

Removal of phosphate from aqueous solutions by iron nano-particle resin Lewatit (FO36)

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Abstract—Lewatit FO36 resin was covered with Fe (III) nano-particles, and it was used as a new way to eliminate phosphate. Column experiments were carried out in 11 stages in fixed bed columns with constant flow rate of 9 ml/min and the empty bed contact time (EBCT) of 2.1 min. The adsorption capacity was calculated for different concentration of phosphate solutions. After resin was regenerated by using NaOH and NaCl solutions, the adsorption capacity of resin was computed for 6 mg/L of phosphate, typically. The adsorption capacity of resin was checked again a typical concentration of phosphate. The adsorption capacity measurements of regenerated resin show that the concentration of phosphate reached to 1.6 mg/g after an 8.5% decrease when the initial concentration of phosphate is 6 mg/L. Competition of anions with phosphate was analyzed using chloride, sulfate, bicarbonate and a combination of these anions. Finally the effect of resin in phosphate removal was studied for a typical real sample, and the data was analyzed using statistical software (SPSS 13). The statistical results indicated that Cl^- , SO_4^{2-} , HCO_3^- and combined competing anions did not have a strong influence on the phosphate removal efficiency.

Key words: Phosphate Removal, Lewatit FO36, Competing Anions, Adsorption

INTRODUCTION

Phosphorus plays an important role as the necessary element for plant growth and as the restricting nutrient in the algal growth and eutrophication in surface water bodies [1]. On the other hand, phosphate is a very important basic material that is highly used in the manufacture of fertilizers, detergents, water softeners, processed foods and drinks and all types of products in which phosphate is the main part. Most countries in world are dependent on phosphate for industrial production processes [2]. Different processes may affect the phosphate removal from aqueous solutions [3,4] such as adsorption [5,6], biological methods [7], crystallization [8] and reverse osmosis [9]. Most physical methods, such as reverse osmosis, are expensive. Biological methods are more effective in phosphate removal [10], yet the chemical method is the most complete and most applicable one [11]. Among the chemical methods the chemical sedimentation with Fe, lime, $\text{Ca}(\text{OH})_2$, to form calcium hydroxyapatite, $\text{Ca}_5\text{OH}(\text{PO}_4)_3$, under alkaline condition, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and Mg is among the most common methods to remove phosphate from the wastewater [12,13]. The adsorption process is an important method in phosphate removal from aqueous solutions in which the adsorption capacity increases with activating the surface [14,15].

Li et al. [16] used a novel adsorbent to remove ammonia nitrogen and phosphate and presented that the new sorbent is very effective and the novel rare earth adsorbent will provide a new way for the treatment of ammonia nitrogen and phosphate in wastewater. Results showed the best adsorption capacity is 25 mg/g and 50 mg/g for ammonia nitrogen and phosphate, respectively, and Chen et al. [17] showed that phosphate immobilization capacity (PIC) of the synthesized zeolites was significantly increased (from 1.2 to

7.6 times).

The novel La (III)-modified zeolite adsorbent (LZA) was used to selectively remove phosphate in the presence of various omnipresent anions, such as sulfates, bicarbonates, and chlorides, which results indicated good selectivity and regeneration of LZA might serve as a potential way for advanced phosphate removal from the sewage containing other anions (Ning et al.) [18].

Regarding the studies of Geelhoed et al. [19] on phosphate and sulfate adsorption with goethite, sulfate did not show any significant inhibition effect on phosphate removal and Blaney et al.'s [20] research on the hybrid anion exchanger competing anions such as sulfate, chloride, and bicarbonate did not show effect on the function of resin in adsorbing phosphate.

Nowadays, chelating resins are more common and more widely used due to their high adsorption capacities, durability, and selectivity [21,22]. These resins are polymers with the functional groups able to form complexes with selected ions. In contrast to the conventional ion exchange resins, chelating resins combine with ion exchange and complex formation, and hence can exhibit high selectivity for some ions or groups of ions, providing a wide range of practical use and industrial applications. The properties of chelating ion exchangers depend on the type of functional groups, though to a lesser extent on grain size and physical properties [23,24]. Selective resins were deemed major options for treating wastewater. Traces of environmentally harmful substances accumulate on the Lewatit FO36 ion-exchange resin and are thereby removed from the wastewater. Lewatit FO36 has high exchange capacity, very good chemical, mechanical and thermal stability. On the other hand, having good ion-exchange kinetics makes it suitable for the treatment of electroplating rinse waters [25]. Gel resins usually have higher efficiencies and lower cost [26]. Lewatit FO36 is among resins with the poly-styrene structure which is similar to the mineral goethite, covered with the surface groups of $\text{FeO}(\text{OH})$ [26,27]. Covering layer

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with nano particles in fixed bed columns or any similar systems prevents sudden pressure decrease [28]. Studies indicate that nano-particles such as Fe (III), Al (III), Zr (IV) and Ti (IV) are able to remove phosphate [29-31]. Application of fertilizers in agricultural fields changes the phosphate content of groundwater, and reduction of phosphate is necessary [32].

