

# Hybrid Adsorbent for Selective Recovery of Phosphorus from Contaminated Water

Shantanu Agrawal, Deepak Jain, and Sudipta Sarkar

**Abstract**— Phosphorus is an essential part of the life's building block, DNA. It acts as an essential nutrient for plant growth and agriculture. Humans have greatly impacted the biogeochemical cycle of phosphorus, mining it from rock and other underground deposits, converting it to fertilizer for its use around the world. Thus, the journey of phosphorus has been almost one way- it starts from phosphate-rich deposits and ends up being dispersed in food chain. The global availability of mineable phosphate is low and is concentrated within a few regions in the world. Therefore, unless phosphorus is recycled within the food chain, it is likely that phosphorus would become a supply-limited nutrient. It would play a major role in determining the future food price and also, on the global food security as well. Land run-offs, from agricultural fields and soil erosion, municipal wastewater carrying human and animal waste, poultry run-off are major sources through which phosphorus is lost from the food chain to the aqueous systems. The runoff containing high concentration of nutrients is known to cause a serious environmental problem known as eutrophication. On the other hand, removal and recovery of phosphorus from these sources have the potential to recycle much of phosphate that would otherwise be lost within the environment. In this study we attempted to develop and validate a hybrid adsorbent for selective removal and recovery of phosphate from contaminated water. The hybrid adsorbent has two phases, one phase has the polymeric backbone having weak base functionality and the other phase is dispersed nanoparticles of iron hydroxide. Batch adsorption studies at different pH values with a background of commonly available anions showed that adsorption closely follows Freundlich isotherm and most efficient at around neutral pH 7. The experimental results of kinetics study show that the adsorption is kinetically controlled by intraparticle diffusion process. The effect of competing ions such as sulfate, chloride or bicarbonate was not significant, thereby confirming the prevalence of inner-sphere complexation process in adsorption. We also carried out fixed-bed column runs, both with synthetic contaminated water as well as secondary treated wastewater. In both the cases, phosphate was successfully removed from the background of other anions for more than 2000 bed volumes. Regeneration performed by a solution of caustic soda was able to recover almost all the adsorbed phosphate, thus allowing for reuse of the adsorbent. The ability to remove and recover phosphate from wastewater demonstrated that it may be commercially feasible to recycle phosphate back into agricultural fields in the form of fertilizer.

**Index Terms**—phosphate removal and recovery, wastewater, hybrid ion exchanger, regeneration

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## I. INTRODUCTION

Phosphate (P) is an essential part of DNA and RNA, the basic building blocks of life on this earth. The origin of P in the environment is from rocks or deposits laid down on the earth. It occurs almost exclusively in nature as orthophosphate ( $\text{PO}_4^{3-}$ ) in the minerals like apatite, monazite, etc. Weathering and erosion of rocks gradually releases phosphorus as phosphate ions which are soluble in water. When plant materials and waste products decay through bacterial action, the phosphate is released and returned to the environment for reuse. Much of the P eventually is washed into the water from erosion and leaching. In freshwater ecosystems, P is considered to be the rate-limiting nutrient, because its concentration in freshwater bodies governs the growth of aquatic organisms. If not enough P is present, the growth is stunted. If too much P is present excess growth may occur, particularly in algae giving rise to a situation known as eutrophication in lakes. Eutrophication causes an ecological imbalance of organisms present in the water bodies, threatening the living organisms in the aquatic life. The total P should not be more than 0.05-0.1 mg P/L in natural water bodies to keep a check on eutrophication [1].

P is essential nutrient for growth of the land plants and plays vital role in food production. A major part of phosphate applied in the fields and of what enters into the food chain, ultimately gets dissolved in the water and enters aquatic ecosystem from where it is not readily available for reuse. Land run-offs, from agricultural fields and soil erosion, municipal wastewater carrying human and animal waste, poultry run-off are major sources through which P is lost from the food chain to the aqueous systems. Unless removed, the amount of phosphorus currently entering the receiving streams and lakes far exceeds the seasonal loading capacity so as to disrupt the aquatic ecosystems and to cause water quality problems, which needs to be resolved.

The recovery of phosphate through waste water treatment plants has proven to be ineffective in bringing down the concentrations of phosphate below the levels recommended by many environmental regulatory authorities. Only a removal of 75-80 % of total phosphate is possible through the generally used process of biological wastewater treatment [2]. The concentration of phosphate is not easily brought below 100 mg/L of P by biological nutrient removal and precipitation – sorption processes [3], [4].

