, if sufficient phosphate is added, the WTR may be converted from a phosphate consumer to a phosphate supplier (Butkus, 1997). A surface complexation model, which quantifies the speciation of phosphate in WTR, may be of significant utility to both practitioners and regulators (Butkus, 1997). Models of WTR-phosphate complexation in the literature that allow for such quantification are unavailable. Although WTR typically contains a large fraction of an amorphous metal hydroxide precipitate (aluminum or iron), it may also contain a significant quantity of organic polymers that are often added during water treatment processes (Butkus, 1997). We hypothesize that phosphate may also bind to such ancillary WTR components. These forms of bound phosphate may be more labile (and possibly available to plants) than phosphate that is bound to oxides and may govern surface reactions in different pH regions. The purpose of this work is to quantify the effects of two WTR components, ferric hydroxide and a sorbed quaternary polyamine added during water treatment operations, on the binding of phosphate as a function of pH. An accepted surface complexation model that can predict the speciation of phosphate in a multicomponent WTR system was used. Quantification of the distribution of phosphate in this system may allow for accurate prediction of available phosphate in land application scenarios.

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BACKGROUND

Coagulation, flocculation, and sedimentation (or coagulation and filtration) are processes used in water treatment to remove color and turbidity. The purpose of coagulation and flocculation is to create an environment in which small particles can combine and form larger aggregates. Coagulation can be considered as three separate and sequential steps: coagulant formation, particle destabilization, and interparticle collisions (Amirtharajah and O'Melia, 1990). Metal salts such as ferric chloride and ferric sulfate are used during the coagulation process to accomplish these steps.

In the case of iron coagulation, iron salts dissolve rapidly when added to water. The iron cation produced will then hydrolyze to form complexes. These complexes will change the solution ionic strength and adsorb onto colloidal particles, which results in particle destabilization. Once particles have been destabilized, interparticle collisions will result in the formation of aggregates. At a specific pH and Fe concentration, an amorphous, gelatinous precipitate of ferric hydroxide is formed. The solid material remaining following the coagulation, flocculation, and solid/liquid separation processes is known as WTR.

The chemistry of ferric hydroxide WTR has not been studied from a fundamental perspective. However, the chemistry of hydrous ferric oxide (also called amorphous ferric hydroxide), that comprises a large fraction of WTR, has received extensive attention (Dzombak and Morel, 1990). Once formed, precipitated amorphous ferric hydroxide will begin to undergo structural changes that may continue with age (Lijklema, 1980). In aqueous solution at 20 to 30°C, hydrous ferric oxide will gradually transform to a crystalline iron oxide, usually goethite and hematite (Lijklema, 1980). A similar aging process has been hypothesized for WTR during dewatering operations (Dempsey et al., 1995; Novak et al., 1995). As hydrous ferric oxide crystallizes, its surface area will change. Surface area can be used to estimate the quantity of surface sites available for surface complexation reactions. A wide range of values for the surface area of hydrous ferric oxide have been reported; values range from 160 m²/g (Crosby et al., 1983) to 600 m²/g (Dzombak and Morel, 1990). Based on the range of sorption maxima reported in the literature, Dzombak and Morel (1990) estimated that there are approximately 0.2 mol sites/mol Fe that can bind with protons, cations, and anions.

The binding of phosphate by iron oxides has also received considerable attention in the literature. Lindsay (1979) reported FeHPO₄⁺ to be the most significant ferric iron-phosphate complex formed in natural systems (based on soil activity at neutral pH conditions). Although iron-phosphate complexes have been observed at relatively high concentrations in solution, uptake of phosphate by iron oxides in the solid phase appears to have the most significant impact on aqueous phosphate activity (Hsu, 1965). Hingston et al. (1972) reported that anions of incompletely dissociated acids, such as H₂PO₄⁻, can be adsorbed in excess of the positive charge and even onto surfaces with a net negative charge. Parfitt et al. (1975, 1976) reported that the adsorption process on synthetic iron oxides is a ligand exchange reaction where pairs

of Fe-OH react with phosphate to give a binuclear bridging FeOP(O₂)OFe complex. Other workers have reported binuclear iron-phosphate complexation reactions (Ryden et al., 1977a; Lijklema, 1980; Stumm and Morgan, 1996). However, recent spectroscopic data suggest that phosphate forms mononuclear complexes with iron oxides (Persson et al., 1996). It has been suspected for several decades (Ryden et al., 1977a; Farley et al., 1985) that phosphate may also form surface precipitates with hydrous oxides at high surface concentrations. More recently, these hypotheses have been confirmed with spectroscopic data (Nanzyo, 1986).

Factors such as ionic strength, pH, crystallinity, moisture content, and organic material appear to affect the sorption of phosphate onto iron. For example, Ryden et al. (1977b) reported that a decrease in surface potential, caused by an increase in concentration and valence of the inert electrolyte, resulted in an increase in P sorption due to van der Waals attractive forces. Hingston et al. (1972) have also shown that phosphate adsorption decreases with increasing pH.

Increased crystallinity of hydrous ferric oxide (for example, goethite) appears to result in a decrease in P uptake, which suggests a decrease in available surface sites for phosphorus sorption (McLaughlin et al., 1981; Lijklema, 1980) and/or less available cation for surface precipitation (Dzombak and Morel, 1990). McLaughlin et al. (1981) reported drying of amorphous iron hydroxide at 80°C resulted in a fourfold decrease in phosphate sorption. Iron particulates may also aggregate, via a phosphate bridge, resulting in a decrease in surface area (Anderson et al., 1985). The impact of aging on crystallization may be affected by the presence of potential sorbates. Kuo (1986) observed no change in phosphate sorption by hydrous iron oxide over a 1-yr incubation period at room temperature. However, x-ray diffraction indicated no goethite or hematite formation. Thus, the presence of phosphate may have prohibited crystal formation.

There are several hypotheses that attempt to explain the impact of organic matter on the adsorption of phosphate onto iron hydroxides. Sibanda and Young (1986) reported that humic acid competed with phosphate for sorption sites on goethite. They also stated that the maximum competition occurred at lower pH levels, where the buffering of the humic acid was high relative to that of phosphate. On the other hand, Borggard et al. (1990) noted that organic matter does not directly compete with phosphate for sorption sites. In fact, they reported that humic substances could actually increase phosphate adsorption due to inhibition of Fe-oxide crystallization. The discrepancy concerning the impact of organic material on phosphate adsorption onto iron oxides may be due to differing experimental conditions and time of reaction between the organics and oxides (Gerke, 1993).

