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Contribution to the removal study of phosphate from aqueous solutions by IRN-78 anion exchange resin

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Abstract

In the present study, static and dynamic experiments were performed to characterize the effectiveness of an anionic resin (IRN78) in the elimination of phosphate ions from aqueous solutions. The phosphate retention by the resin is characterized by infrared analyses. The results of the macroscopic tests show that the elimination kinetics is characterized by a quick first step and a second slow. It is well described by the pseudo-second order model. The Langmuir isotherm generates the better agreement with the experimental data for the adsorption system in comparison with Freundlich isotherm. The maximum exchange capacity of the resin for phosphate is estimated to 42mg/g. In the pH range studied, the phosphate removal increases with the increase of pH.

Keywords: phosphate; ion exchange; anion resin; water treatment; IRN78

1. Introduction

The increase of phosphorus in surface freshwater systems will lead to excessive algae growth causing eutrophication problems in lakes and rivers. Consequently, phosphorus removal from waste water is of great significance for the preservation of water quality. Among the various techniques proposed, adsorption has given satisfactory results in many studies (1-5). However, the depletion of phosphorus as an important nutrient element requires its recovery from wastewater which can be considered as a secondary source of phosphorus (6). As the principal phosphorus compounds in wastewater are generally orthophosphates (7), anion exchange can be considered as a possible process for phosphorus removal in several types of wastewaters treatment. It is well recognized as one of the simplest and the safest methods used for the water treatment. Various types of ion exchange adsorbents were proposed to reduce concentrations of anions such as phosphate in water and wastewater (8-12). The present study reports the results of investigation on phosphate removal by the anion exchange resin IRN-78.

2. Materials and methods

All chemicals used in this study were of analytical grade reagent and no purification was used. All experimental vessels and storage containers were Pyrex glass. Phosphate solutions were prepared by dissolving KH_2PO_4 obtained from Codex. Prior to each experiment, the pH was adjusted by adding solution of NaOH or HCl (0.1M). The resin (IRN78) purchased from Prolabo was regenerated by NaOH (5%), rinsed with distilled water and dried at 40°C. The removal of phosphate ions was performed by experiments in static (batch) and dynamic (column) conditions.

In batch system, the effects of resin dose, contact time, initial phosphate concentration and pH were evaluated. In each experiment, a given dose of resin was added to 100mL of phosphate solution; the formed suspension was agitated for a suitable time. After centrifugation, residual phosphate concentration was measured in the recovered solution.

In dynamic system, the experimental device consisted of a glass column where the resin bed (bed depth: 1.5cm) was held by a filter support. The solution of phosphate ions was introduced at the top of the column (flow rate: 5mL/min).

Phosphate concentration was determined by a UV-visible spectrophotometer (Shimadzu 1650PC) using the molybdenum method. In this method, a phosphomolybdic complex is formed in the presence of sulfuric acid, and then reduced by ascorbic acid developing a blue color in the presence of potassium and antimony tartrate. The equilibrium exchange capacity (Q(mg/g)) is calculated according to the following relation: $Q = (C_0-C_f)*V/m$; where C_0 and C_f (mg/L) are the initial and the final concentration of phosphate respectively, V(L) is the solution volume and m(g) is the resin amount used.

The dried resin samples prepared before and after phosphate removal, were ground and mixed with powdered pure KBr in an agate mortar and compressed into small disks used for recording the IR spectra between 400 and 4000 cm^{-1} using Hyper IR Shimadzu E spectrophotometer.

3. Results and discussion

3.1. Effect of resin dose

As shown in Figure 1, the increase of the resin dose induces an increase in binding capacity of phosphate ions due to the increase in the number of exchange sites. The maximum removal percentage is achieved at a resin weight of 0.1g/100 mL. With the initial phosphate concentration tested, the increase of the resin dose from 0.2 g/L to 1g/L induces an increase of phosphate removal from 69.6% to 92.4% respectively.

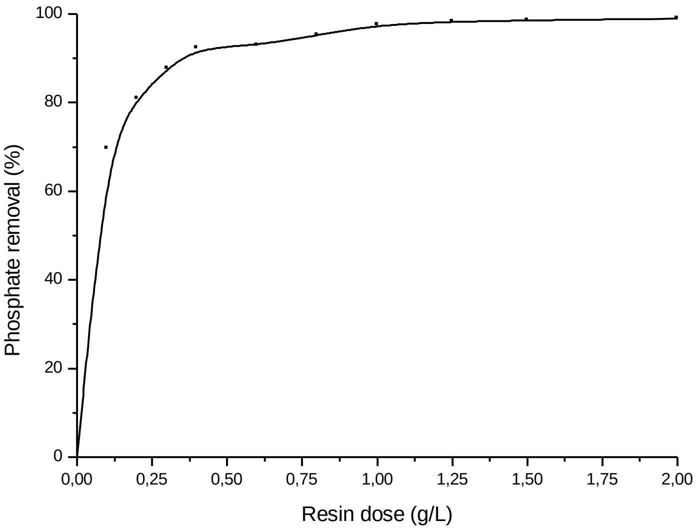

Figure 1: Effect of resin dose on phosphate removal by IRN78 (C_0:19mg/L; t:60 min)

