NOVEL HYBRID EXCHANGER FOR PHOSPHATE REMOVAL FROM WATER AND WASTEWATER

SANDIP DESHMUKH[+], RENU SARAPH [*], SANJAY MEHENDALE[+] AND SANJAY DESHMUKH[#]

[+] Ion Exchange(I) Ltd., Dhirubhai Ambani Knowledge City Park (Koparkhairane) , India

ABSTRACT

Phosphate discharged into surface waters can stimulate plant growth, resulting in eutrophication of rivers and lakes. Environmental problems may develop as P moves off-site into aquatic systems. Removal of P from wastewaters has long been a concern of municipalities, and technologies have been developed to lower P concentrations in wastewaters. This study presents the development and performance of a new phosphate-selective sorbent, referred to as hybrid anion exchanger or HEX. HEX combines durability and mechanical strength of polymeric anion exchange resins with high sorption affinity of hydrated ferric oxide (HFO) toward phosphate. Laboratory kinetic studies show that HEX selectively removes phosphate from the background of much higher concentrations of competing sulfate, chloride and bicarbonate anions due to the combined presence of Coulombic and Lewis acid–base interactions. The film diffusion equation was used to examine the kinetic data and the exchange rate was found to be governed by the film diffusion process. Column and field trials also show consistent results in the operating capacity of HEX resin with minimal phosphate leakage.

INTRODUCTION

In Indian economy, leather industry occupies an important role. Phosphorus is an essential nutrient and is often second, only to N, as a limiting mineral nutrient to plant production. Phosphorus is present as either H_2PO4^{2-} in alkaline soils or H_2PO4^{2-} in acidic soils, and apatite (Ca phosphate) is the most common P mineral found in soils (Southern Cooperative Se-

ries, 1998). Phosphorus inputs to the environment can originate both from point and nonpoint sources. Point sources include industrial operations, municipal waste treatment plants, and large, confined livestock operations (Pierzynski *et al.*, 2000). Nonpoint sources of P include soil erosion and water runoff from cropland, lawns and gardens, urban areas, small livestock confinement operations, and livestock grazing operations (Pierzynski *et al.,* 2000).

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*Address Correspondence to: Mrs. Renu Saraph, Divisional Manager-Technology,
E mail:renu.saraf@ionexchange.co.in

stimulate plant growth, resulting in eutrophication of rivers and lakes. Environmental problems may develop as P moves off-site into aquatic systems. An efficient removal of phosphate during waste- water treatment is therefore an important factor in preserving the water quality of eutrophic lakes. Removal of P from wastewaters has long been a concern of municipalities, and technologies have been developed to lower P concentrations in wastewaters. Advanced Chemical precipitation, biological P removal, crystallization, Magnetic technology, adsorbents, tertiary filtration technologies and ion exchange technologies are the most common for P removal and recovery from waste water.

In the past decades, adsorption on hydrated Fe (III) oxide (HFO) has been widely used as it is innocuous, inexpensive, readily available and chemically stable over a wide pH range. In general, HFO exhibit amphoteric sorption behaviour around neutral pH, that is, they can selectively bind both transitional metal cations as well as anion ligands through electrostatic (ion exchange) and Lewis acid base (metal ligand) interactions. But, as a non porous material, the freshly precipitated amorphous HFO (20-100nm) increases the pressure drop due to poor mechanical strength, it is found unusable for fix bed system. To overcome the problem, we have developed a new class of hybrid sorbents by impregnating amorphous HFO particles within a strong base anion exchange resin in a polymer matrix. This resulted in enhanced permeability of ions from the bulk solution onto the interior surface of the sorbent. Such an enhancement in sorption capacity results from the Donnan membrane effect exerted by the fixed positive charges of an anion exchanger. Also, increased durability and mechanical strength is expected to improve the life time of sorbent.