Cationic and anionic organic polymers (polyelectrolytes) are commonly used in the water treatment process. Cationic polyelectrolytes are typically used to supplement iron and aluminum salts as the primary coagulant for color and turbidity removal. They typically have a high charge density and function via charge neutralization and interparticle bridging mechanisms (Luttinger, 1981). Anionic polyelectrolytes are typically used as filter aid and for sludge conditioning. Use of polyelectrolytes can reduce overall operating and material costs (Luttinger, 1981). The cationic polyelectrolyte investigated in this study was Magnafloc 572C (Cytec Industries, West Pattern, NJ), a quaternary polyamine. The chemical structure of a quaternary polyamine is shown in Fig. 1.

MATERIALS AND METHODS

Water Treatment Plant Residuals Characteristics

The WTR used in this study was generated from July 1995 to August 1996 at the Lake Gaillard Water Treatment Plant,

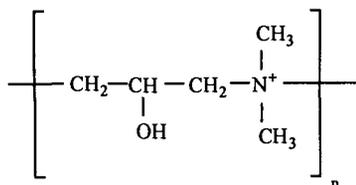


Fig. 1. Chemical structure of quaternary polyamine (Cytec Industries, West Pattern, NJ)

in New Haven, CT, operated by the South Central Connecticut Regional Water Authority. The primary coagulant used at the plant was $\text{Fe}_2(\text{SO}_4)_3$. The plant produced drinking water at an annual average of 36 million gallons/d and generated WTR at a rate of 16 000 gallons/d (1–2% solids). Ferric sulfate was added at a dose of 10.4 mg/L while Magnafloc 572C (a 50% cationic quaternary polyamine solution) was added at a dose of 2.3 mg/L and Magnafloc 1849A (a 30% anionic polyacrylamide solution) was added to the backwash water at a dose of 0.1 mg/L. Quaternary polyamine and polyacrylamide are typically assumed to remain as a fraction of WTR following filter backwashing operations (Cytech Industries, West Pattern, NJ). Plant influent total organic carbon (TOC), from Lake Gaillard, typically averages 3 mg/L.

Dried WTR (15–35% solids) was obtained from drying beds located adjacent to the water treatment plant. This material was oven dried at 40°C and stored in 1 L nalgene bottles. The WTR used in this study contained approximately 50% sand deriving from the drying beds. The TOC of dried WTR (corrected for mass of sand) was found to be approximately 42% (Butkus, 1997).

Sorption Studies

Sorption studies were conducted to quantify phosphate/WTR-partitioning speciation as a function of pH (pH sorption edges). Each experiment was conducted using a specific initial phosphate to WTR ratio. All experiments were conducted in 0.01 M NaCl and 0.02% NaN_3 (Dohse and Lion, 1994). Various volumes of 6 M HCl or 4 M NaOH were added to adjust pH. Solutions were prepared by adding $(\text{NH}_4)_2\text{HPO}_4$, NaCl, NaN_3 , and HCl or NaOH to 100 mL volumetric flasks. Conducted in triplicate, 18 mL volume of each solution was placed in 35 mL Nalgene Oak Ridge centrifuge tubes and combined with 2 g of dried WTR. All samples were capped, laid horizontally on a Braun Auto Shake table, and agitated for 7 d at 160 rpm to allow for equilibration. Kinetic studies indicated that equilibrium was achieved within 2 d (Butkus, 1997). Other workers (Ryden et al., 1977b; White and Taylor, 1977; Nair et al., 1984; Persson et al., 1996) have reported that a 1 to 2 d equilibration period was adequate to achieve equilibrium in iron-phosphate surface complexation experiments. Following the equilibration period, the pH of each sample was measured. Samples were then centrifuged and vacuum filtered through 0.45 μm nominal pore size nylon filters (Micron Separations Inc., No. RO4SP04700, Westboro, MA). Aqueous extracts were analyzed for phosphate using ion chromatography (Dionex Corp., series 4000, Sunnyvale, CA). Sorption experiments conducted with blanks and sand suggested that phosphate binding by these substrates was negligible compared to WTR. All results reported in this work have been corrected for mass of sand.

BET Surface Area

BET surface area measurements, using N_2 gas, were conducted with an Omicron Aquapore 1000 phase transition porosimeter. Measurements were conducted on WTR, which was oven dried at 40°C.

Attenuated Total Reflectance-Fourier Transform Infrared Analysis

Infrared spectroscopy was used to investigate the interaction of phosphate with the cationic polymer. The ATR sampling technique was used to analyze in situ the cationic polymer-phosphate aqueous solutions. The ATR-FTIR spectroscopy was performed using a Perkin Elmer FTIR 1600 spectrophotometer equipped with a DTGS-detector. A Squar-

ecol (Specac) liquid ATR cell was employed. The angle of incidence was 45 degrees. The spectra were recorded between 2000 and 500 cm^{-1} at a 2 cm^{-1} resolution and a total number of 64 scans. The empty cell was used as a background.

The following three samples were analyzed: 0.1 M KH_2PO_4 solution at pH 6 and 9; 8% (w/w) quaternary polyamine solution at pH 6; 0.1 M KH_2PO_4 in 8% (w/w) quaternary polyamine mixture at pH 4, 6, and 8.5.

The single spectra of the solutions were dominated by the strong absorption of water. To obtain a useful spectrum of the compound(s) of interest, a reference spectrum of water with the same pH and similar ionic strength (0.1 M NaCl) was subtracted from the sample spectrum.

Proton Release

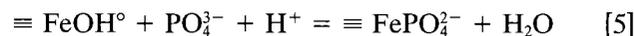
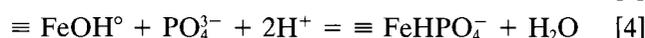
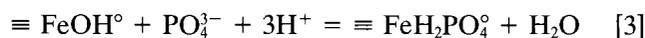
Proton release during phosphate/quaternary polyamine reactions was monitored. Increments of 0.5 mL of KH_2PO_4 (0.05–0.1 M) were added to solutions of 0.117 g of quaternary polyamine (Magnafloc 572C) in 40 mL of either distilled water or 0.1 M NaCl. The pH of the phosphate solutions was adjusted to that of the polymer solution prior to titrating. These solutions were titrated at various initial pH values ranging from 4.0 to 8.5. Changes in pH after mixing were back titrated to the initial pH using either 0.2 M HCl or 0.1 M NaOH.

All labware was steam washed, soaked overnight in 10% HNO_3 , soaked in distilled (DI) water, and rinsed twice in DI water. Solutions were prepared with ACS reagent-grade chemicals and DI water.

Modeling

A primary objective of this work was to employ a simple equilibrium model to describe the speciation of phosphate in a ferric hydroxide WTR matrix. Due to the complexity of the WTR matrix, we presumed a priori that two components of the WTR (hydrous ferric oxide and quaternary polyamine) formed substantial complexes with phosphate. We maximized use of literature values to describe these complexes to justify our choice of dominant phosphate-WTR complexes. Many physical models exist that can be used to describe sorption phenomena. This work used the diffuse double layer model, which has proven to be successful in predicting surface speciation over a wide range of chemical conditions (Dzombak and Morel 1990; Sposito, 1990; Grasso et al., 1997).