3.2. Effect of contact time - Adsorption kinetics

As a function of time, the binding of phosphate ions occurs in two combined stages, a first rapid followed by a second slow. It increases rapidly with time during the first 20minutes to attain 16.8 mg/g and then slowed to stabilize and reach equilibrium at 60 min corresponding to 17.6mg/g. The experimental data are fitted by the first order and second order models. The obtained parameters are included in Table 1 (R is the correlation coefficient, Q_e is the adsorption capacity (mg/g) at equilibrium, K is the rate constant).

Table 1: Parameters of the kinetic models of phosphate removal by IRN78

Kinetics model	R	k	Q_e
First order $\ln (Q_e-Q_t)=\ln Q_e-k.t$	0.897	0.026	3.04
Second order $t/Q_t= 1/kQ_e^2 +(1/Q_e).t$	0.999	0.037	17.90

According to the calculated correlation coefficients, the second kinetics model is more suitable for describing the experimental data. This result is reinforced by the calculated curve which coincides with the experimental data (Figure2).

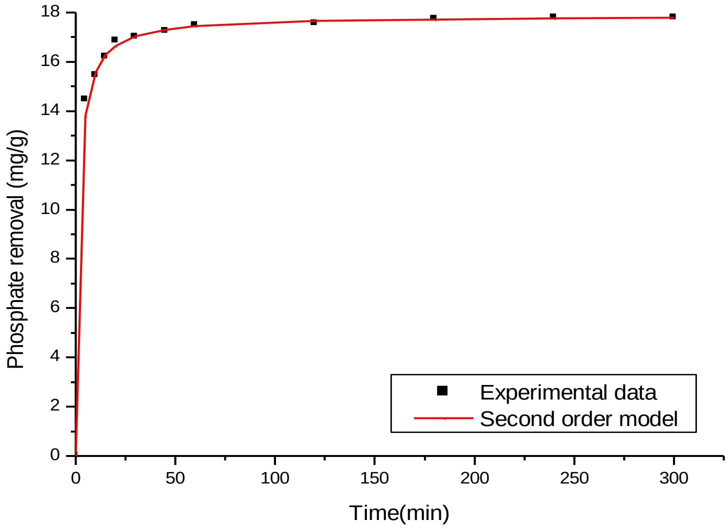

Figure 2: kinetics of phosphate removal by IRN78 (C_0:19 mg/L, resin dose: 1g/L).

Taking into consideration only the first step, the adsorption kinetics can be also described by inter-particles diffusion model (Figure 3); the plot of its linearized equation gives a satisfactory correlation coefficient (R=0.992) and a diffusion constant equal to 0.0099mn^{-1}.

