REMOVING PHOSPHONATE ANTISCALANTS FROM MEMBRANE

CONCENTRATE SOLUTIONS USING FERRIC HYDROXIDE ADSORBENTS

by

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APPROVAL BY THESIS DIRECTOR

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Abstract

Phosphonate antiscalants are commonly used in nanofiltration and reverse osmosis water treatment to prevent membrane fouling by mineral scale. In many circumstances it is desirable to remove these phosphonate compounds before concentrate disposal or further treatment. This research investigated the removal of phosphonate compounds from simulated membrane concentrate solutions using ferric hydroxide adsorbents. Two phosphonate antiscalants were investigated, Permatreat 191® (PT191) and nitrilotrimethylphosphonic acid (NTMP). Batch adsorption isotherms and column breakthrough and regeneration experiments were performed on two commercial adsorbents and a ferric hydroxide loaded polyacrylonitrile fiber adsorbent prepared in our laboratory. The best performing adsorbent was Granular Ferric Hydroxide® (GFH) obtained from GEH Wasserchemie. Adsorption isotherms measured after 24-hour equilibration periods showed initial concentration effects, whereby the isotherms were dependent on the initial adsorbate concentration in solution. Significant differences in adsorption behavior were observed between the PT191 and the NTMP adsorbates. Differences in adsorption behavior between NTMP and PT191 are all consistent with the PT191 containing fewer phosphonate functional groups per molecule than NTMP. Desorption rates were bimodal, with 40-50% of the adsorbed phosphonate being released on a time scale of 10-24 hours, while the remaining fraction was released approximately one order of magnitude more slowly. The slow desorbing fraction primarily resulted from equilibrium effects resulting from significant phosphonate adsorption, even in 1.0 mol/L NaOH solutions. Complete regeneration could not be achieved, even after eluting the adsorbent columns with more than 300 bed volumes of 1.0 mol/L NaOH. However, the incomplete regeneration had only a minor effect on phosphonate uptake in subsequent column breakthrough experiments.

1 Introduction

Antiscalant compounds are commonly used during nanofiltration (NF) and reverse osmosis (RO) to prevent membrane fouling by mineral scale. The most commonly used type of antiscalants are phosphonate compounds. Similar to phosphate, phosphonate compounds have a high affinity for Ca^{2+} and other scale forming ions, such as Ba^{2+}, Mg^{2+} and Fe^{3+}.[1] Phosphonate compounds inhibit scale formation by interfering with crystallization of scale forming minerals, and delaying or completely preventing nucleation of mineral precipitates.[2]

In many water treatment operations, the membrane concentrate is subjected to a second stage NF/RO process. Increased water recovery can be achieved using multistage processes that include a precipitation step on the primary NF/RO concentrate.[3] When antiscalant compounds are used, they interfere with mineral precipitation from the concentrate solution. Thus, it is desirable to remove antiscalant compounds from the primary concentrate prior to the precipitation step. In situations where the membrane concentrate is disposed of in the ocean, phosphonate removal is also desirable to avoid adding phosphate that may promote algal blooms. [4]

Several previous studies have investigated the removal of phosphonate compounds from membrane concentrate solutions. One study investigated the use of ion exchange media and activated carbon for removing nitrilotri(methylphosphonic) acid (NTMP) from solution.[5] Another study investigated removing NTMP from solution is via adsorption onto ferric hydroxide.[6] Adsorption rates of NTMP by ferric hydroxide were measured in batch reactors. The adsorption kinetics were described by a numerical model incorporating boundary layer mass transfer resistance and intragranular diffusion resistance. Adsorption onto ferric hydroxide was

found to be a superior method to ion exchange for phosphonate removal since it was not adversely impacted by the presence of high concentrations of other anions.[5]

The mechanism of phosphonate uptake by ferric hydroxides is complex, and involves several adsorption mechanisms that include both physical and chemical adsorption. A recent study using quantum chemistry simulations showed that physical adsorption of NTMP on ferric hydroxide is promoted by electrostatic effects and charge assisted hydrogen bonding.[7] NTMP is a polyprotic acid containing 6 ionizable -POH groups and one strong base group. The pK_a values for the six phosphoric acid groups are: <0, <0, 1.50, 4.62, 5.90, 7.25, and the pK_a for the strong base group is 14.2.[8] Thus, at circumneutral pH values, NTMP will carry a net negative charge ranging from -3 to -5 that increases with increasing pH value. In addition to physical adsorption, phosphonate compounds are known to form chemical adsorption complexes with ferric hydroxide.[9] These complexes involve ligand exchange reactions in which an -OH or -OH_2 ligand attached to Fe^{3+} is replaced by a phosphonate, as illustrated in Figure 1. In addition to monodentate mononuclear complexes, that involve a single P-O-Fe bond, bidentate binuclear complexes involving two P-O-Fe bonds on different Fe atoms may also form if the phosphonate compound contains more than one phosphonate group.[7]
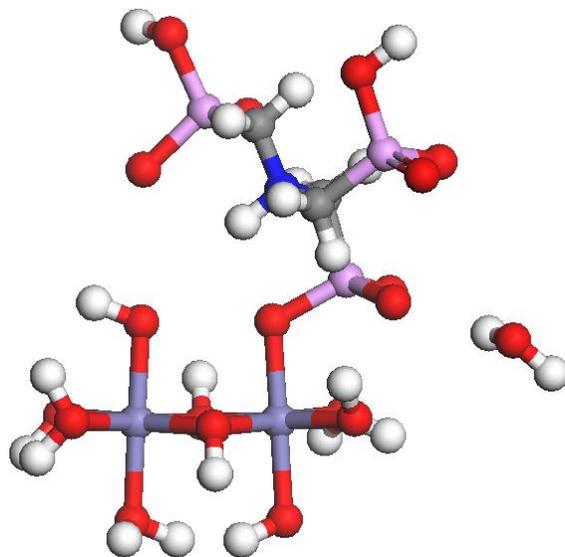
Figure 1. Monodentate adsorption complex between nitrilotri(methylphosphonate) [NH(CH$_2$)$_3$(HPO$_3^-$)$_3$] and ferric hydroxide [Fe$_2$O$_3$(H$_2$O)$_7$]. Atom color key: Fe (blue-gray); O (red); N (blue) C (gray); P (pink-lavender); H (white).