Surface complexation of phosphate onto WTR iron oxide sites was modeled using accepted relationships (Dzombak and Morel, 1990). We assumed that iron was the only metal that formed surface complexes with phosphate for two reasons. First, concentrations of other metals such as aluminum were found to be orders of magnitude lower than iron on a mass basis (Butkus, 1997). Moreover, Kuo (1986) reported that sorption of phosphate was unaffected by concurrent sorption of selected cations (Zn, Cd, and Ca) by hydrous ferric oxide. Surface complexation of phosphate with WTR was modeled via the following reactions:



Stability constants for reactions are summarized in Table 1.

Converting WTR from a phosphate consumer to a phosphate supplier may require a considerable quantity of phosphate. At sorbate/sorbent ratios of >10%, multihydroxylated surface species may be significant (Farley et al., 1985; Dzom-

Table 1. Thermodynamic parameters used to model the complexation of phosphate to hydrous ferric oxide.

Species	Equation	logK ^{int}	Reference
XOH	1	-7.29	Dzombak and Morel, 1990
XO ⁻	2	-8.93	Dzombak and Morel, 1990
XOH ₂ PO ₄	3	31.29	Dzombak and Morel, 1990
XOHPO ₄ ⁻	4	25.39	Dzombak and Morel, 1990
XOPO ₄ ²⁻	5	17.72	Dzombak and Morel, 1990
Fe(OH) ₃	8	-3	Stumm and Morgan, 1996
Fe(PO ₄)	8	26	Stumm and Morgan, 1996

bak and Morel, 1990; Katz and Hayes, 1995). For anions, this so-called "surface precipitation" phenomenon is essentially coprecipitation of the ligand with the sorbate cation and original metal oxide surface phase. Farley et al. (1985) have developed a model that accounts for the transition from surface complexation to surface precipitation. This model is based on a mathematical approach for continuously increasing the activity of the coprecipitating ligand-metal from approximately zero to one as surface precipitation increases in the solid solution. For the WTR studied here, the solid activities are defined as:

$$\{FePO_{4(s)}\} = \frac{[FePO_{4(s)}]}{T_s} \quad [6]$$

$$\{FeOH_{3(s)}\} = \frac{[Fe(OH)_{3(s)}]}{T_s} \quad [7]$$

where [] imply concentrations and { } imply activities. The total mass of the solid solution (T_s) is given by:

$$T_s = [FePO_{4(s)}] + [Fe(OH)_{3(s)}] \quad [8]$$

The activity of each species in the solid solution is constrained via the following relationship:

$$\{FePO_{4(s)}\} + \{Fe(OH)_{3(s)}\} = 1 \quad [9]$$

Thus, precipitation may occur in the solid solution at phosphate concentrations lower than that required in the bulk (for a more detailed explanation, cf. Dzombak and Morel, 1990; Katz and Hayes, 1995). Surface complexation and surface precipitation of phosphate onto iron, on the WTR surface, was modeled using a modified version of MICROQL according to Dzombak (1989).

We also modeled the complexation of phosphate by functional groups on quaternary polyamine. For the sake of brevity, we will refer to the charged functional group on quaternary polyamine, $R'-(CH_3)_2CHN^+-R''$, as Q^+ . We assumed that charged functional groups are affected by pH via:



Based on the phosphate pH adsorption edges, FTIR measurements, and titration experiments, we postulated the following set of possible complexes between Q^+ and phosphate (see the results section of this work for a discussion of the basis for our assumptions):



Equilibrium constants for Eq. [11] and [12] were determined using FITEQL (Westall and Morel, 1977; Westall, 1982).

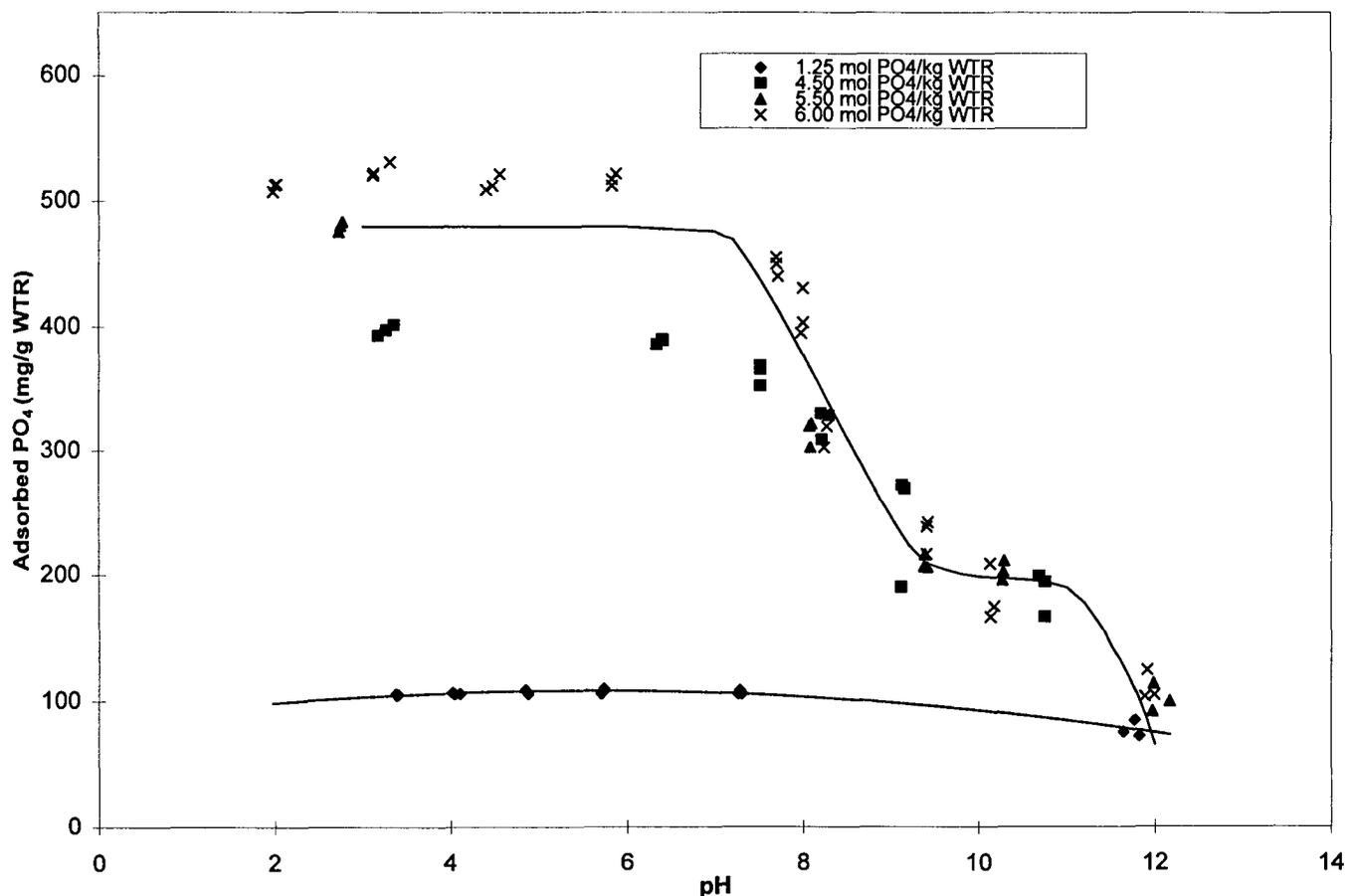


Fig. 2. Phosphate-WTR pH adsorption edge data (0.01 M NaCl). Curves are provided to illustrate trends in data.