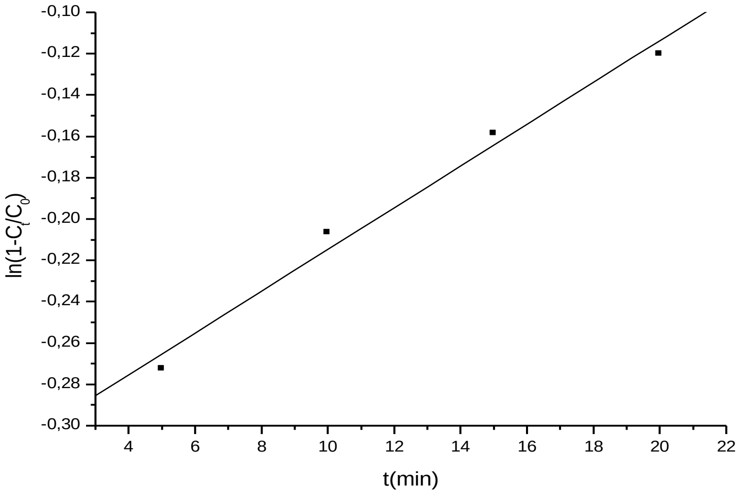

Figure 3: Inter particules diffusion plot

3.3. Effect of phosphate concentration

The increase of the phosphate quantity removed by the resin with the increase of the initial concentration is due to the sufficient availability of the exchange sites. Adsorption is often described by the isotherms reflecting the relationship between the amounts adsorbed and the concentrations of the solution under equilibrium conditions at constant temperature. Several models have been developed to describe this relationship. The application of Langmuir and Freundlich equations to our results gives the parameters shown in Table 2. The correlation coefficients values are higher than 0.95 indicating that the two models can be used for describing the experimental data. In order to determine the most appropriate model, we have plotted the nonlinear isotherms for each model. The obtained curves (Figure 4) show that the Langmuir model is more suitable to describe the experimental isotherm. The calculated maximum adsorption capacity is equal to 42.81mg/g. This capacity is included in the range given for various commercials resins (13).

Table 2: Isotherm parameters of phosphate removal by IRN78

Isotherm model	R^2	Q_{max}	k	n
Langmuir $Q=Q_{max}(k.C/(1+ k.C))$	0.991	42.81	1.51	-
Freundlich $Q=k.C^{1/n}$	0.962	-	22.32	2.44

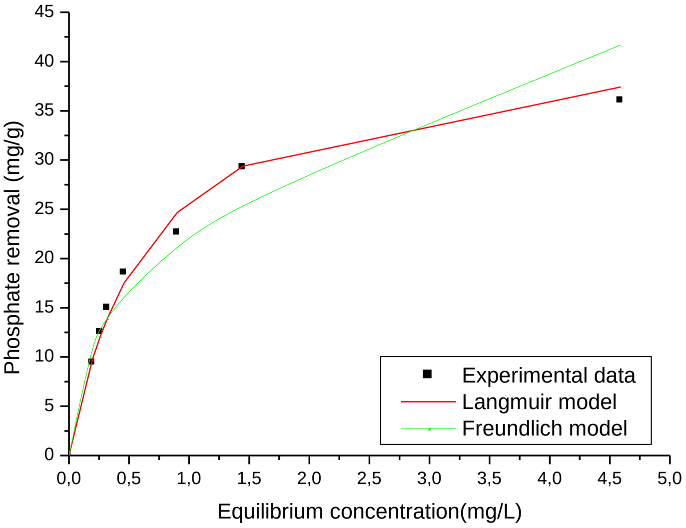

Figure 4: Isotherm of phosphate removal by IRN78 (t:60 min; resin dose:1g/L)

3.4. Effect of pH

From the Figure 5, it is apparent that there is a good elimination of phosphate ions in the pH range studied. The phosphate adsorption capacity increases gradually as the solution pH increases to attain a maximum at pH > 7 where HPO4^{2-} is the dominant species. In aqueous solution, phosphate can exist in the form of H_3PO_4 at pH <2, $H_2PO_4^-$ in the pH range 2-7 and HPO_4^{2-} in the pH range 7-12.5.

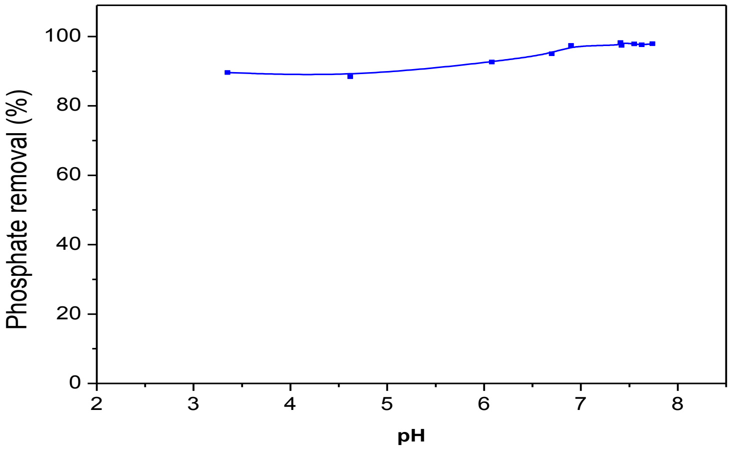

Figure 5: Effect of solution pH on phosphate removal by IRN78
(C_0: 19 mg/L, t:60 min; resin dose: 1g/L)

3.5. Column test

The breakthrough curve is expressed in terms of concentration defined as the ratio of the effluent concentration to inlet concentration (C/C_0). The column adsorption capacity was calculated as a function of bed volume for a given bed height. According to the results of the present study (Figure 6), it can be seen that the concentrations ratio (C/C_0) remains constant up to 266 bed volume then it begins to increase rapidly as phosphate solution continues to flow. The column is gradually saturated with phosphate ions and becomes less effective for additional adsorption. The saturation of IRN 78 resin is obtained for a bed volume of 426.6.