In this study, the efficiency of a nano particles ion exchange resin, i.e., Lewatit FO36, for removal phosphate from aqueous solutions has been investigated using fixed-bed technique. Then, the effect of anions such as Cl^- , SO_4^{2-} , HCO_3^- and the combined anions on removal of phosphate anion have been investigated. Also, UV-Vis spectrophotometric technique was applied to determine phosphate concentration using vanadate-molybdate reagent.

MATERIALS AND METHODS

Lewatit FO36 resin was purchased from the Lanxess Company (Germany). Resin contains a layer of nano iron oxide binds in a specific surface complex. The typical characteristics of Lewatit FO36 are summarized in Table 1 [33]. All other chemicals were purchased from Merck with analytical grade, and were used as received without further purification.

Stock solutions (50 mg/L) of the phosphate ion were prepared by dissolving an appropriate weight of pure KH_2PO_4 salt in distilled water according to instruction P-4500 Standard Method [34]. Individual phosphate solutions with specified concentrations (1-6 mg/L) were prepared by diluting the stock solution in distilled water.

The performance of the adsorption was studied at room temperature as were the effects of important parameters on removal efficiency. All experiments were performed in duplicate and the result was taken as the average value of the experiment.

A chloride solution with 70 mg/L, the bicarbonate solution with 100 mg/L, and a sulfate solution with 60 mg/L concentrations (based on the medium strength wastewater) were prepared by dissolving an appropriate weight of their salts (NaCl , NaHCO_3 and Na_2SO_4).

The ion-exchange experiments were carried out at room temperature ($25 \pm 1^\circ\text{C}$). The initial pH of the sample solutions was adjusted in the range of 7.0 using 0.1 N of HCl or diluted NaOH. All pH measurements were performed with a Metrohm E520 pH meter.

The experiments were performed in fixed bed columns having 1 cm diameters and 30 cm height and a flow rate of 9 ml/min with empty bed contact time (EBCT) equal to 2.1 min. The column was filled with 2 g of resin, which takes about 1.6 ml of the column.

Table 1. Physical and chemical properties of Lewatit FO 36

Property	Value
Uniformity coefficient	1.1
Density	g/ml 1.25
Bulk density	g/L 0.765
pH - range stability at	4-14
Operating pH - range	4-11
Storability temperature range	Until +40-20
Storability of the product	2 Years · max
Total arsenic capacity	min · g/L ≥ 40
Regenerate	NaOH+NaCl (with a mass-ratio of 1 : 1)

The aqueous solution containing phosphate was delivered from down-flow to the column at a flow rate of specific velocity defined as bed volume per hour (SV) equal to 337.5 BVh^{-1} . Linear flow velocity (LV) equal to 1.2 mh^{-1} was checked and adjusted at each sampling.

Column experiments were run eleven stages. In the primary of six stages, the column was formed for the distinct concentrations of 1 to 6 mg/L of phosphate for determining adsorption capacity. In the next stage, after regeneration of resin, the concentration of 6 mg/L was selected and the above procedure was repeated again. Then the experiments were carried out in four stages with the presence of competing ions such as chloride, bicarbonate, sulfate and their combinations. After all these stages a real sample was introduced to the column for the effluent wastewater plant of Shahrak-e-Quds in Tehran.

In the primary of six stages, the phosphate solution with different concentrations (1 to 6 mg/L) was passed through the resin to determine its adsorption capacity, and sampling continued until the concentration of the exiting phosphate reached the primary concentration. In the next stage after regeneration, the first stage was repeated again. Four series of solutions containing 70 mg/L Cl^- , 60 mg/L SO_4^{2-} and 100 mg/L HCO_3^- were run through the column to determine anion competition on phosphate removal. In the last stage, a combination of competing anions (70 mg/L Cl^- , 60 mg/L SO_4^{2-} and 100 mg/L HCO_3^-) passed through the column. Finally, a sample solution of effluent in the Shahrak-e-Quds refinery of Tehran, as a typical real sample, which contained 3 mg/l of phosphate, was used in the adsorption experiment.