The objectives of this study is

• To determine the selective performance of HEX towards phosphate ions, by conducting batch and column tests.
• To investigate the regenerability and reusability of HEX for multiple cycles.
• To elucidate the underlying mechanism of phosphate removal by HEX.
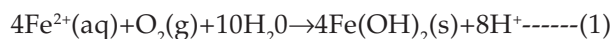
Theoretical background

Phosphate is the predominant form of phosphorus in natural waters and in wastewaters (Clesceri *et al.*, 1989). In lake systems, 90% of all phosphorus is bound in the solid phase as organic phosphates, either as cellular constituents in the living biota, or associated with dead particulate organic materials and detritus.
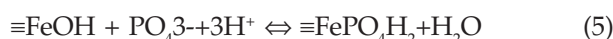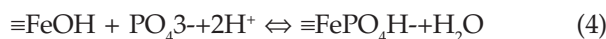
Basic Chemistry of HEX

Monovalent and divalent phosphate ($H_2PO_4^-$ and HPO_4^{2-}, respectively) ions bind to HFO surface sites through the formation of inner-sphere complexes. In comparison, sulfate and chloride form only outer-sphere complexes through Coulombic interaction and hence, are less selectively bound.

Freshly precipitated hydrated Fe(III) oxide particle surfaces are considered to be a diprotic acid with two dissociation constants

$$4Fe^{2+}(aq) + O_2(g) + 10H_2O \rightarrow 4Fe(OH)_2(s) + 8H^+ \text{------} (1)$$

$$I\ FeOH_2 + \leftrightarrow H^+ + I\ FeOH \qquad (2)$$

$$I\ FeOH \leftrightarrow H^+ + I\ FeO- \qquad (3)$$

In Equations 2 and 3 straight lines indicate the solid phase. At neutral pH, $FeOH_2+$ and $FeOH$ are predominant HFO species. Phosphate adsorption on HFO can be described by surface complexation model as shown in Figure 1.

$$\equiv FeOH + PO_43- + 2H^+ \Leftrightarrow \equiv FePO_4H- + H_2O \qquad (4)$$

$$\equiv FeOH + PO_43- + 3H^+ \Leftrightarrow \equiv FePO_4H_2 + H_2O \qquad (5)$$

Experimental materials and methods

A. Materials

All chemicals were reagent grade or above and used without further purification. Demineralised water was used for preparation of all reagent solutions. Potassium Dihydrogen phosphate (99%) was obtained from Qualigen Chemicals. Strong Base anion exchange sample was used from Ion Exchange (I) Ltd. Reagent grade ferric salts were used for preparation of sorbent. Corning glass column of 25 mm diameter and 1200 mm height were used for fixed bed arsenic adsorption capacity. Magnetic stirrer was used for Batch tests

B. Preparation of Sorbent

The sorbent is developed on a polymer matrix by a novel technique where iron oxide particles are uniformly distributed throughout the resin matrix. This was achieved by an anion exchange resin, pre-concentrated with targeted anion of ferric sulphate followed by hydrolysis with alkali and oxi-
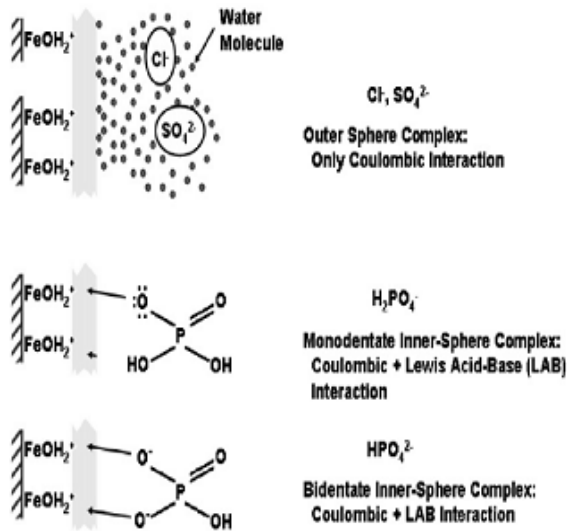
Fig. 1 Schematic illustration of the formation of mono and bi-dentate inner sphere complexes between phosphate and HFO surface groups; competing anions such as sulphate and chloride form only outer sphere complex.

dation treatment.

C. Batch Tests

Stock solutions of 2000 mg/L PO_4^{3-} were prepared from reagent grade KH_2PO_4 in demineralised water. To series of 500 mL beakers, 200 mL of 2000 ppm phosphate solution with varying amount of TDS levels (50 ppm, 500 ppm, 1000 ppm) and 10 gms of HFO were added. The samples were stirred at room temperature (30°C) and were allowed to reach equilibration time. The supernatant liquid was analyzed for PO_4^{3-} at suitable time intervals. The quantity of PO_4^{3-} uptake by HEX was calculated by the decrease of its concentration in the solution. Repeatability tests also demonstrated less than 5% experimental error.