The goal of this study was to investigate the effectiveness of three ferric hydroxide adsorbents for removing phosphonate antiscalants from simulated membrane concentrates. Column breakthrough experiments and equilibrium adsorption isotherms were measured for a commercial phosphonate antiscalant and for NTMP on ferric hydroxide. The effectiveness of adsorbent regeneration using 0.10 and 1.0 mol/L NaOH solutions was also investigated.

2 Materials and Methods

2.1 Adsorbents

Two commercially available ferric hydroxide adsorbents and one adsorbent prepared in our laboratory were used in this study. These adsorbents were developed for the removal of arsenate and arsenite from potable water.[10-13] One adsorbent was Granular Ferric Hydroxide® (GFH) and was obtained from GEH Wasserchemie (Osnabruck, Germany).   GFH consists

predominantly of akaganeite, which is β-FeOOH. The manufacturer's reported specific surface was approximately 300 m^2/g and reported particle size ranged from 0.2 to 2.0 mm. All results are presented on an as-received mass basis. The second adsorbent used was Bayoxide E33$^{®}$ media, obtained from AdEdge Technologies (Buford, GA). The E33 media is a synthetic iron oxide composed of 90% α-FeOOH.[12] As reported by the manufacturer, the specific surface area ranges from 120 to 200 m^2/g with particle diameters ranging from 0.5 to 2 mm. The third adsorbent consisted of a homopolymer polyacrylonitrile (PAN) fabric coated with amorphous ferric hydroxide. The PAN fiber adsorbent (PAN) was included in this study due to its much faster mass transfer kinetics for arsenate removal as compared to the two granular adsorbents.[13] The PAN fibers were 15 µm in diameter and were uniformly coated with ferric hydroxide nanoparticles at a loading of 140 mg Fe/g dry fiber. Other properties of the PAN fiber adsorbent and preparation procedures are detailed in previous publications.[13][14]

2.2 Synthetic NF Concentrate

The composition of the water used in the isotherm and column experiments was based on NF concentrate generated in a previous investigation.[15] The NF concentrate was produced from Central Arizona Project (CAP) water as delivered to Tucson, AZ at 85% recovery. The simulated NF concentrate included only the major ions listed in Table 1. Solutions were prepared in 18 MΩ-cm ultrapure water (UPW) using ACS grade H_2SO_4, $CaCl_2$, Na_2CO_3, Na_2SO_4, $MgCl_2$, NaOH, and HCl from Fisher Scientific. Two different antiscalants were tested, PermaTreat 191$^{®}$ (PT191) from Nalco (Naperville, IL), and NTMP of $\geq$97% purity from Sigma-Aldrich (St. Louis, MO). PT191 is a proprietary mixture of phosphonate compounds plus a terpolymer composed of acrylic acid, acrylamide, and acrylamidomethylsulphonic acid.[16] In preparing the NF concentrate, the antiscalants were dosed in accord with the manufacturer's

recommendation. Because the composition of the phosphonate compounds in the PT191 are unknown, phosphonate concentrations are reported on a mg phosphorous per liter basis. Phosphorous concentrations were measured using an Agilent model 5100 synchronous vertical dual view inductively coupled plasma optical emission spectrophotometer (ICP-OES).

Table 1. Composition of the pH=8.3 synthetic NF concentrate used in isotherm and column experiments.

Cation	Concentration (mmol/L)	Concentration (mg/L)	Anion	Concentration (mmol/L)	Concentration (mg/L)
Na^+	29.0	667	SO_4^{2-}	13.0	1250
Ca^{2+}	8.50	340	Cl-	29.5	1050
Mg^{2+}	6.25	150	HCO_3^-	3.00	300 as $CaCO_3$

2.3 Column Breakthrough and Regeneration Experiments

Column breakthrough experiments were performed using 1-2 grams of each adsorbent packed into a 0.8 cm diameter by 9 cm long glass column and held in place using glass wool. The columns were operated in up-flow mode at a flow rate of 1.0 ml/min using liquid chromatography pumps. The regeneration experiments were performed using 0.10 mol/L or 1.0 mol/L NaOH at flow rates of 0.05 ml/min or 0.25 ml/min. After regeneration, the columns were rinsed with UPW to bring down the effluent pH to ~8.5 before reuse. Effluent samples from each column were collected using a Gilson FC204 fraction collector. As a check on the mass balance of each adsorbate, samples of the adsorbent were removed from the columns after use and dissolved in 1.5 mol/L HCl. The liquor was then analyzed for its phosphorous content to

determine the amount of adsorbed phosphonate that was not removed during the regeneration process.

2.4 Adsorption Isotherm Experiments

Equilibrium adsorption isotherms were obtained via addition of 10 to 4000 mg of each adsorbent to synthetic concentrate solutions contained in polyethylene bottles. Three initial phosphorous concentrations for each adsorbate were tested: 0.60, 3.0 and 9.0 mg/L. For the NTMP, these phosphorous concentrations corresponded to 2.0, 10 and 30 mg NTMP/L. Isotherms were measured at 20 °C at initial pH values of 6.0 and 8.3. Desorption isotherms were measured via replacing the simulated concentrate solution in each bottle with 0.10 mol/L NaOH, yielding a solution pH value of 12.7. The suspensions were mixed using a shaker table operated at 80 rpm for 24 hours. Samples were filtered with 0.45 µm syringe filters and acidified before analysis using HNO_3. Triplicate samples were taken and the reported values represent the mean of the three samples.