RESULTS AND DISCUSSION

Experimental

Sorption studies were conducted to determine the effect of pH on the uptake of phosphate by WTR. Figure 2 shows results for ferric sulfate WTR obtained from the Lake Gaillard Water Treatment Plant. This figure illustrates results for four phosphate amendments (6.0 mol PO_4/kg WTR, 5.5 mol PO_4/kg WTR, 4.5 mol PO_4/kg WTR, and 1.25 mol PO_4/kg WTR).

As indicated by the 6.0 mol PO_4/kg WTR data in Fig. 2, phosphate-WTR complexation was relatively constant between pH values of approximately 2 to 7. Phosphate uptake decreased at pH values greater than about 7. Between pH 3 to 9, the data is similar to that reported by Lijklema (1980) for phosphate-iron(III) hydroxide complexation. However, as indicated by the trend line for high initial phosphate values beyond a pH of approximately 9, the solid phase concentration reached a shoulder and then decreased precipitously at a pH of about 12. This behavior is not indicative of typically reported iron phosphate reactions; for example, data from Lijklema (1980) suggests that sorption of phosphate onto iron hydroxide approached zero as pH values approached 10. Therefore, the presence of a shoulder (about 200 mg PO_4/g WTR) may be indicative of an additional competitive reaction for phosphate (in addition to iron hydroxide) on the WTR surface. It was hypothesized that phosphate cationic polymer binding may have been responsible for this behavior.

The interaction between phosphate and Q^+ was investigated using ATR-FTIR. This technique offers the advantage of in situ investigations of chemical species in aqueous solutions and suspensions and can provide information about the interaction between Q^+ and phosphate at the molecular level. The interpretation of spectra of complexed species in ATR-FTIR spectroscopy is based on the comparison with the corresponding free solution species (Tejedor-Tejedor et al., 1990). Figure 3a and b show the spectra of aqueous solution of 0.1 M KH_2PO_4 at pH 6 and 9, respectively. The H_2PO_4^- anion is the predominant solution phosphate species at pH 6 (Stumm and Morgan, 1996). The H_2PO_4^- anion has a C_{2v} symmetry and the bands in Fig. 3a are typical for this phosphate monoanion. The 1075 cm^{-1} band can be assigned to a symmetric P-O stretching vibration, the 1154 cm^{-1} to an asymmetric P-O stretching vibration and the 940 cm^{-1} to an asymmetric P-OH stretching vibration (Nakamoto, 1986; Tejedor-Tejedor and Anderson, 1990). Figure 3b represents the spectrum of the HPO_4^{2-} anion, which is predominant at pH 9. This phosphate dianion has a C_{3v} symmetry; in this symmetry species the band at 1077 cm^{-1} can be assigned to the asymmetric P-O stretching vibration and the 988 cm^{-1} can be assigned to the symmetric P-O stretching vibration.

Figure 3c shows the spectrum of a solution of 0.1 M KH_2PO_4 and 8% Q^+ at pH 6. Bands due to phosphate dominate this spectrum. The spectrum of the 8% Q^+ solution shows only weak bands in the spectral range of phosphate vibrations, as can be observed in Fig. 3d.

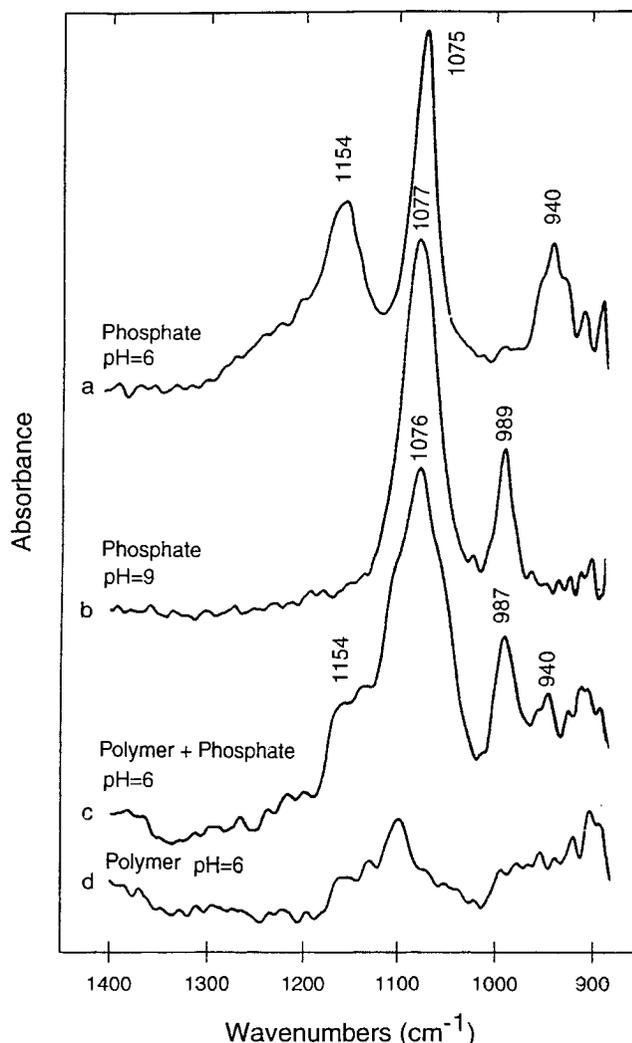


Fig. 3. ATR-FTIR spectra of (a) 0.1 M KH_2PO_4 solution at pH 6; (b) 0.1 M KH_2PO_4 solution at pH 9; (c) mixture of 8% Q^+ solution and 0.1 M KH_2PO_4 at pH 6; (d) 8% Q^+ solution at pH 6.

