Phosphate adsorption on granular ferric hydroxide to increase product water recovery in reverse osmosis-desalination of secondary effluents

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HIGHLIGHTS

- Phosphate adsorption on GFH prevents scaling in multistage effluent desalination.
- Optimal hydraulic conditions for P adsorption and GFH regeneration were formulated.
- Over 95% P removal was achieved keeping a breakthrough concentration of 0.2 mg P/L.
- Fixed bed GFH set-up in between stages allows pressure recovery in two stage-RO.
- Brines released are suitable for high recovery rate-subsequent desalination.

ARTICLE INFO

ABSTRACT

Calcium phosphate precipitation, and in particular calcium hydroxyapatite (HAP)-Ca$_5$(PO$_4$)$_3$OH scaling, is a major factor limiting high recovery in reverse osmosis (RO) of treated effluents. This study evaluated the feasibility of phosphate adsorption in continuous regime on granular ferric hydroxide (GFH) from 2-fold concentrated RO-brines (1st stage of a 2-stage RO desalination train) of secondary effluents. Fixed bed adsorption on granular media was chosen to ensure low turbidity and preserve brine pressure for the 2nd RO stage. Optimal hydraulic conditions for adsorption and a method for GFH regeneration were formulated. Simultaneous analysis of bed mass transfer zone and adsorbent concentration yielded optimum at empty bed contact time (EBCT) > 3.5 min and 10 < hydraulic load (HL) < 15 m/h. Breakthrough P-concentration was set at 0.2 mg/L to maintain HAP-solubility index ≤7. A constant adsorption rate of 1.6 mg P/g GFH was maintained during nine adsorption/regeneration cycles at feed phosphate concentration of 9.3 ± 0.9 mg/L (as P), approx. 3300 bed volumes (BV) per batch. A NaOH regeneration solution was effectively recycled over 2300 BV until reactivation was required. Considering that phosphate concentration in effluents of well performing wastewater treatment plants is far below 10 mg/L, in practice column capacity will be considerable higher than 3300 BV.

1. Introduction

Water recycle for agriculture, which is considered a central water management issue in arid and semiarid regions, is becoming a major concern worldwide because of dwindling of fresh water resources and pollution of existing ones. In Israel, for example, about 85% of the treated municipal effluents are recycled for irrigation, accounting for about one-half of the total water demand for agriculture [1].

Reuse and discharge of conventionally treated wastewater effluents for irrigation involve public health considerations aimed at preventing the spread of salts, viruses, endocrine disrupting compounds, suspected carcinogenic materials, nanomaterials and other contaminants [2]. Because of their broad capability and flexibility, dense pressure-driven membranes such reverse osmosis (RO), represent a central technology to confine all these contaminants in the brines when applied to treat effluents [3,4], while releasing high quality water for unrestricted irrigation. This conception can exclude the salts and organic contamination from circulating and contribute to a sustainable wastewater disposal. However, a proper pretreatment of

treated effluents is necessary prior to desalination. Besides biofouling, mineral scaling is a major obstacle for effluent desalination, and in particular calcium phosphates, which limit high recovery rates. Although biological nutrient removal performed in most conventional wastewater treatment plants (WWTPs) is efficient for nitrogen species removal [5], it displays unsteady and fluctuating results for phosphorous species. Therefore, targeted pretreatment for efficient P removal is required prior to or during desalination to ensure high recoveries [6]. Working at 90% recovery (about ten-fold concentration), most complex anions present in effluents, e.g., bicarbonate, sulfate and in particular phosphate, eventually exceed the saturation level [7].

Allowed phosphorus concentration for effluents discharge is up to 1 mg/L in most countries, with orthophosphates being the common specie and traces amounts of polyphosphates and organic phosphate. Calcium hydroxyapatite (HAP)-$Ca_5(PO_4)_3OH$ precipitation is the most common phosphate scaling species in RO desalination of secondary effluent, due to its low solubility ($pK_{sp} \approx 58$). The normally high alkalinity of the concentrate stream (~2200 mg/L for a 10-fold concentrate) makes it unfeasible to lower the pH below the K_{sp} at a reasonable cost, even in the presence of high dose of commercially available antiscalants [8,9]. Therefore, effluent pretreatment for phosphate or calcium removal is imperative for high recovery rates. Conventional phosphate precipitation by dosing of Al and Fe(III) salts or (hydro)oxides is normally kinetically unfavorable because of the relatively low and fluctuating phosphate concentration in the feedwater [10,11]. A Fe(III):P mass ratio $\geq 2.5{:}1$ is theoretically required for 90% phosphate precipitation as strengite from 2-fold concentrated brines. However, a least ratio 6:1 Fe:P is needed in practice for 90% phosphate removal due to complexation with organic materials which inhibit strengite precipitation [12]. A better efficiency was achieved combining adsorption on FeO/OH nanoparticles with ultrafiltration, a process that needs to be developed in parallel [13,14]. Adsorption of phosphate on a bed of active carbon covered with iron(3)oxide-nanoparticles is also a possible method that needs more attention [15].

