Phosphate removal from water using an iron oxide impregnated strong base anion exchange resin

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ABSTRACT

Removing phosphate from water is important as it causes eutrophication, which in turn has a harmful effect on aquatic life, resulting in a reduction in biodiversity. On the other hand, recovery of phosphate from phosphorus containing wastewater is essential for developing an alternative source of phosphorus to overcome the global challenge of phosphorus scarcity. Phosphate removal from aqueous solutions was studied using an iron oxide impregnated strong base anion exchange resin, Purolite FerrIX A33E in batch and fixed-bed column experiments. Phosphate adsorption in the batch study satisfactorily fitted to the Langmuir isotherm with a maximum adsorption capacity of 48 mg P/g. In the column study, increase in inlet phosphate concentration (5–30 mg P/L), and filtration velocity (2.5–10 m/h) resulted in faster breakthrough times and increase in breakthrough adsorption capacities. Increase in bed height (3–19 cm) also increased adsorption capacity but the breakthrough time was slower. The breakthrough data were reasonably well described using the empirical models of Bohart–Adams, Thomas, and Yoon–Nelson, except for high bed heights. Phosphate adsorbed was effectively desorbed using 1 M NaOH and the adsorbent was regenerated after each of three adsorption/desorption cycles by maintaining the adsorption capacity at >90% of the original value. Greater than 99.5% of the desorbed P was recovered by precipitation using $CaCl_2$.

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1. Introduction

Phosphorus (P) is an essential nutrient for the growth of plants and microorganisms. It is also an important chemical element for many industries and a major nutrient contaminant in water. It is released to water bodies in the form of organic and inorganic phosphates by domestic, mining, industrial and agricultural activities and municipal discharges. Excessive concentration of P in water causes eutrophication. Eutrophication is a major environmental problem as it can lead to abundant development of aquatic plants, including algae, threaten fish and other aquatic life, and disturb the ecological balance of organisms present in the water. The excessive P in water should be removed for controlling eutrophication and maintaining a sustainable green environment for future generations. To control eutrophication, environmental protection agencies in many countries have recommended that total P should not exceed 0.005–0.1 mg P/L in natural water bodies [1,2].

Several physical, biological and chemical processes have been investigated for the removal of dissolved phosphates in water and wastewaters. These processes include adsorption/ion exchange, chemical precipitation/coagulation, crystallization and membrane filtration/reverse osmosis. Of the various methods of P removal, adsorption/ion exchange methods are promising, because they are simple and economical, result in less sludge production and therefore experience minimal disposal problems [3]. Furthermore, these methods seem to be the most suitable for small water supplies contaminated by P because of its simplicity, effectiveness, selective removal in the presence of other ions, easy recovery of P and relatively low cost [4]. These methods are also able to handle shock loadings and operate over a wide range of temperatures.

The performances of the adsorbents with reference to phosphate removal have been reported in literature with varying degrees of success [3]. Generally, ion exchangers are able to effectively remove nitrate from water, but they have not been successful in removing phosphate. For example, Gupta et al. [5] reported that Purolite 500 A anion exchange resin had a Langmuir adsorption capacity of 64 mg N/g for nitrate adsorption whereas it had only 7 mg P/g for phosphate adsorption. Therefore, they used two columns in series, one with Purolite for removing nitrate followed by the other with hydrous ferric oxide for the removal of phosphate from water containing both these anions. Others used

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polymeric anion exchanger bound with ferric oxide nanoparticles to successfully remove phosphate [4,6]. These studies showed that adsorbents containing ferric oxide are required for effectively remove phosphate. Purolite FerrIX A33E media is another nanoparticle derived resin designed to selectively remove arsenic (arsenate and arsenite) from water supply [7]. This resin unites a unique blend of hydrous iron oxide nanoparticles that have a very high attraction for arsenic with a durable, non-friable, spherical polymer substrate. As this resin was found to be effective in removing arsenic anions, it is expected to have strong affinity for phosphate anions as well, because phosphate like arsenic is specifically adsorbed on iron oxides [3]. However, no detailed study has been conducted on phosphate adsorption by this ion exchange resin.

The aim of the present research is to study and model the removal of phosphate from synthetic wastewater employing the ion exchange resin, Purolite FerrIX A33E in batch and fixed-bed column systems. The effects of bed height, initial phosphate concentration and filtration velocity were investigated in the column study. The empirical models of Bohart–Adams, Thomas and Yoon–Nelson were tested for their ability to describe the column adsorption data. A study was also conducted to develop a suitable method to regenerate the adsorbent for reuse, as well as recovery of the desorbed P for beneficial use.