Amongst the many physico-chemical process for phosphate removal from water and wastewater that have been studied extensively like chemical precipitation and coagulation, membrane filter, reverse osmosis, crystallization, only adsorption/ion exchange methods are the

most efficient to reduce phosphate concentrations below the regulatory standards. Of the various methods of P removal, adsorption/ion exchange methods are promising. These processes generally take place in fixed beds such as plug flow reactors which, by virtue of its fundamental design advantage, produce only zero to very low concentration of P in the effluent. Moreover, these processes are simple and economical, result in less sludge production and therefore experience minimal disposal problems [5].

The use of ferric oxides (in its hydrated form) as an adsorbent for removal of anionic pollutants like phosphate has well been established [6]. These ferric oxides have been doped with adsorbents of larger size. The mechanical strength and durability of polymeric material, the adsorbent, needs to be coupled in selectivity towards removal of phosphate for them to be used efficiently in the treatment process. A new hybrid adsorbent HAIX was synthesized by dispersing HFO nanoparticles within a polymeric anion exchanger. IRA-900, a strong base anion exchange resin was used for the production of HAIX [7]. There are other evidences that strong base anion exchange resins have been used as the host material for dispersal of ferric HFO nanoparticles so that effective removal of phosphate from water and waste water can take place. But no extensive study has been undertaken to synthesize hybrid ion exchanger with weak base anion exchange resins as host material for phosphate removal and recovery. This study aims to use weak base anion exchange resin, IRA-67, for the dispersion of HFO nanoparticles inside to create an adsorbent for effective and selective removal of phosphate. The hybrid adsorbent, HFO-IRA67, was also validated for phosphate removal capacity and extent of recovery of phosphate possible.

## II. MATERIALS AND METHODS

### 2.1 Materials

IRA-67 used for the synthesis of HFO-IRA67 was procured from Rohm and Haas Co. (Philadelphia, PA, USA). IRA-67 has a matrix of cross-linked acrylic gel structure and tertiary amine functional group. Ferric chloride and sodium hydroxide used for synthesis were of reagent grade. All other chemicals used for determination of phosphate and for preparation of synthetic water were of certified analytical grade.

### 2.2 Preparation of HFO-IRA67

IRA 67 resins were washed with deionized water and were subjected to 5M solution of  $\text{FeCl}_3$ .  $\text{Fe}^{3+}$  ions bind to nitrogen atom of the tertiary amine functional group through Lewis acid base interaction by sharing of lone pair of electrons. The resins were then contacted with 2N solution of NaOH when  $\text{Fe}^{3+}$  ions react with hydroxyl ions to form precipitates of ferric hydroxide or HFO within the internal pore of the ion exchanger. The cyclic mixing of IRA-67 resins with  $\text{FeCl}_3$  and NaOH led to dark brown coloration of IRA-67 resins because of the impregnation of HFO particles inside IRA-67. After three cycles loading with HFO, the hybrid resins were subjected to dilute solution of HCl so that the HFO functional groups remain protonated as well as the weak base functional

groups become ionized. After a wash with deionized water, the hybrid resins were left to dry in air before they are used for further adsorption studies. Fig. 1 shows schematically the method of synthesis of the hybrid ion exchange resin HFO-IRA67.

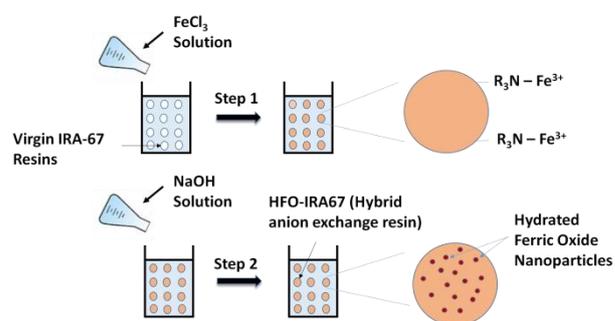


Fig. 1 - Schematic showing the preparation of hybrid ion exchanger HFO-IRA67.

## 2.3 Batch Studies

2.3.1 Batch adsorption isotherms were carried at different pH values with solutions containing initial phosphate concentration of 0.5 mg/L and a standard background concentration of anions, to which varying amount of adsorbents were added. After equilibration for 24 hours on a platform shaker, the final phosphate concentration was analyzed. Unless otherwise stated, all batch studies were performed using a synthetic phosphate solution having a background of commonly occurring anions such as  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ . The solution pH was constantly maintained at their respective values by adding HCl/NaOH as required.

2.3.2 In another set of experiments, run at pH 6.5, adsorption isotherms were prepared at different  $\text{SO}_4^{2-}$  concentrations but with same phosphate and background concentration of other anions. The amount of resins, HFO-IRA-67, for each isotherm was also kept constant.