Unlike the spectrum of free phosphate at pH 6 in Fig. 3a, the spectrum of the mixture with Q^+ and phosphate in Fig. 3c shows a strong band at 987 cm^{-1} , while the bands at 1154 and 940 cm^{-1} are reduced. Comparing the spectrum in Fig. 3c with the spectrum of solution phosphate at pH 9 in Fig. 3b, one can clearly observe the similarity in the presence of the bands at 1077 and 988 cm^{-1} due to the HPO_4^{2-} species. These results indicate that in the mixture of Q^+ and P at pH 6, phosphate is predominantly present as the HPO_4^{2-} species with a minor fraction present as the H_2PO_4^- species. Apparently, the interaction of phosphate with Q^+ results in a complex that favors the formation of the dianionic species.

Mixtures of Q^+ and phosphate at pH 8.5 and 4 were also analyzed (data not shown). The spectrum of the mixture at pH 8.5 showed the same strong bands at 1077 and 989 cm^{-1} . The band at 940 cm^{-1} was not observed in this spectrum, indicating that only the HPO_4^{2-} species was present in that mixture. The spectrum of the mixture at pH 4 showed bands at 1154, 1077, 989, and 940 cm^{-1} . This indicates that both H_2PO_4^- and HPO_4^{2-} species were

present at pH 4. The difference in intensity of the bands at 989 and 940 cm^{-1} indicated that H_2PO_4^- was the predominant species.

A similar behavior of inorganic phosphate has been observed with its binding to aspartate aminotransferase apoenzyme (Martinez-Liarte et al., 1992). Using FTIR spectroscopy following the phosphate band at 989 cm^{-1} , they concluded that bound phosphate remained in the dianionic (HPO_4^{2-}) state throughout the studied pH range of 5.3 to 8.3. They suggested that electrostatic interactions and H-bonding were the important factors in the affinity of phosphate for this enzyme. Based on the infrared data in this study, we suggest that phosphate forms a complex with Q^+ through electrostatic interactions. H-bonding of phosphate with Q^+ is also possible based on the molecular structure of Q^+ . The complex apparently favors the formation of the dianionic phosphate species.

The FTIR data indicate that the H_2PO_4^- dissociates a proton upon complexation with Q^+ . Experiments were done to evaluate the effect of complexation on the solution pH. The addition of H_2PO_4^- to the polymer at pH 4.0 and 5.3 resulted in a decrease in pH, which confirms the FTIR spectra of a complexed HPO_4^{2-} species at low pH. That is, the dominant H_2PO_4^- species in solution must release a proton to form the HPO_4^{2-} complex. The molar stoichiometry (moles of H released per mole of P added) of this reaction was 0.2 at pH 4.0 and 0.6 at pH 5.3 based on the amount of base needed to return the mixture to the initial pH conditions. The molar stoichiometry decreased rapidly to zero as more P was added to the mixture. In the presence of NaCl, fewer protons were released at pH 5.9 (stoichiometry was 0.3–0.4), and no proton release was noted at pH 4.1.

At pH 7.9 and 8.5, the addition of phosphate to the polymer resulted in a pH increase. This is explained based on earlier polymer titration results (Butkus, 1997). The titration of the polymer showed that the cationic polymer above pH 7 consumes OH^- . Based on our competitive model of hydroxyl and phosphate species for the polymer cationic sites, the release of OH^- was expected. The molar stoichiometry of OH^- release to phosphate added ranged initially from 0.3 to 0.5, and it quickly decreased to zero as more P was added to the mixture at pH 7.9.

While the FTIR spectra confirm that HPO_4^{2-} is complexing with the polymer and the proton release experiments support the reactivity of HPO_4^{2-} with the polymer, these experiments neither confirm nor disprove that H_2PO_4^- is complexing with the polymer. With the FTIR spectra, the H_2PO_4^- bands may originate from either complexed phosphate or free-phosphate species. With the proton release experiments, the formation of H_2PO_4^- complexes with the polymer at low pH should neither release nor consume protons. Because the binding mechanism of HPO_4^{2-} is believed to be through electrostatic interactions (based on our FTIR data), there is a high probability that the H_2PO_4^- species would be sequestered by a similar mechanism also.

Modeling

Hypothesized WTR surface complexation reactions are illustrated in Fig. 4. Organic surface sites, Q^+ , have

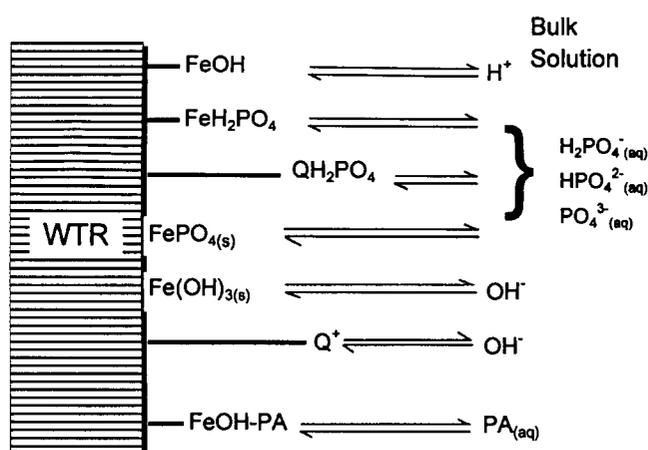


Fig. 4. Hypothesized WTR surface reactions. PA represents partially hydrolyzed polyacrylamide. All other species are defined in Eq. [1] through [12].

been placed away from the WTR surface to simulate polymer loops and tails (Lyklema, 1978; Stumm, 1992). As previously stated, we presume that phosphate may bind to these sites. Phosphate may also bind to iron oxide surface sites and form a surface precipitate with iron. Figure 4 also illustrates that partially hydrolyzed polyacrylamide (PA), which is a negatively charged polymer added during filter backwashing operations, may compete with phosphate for iron oxide sites. Based on the mass of this polymer added, these reactions were considered minor and consequently not modeled.

Model parameters for Q^+ and hydrous ferric oxide were determined independently. Parameters required for modeling surface complexation of phosphate with Q^+ were determined using the FITEQL optimization program. Parameters for modeling phosphate onto hydrous ferric oxide were determined using MICROQL. Results of each model were combined to predict the total quantity of phosphate adsorbed as a function of aqueous phosphate concentration and pH.

Equilibrium constants and the total number of Q^+ functional groups for Eq. [11] and [12] were optimized with data from a WTR-phosphate adsorption edge in the alkaline pH region. The equilibrium constant for Eq. [10] was obtained from potentiometric titration data (Butkus, 1997). Polyelectrolyte titration data modeling, using a gaussian distribution as described by Stevenson (1994), cannot be directly adapted into current optimization programs. That is, these models are limited to standard mass balance equations and predictions, which may not fully describe polyelectrolyte reactions. As a first approximation, a 1:1 mass balance equation, depicted in Eq. [10], was used to model the ionization of Q^+ . A pK_a of 9.5 for Eq. [10] was found to yield a minimal ionization error (<10%) up to a pH of 9. Measurements from the 5.5 mol PO_4/kg WTR treatment (pH > 9), illustrated on Fig. 2, were input into FITEQL as serial data. (The FITEQL program uses serial data to optimize adjustable parameters.) The Q^+ -phosphate complex was assumed to plateau at pH values <9. The FTIR and proton release observations discussed above support the hypothesis that the Q^+ -phosphate complex exists at pH of 6. All parameters were optimized simultaneously to obtain a unique solution. The total number of Q^+ sites,

Table 2. Thermodynamic parameters used to model the complexation of phosphate to quaternary polyamine (Q⁺).