2. Materials and methods

2.1. Ion exchange resin

A commercially available and reasonably economical iron oxide impregnated Type II hybrid strong base anion exchange resin, Purolite FerrIX A33E obtained from the Purolite Company, U.S.A. [7] was used as the adsorbent in this study. This adsorbent is a blend of hydrous iron oxide nanoparticles and highly porous polystyrene cross-linked with divinylbenzene polymer having an arsenic operating capacity of 0.5–4 g As/L and available in the form of spherical beads (0.3–1.2 mm diameter). The highly porous nature of the resin bead allows for maximum utilization of the impregnated iron oxide. The polymer component of the adsorbent had positively charged quarternary ammonium functional groups with chloride as counter ion [8]. The resin contained 13% Fe.

2.2. Feed solutions

The feed solutions were prepared using KH_2PO_4 with distilled water spiked with different concentrations of phosphate (5–30 mg P/L). The pH of the solutions ranged from 7.2 to 7.6.

2.3. Chemical analysis

The analysis of phosphate ion was carried out using a Metrohm ion chromatograph (model 790 Personal IC) equipped with an auto sampler and conductivity cell detector. The separation was achieved using an A SUPP column 3 (150 mm × 4 mm). Na_2CO_3 (3.2 mmol/L) and $NaHCO_3$ (1.0 mmol/L) were used as mobile phase with a flow rate of 0.9 mL/min.

2.4. Batch adsorption experiment

Equilibrium adsorption experiments were conducted in a set of glass flasks with 100 mL solutions spiked with phosphate (10 mg P/L) and ion exchange resin concentrations of 0.1–10 g/L at room temperature (24 ± 1 °C). The suspensions were agitated in a flat shaker at a shaking speed of 120 rpm for 72 h to ensure that the adsorption equilibrium is reached. However, preliminary experiments showed that the adsorption equilibrium was achieved within

48 h. The experiments were duplicated and the average values were taken for data analysis. The difference between duplicate values was within $\pm 2\%$. The amount of phosphate adsorption at equilibrium, q_e (mg P/g), was calculated using Eq. (1),

$$q_e = \frac{(C_0 - C_e)V}{M} \tag{1}$$

where C_0 = initial concentration of phosphate (mg P/L); C_e = equilibrium concentration of the phosphate (mg P/L); V = volume of the solution (L) and M = mass of adsorbent (g).

2.5. Column mode experiments

The fixed-bed column was made of 2.0 cm inner diameter pyrex glass tube. At the bottom of the column, a stainless steel sieve was attached followed by a layer of glass beads in order to provide a uniform flow of the solution through the column. A known quantity (12–86 g) of the resin was packed in the column to yield the desired bed height (3–19 cm) of the adsorbent. Phosphate solutions of known concentrations (5, 10, 15, 20 and 30 mg P/L) was pumped upward through the column at a desired filtration velocity (2.5, 5.0 and 10.0 m/h) controlled by a peristaltic pump. The effluents at the outlet of the column were collected at regular time intervals and the phosphate concentration was measured using ion-chromatograph.

The breakthrough curves show the loading behaviour of phosphate to be removed from solution in a fixed-bed column and are usually expressed in terms of adsorbed phosphate-P concentration (C_{ad}), inlet phosphate-P concentration (C_o), outlet phosphate-P concentration (C) or normalized concentration defined as the ratio of outlet phosphate concentration to inlet phosphate concentration (C/C_o) as a function of time. The maximum column capacity, q_{total} (mg P), for a given feed concentration and filtration velocity is equal to the area under the plot of the adsorbed phosphate-P concentration, C_{ad} ($C_{ad} = C_o - C$) (mg/L) versus effluent time (t, min) and is calculated from Eq. (2).

$$q_{total} = \frac{Q}{1000} \int_{t-0}^{t-total} C_{ad}dt \tag{2}$$

Equilibrium uptake q_{eq} (mg P/g) or maximum capacity of the column is defined by Eq. (3) as the total amount of adsorbed phosphate-P concentration (q_{total}) per g of adsorbent (M) at the end of the total flow time:

$$q_{eq} = \frac{q_{total}}{M} \tag{3}$$

The detention times of Purolite FerrIX A33E during fluidization are calculated using Eq. (4).

$$t = \frac{H}{v} \tag{4}$$

where t is the detention time (h), H is the column bed height (m) and v is the upflow filtration velocity (m/h).

2.6. Batch adsorption isotherm modelling

Batch adsorption data were modelled using Langmuir adsorption isotherm equation [9] expressed as follows:

$$Q_e = \frac{q_{max}K_LC_e}{1 + K_LC_e} \tag{5}$$

where q_{max} = the maximum amount of the phosphate-P concentration per unit weight of the adsorbent (mg P/g), K_L = Langmuir adsorption constant (L/mg).