Infinite bath method was used to study the kinetics of phosphate sorption. An exact 10 gms of HEX resin was poured in 200 mL of PO_4^{3-} solution having a concentration of 1000 mg/L at the desired temperature. At various time intervals, supernatant liquid was withdrawn and was analysed for phosphate using UV -Visible spectrophotometer (HACH DR 5000).

D. Column Tests

Fixed bed column experiments were conducted using glass columns of 17.0 mm diameter and 800 mm bed depth at a constant flow rate of 50-60 mL/minute. Feed was allowed to enter the top of the column and was made to pass through the resin bed

of HEX particles and was discharged to the collectors, where treated water was collected and stored. Several runs were conducted and samples were collected at suitable time intervals and were analyzed. Also, Superficial liquid velocity and Empty Bed Contact Time (EBCT) were monitored for every run.

E. Chemical Analyses

The phosphate concentration was estimated on UV -Visible spectrophotometer (HACH DR 5000). The arsenic concentration was estimated on Atomic Absorption Spectroscopy-Hydride system by Chemito-AA203D model.

RESULTS AND DISCUSSION

1. Effect of Total Dissolved solids

The results of adsorption equilibrium experiments using phosphate solutions of concentration 2000 ppm with different levels of Total Dissolved solids (TDS = 50 ppm, 500 ppm and 1000 ppm) were carried out. Figure 2 shows the adsorption behaviour with increasing TDS levels.

It was observed that there was a slight decrease in the amount of phosphate sorbed, q (mg/gm) with the increase in the level of total dissolved solids. This indicates poor affinity of other common ions present in water towards HEX and selective affinity towards phosphate ions. Static adsorption capacity of the resin is calculated by mass balance on the solute before and after the test and is found to be 31 mg PO_4^{3-}/gm of resin.

2. Sorption Kinetics

Phosphate sorption kinetics was determined and the results are shown in Figure 3. It can be seen that phosphate sorption onto HEX slightly increases with increase in temperature. This may be attributed to the enhancement of pore size or inactivation of the surface of the sorbent.

The kinetics of sorption on HEX was observed to be described with the help of film diffusion equation. The expression for the film diffusion equation is given below:

$$-\ln(1-F)=K_u*t \qquad (6)$$

Where F is the ratio of amount adsorbed after time t to the amount adsorbed at equilibrium and K_o is the rate constant. According to equation 6, when the
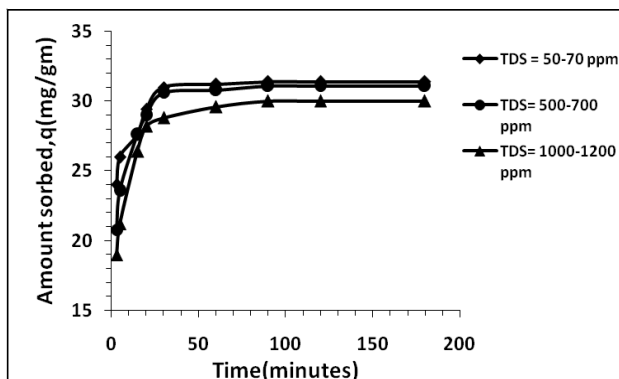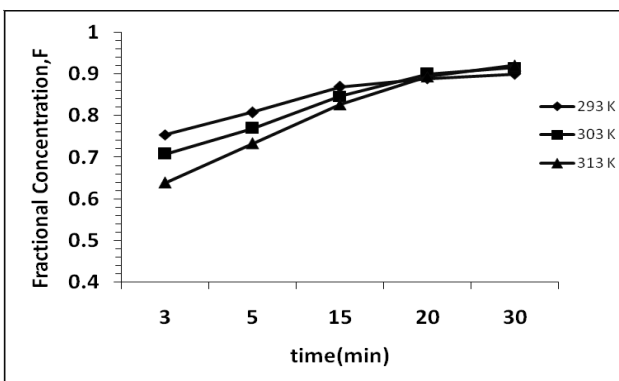
Fig. 2 Effect of TDS on Phosphate Sorption

Fig. 4 Film Diffusion plots for HEX at different Temperatures

where a straight line is obtained with a slope and intercept equal to E_a/RT and $\ln(A)$.

The value of activation energy for the film diffusion process is found to be 18.81kJ/mol (Table 1). As the value of activation energy is found to be less than 21kJ/mol, it can be confirmed that film diffusion process.