3 Results and Discussion

3.1 Adsorbent Comparison

Figure 2 shows column breakthrough data for the E33, GFH and PAN fiber adsorbents measured with influent PT191 concentrations of 0.60 mg P/L. Empty bed contact times for each column were 2.6 min for the E33, 2.0 min for the GFH, and 2.5 min for the PAN fiber. Immediate breakthrough was observed for the E33 and PAN fiber media, while the GFH media showed near complete removal for 2600 bed volumes. The better performance of the GFH media can likely be attributed to its higher surface area and greater iron content, as compared to the other media. Due to its better performance, the remainder of this investigation focused only on the GFH media.
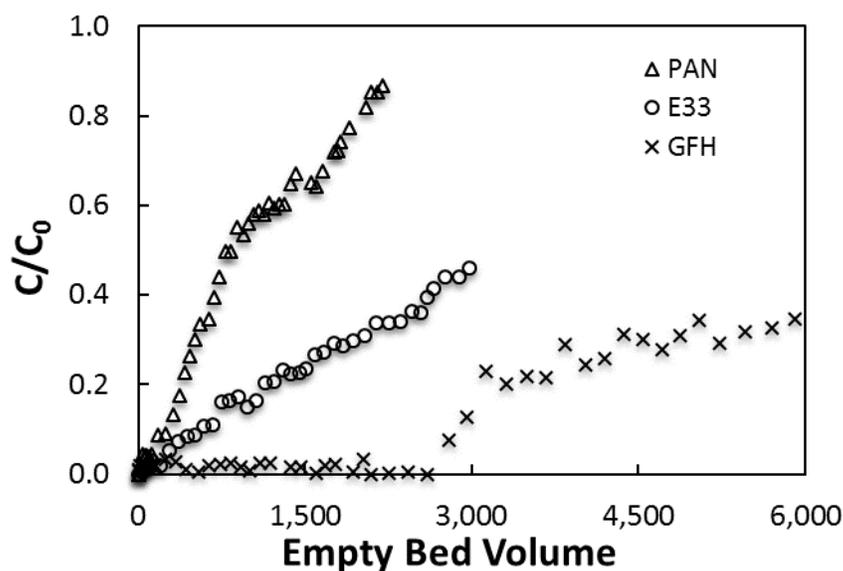
Figure 2. Column breakthrough profiles for PT191 on PAN, E33 and GFH adsorbents. Initial PT191 concentration was 0.60 mg P/L.

3.2 Adsorption Isotherms

Adsorption isotherms for PT191 and NTMP were measured on GFH to determine the adsorbent loading as a function of the aqueous concentration. Adsorption isotherms for PT191 for three initial solution concentrations at pH=8.3 are shown in Figure 3. The isotherms could be adequately described by the Langmuir isotherm model, whose parameters are given in Table 2. Interestingly, the initial concentration in the solution had a significant effect on the amount of phosphonate uptake after 24 hours. This phenomenon has been previously reported for arsenate adsorption on titanium dioxide, and has been termed the "initial concentration effect".[17] This effect can be attributed to kinetically irreversible adsorption, where rates of desorption can be orders of magnitude slower than rates of adsorption.[18][13] In this case, exposure of the outer layer of an adsorbent granule to a high concentration of an adsorbate results in a high amount of

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uptake in that layer that is not released and redistributed over the entire granule when the overall solution concentration decreases to its lower final value. Low activation barriers for adsorption accompanied by high activation barriers for desorption have recently been shown for chemisorption of NTMP on ferric hydroxide using quantum chemistry modeling.[7]

Figure 4 shows adsorption isotherms for NTMP on GFH for three initial aqueous NTMP concentrations. Table 2 lists Langmuir isotherm parameters for each data set. On a mg P/g adsorbed basis, NTMP adsorption on GFH ranged from 15%-70% lower than PT191 adsorption for the isotherms measured at the highest initial P concentration of 9.0 mg/L. However, for the lowest initial aqueous concentration, the uptake of NTMP ranged from 56% to 123% greater than that for PT191. The NTMP isotherms also show an initial concentration effect. However, the effect was opposite of that shown by the PT191, where greater adsorption was shown for lower initial concentrations. We are not aware of any previous reports of this phenomenon. However, the porous structure of akaganeite may provide an explanation for this type of behavior.[14]

The structure of akaganeite is composed of Fe^{3+} in octahedral coordination with oxygen atoms. These octahedral structures are arranged in a manner that forms channels with a diameter of 5.6 Å. Because NTMP has more than one phosphonate group, it can form a bidentate, binuclear complex with two Fe^{3+} atoms at the opening of a channel. This would result in blocking the diffusion of other NTMP species to adsorption sites inside the channel. Thus, one possible explanation for the unusual initial concentration effect observed in Figure 4, is that a higher initial concentration of NTMP in solution resulted in a greater amount of slowly reversible pore blocking by bindentate binuclear complexes. Thus, pores blocked by high initial NTMP adsorption when first exposed to the solution do not become unblocked as the NTMP

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solution concentration declines during the equilibration period. In this manner, higher initial

NTMP concentrations result in greater blockage of interior adsorption sites. The fact that this

behavior was not observed with the phosphonate compounds in the PT191 may result from these

phosphonates having only a single $-PO_3$ functional group, and thus can only form mononuclear

complexes.

Table 2 . Langmuir isotherm parameters for PT191 and NTMP on GFH for three initial solution

concentrations. The Langmuir model is given by: $C_s = \frac{C_{smax} \times b \times C_{aq}}{1 + b \times C_{aq}}$

	Initial Concentration (mg P/L)	C_{smax} (mg/g)	b (L/mg)	Adjusted R^2
PT191	0.60	3.72	1.73	0.98
	3.0	19.6	0.19	0.99
	9.0	42.5	0.23	0.98
NTMP	0.60	10.1	1.00	0.98
	3.0	1.38×10^4	1.46×10^{-4}	1.00
	9.0	1.84×10^4	5.99×10^{-5}	0.99