Species	Equation number	log K^{int}	Reference
QOH	10	-9.5	Butkus, 1997
QH ₂ PO ₄	11	22.31	This study
QHPO ₄	12	15.66	This study

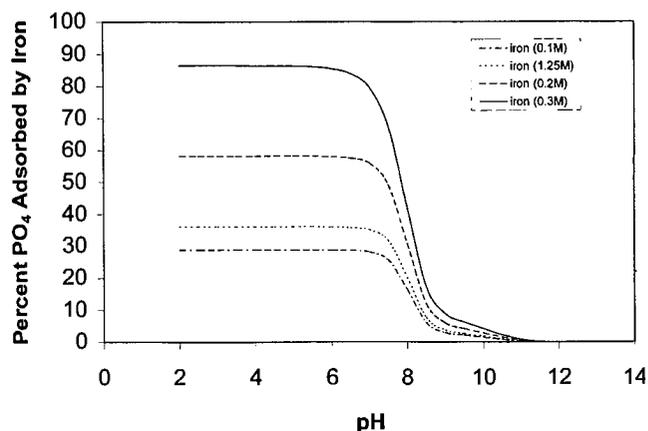
obtained from the FITEQL optimization, was found to be 2.19 mol Q⁺/g WTR. Using the FITEQL result for total number of Q⁺ sites and based on the expected Q⁺ site density of 9.8E-3 mol sites/g Q⁺ (Cytech Industries, West Pattern, NJ), the fraction of polymer in the WTR can be approximated at 0.22 g Q⁺/g WTR. This value is comparable to the water treatment plant Q⁺ dosages identified earlier. Equilibrium constants obtained from FITEQL are summarized in Table 2. The errors associated with the optimization (weighted sum of squares divided by degrees of freedom, WSOS/DF) was 41. This error may be slightly high due to data scatter. The results of the optimization, derived from FITEQL, were input into MINEQL⁺ (Westall et al., 1976; Schecher and McAvoy, 1994) to readily predict Q⁺-phosphate speciation at equilibrium as a function of pH.

Surface complexation of phosphate onto iron oxide was modeled using the MICROQL program. Model input parameters are given in Tables 1 and 3. All parameters used in this model were determined experimentally or taken from the literature with the exception to total iron (TOTFe). This parameter is a function of particle size, shape, and morphology (Katz and Hayes, 1995). Katz and Hayes (1995) reported that only the surface and some of the first few layers of the sorbent will participate in the formation of the solid solution. Because WTR may crystallize as a function of drying/aging, the value of TOTFe for WTR may change with time. The optimized value for TOTFe was found to be 3.48E-3 mol/g WTR, which falls within the range for percent iron in our WTR as determined by inductively coupled plasma (Thomas Morris, 1997, personal communication, Dep. of Plant Science, Univ. of Connecticut, Storrs). A sensitivity analysis was conducted to determine the impact of changing TOTFe on the MICROQL predictions. The model was subjected to a total phosphate concentration of 0.333 M while TOTFe and pH were adjusted. Results of the analysis, illustrated in Fig. 5, suggest that an increase in TOTFe will result in a significant increase in iron-phosphate complexation/precipitation over the pH range of 2 to 7. The model appears to be less sensitive to TOTFe at pH >7.

Following optimization of parameters for phosphate complexation with Q⁺ (FITEQL model) and hydrous ferric oxide (MICROQL model), phosphate speciation was predicted for each complex as a function of total phosphate, pH, and ionic strength. The total phosphate available to bind with Q⁺ was set equal to the total

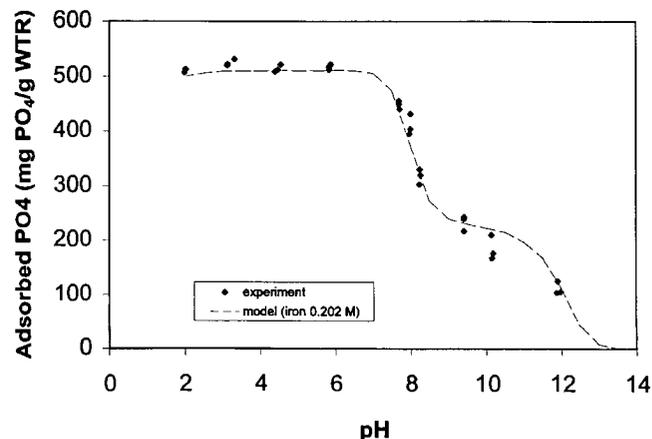
Table 3. MICROQL input parameters for phosphate-WTR surface complexation and surface precipitation.

Parameter	Value	Reference
TOTXOH, mol/g WTR	6.97E-4	This study
TOTFe, mol/g WTR	3.48E-3	This study
Surface area, m ² /g WTR	10	This study
Solids, g/L	18	This study

**Fig. 5. MICROQL model sensitivity analysis: effect of changes in total iron on the surface complexation/precipitation of phosphate. Total PO₄ = 0.33 M (0.01 M NaCl).**

phosphate in the system less than that which was bound to the iron. Results from each model were superimposed to give the total quantity of phosphate bound by the WTR. Figure 6 illustrates the results of the model calibration. A plot of the model predictions vs. experimental data resulted in a slope of 0.930 ($r^2 = 0.987$). The model was validated using isotherm data at pH values of 6 and 8. A plot of the model predictions vs. experimental data resulted in a slope of 0.996 ($r^2 = 0.997$) for pH 6 and a slope of 0.932 ($r^2 = 0.927$) for pH 8. Although the model predictions of adsorbed phosphate are satisfactory (based on the slope of model predictions vs. experimental data) the model appears to slightly under predict the quantity of aqueous phosphate. However, because most of the total phosphate is adsorbed the aqueous phosphate is highly sensitive to minor changes in adsorbed phosphate. For example, a decrease in adsorbed phosphate from 330 mg PO₄/g WTR to 310 mg PO₄/g WTR would result in a concomitant decrease in aqueous phosphate from 1.65 g PO₄/L to 0.504 g PO₄/L.