The amount of phosphate in each stage was measured using a SHIMADZU-UV1700 spectrophotometer in 420 nm using molybdate-vanadate reagent according to standard method [34]. The adsorption capacity of resin was calculated in each of the above-mentioned stages using Data Studio software.

RESULTS AND DISCUSSION

1. Determining the Adsorption Capacity

Six concentrations of phosphate were passed through the indi-

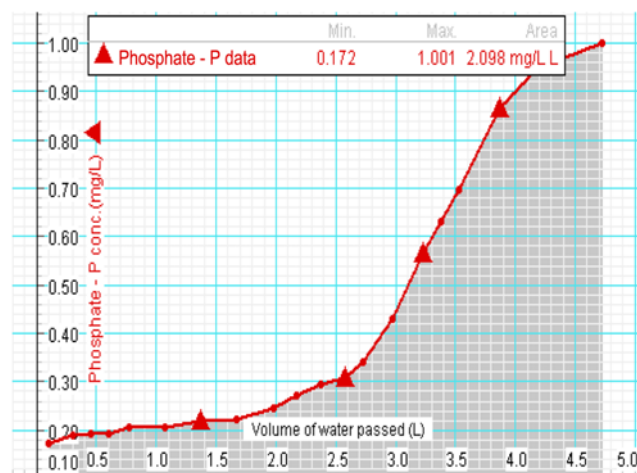


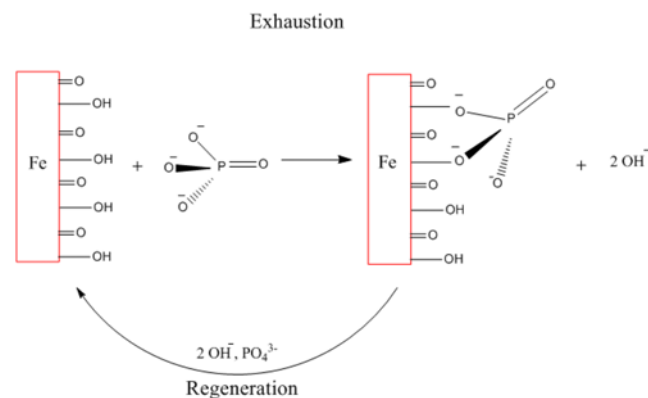
Fig. 1. Adsorption capacity diagram of Lewatit FO36 obtained by the data studio software phosphate - p: 1 mg/l, EBCT: 2.1 min (typically).

vidual columns and the sampling continued until phosphate concentration in the outlet reached to concentration in feed. Fig. 1 shows a typical plot of outlet phosphate concentration versus volume of water passed. The area under the curve shows the amount of phosphate which is not adsorbed by the resin and exited through the column. Thus, 2.0 g resin adsorbed 2.627 mg phosphate and adsorption capacity of resin is 1.31 mg/g. This value was obtained for 1 mg/L of phosphate solution. For the other phosphate concentrations, i.e., 2 to 6 mg/L, adsorption capacity was calculated as 1.35, 1.53, 1.64, 1.7 and 1.75 mg/g, respectively. Statistical analysis showed that P value=0.04 for the primary of six stages.

The layer of iron oxide binds phosphate in a specific surface complex. It adsorbs phosphate as well as other anions and heavy metal ions. A simplified scheme of the adsorption is presented in Scheme 1 [uptake of PO_4^{3-}]. An equivalent reaction scheme can also be created for binding other ions on the iron oxide surface.

2. Determining the Adsorption Capacity after Regeneration

For a typical 6 mg/L phosphate solution feed, after saturation of resin, i.e., when the concentration exiting the column reaches the primary concentration of 6 mg/L, resin was regenerated using a mixture of NaCl and NaOH with a mass-ratio of 1 : 1. Following regeneration, the column was rinsed with distilled water. The total



Scheme 1. Simplified reaction scheme of phosphate anion uptake.