Figure 3. Adsorption isotherms for PT191 on GFH with initial concentrations (C_0) of 0.60, 3.0 and 9.0 mg P/L. Also shown are fits to the Langmuir isotherm model with parameters listed in Table 2. Note the logarithmic scale on the ordinate in order to achieve better visual separation between data sets.
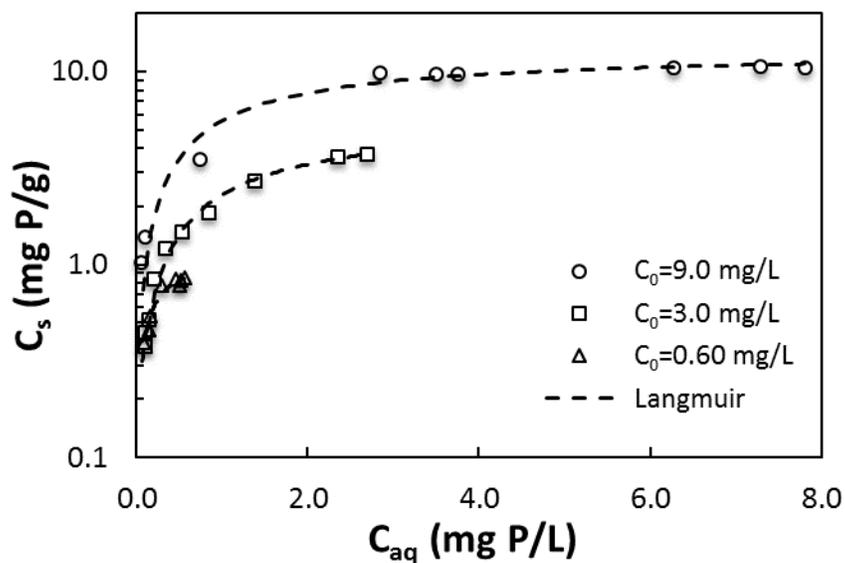
Figure 4. Adsorption isotherms for NTMP on GFH with initial concentrations (C_0) of 0.60, 3.0 and 9.0 mg P/L. Also shown are fits to the Langmuir isotherm model with parameters listed in Table 2. Note the logarithmic scale on the ordinate in order to achieve better visual separation between data sets.
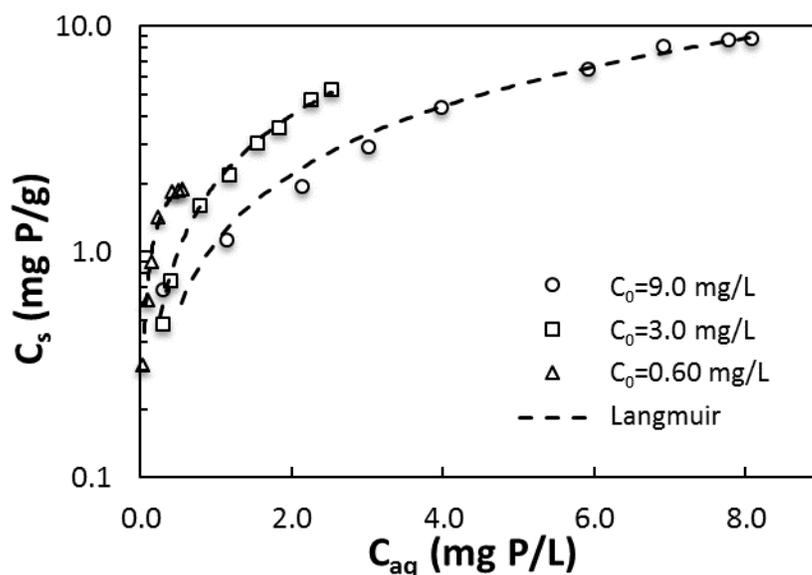
The feed solutions to RO and NF are often acidified to pH values of ~6 in order to reduce scale formation potential. Thus, it is important to understand the effect of pH on phosphonate adsorption to ferric hydroxide. Figure 5 compares adsorption isotherms for PT191 at pH values of 6 and 8.3 in the simulated NF concentrate. At P concentrations greater than 1.0 mg/L, phosphonate adsorption was greater at the lower pH value. This can be explained by electrostatic effects. Raising the pH resulted in increasing the negative charge on the phosphonate, and increasing the negative charge on the akaganeite, whose pH of zero charge (pzc) is 7.2.[14] The effect of pH on adsorption at phosphorous concentrations less than 1.0 mg/L is the opposite of that observed at higher concentrations. This effect may be the result of

the polymeric additive in the PT191. Lowering the pH value may have lowered the solubility of the polymer by increasing protonation of carboxylate functional groups. This may result in adsorption of the polymer on the akaganeite surface and the blocking of adsorption sites.

The effect of raising the pH value on PT191 desorption was also investigated by replacing the solution for the samples equilibrated at pH=8.3 with 0.10 mol/L NaOH solution. This desorption isotherm at a pH value of 12.7 is shown in Figure 5. Replacing the simulated NF concentrate/PT191 solution with 0.10 mol/L NaOH decreased the amount of PT191 adsorption by only 8 to 30%. This indicates that NaOH concentrations higher than 0.10 mol/L will be needed for adsorbent regeneration.

The solution pH value also affected NTMP adsorption on GFH, as illustrated in Figure 6. Greater adsorption at the lower pH value can be explained by the previously described electrostatic effects. Interestingly, the effect of pH on NTMP adsorption decreased with increasing adsorbed phase loadings, and was negligible as surface saturation was approached. The different NTMP behavior at pH=6 as compared to the PT191 is consistent with the absence of the polymeric additive interfering with phosphonate adsorption. Release of NTMP by the 0.10 mol/L NaOH solution was greater than that observed for PT191 release. The fraction of NTMP released by the pH increase ranged from 37% at low concentrations to 91% at high concentrations. The greater effect of high pH on NTMP release is consistent with the NTMP having more ionizable phosphonic acid groups than PT191. With NTMP, increasing the solution pH value increased the negative charge on both the GFH and the NTMP molecule. However, if the PT191 has only one phosphonate group there will be a smaller effect of pH on increasing the negative charge of the adsorbate.
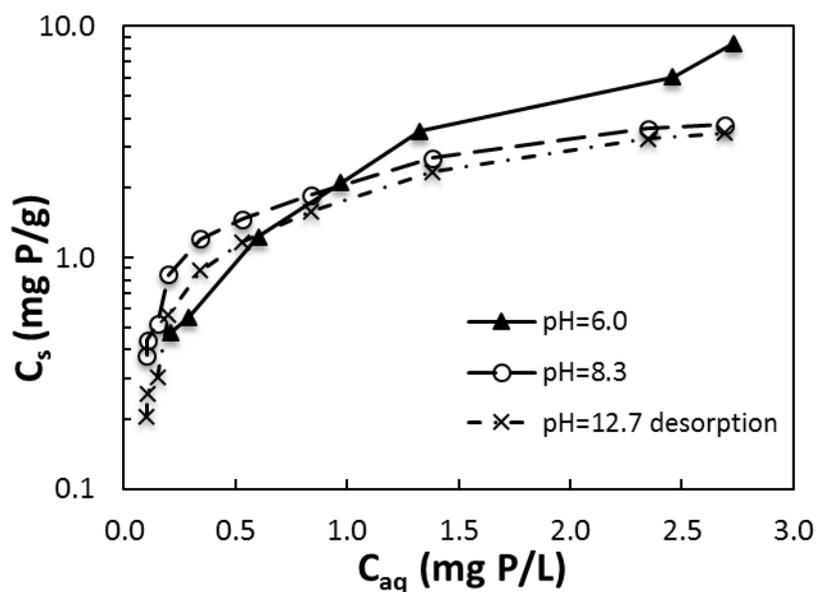
Figure 5. Adsorption isotherms for PT191 by GFH at different solution pH values. Initial