3. Fixed Bed Column runs

Figure 6 shows the effluent histories of phosphate using HEX resin for a number of consecutive runs. For all the runs, the influent composition, pH and hydrodynamic conditions, namely EBCT and SLV were identical and are provided. It can be seen that phosphate leakage is less than 0.03 ppm for several runs upto 1000 Bed Volumes. The resin is effectively regenerated using caustic and brine and is consecutively used for several cycles.

Fig. 3 Effect of Temperature on Phosphate sorption.

kinetic data obtained for a series of F values are plotted against t, a straight line is obtained having a slope equal to rate constant as shown in Figure 4.

Table 1. Kinetic parameters for Film Diffusion process on HEX

Temperature (K)	Rate constant (K_u) (min^{-1})	Activation Energy, E_a (KJ/mol)
293	0.0325	
303	0.0462	18.8179
313	0.0525	

The energy of activation (Ea) for the film diffusion process can be calculated using Arrhenius equation as

$$\ln(K_u)=\ln(A)-E_a/RT \qquad (7)$$

Where K_u is the film diffusion rate constant, A is Arrhenius factor, T is absolute temperature and R is the molar gas constant.

The plots of $\ln(K_u)$ versus $1/T$ according to equation 7 for film diffusion process are shown in Fig. 5
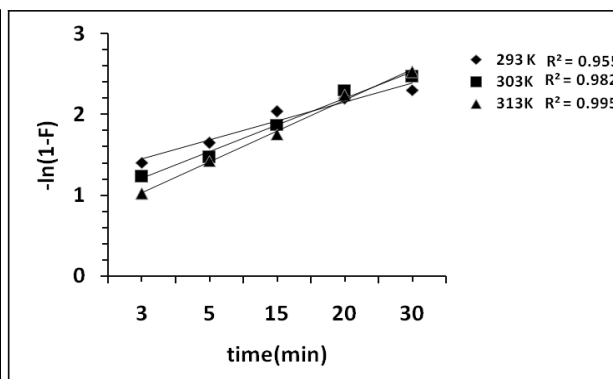
Table 2. Influent Conditions for Column runs

Parameter	Results
pH	7.35-7.43
Conductivity µs/cm	678-682
Total Hardness ppm as CaCO3	168-196
Calcium Hardness ppm as CaCO3	100-120
Magnesium Hardness ppm as CaCO3	68-76
Total Alkalinity ppm as CaCO3	160-176
Phosphate conc. ppm as PO4	5.29-7.20
COD ppm	16-33.2

4. Field Validation of HEX Resin

The consecutive column runs were carried out with secondary waste water from Dhirubhai Ambani Knowledge City (DAKC). Phosphate was present with other competing ions and dissolved organic
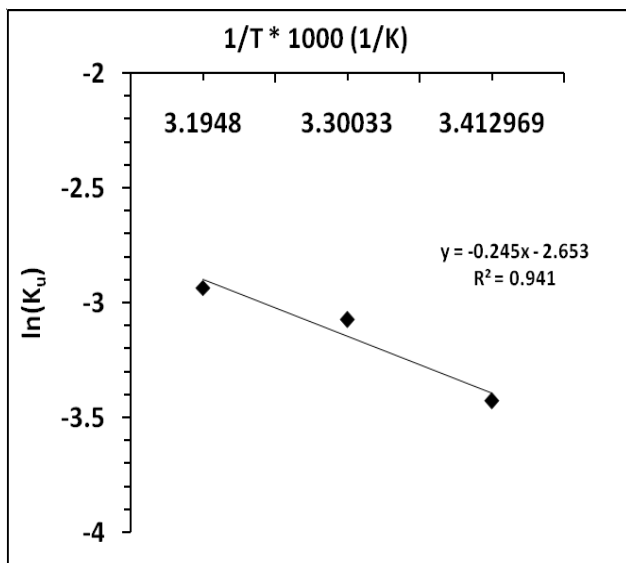
Fig. 5 Arrhenius plot for film diffusion process

Fig. 6 Phosphate elution histories for several column runs using HEX resin

matter. It was noted that Phosphate Breakthrough took place well over 800 Bed Volumes, even in the presence of other ions and organic matter (COD= 3ppm). The column was regenerated after every run. Most importantly, the phosphate breakthrough curve remained unchanged following regeneration confirming the reusability of HEX without any notable change in phosphate removal capacity indicating the efficient and consistent performance of HEX. Figure 7 shows the Phosphate effluent history for the pilot plant runs at DAKC.