The model predicts that the quantity of bound phosphate will plateau. The reason for the plateau, which would not be expected for surface precipitation of cations, is due to the finite quantity of iron available to precipitate with the phosphate. However, the quantity adsorbed at the plateau is much greater than that expected for surface complexation of phosphate by iron

**Fig. 6. Model calibration results for 6.0 mol PO₄/kg WTR, 0.01 M NaCl.**

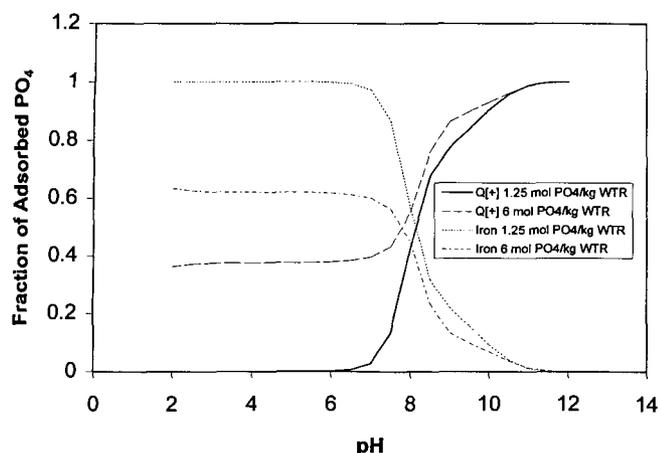


Fig. 7. Distribution of bound phosphate, between iron and quaternary polyamine (Q^+), as a function of pH and total system phosphate.

alone (Ryden et al., 1977a; Goldberg and Sposito, 1984), and may be attributed to complexation by the polymer in addition to surface precipitation.

Figure 7 illustrates the distribution of phosphate between iron and Q^+ as a function of pH and total phosphate. Under field pH conditions (pH 5.5–6.5) the model predicts that phosphate will preferentially bind with iron at low phosphate doses. However, the model suggests that the quantity of phosphate bound to Q^+ will increase as the total phosphate is increased. For a loading of 6 mol PO_4/kg WTR, the model predicted that phosphate associated with Q^+ may make up to almost 40% of the total adsorbed phosphate.

The findings presented herein indicate that phosphate may form complexes with both iron and cationic polymers, which are present in selected WTRs. Previous studies on land application of WTR have failed to identify this latter mechanism of phosphate adsorption. The ability of phosphate to desorb from these polymers remains unknown; however, field studies suggest that plant response to phosphate-amended WTR may have been more favorable than that which would have been expected from phosphate-amended hydrous ferric oxide (Thomas Morris, personal communication, Dep. of Plant Science, Univ. of Connecticut, Storrs).

CONCLUSION

Use of WTR as a soil amendment may hold significant promise as a viable reuse alternative, in lieu of land-filling. However, WTR has been reported to bind soil phosphate, which can result in phosphate-deficient crops. Uptake of phosphate by WTR has often been attributed to metal oxides, typically present at high concentrations. This study examined phosphate binding by a ferric hydroxide WTR. Phosphate-WTR pH adsorption edges and ATR-FTIR analyses suggest that cationic organic polyelectrolytes present in selected WTRs form complexes with phosphate via a complexation reaction. This reaction may explain why the total quantity of bound phosphate exceeded maxima reported in the literature for hydrous ferric oxide surface complexation. The nature of this complex may result in an unexpected

plant response to phosphate-amended WTR. Uptake of phosphate by WTR was modeled using a diffuse double layer model, which included surface precipitation of iron and phosphate as well as complexation reactions between phosphate and the quaternary polyamine. The model predicted that phosphate associated with quaternary polyamine may constitute up to almost 40% of phosphate bound by WTR at high phosphate loadings.

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REFERENCES

- Amirtharajah, A., and C.R. O'Melia. 1990. Coagulation processes: Destabilization, mixing, and flocculation. p. 269–361. *In* F.W. Pontius (ed.) *Water quality and treatment*. Am. Water Works Assoc., McGraw-Hill, New York.
- Anderson, M.A., M.I. Tejedor-Tejedor, and R.R. Stanforth. 1985. Influence of aggregation on the uptake kinetics of phosphate by goethite. *Environ. Sci. Technol.* 19:632–637.
- Borggard, O.K., S.S. Jorgensen, J.P. Moberg, and B. Raben-Lange. 1990. Influence of organic matter on phosphate adsorption by aluminum and iron oxides in sandy soils. *J. Soil Sci.* 41:443–449.
- Bugbee, G.J., and C.R. Frink. 1985. Alum sludge as a soil amendment: Effects on soil properties and plant growth. *New Haven Connecticut Agric. Exp. Stn. Bull.* 827.
- Butkus, M.A. 1997. Impact of phosphate on the surficial properties of a ferric hydroxide matrix: Linkage between surface complexation and colloid stability. Ph.D. diss. Univ. of Connecticut, Storrs (Diss. Abstr. 98-10505).
- Crosby, S.A., D.R. Glasson, A.H. Cuttler, I. Butler, D.R. Turner, M. Whitfield, and G.E. Millward. 1983. Surface areas and porosities of Fe(III) and Fe(II) derived oxyhydroxides. *Environ. Sci. Technol.* 17:709–713.
- Dempsey, B.A., J. Dewolfe, S. Elias, and M. Lunetta. 1995. Freezethaw dewatering of water treatment residuals—Chemical effects. p. 9-25–9-32. *In* 4th Joint WEF & AWWA Residuals/Biosolids Conf., Kansas City, MO. 23–26 July 1995. Water Environment Federation, Alexandria, VA.
- Dohse, D.M., and L.W. Lion. 1994. Effect of microbial polymers on the sorption and transport of phenanthrene in a low-carbon sand. *Environ. Sci. Technol.* 28:541–548.
- Dzombak, D.A. 1989. Computer programs for implementation of the generalized two-layer model. Tech. Rep., Dep. of Civil Engineering, Carnegie Mellon University, Pittsburgh, PA.
- Dzombak, D.A., and F.M.M. Morel. 1990. Surface complexation modeling: Hydrous ferric oxide. John Wiley & Sons, New York.
- Elliot, H.A., B.A. Dempsey, D.W. Hamilton, and J.R. DeWolf. 1990. Land application of water treatment sludges: Impacts and management. Am. Water Works Assoc. Res. Foundation, Denver, CO.
- El-Swaify, S.A., and W.W. Emerson. 1975. Changes in the physical properties of soil clays due to precipitated aluminum and iron hydroxides: I. Swelling and aggregate stability after drying. *Soil Sci. Soc. Am. J.* 39:1056–1063.
- Farley, K.J., D.A. Dzombak, and F.M.M. Morel. 1985. A surface precipitation model for the sorption of cations on metal oxides. *J. Coll. Interf. Sci.* 106:226–242.
- Gerke, J. 1993. Phosphate adsorption by humic/Fe-oxide mixtures