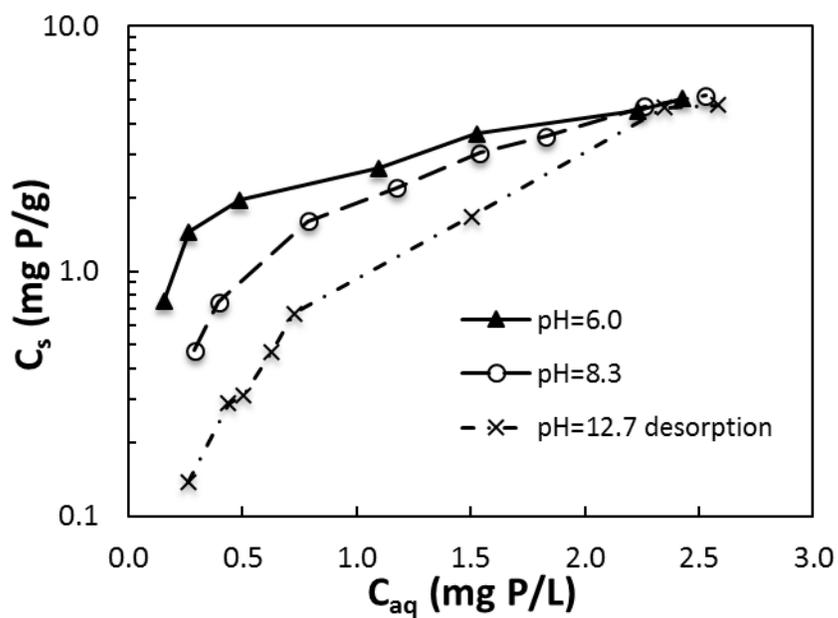phosphorous concentration = 3.0 mg P/L.

Figure 6. Adsorption isotherms for NTMP by GFH at different solution pH values. Initial

phosphorous concentration = 3.0 mg P/L.

The effect of hardness ions on phosphonate adsorption was also investigated. Figure 7 compares isotherms for PT191 in the simulated NF concentrate and NaCl solutions, both at pH=8.3 and an ionic strength of 86.25 mmol/L. The nearly identical isotherms in both solutions indicates that Ca^{2+} and Mg^{2+} ions had no effect on phosphonate adsorption from the PT191 solutions. This behavior contrasts with that shown by the NTMP, as illustrated in Figure 8. The presence of hardness ions increased NTMP adsorption by approximately a factor of 2.5. This can be explained by the high affinity of NTMP for divalent cations. Complexation of ionized phosphonate groups with Ca^{2+} or Mg^{2+} will neutralize some of the negative charges on the NTMP molecule, thereby decreasing its aqueous solubility and increasing its adsorption. The absence of any effect of hardness ions on adsorption of PT191 is consistent with the phosphonate in PT191 not being able to simultaneously form complexes with ferric hydroxide and divalent cations. This suggests that the PT191 contains only monofunctional phosphonate compounds.

Figure 7. Adsorption isotherms for PT191 by GFH in synthetic NF concentrate and NaCl solutions, both at an ionic strength of 86.25 mmol/L. Initial phosphorous concentration= 3.0 mg P/L.

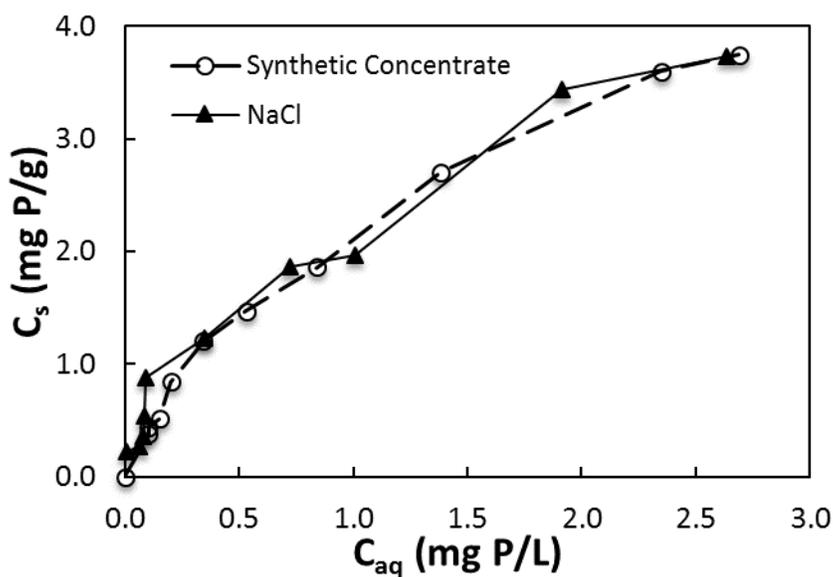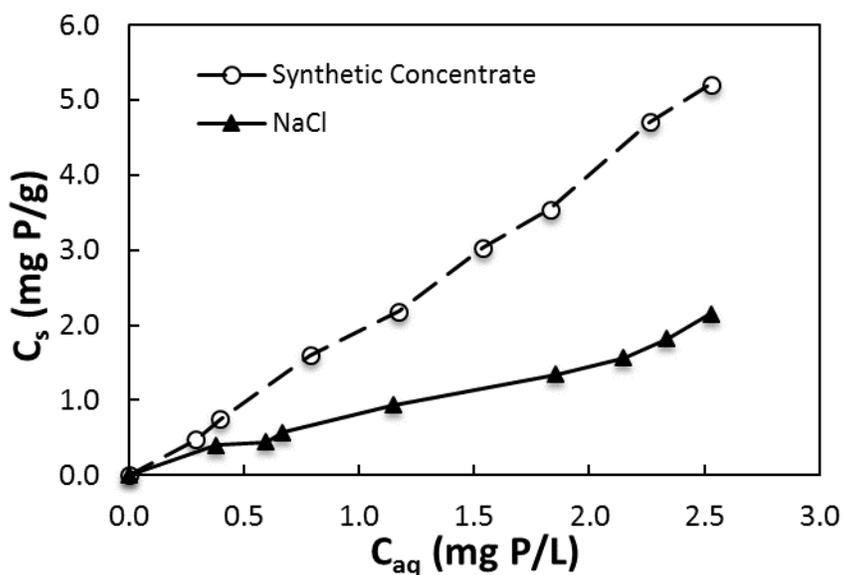
Figure 8. Adsorption isotherms for NTMP by GFH in synthetic NF concentrate and NaCl solutions, both at an ionic strength of 86.25 mmol/L. Initial phosphorous concentration = 3.0 mg P/L.