This research focused on phosphate removal by adsorption on granular ferric hydroxide (GFH). This granular media is used for arsenic removal from drinking water but has also been implemented for phosphate adsorption from wastewater effluents and nanofiltration concentrates [16,17]. Affinity of phosphate towards ferric hydroxide surface is higher than other anions, displaying high specific binding. Due to the well-defined structure of naturally occurring and synthetic crystals, hydrous ferric oxide, goethite and hematite have often been used as model adsorbents for phosphate [18–22]. Adsorption of phosphate anions (PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$) onto GFH was described similar to that on goethite, by three mononuclear surface complexes [23]. It was found that adsorption capacity depends on crystal morphology [24]. The mechanism is mutually dependent on the water matrix composition along with phosphate concentration and crystal properties of GFH. Since GFH is a commercial adsorbent media, poorly crystallized and inhomogeneous, it has wide variations in adsorption capacity [25] and needs to be characterized based on the water matrix characteristics.

The main objective of this study was to evaluate the feasibility of phosphate removal by GFH adsorption in continuous regime from the 1st-stage brines (50% recovery ≡ 2-fold concentrated) of a 2-stage desalination train based on the Technion secondary effluent desalination pilot [26]. Phosphate adsorption in a fixed bed was chosen in order to ensure low turbidity, diminish problems associated with the fluctuation of phosphate concentration and preserve the energy of the concentrate stream in order to use it for the 2nd RO stage. This makes the water quality suitable for feeding 2nd RO stage and ensure high recovery rate. The quantitative adsorption capability of GFH was evaluated, establishing optimal hydraulic conditions for the adsorption process. A methodology for best GFH media reuse and regeneration was formulated.

2. Material and methods

2.1. Granular ferric hydroxide (GFH)

GFH was obtained from GEH Wasserchemie GmbH & Co. KG, catalog number GEH 104. The GFH is supplied as granulated media with typical water content of 45% and nominal surface area >220 m^2/g dry weight, according to the manufacture specifications. The particle size distribution measured by a Hydro 2000S mastersizer (Malvern) is presented in Fig. S1 (Supplementary information). Particle size was in the range 0.2–2 mm with a main typical size of about 0.44 mm. Iron content measured by ICP upon digestion of GFH particles (214 mg) in 65% HNO_3 at 80 °C until complete dissolution was 66.5% (dry weight).

2.2. RO brines

Experiments were performed with fresh RO brines spiked with the indicated concentration of orthophosphate. Brines were obtained from the Technion secondary effluent desalination-pilot plant located at a commercial wastewater treatment plant in northwest Israel. The pilot comprises a pre-filtration stage (100 μm disk filter, Arkal), then an ultra-filtration stage (~40–80 nm, Dow) followed by a two stage-RO system (RO1-8″ and RO2-4″ BW Toray membranes, respectively) as detailed elsewhere [26–28]. The experiments were performed with RO1 brines (2-fold concentrated).

Table S1 (Supplementary information) shows the performance of different runs of RO1 stage within a 6-month period, with emphasis was on the pertinent parameters related to phosphorous removal, depicting the typical fluctuations of the individual parameters in the feed. An overall concentration factor of 1.8 ± 0.2 was observed at a very high rejection of all parameters.

2.3. Experimental

2.3.1. Adsorption isotherms

Adsorption isotherms were conducted in 2 L shaken flasks containing 1 L RO1 brines and varying amounts of GFH (0.2–3 g) for 96 h at a temperature of 25 °C. Experiments were performed in triplicates with the same batch of RO1 brines (~20 mg/L TOC, pH 7–8) amended with Na_2HPO_4 to an initial phosphorus concentration of 17 mg P/L.

Langmuir adsorption isotherm was used to describe the equilibrium between solid (q) and solution (C_{eq}) concentration (Eq. (1)):

$$q = q_{max} \times \frac{K_L \cdot C_{eq}}{1 + K_L \cdot C_{eq}} \tag{1}$$

where K_L is the Langmuir coefficient and q_{max} is the maximum surface concentration, indicating a monolayer coverage. Langmuir coefficients q_{max} and K_L were obtained from linearization of Eq. (1).The potential of phosphate removal from brines of GFH was tested in continuous flow with full recirculation (batch mode) in glass columns (2.2 × 30 cm) in the range of 1–15 mg P/L total phosphorus concentration. Columns were packed with 10 g GFH and run at an approximate velocity of 10 m/h for 48 h with 4 L RO1 brines.

2.3.2. Optimization of hydraulic conditions in flow through-columns

In order to characterize the adsorption of phosphate from RO1 brines onto GFH in continuous process, different hydraulic conditions were investigated. A wide range of empty bed contact times (EBCTs) and hydraulic loads (HLs) were tested within manufacturer recommended range. The runs were performed in continuous mode with single pass using glass columns similar to those described above. EBCT was controlled by addition/removal of columns. A total of 18 breakthrough experiments were conducted.