Table 3. Influent Conditions for several runs at DAKC

	Cycle 1	Cycle 2	Cycle 3	Cycle 4
pH	7.5	7.6	7.6	7.7-7.8
Conductivity	650	660-760	730	620-720
Flow rate(lpm)	6-7	7-8	7-8	9-11
Phosphate Concentration (ppm)	7.8	8.3	8.3-8.8	8.0-8.3

The operating capacity (g/L) was evaluated for every single run and was found to be consistent (Figure 8). Phosphate leakage was found to be minimal (<0.03 ppm). HEX can be effectively regenerated and can be used for several cycles. HEX is mechanically strong, durable and did not show any sign of fragmentation during repeated use lab and field trials. This superior feature makes it suitable for long term applications.
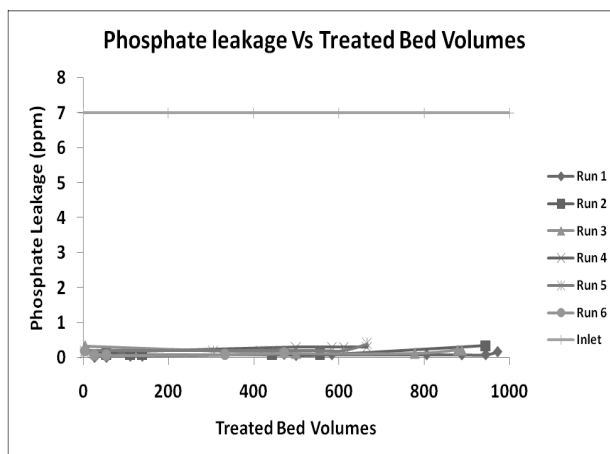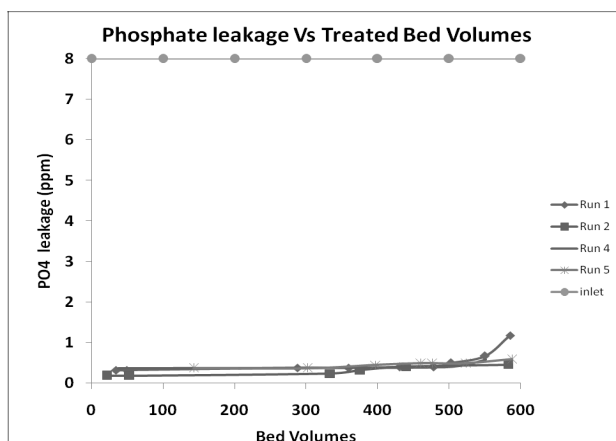

Fig. 7 Phosphate Elution histories using secondary wastewater from DAKC
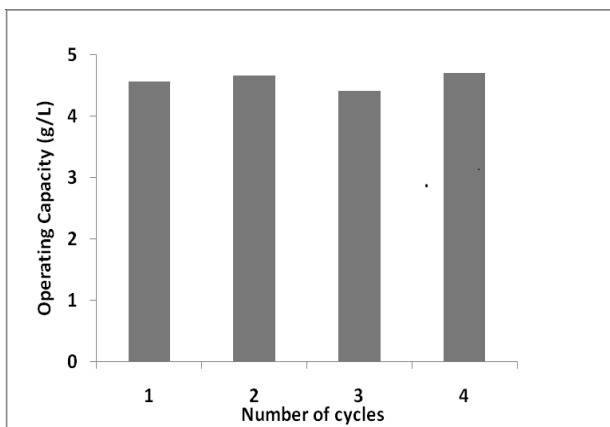
Fig.8 Operating capacity for several cycles

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CONCLUSION

In the present study, a unique chemistry based on impregnation of HFO on a durable polymer substrate, developed by a novel technique, for selective removal of phosphate from water and wastewater without affecting other water quality parameters. Major conclusions derived from this study are summarized as follows:-

1. All batch analyses shows that HEX offers high phosphate selectivity in the presence of other common ions and the effect of Total Dissolved solids is minimal on the phosphate sorption capacity.

2. Kinetics of the system fit the Film Diffusion model and lower activation energy confirms the diffusional nature of sorption process.

3. HEX Resin was used for multiple cycles for Column runs and field trials and results show high efficiency and consistent of removal of phosphate for several runs. HEX can be effectively regenerated using caustic and brine.

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