3.3 Adsorbent Regeneration

During adsorbent regeneration there are several opposing factors that need to be minimized, these include: 1) the mass of base used for producing the regenerant solution; 2) the volume of the regenerant solution; and 3) the time required for regeneration. Optimizing these parameters requires an understanding of the mechanisms controlling desorption. The rate of desorption can be controlled by either kinetic or equilibrium effects. Kinetic limitations on desorption include the reaction rate of the desorption reaction and diffusional mass transfer. Equilibrium limitations on the desorption rate primarily depend on differences in the adsorption isotherms under loading and regeneration conditions, and in this case depend primarily on the solution pH value and temperature. Insight into these effects can be gained by varying the regenerant solution concentration, flow rate, and temperature.

Figure 9 shows the fraction of PT191 desorbed versus eluant bed volumes from a column of GFH using 0.10 mol/L and 1.0 mol/L NaOH solutions. Using a 0.10 mol/L NaOH solution at 20 °C, 39% of the adsorbed PT191 was desorbed after 30 bed volumes (1050 minutes), however, after that point, the desorption rate was much slower. An additional 300 bed volumes (10,500 min) released only 39% more PT191. This indicates that the release rate for the slow desorbing fraction was an order of magnitude lower than that for the fast desorbing fraction. This type of desorption behavior has previously been attributed to intragranular diffusional mass transfer limitations.[5]

The effect of the eluant concentration on PT191 desorption suggests that some of this dual rate behavior can be attributed to equilibrium effects. Increasing the eluant concentration from 0.10 to 1.0 mol/L increased both the release rate of the fast desorbing fraction and the fraction of PT191 that was quickly released. This indicates that the release rate over the first ~50 bed

volumes in the 0.10 mol/L NaOH solution was not limited by mass transfer limitations, since the eluant concentration should only minimally affect rates of diffusion. In the 1.0 mol/L eluant, the weaker adsorption at higher pH values increased the thermodynamic driving force for PT191 desorption and increased the mass of fast desorbing PT191. This is an equilibrium effect.

An increase in temperature should affect both kinetic and equilibrium limitations on the desorption rate. An increase in temperature should increase both the rate of the desorption reaction and the rate of intragranular diffusion. An increase in temperature should also affect the equilibrium partitioning between adsorbed and solution phases.   According to quantum chemistry simulations, chemisorption of phosphonates on ferric hydroxide is exothermic, and thus there should be less adsorption at higher temperature.[6]   As shown in Figure 9, increasing the temperature to 50 °C during the regeneration process increased the release rate of the fast desorbing fraction. Increasing the temperature by 30 °C, increased the initial release rate (first 25% desorbed) by a factor of 3.6. This increase in rate corresponds to an apparent activation energy for the desorption process of 29 kJ/mol. This value is much higher than apparent activation energies for aqueous diffusion. According to the Wilke-Chang equation, diffusion coefficients calculated for NTMP at 20 °C and 50 °C yield an apparent activation energy of 0.023 kJ/mol.[19] Thus, it is not likely that the initial release of PT191 was limited by a simple aqueous diffusional mass transport process. The small impact of the increase in temperature on the fraction of slowly released PT191 suggests that the impact of temperature on equilibrium partitioning is small.
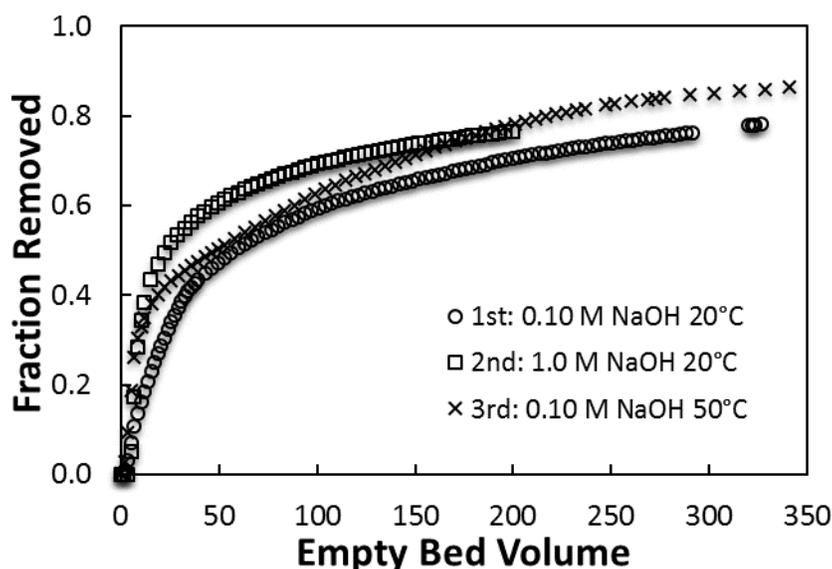
Figure 9. Fraction of PT191 removed from GFH as a function of regenerant solution bed volumes at a flow rate of 0.05 ml/min (35 min EBCT).