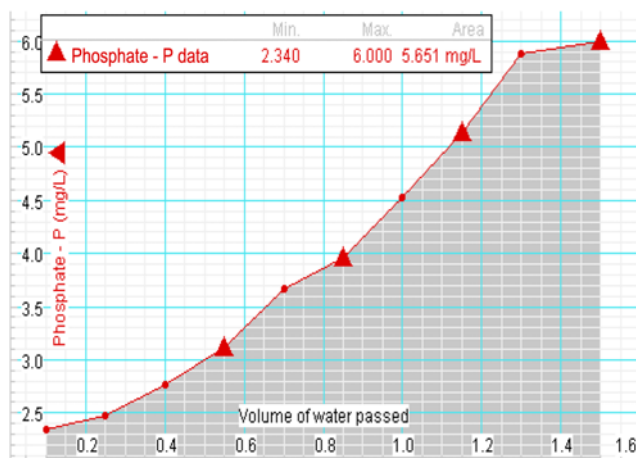


Fig. 2. Adsorption capacity diagram of Lewatit FO36 after regeneration obtained by the Data Studio software phosphate- p: 6 mg/L, EBCT: 2.1 min.

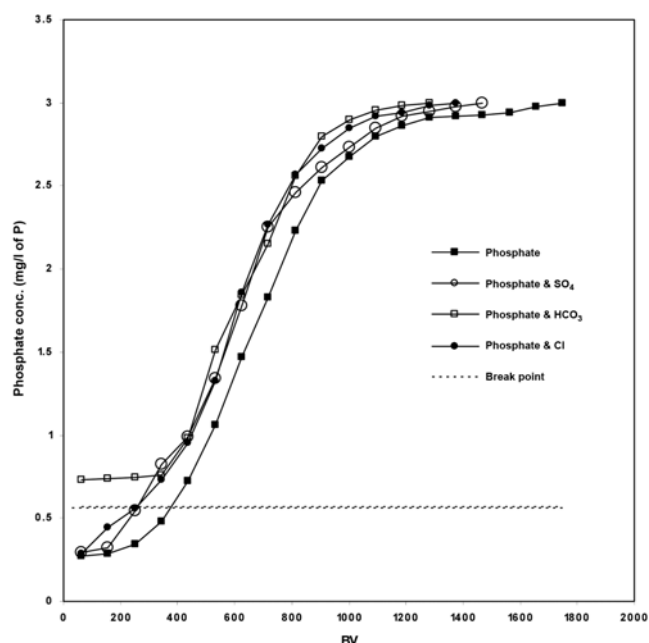


Fig. 3. Effects of chloride (●), sulfate (○) and bicarbonate (□) on phosphate removal separately (phosphate - p: 3 mg/L, Cl: 70 mg/L, HCO_3^- : 100 mg/L, SO_4^{2-} : 60 mg/L & EBCT: 2.1 min).

amount 500 BV distilled water was used for several rinses of the column during the regeneration process.

Now, the column was ready for the next sorption cycle. Again, 6 mg/L of phosphate solution was passed through from the column (Fig. 2). The capacity, with an 8.5% decrease, was reduced from 1.75 mg/g to 1.6 mg/g following regeneration. The adsorption capacity of resin was calculated after the recovery process using Data Studio Software (Fig. 2).

3. Effect of Competing Anions

The adsorptive behavior of phosphate in the presence of chloride is shown in Fig. 3 (filled circles). In the 3 mg/l of phosphate, 1,375 bed volumes (BV) was reached in the presence and 2950 BVs in the absence of chloride anion. According to Two-Sample T-Test analysis, the amount of P value was equal to 0.85 in the presence and absence of chloride anion. The same plot of above-mentioned adsorptive behavior of phosphate in the presence of bicarbonate anion was observed in Fig. 3 (open squares). In the presence of bicarbonate, the effluence reached to 3 mg/L phosphate after 1,281.25 BVs, while distilled water with phosphate reached to this point after approximately 2,950 BVs. According to Two-Sample T-Test analysis the amount of P value was calculated to be 0.88 in the presence and absence of bicarbonate anion. Also, the effects of sulfate ions on removal of phosphate are illustrated in Fig. 3 (open circles). As shown, in the presence of sulfate anion, phosphate reached 3 mg/L after 1468.75 BVs, and in the absence of sulfate anion after 2,950 BVs was reached. According to Two-Sample T Test analysis, P value=0.88 was calculated in the presence and absence of sulfate anion.