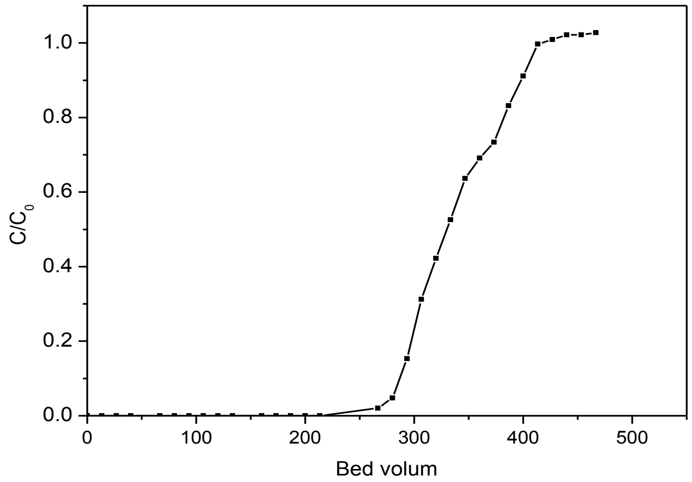

Figure 6: Breakthrough curve of phosphate removal by IRN78 (Flow rate: 5mL/min)

3.6. Spectroscopic analyses

The comparison of the infrared spectra obtained before and after phosphate exchange (Figure 7) reveals the appearance of new bands at 1018 cm^{-1}, 619cm^{-1} and 543cm^{-1} which are characteristic of the presence of phosphate ions and are attributed to the asymmetric stretch vibration of P–O and bend vibration of O–P–O respectively (14, 15).

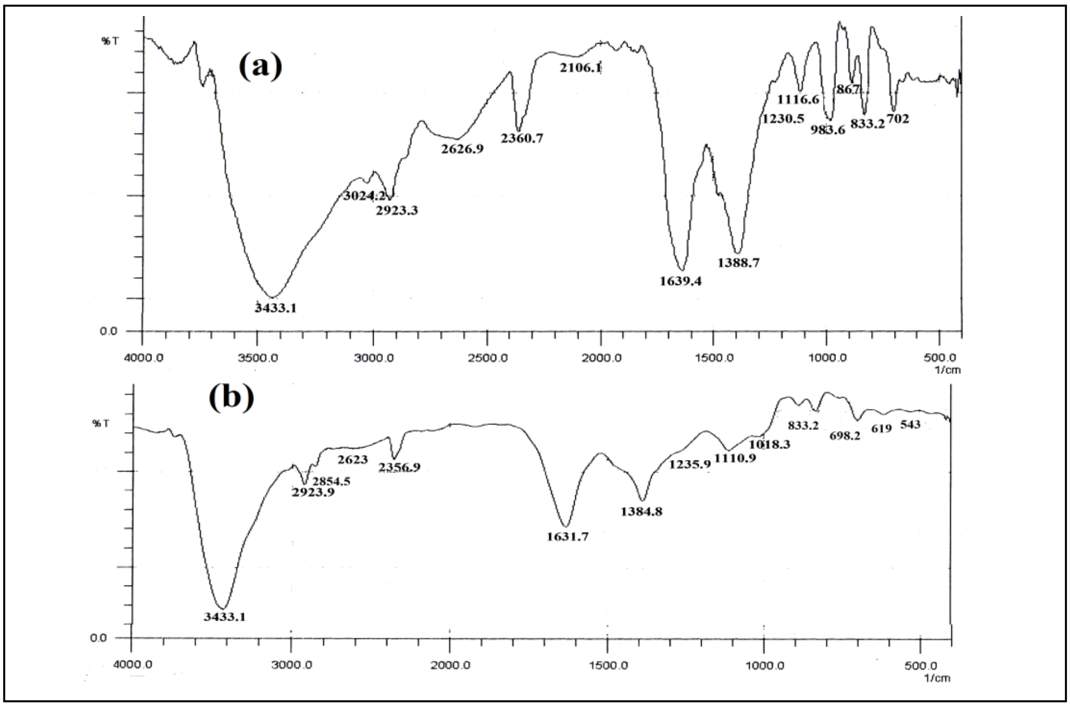

Figure 7: IR spectra of IRN 78 (a) and in the presence of phosphate ions (b)

Conclusion

Through bath experiments, the present study shows that the use of IRN78 is effective for the rapid removal of phosphate ions from water. The adsorption efficiency exceeds 85% within a wide pH range. The maximum adsorption capacity is 42mg/g. The results of the column experiment, imply the satisfactory application of IRN78 in phosphate removal in dynamic system.

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