Further insight into the mechanisms controlling release of adsorbed phosphonate can be seen by varying the flow rate and eluant concentration during a single experiment. In these experiments, the regeneration cycle was divided into 4 parts: a) 0.10 mol/L NaOH at 0.05 ml/min; b) 0.10 mol/L NaOH at 0.25 ml/min; c) 1.0 mol/L NaOH at 0.25 ml/min; and d) 1.0 mol/L NaOH at 0.05 ml/min. The flow rate at 0.05 ml/min corresponds to an empty bed contact time of 35 min and 0.25 ml/min corresponds to 7.0 min. Figure 10 shows the fraction of NTMP removed from a column of GFH using 0.10 mol/L NaOH at a flow rate of 0.05 ml/min for 5700 min (163 bed volumes). Similar to the PT191, there was a fast desorbing fraction and a slow desorbing fraction. At 5700 min elapsed, the eluant flow rate was increased to 0.25 ml/min. This resulted in a factor of 4.1 increase in the NTMP release rate from 4.40×10^{-4} to 1.82×10^{-3} mg NTMP/min. This indicates that equilibrium factors were limiting the desorption rate of the slow

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desorbing fraction. At 6400 minutes elapsed the eluant concentration was increased to 1.0 mol/L. This resulted in a factor of 5.4 increase in the desorption rate from 1.21×10^{-3} to 6.55×10^{-3} mg NTMP/min, which is also indicative of an equilibrium effect. Similar results were observed for PT191 desorption, as shown in Figure 11. Increasing the eluant flow rate from 0.05 to 0.25 ml/min increased the desorption rate by a factor of 3.9. Increasing the eluant concentration from 0.10 to 1.0 mol/L increased the desorption rate by a factor of 6.7. Thus, equilibrium considerations strongly affected the release rate of the slow desorbing fraction of PT191. This suggests that batch regeneration procedures where the eluent solution is recirculated through the adsorbent column may not be an effective regeneration strategy.[5] Overall, removal of phosphonate from the GFH media was much more difficult than regeneration of ion exchange media, which typically requires fewer than 10 bed volumes for near complete regeneration. The difficulty of removing adsorbed phosphonate stems from its strong adsorption, even in 1.0 mol/L NaOH solutions.
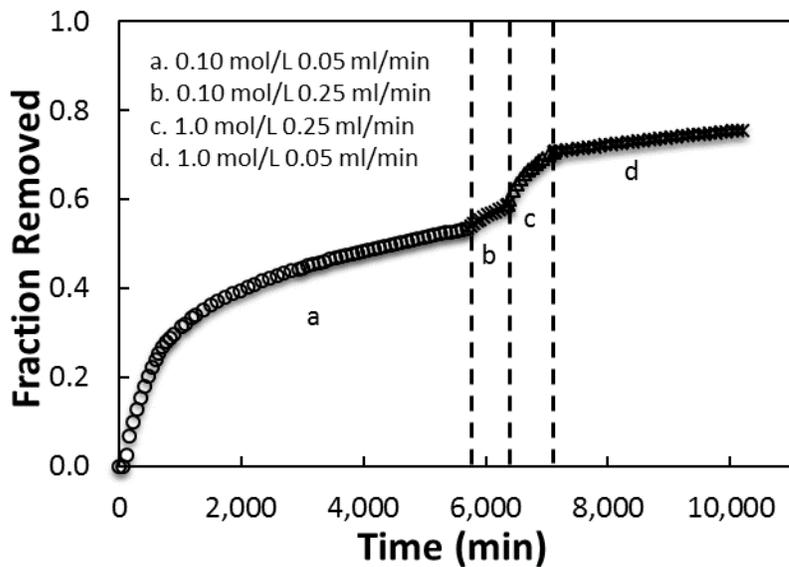
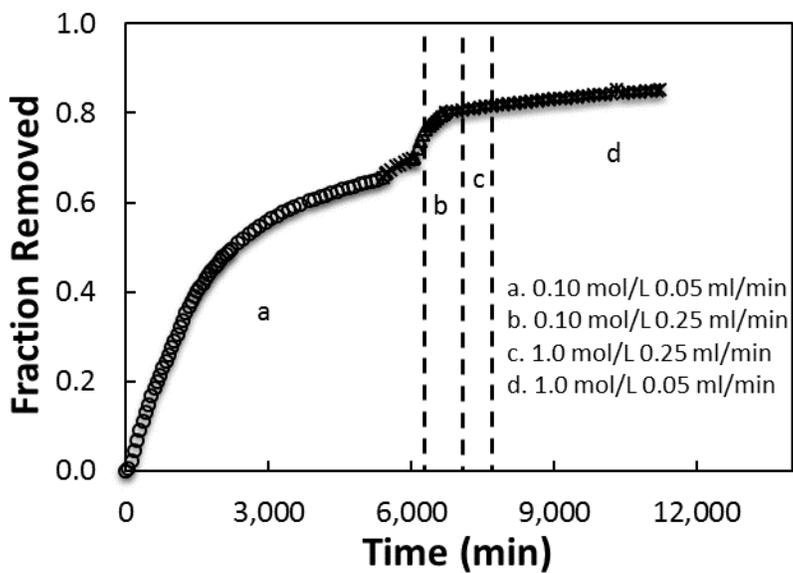Figure 10. Fraction of adsorbed NTMP removed from GFH under four different elution conditions.

Figure 11. Fraction of adsorbed PT191 removed from GFH under four different elution conditions.

3.4 Adsorbent Reuse

The incomplete regeneration of the GFH adsorbent may result in decreased phosphonate uptake during subsequent adsorption cycles. Figure 12 shows three PT191 breakthrough experiments on a column of GFH, and Table 3 summarizes the mass of phosphorous adsorbed and desorbed during each experiment. During the first breakthrough experiment, near complete PT191 removal was observed for 2600 bed volumes and the total uptake was 3.07 mg P/g after 6400 bed volumes. When this column was regenerated using 0.10 mol/L NaOH, only 78% of the adsorbed PT191 was removed after 327 bed volumes. The incomplete regeneration resulted in immediate breakthrough of PT191 during the second breakthrough experiment. However, the uptake of PT191 over the first 6000 bed volumes of 3.04 mg P/g during the second breakthrough was greater than the uptake during the first breakthrough experiment after 6000 bed volumes. During regeneration after the second adsorption experiment, only 66% of the total PT191 in the column was desorbed. However, the uptake over the first 6000 bed volumes during the third breakthrough experiment of 2.91 mg P/g was close to that for the first experiment (2.89 mg P/g), despite the fact that the column already contained 1.62 mg P/g at the start of the third breakthrough. After the third regeneration, the PT191 mass balance difference between integrating the uptake and desorption profiles yielded a residual loading of 1.83 mg P/g. Extraction of the adsorbent samples yielded a residual of 1.66 mg P/g, indicating a mass balance error of ~10%.