2.3.3 In the kinetics study, 3gm of adsorbent (HFO-IRA-67) was introduced in a 4L solution having an initial phosphate concentration of 2 mg/L and a standard background concentration of anions, and the suspension was put on a shaker. The kinetics study was performed at two different rpm values of 100 and 200. The liquid samples were collected at specified time intervals and were analyzed for phosphate concentration.

## 2.4 Column Studies

Fixed bed column run experiments were carried out using a glass column, having a diameter of 11mm. The glass column was filled by the adsorbents up to a specified height and the volume of the bed was recorded. A 0.55 mg/L as P solution of phosphate with a standard background solution was passed through the column at a flow rate of 6 ml/min. The effluent samples from the column run were collected at regular intervals of time and analyzed for phosphate.

## 2.5 Analysis

The phosphate concentrations in all the samples that were collected and tested were measured using a HACH spectrophotometer, DR5000, by the standard stannous chloride method for phosphate analysis.

### III. RESULTS AND DISCUSSIONS

#### 3.1 Adsorption Isotherm

The Langmuir adsorption isotherm can be written as:

$$q_e = \frac{Q_{max} b C_e}{1 + b C_e} \quad (1)$$

where  $C_e$  is the equilibrium adsorbate concentration (mg/l),  $q_e$  is the mass of adsorbate per unit mass of adsorbent at equilibrium (mg/g),  $Q_{max}$  is the maximum mass adsorbed at saturation conditions per unit mass of adsorbent (mg/g),  $b$  is the empirical constant.

The Freundlich adsorption Isotherm can be written as:

$$q_e = K C_e^{1/n} \quad (2)$$

where  $q_e$  is solid phase adsorbate concentration in equilibrium (mg/g),  $C_e$  is the liquid phase adsorbate concentration in equilibrium (mg/l),  $K$  is the freundlich constant and  $n$  is the heterogeneity factor.

Fig. 2 shows the results of the isotherm study. The Freundlich isotherm model showed a much better fit compared to the Langmuir model. The fitted models with derived equations have been included in Fig. 2.

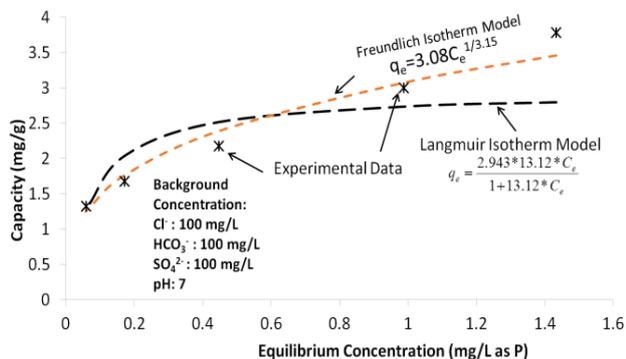


Fig. 2 - Results of isotherm study for phosphate adsorption on hybrid anion exchanger showing fit of Langmuir and Freundlich Isotherm models.

#### 3.2 Effects of pH on Adsorption

Fig. 3 shows the variation of adsorption capacity of HFO-IRA67 at different pH values of the solution containing phosphate. The adsorption capacity was the maximum at near-neutral pH; it got diminished when the pH was either lowered or made higher.

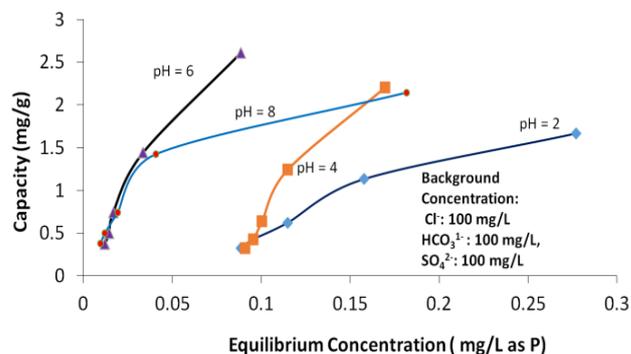


Fig. 3 - Effects of pH on the phosphate adsorption capacity of the hybrid anion exchanger HFO-IRA67

#### 3.3 Adsorption Kinetics

Fig. 4 shows the kinetics of removal of phosphate by HFO-IRA67 from a solution containing 2mg/L of P along with a background concentration of different anions at different degree of turbulence measured as rpm of the agitation. It may be noted that the equilibrium concentration was reached faster at an rpm of 200 as compared to 100 rpm. The time required to reach equilibrium reduced from 100 minutes to 50 minutes when the speed of the agitation was changed from 100 rpm to 50 rpm. It shows that adsorption kinetics is rate limited by film diffusion phenomena.