Based on Fig. 4, in the presence of all anions, the number of bed volumes versus the concentration at which the effluent reaches our maximum allowable concentration (3 mg/L) is 1,093.75. According

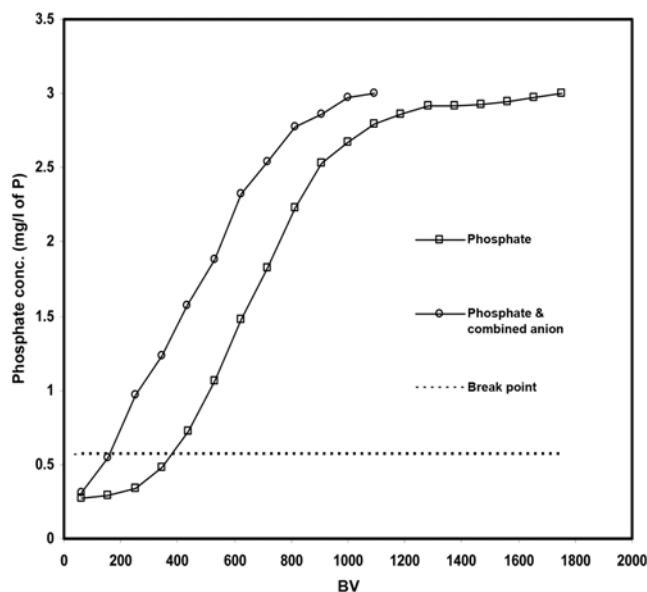


Fig. 4. Effect of combined ions on phosphate removal (phosphate - p: 3 mg/L, Cl^- : 70 mg/L, SO_4^{2-} : 60 mg/L, HCO_3^- : 100 mg/L, EBCT: 2.1 min).

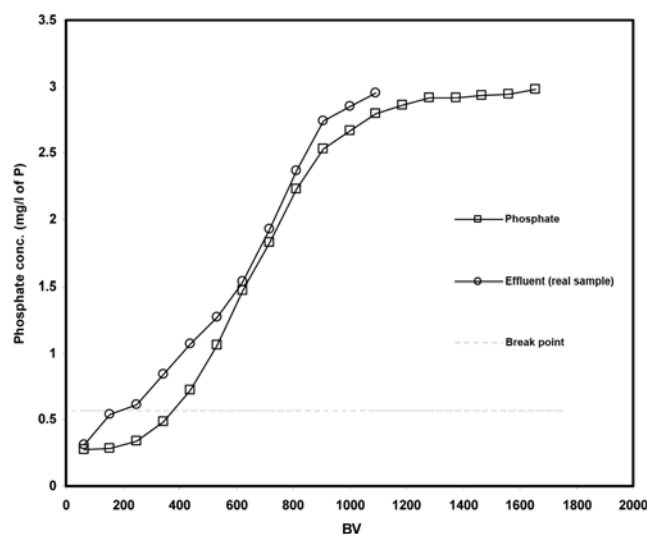


Fig. 5. Effluent sample of Shahrak-e Quds wastewater treatment plant (phosphate - p: 3 mg/L, Cl^- : 75 mg/L, SO_4^{2-} : 62 mg/L, HCO_3^- : 120 mg/L, EBCT: 2.1 min).

to Two-Sample T Test the amount of P was found to be P value= 0.89 in the presence and absence of combined anion.

4. Study of a Real Sample

Fig. 5 shows resin behavior on the effluent sample of Shahrak-e Quds refinery of Tehran. After crossing 1,187.5 BVs the adsorptive behavior of resin turns phosphate to the primary concentration, and is compared to 3 mg/l phosphate formed synthetically.

CONCLUSIONS

The experimental results indicated that Lewatit FO36 can be successfully used for the adsorption of phosphate from aqueous solu-

tions using a fixed bed column. Statistical analysis of six primary concentrations of 1-6 mg/l of phosphate shows the relation between the concentration level and the adsorption capacity of resin. On the other hand, the calculated P value shows that the adsorption capacity of the resin was increased with increasing of the concentration of phosphate.

A single-step with a mixture of NaOH and NaCl regeneration consistently recovered over 90% phosphate in 937.5 bed volumes. Subsequently, a rinse with distilled water made Lewatit suitable for the next cycle of phosphate removal.

Statistical analysis of competing anions and different amounts of obtained P value showed that anions such as chloride, bicarbonate, sulfate, and the combined competing anions do not influence phosphate adsorption; therefore Lewatit offered high phosphate selectivity in the presence of other commonly encountered anions, namely, sulfate, chloride, and bicarbonate.

Lewatit FO36 is an appropriate sorbent for phosphate removal from aqueous solutions.

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