Removing phosphonate antiscalants from membrane concentrate solutions using granular ferric hydroxide

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ABSTRACT

Phosphonate antiscalants are commonly used in membrane desalination to prevent fouling by mineral scale. In many circumstances, it is desirable to remove these compounds before concentrate disposal or further treatment. The goal of this research was to determine if the kinetics of phosphonate adsorption and desorption from granular ferric hydroxide (GFH) are sufficiently fast for GFH to be used in packed bed adsorption systems for antiscalant removal from membrane concentrate solutions. Well-stirred batch experiments were performed to investigate the adsorption kinetics of Permatreat 191* (PT191) and nitrilotri(methylphosphonic) acid (NTMP) onto GFH. Uptake of both compounds was slow and continued over the course of 6 days. Adsorption isotherms measured after 24 h elapsed showed initial concentration effects, whereby the isotherms were dependent on the initial adsorbate concentration in solution. This can be attributed to chemical adsorption reactions with faster rates of bond formation than bond breaking. Strong phosphonate adsorption in high pH solutions and high activation barriers for desorption resulted in slow kinetics for adsorbent regeneration by NaOH solutions. Desorption rates were bimodal, with 40–50% of the adsorbed phosphonate being released on a time scale of 10–24 h, while the remaining fraction was released approximately one order of magnitude more slowly. Complete regeneration could not be achieved, even after eluting the adsorbent columns with more than 300 bed volumes of 1.0 mol/L NaOH. The inability to regenerate the adsorbent in an efficient manner likely precludes its use for cost-effective antiscalant removal from membrane concentrate solutions.

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 [4]. 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 [5].

Removal of phosphonate compounds from membrane concentrate solutions requires an adsorbent that reacts with the phosphonate group via chemical adsorption, rather than by electrostatic attraction or ion exchange. This is necessary since the concentration of the antiscalant compound is usually less than 0.1 mM, while the concentrations of other anions, such as Cl^-, SO_4^{2-}, and HCO_3^- are typically one to two orders of magnitude greater. Adsorbents based on ferric hydroxide have been proposed for removing phosphonate antiscalants from membrane concentrate solutions [6–8].

The mechanisms of phosphonate adsorption to iron oxide minerals and amorphous ferric hydroxide have been studied by several investigators using spectroscopic and quantum chemistry methods [9–14]. The mechanisms of phosphonate uptake by ferric hydroxides are complex, and involve several adsorption mechanisms that include both physical and chemical adsorption. A recent study using quantum chemistry simulations showed that physical adsorption of the antiscalant, nitrilotri(methylphosphonic) acid (NTMP), on ferric hydroxide is promoted by electrostatic effects, and charge assisted hydrogen

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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 $CaCO_3$

bonding [9]. NTMP is a polyprotic acid containing six 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 [15]. 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 [9,12–14]. These complexes involve ligand exchange reactions in which an −OH or −OH2 ligand attached to Fe^{3+} is replaced by a phosphonate. Adsorption complexes involving a single P−O−Fe bond are termed, monodentate mononuclear complexes. Bidentate mononuclear complexes may form that involve two Fe−O−P bonds to the same Fe atom. Two P−O−Fe bonds on adjacent Fe atoms may also form. This type of complex is known as a bidentate binuclear complex. For phosphonate compounds that contain more than one phosphonate group, multiple types of bonding may occur for a single adsorbate molecule [9]. In addition, Ca^{2+} ions may also be involved in ternary complexes between ferric hydroxide and phosphonate groups [9,16].

Chemical adsorption reactions generally have activation barriers associated with breaking and forming chemical bonds. A previous study using quantum chemistry modeling has shown that adsorption of NTMP on ferric hydroxide has activation barriers ranging from 0 kcal/mol for physical adsorption, and 8.5–53 kcal/mol for chemical adsorption [9]. For desorption of NTMP from ferric hydroxide, activation barriers ranged from 36 to 53 kcal/mol, depending on the type of complex [9]. At room temperature, these activation barriers are significantly greater than the average thermal energy per molecule, and can result in slow equilibration for both adsorption and desorption reactions. Higher activation barriers for desorption, as compared to adsorption, can result in metastable equilibrium and adsorption isotherms that are apparently influenced by the initial concentration of the adsorbate in solution [9].

A previous study has reported that adsorption of NTMP on a granular ferric hydroxide (GFH) adsorbent required 3–9 h to reach equilibrium, and depended on the initial concentration of NTMP in solution [6]. The slow approach to equilibrium was attributed to diffusional mass transfer limitations, and the effect of activation barriers on rates of adsorption and desorption were not considered. Batch adsorption isotherms were measured after 24 h of equilibration. Similarly, a second batch study has reported adsorption isotherms for NTMP on GFH measured after 24 h of equilibration [8].

We hypothesize that high activation barriers for chemical bond formation and bond breaking of phosphonate antiscalants will result in slow kinetics for both adsorption and desorption in packed bed treatment systems. Slow adsorption kinetics may result in early breakthrough in flow-through adsorbent beds. Slow desorption will make adsorbent regeneration difficult, possibly requiring large volumes of regenerant solution. The goal of this study was to investigate whether the kinetics of phosphonate adsorption and desorption from GFH are sufficiently fast to enable it to be used in practical treatment systems for antiscalant removal. Practical treatment systems commonly employ empty bed contact times on the order of 10 min and can be regenerated on-site. Towards those ends, column breakthrough experiments and adsorption isotherms were measured for a commercial phosphonate antiscalant and for NTMP on a commercially available GFH adsorbent. The effectiveness of adsorbent regeneration using 0.10 and 1.0 mol/L NaOH solutions was also investigated.

2. Materials and methods

2.1. Adsorbent

The adsorbent used in this study was Granular Ferric Hydroxide® (GFH), and was obtained from GEH Wasserchemie (Osnabruck, Germany). GFH consists predominantly of the mineral akaganeite (β-FeOOH), and was developed for removal of arsenate and arsenite from potable water [17–19]. The material was used as-received, with manufacturer's reported specifications of 300 m^2/g surface area, and 0.2–2.0 mm particle diameters. Drying the GFH for 24 h at 120 °C resulted in a 45% weight loss, which is indicative of the water content. All results are presented on an as-received mass basis.

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 [4]. 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 ≥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 [20]. 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 (mg-P/L). Phosphorous concentrations were measured using an Agilent model 5100 synchronous vertical dual view inductively coupled plasma optical emission spectrophotometer (ICP-OES) using a wavelength of 213.618 nm. Three calibration standards with concentrations of 0.10, 1.0 and 10.0 mg-P/L were prepared in UPW. The linear calibration curve had an R^2 value of 0.9999.

2.3. Column breakthrough and regeneration experiments

Column breakthrough experiments were performed using 2 g of GFH packed into a 0.8 cm diameter by 9 cm long glass column and held in place using glass wool. The columns were operated at an empty bed contact time of 2.0 min 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.