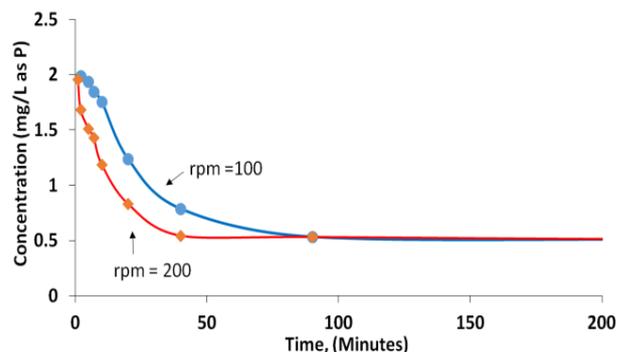


Fig. 4 - Effects of change in rpm of the agitator on the concentration of P in solution over time

#### 3.4 Effects of Sulphate concentration on adsorption capacity

As the concentration of sulphate, as a competing ion for adsorption, was increased from 25mg/L to 150mg/L with a fixed background solution of competing anions, the percentage adsorption of phosphate did not have any appreciable change. At the pH of the experiment, had it been only the ion exchange functional groups that are responsible for phosphate removal, the sulfate being a divalent ion present at much higher concentration in the solution, would have had a strong effect on the adsorption capacity. But the absence of any strong competition by sulfate indicates that the adsorption is occurring mainly at the HFO functional groups where phosphate is preferentially adsorbed over sulfate due to inner sphere complexation through Lewis acid base interaction; such interaction is absent in case of interaction of sulfate ions with functional groups of HFO [7], [8].

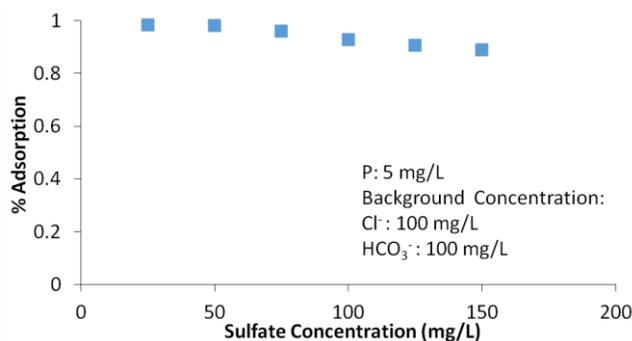


Fig. 5 - Effects of change of sulfate ion concentration on percentage adsorption of phosphate

### 3.5 Column Run at pH 6

A fixed bed column run was performed with the hybrid anion exchanger HFO-IRA67 as the adsorbent and synthetic phosphate solution as the feed. The inlet solution had a phosphorus concentration of 0.55 mg/L as P as the feed along with the standard background concentration of competing anions. The pH of the inlet feed was maintained at 6. The samples taken from time to time were analyzed for concentration of phosphate. The column ran for about 3500 bed volumes before it showed a complete breakthrough of phosphorus. Fig. 6 shows the concentration of phosphate in the effluent from the water with respect to bed volume of water treated.

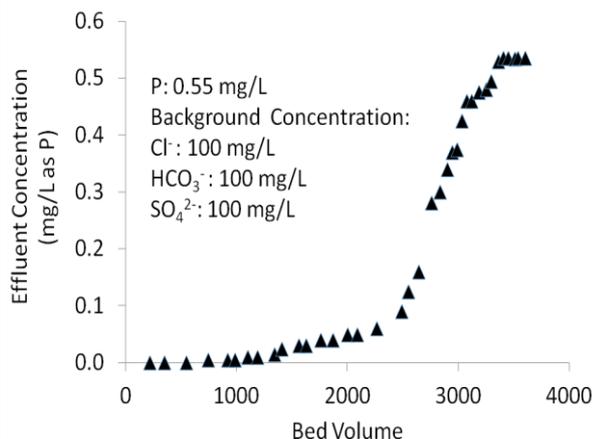


Fig 6. Phosphate breakthrough profile in the effluent from the column

## IV. CONCLUSION

A hybrid anion exchange resin with weak base anion exchange resin as the host material has been synthesized with HFO nanoparticles dispersed inside. Adsorption capacity and adsorption kinetics were experimentally assessed. The adsorption was found to closely follow Freundlich isotherm. The adsorption capacity was maximum at near neutral pH and at higher pH it showed diminished adsorption capacity. The regeneration of the hybrid anion exchanger should be easier than those synthesized from strong base anion exchanger. However, in this study we have not reported the

regeneration of the hybrid adsorbent and also, the recovery of phosphate. Cyclic repetitive column runs with real wastewater followed by regeneration shall prove the capability of the hybrid adsorbent for recovery of phosphate.

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