- aged at pH 4 and 7 and by poorly ordered Fe-oxide. *Geoderma* 59:289-310.
- Goldberg, S., and G. Sposito. 1984. A chemical model of phosphate adsorption by soils: ii. noncalcareous soils. *Soil Sci. Soc. Am. J.* 48:779-783.
- Grasso, D., M.A. Butkus, D. O'Sullivan, and N.P. Nikolaidis. 1997. Soil-washing design methodology for a lead-contaminated sandy soil. *Water Res.* 31(12):3045-3056.
- Heil, D.M., and K.A. Barbarick. 1989. Water treatment sludge influence on the growth of sorghum-sudangrass. *J. Environ. Qual.* 18: 292-298.
- Hingston, F.J., A.M. Posner, and J.P. Quirk. 1972. Anion adsorption by goethite and gibbsite. I. The role of the proton in determining adsorption envelopes. *J. Soil Sci.* 23:177-192.
- Hsu, P.H. 1965. Fixation of phosphate by aluminum and iron in acidic soils. *Soil Sci.* 99:398-402.
- Katz, L.E., and K.F. Hayes. 1995. Surface complexation modeling. II. Strategy for modeling polymer and precipitation reactions at high surface coverage. *J. Colloid Interface Sci.* 170:491-501.
- Kuo, S. 1986. Concurrent sorption of phosphate and zinc, cadmium, or calcium by a hydrous ferric oxide. *Soil Sci. Soc. Am. J.* 50: 1412-1419.
- Lijklema, L. 1980. Interactions of orthophosphate with iron (III) and aluminum hydroxides. *Environ. Sci. Technol.* 14:537-541.
- Lindsay, W.L. 1979. *Chemical equilibria in soils.* John Wiley & Sons, New York.
- Luttinger, L.B. 1981. The use of polyelectrolytes in filtration processes. p. 211-242. *In* W.L.K. Schwoyer (ed.) *Polyelectrolytes for water and wastewater treatment.* CRC Press, Boca Raton, FL.
- Lyklema, J. 1978. Surface chemistry of colloids in connection with stability. p. 3-36. *In* K.J. Ives (ed.) *The scientific basis of flocculation.* Sijhoff and Noordhoff, the Netherlands.
- Martinez-Liarte, J.H., A. Iriarte, and M. Martinez-Carrion. 1992. Inorganic phosphate binding and electrostatic effects in the active center of aspartate aminotransferase apoenzyme. *Biochemistry* 31: 2712-2719.
- McLaughlin, J.R., J.C. Ryden, and J.K. Syers. 1981. Sorption of inorganic phosphate by iron- and aluminum-containing components. *J. Soil Sci.* 32:365-377.
- Nair, P.S., T.J. Logan, A.N. Sharpley, L.E. Sommers, M.A. Tabatabai, and T.L. Yuan. 1984. Interlaboratory comparison of a standardized phosphorus adsorption procedure. *J. Environ. Qual.* 13:591-595.
- Nakamoto, K. 1986. *Infrared and raman spectra of inorganic and coordination compounds.* John Wiley & Sons, New York.
- Nanzyo, M. 1986. Infrared spectra of phosphate sorbed on iron hydroxide gel and the sorption products. *Soil Sci. Plant Nutr.* 32:51-58.
- Novak, J.T., W.R. Knocke, W. Geertsema, D. Dove, A. Taylor, and R. Mutter. 1995. An assessment of cropland application of water treatment residuals. *Am. Water Works Assoc. Res. Foundation, Denver, CO.*
- Parfitt, R.L. 1979. The availability of P from phosphate-goethite bridging complexes. Desorption and uptake by ryegrass. *Plant Soil* 53: 55-65.
- Parfitt, R.L., R.J. Atkinson, and R.St.C. Smart. 1975. The mechanism of phosphate fixation by iron oxides. *Soil Sci. Soc. Am. Proc.* 39:837-841.
- Parfitt, R.L., J.D. Russell, and V.C. Farmer. 1976. Confirmation of the surface structures of goethite and phosphated goethite by infrared spectroscopy. *J. Chem. Soc. Faraday Trans. 1* 72:1082-1087.
- Persson, P., N. Nilsson, and S. Sjöberg. 1996. Structure and bonding of orthophosphate ions at the iron oxide-aqueous interface. *J. Colloid Interf. Sci.* 177:263-275.
- Ryden, J.C., J.R. McLaughlin, and J.K. Syers. 1977a. Mechanisms of phosphate sorption by soils and hydrous ferric oxide gel. *J. Soil Sci.* 28:72-92.
- Ryden, J.C., J.K. Syers, and J.R. McLaughlin. 1977b. Effects of ionic strength on chemisorption and potential-determining sorption of phosphate by soils. *J. Soil Sci.* 28:62-71.
- Schecher, W.D., and D.C. McAvoy. 1994. *Mineql⁺: A chemical equilibrium program for personal computers.* Environ. Res. Software, Hallowell, ME.
- Sibanda, H.M., and S.D. Young. 1986. Competitive adsorption of humus acids and phosphate on goethite, gibbsite and two tropical soils. *J. Soil Sci.* 37:197-204.
- Sposito, G. 1990. Molecular models of ion adsorption on mineral surfaces. *Rev. Mineral.* 23:261-279.
- Stevenson, F.J. 1994. *Humus chemistry: Genesis, composition, reactions.* John Wiley & Sons, New York.
- Stumm, W. 1992. *Chemistry of the solid-water interface.* John Wiley & Sons, New York.
- Stumm, W., and J.J. Morgan. 1996. *Aquatic chemistry.* 3rd ed. John Wiley & Sons, New York.
- Tejedor-Tejedor, M.I., and M.A. Anderson. 1990. Protonation of phosphate on the surface of goethite as studied by CIR-FTIR and electrophoretic mobility. *Langmuir* 6:602-611.
- Tejedor-Tejedor, M.I., E.C. Yost, and M.A. Anderson. 1990. Characterization of benzoic and phenolic complexes at the goethite/aqueous solution interface using cylindrical internal reflection Fourier transformed infrared spectroscopy. Part 1. Methodology. *Langmuir* 6:979-987.
- Westall, J.C. 1982. FITEQL: A program for the determination of chemical equilibrium constants from experimental data. *Tech. Rep. Chemistry Dep., Oregon State Univ., Corvallis.*
- Westall, J.C. and F.M.M. Morel. 1977. FITEQL: A general algorithm for the determination of metal-ligand complex stability constants from experimental data. *Tech. Note 19.* Ralph M Parsons Lab., Dep. of Civil Eng., Massachusetts Inst. of Technology, Cambridge.
- Westall, J.C., Zachary, J.L., and F.M.M. Morel. 1976. *Mineql: A computer program for the calculation of chemical equilibrium composition of aqueous systems.* *Tech. Note 18.* Ralph M. Parsons Lab., Dep. of Civil Engineering, Massachusetts Inst. of Technology, Cambridge.
- White, R.E., and A.W. Taylor. 1977. Effect of pH on phosphate adsorption and isotopic exchange in acid soils at low and high additions of soluble phosphate. *J. Soil Sci.* 28:48-61.