The effect of incomplete regeneration on subsequent adsorption capacity was greater for NTMP than for the PT191, as shown in Figure 13. Similar to the PT191, the regeneration efficiency was 78% after the first breakthrough experiment. However, the NTMP uptake over the first 6000 bed volumes was reduced by 28% in the second breakthrough experiment. The

greater effect of incomplete regeneration on subsequent uptake for NTMP than for the PT191 is consistent with the previous hypotheses that the NTMP had more phosphonate functional groups than the PT191. Given that all six of the phosphonic acid groups are near completely ionized at pH=8.3, exchange of a NTMP ligand for a -H_2O ligand will result in a significant decrease in the surface charge of the adsorbent. This decrease in surface charge will decrease the energetic favorability for further NTMP adsorption. If the NTMP is more negatively charged than the PT191 adsorbate, the adverse effects of incomplete regeneration would be greater for the NTMP.
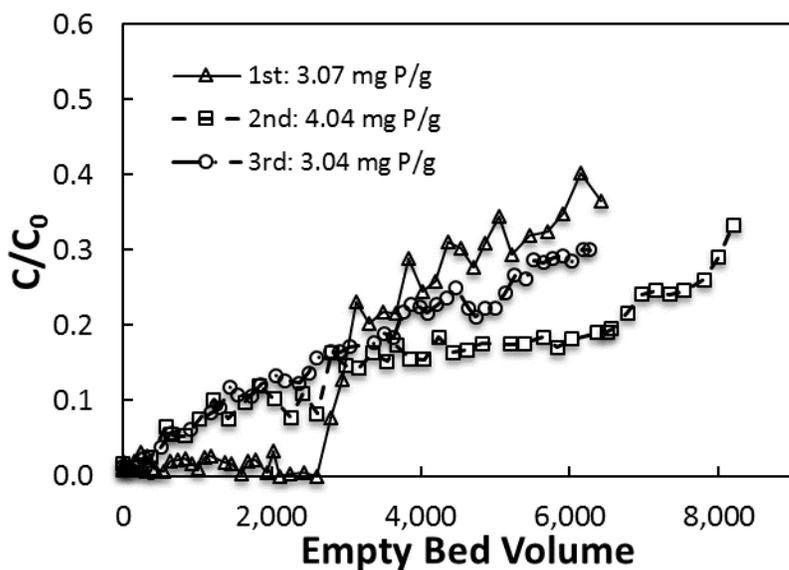

Figure 12. Column breakthrough profiles in simulated NF concentrate at pH=8.3 for PT191 on GFH with feed concentrations of 0.60 mg P/L. Uptake during each breakthrough experiment is shown for each data set. The same column was loaded and regenerated three times using 0.10 mol/L and 1.0 mol/L NaOH.
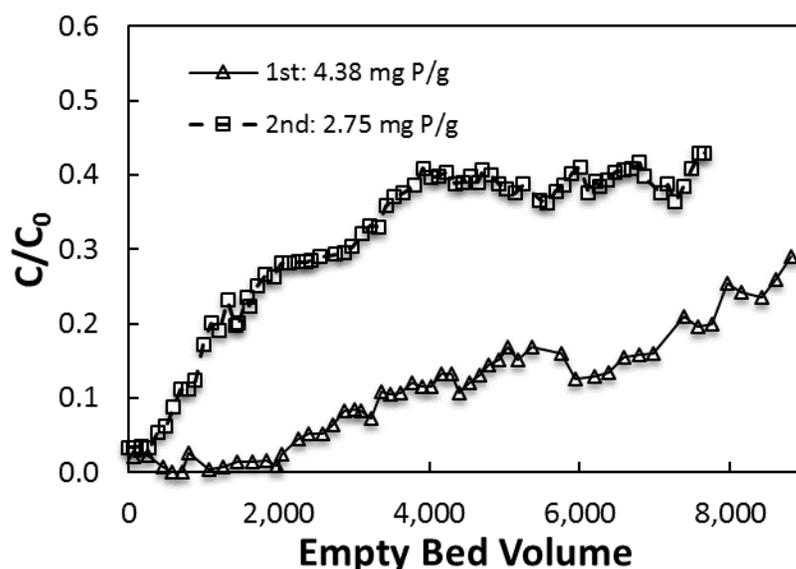
Figure 13. Column breakthrough profiles for NTMP in simulated NF concentrate at pH=8.3 on GFH with feed concentrations of 0.60 mg P/L. Uptake during each breakthrough experiment is shown for each data set. The same column was loaded and regenerated two times using 0.10 mol/L and 1.0 mol/L NaOH.

Table 3 The loading and regeneration of PT191 and NTMP on GFH. (Units are mg P/g)

PT191	Uptake by 6000 Bed Volumes	Final Uptake	Total in Column	Regeneration	Residual	Recovery %	Extracted Residual
1st	2.89	3.07	3.07	2.40	0.67	78%	
2nd	3.04	4.05	4.72	3.10	1.62	66%	
3rd	2.91	3.04	4.66	2.83	1.83	61%	
Total		10.16		8.33	1.83		1.66
NTMP	Uptake by 6000 Bed Volumes	Final Loading	Total in Column	Regeneration	Residual	Recovery %	Extracted Residual
1st	3.09	4.38	4.38	3.40	0.98	78%	
2nd	2.24	2.75	3.73	2.08	1.65	56%	
Total		7.13		5.48	1.65		1.83

4. Conclusion

This research showed that phosphonate compounds adsorb strongly to ferric hydroxide, even in the presence of high concentrations of other anions. This is indicative that the adsorption mechanism involves inner-sphere complexation. The initial concentration effects shown for both PT191 and NTMP indicate that the adsorption reactions are not kinetically reversible. Strong phosphonate adsorption, even in high pH solutions, renders conventional regeneration methods impractical. To overcome the high volume of NaOH solutions required for regeneration, previous investigators have suggested the use of NF for separating the phosphonate compounds from the regenerant solutions.[5] While this process works in short-term laboratory experiments, most NF membranes are limited to operational pH values of 11 or lower.[20] Thus, more research is needed in order to develop improved methods of regeneration.

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