Study of iron adsorption on ion exchange resins for the removal of pollutants from aqueous effluents

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Abstract

The ion exchange method using commercial resins is a known treatment for industrial effluents. These resins can retain metal ions in solution on their surface by adsorption. To evaluate the applicability of this method, the best conditions for iron adsorption using a cationic exchange resin were investigated. To establish the ideal adsorption conditions, parameters such as stirring time and speed, resin mass dosage, pH and contact time were investigated. The tests were carried out for three different iron concentrations: 50, 100 and 150 mg L^{-1}. The experiments indicated that a stirring time of 20 minutes was satisfactory. In relation to the pH, the better results were observed for a pH 1.0. The mass of resin was varied between 0.2 to 0.6 g, the latter being the most efficient. The stirring speed was optimized with different values, so that a speed of 250 rpm resulted in a higher adsorption content. Using optimized conditions, it was possible to obtain a maximum adsorption of Fe (III) of approximately 99%. The correlation coefficient (R^2) values of the pseudo-first order model was 0.6868 for Fe (III) adsorption, while pseudo-second order model correlation coefficient (R^2) value was 0.9913. The theorical k_2 value calculated was 0.0456 g mg^{-1} min^{-1}. The experimental q_e value (11.80 mg g^{-1}) showed good correlation with the calculated value (12.06 mg g^{-1}) from pseudo-second order model. Therefore, it can be concluded that the pseudo-second order model was better in describing the adsorption kinetics.

Keywords: adsorption process; ion exchange; cationic resin; metalic especies; aqueous effluent

1. Introduction

In reverse cation flotation, it is crucial to address the harmful effects of alkali metal cations, as well as divalent/polyvalent ions and their hydroxy-complexes in aqueous media when using amines and ether-amines as collectors to achieve satisfactory performance. This occurs because the pH range in which flotation is carried out ($9 < $ pH $ < 10.5$) includes values above the isoelectric points of iron and quartz minerals (pH between 2-7), giving them a negative surface charge. Thus, the cations present in the environment end up being electrostatically attracted to the negative charges of the minerals, modifying their surface charge and thus interfering with the action of the flotation reagents [1]. Among the methods for removing cations from aqueous effluents are the ion exchange processes using resins [2,3,4]. These resins can retain metal ions in solution on their surface by adsorption [4]. Considering the aspects discussed above, this work aims to evaluate the efficiency and applicability of the ion exchange method for removing iron from reuse water from the iron ore reverse flotation process.

2. Experimental

2.1. Materials

The cationic resin, Amberlite IR-120, hydrogen form with active group $-SO_3H^+$ (Supelco) was employed without any further purification. The resin was activated by immersing it in 1 mol/L HCl for 24 h. The resin was then washed several times by deionized water to remove all chloride content. Then the resin was dried at temperature 45 $^\circ$C. The synthetic solution containing iron 50 – 150 mg/L was prepared from stock solution of 1000 mg L^{-1} (SpecSol) using deionized water. The chemical reagents such as iron, hydrochloric acid, sodium hydroxide, etc. were laboratory reagent grade.

2.2. Procedure

Batch sorption studies were performed by mixing 0.2 – 0.6 g dry resin particles with 50 mL iron solution of 50 – 150 mol/L in a 125 mL Erlenmeyer flask. The mixtures were shaken in an orbital shaker (Tecnal) at ambient temperatures for different times. Aliquot samples of 200 μL were taken from the flask at appropriate time intervals as necessary and the concentration of iron was determined using an atomic absorption spectrometer, Thermo Scientific, model Solaar M5. An investigation of the effect of rate of agitation was carried out at stirring speed ranged between 150 – 250 rpm at different times. The effect of pH on iron sorption was performed. The process was evaluated using the sorbent in a pH range of 1 – 3 and adjusted, when necessary, with 1.0 mol/L NaOH solutions. The amount of Fe (III) sorbed onto the resin (mg g^{-1}) and the uptake percent (Ad (%)) were respectively determined using the following relations [2]:

$$q = ((C_0 - C_e)V)/m \qquad (1)$$

$$Ad\ (\%) = ((C_o - C_e)/Ce)\ x\ 100 \qquad (2)$$

where C_0 and C_e are the initial and equilibrium concentrations of Fe (III) in the solution (mol L^{-1}), V is the volume of solution (L), m is the weight of the resin (g). All experiments were performed at pH near to 1.0 in duplicate and the averaged values were taken.

3. Results

3.1. Effect of stirring time

The effect of stirring time on adsorption of iron was studied using Amberlite IR-120 resin. The

stirring speed was kept constant at 150 rpm. The percentage adsorption vs. time curve was obtained. The curve leading to the iron adsorption equilibrium on the resin surface was obtained. As the contact time increased to 10 min, the percentage of Fe (III) adsorption increased until it reached 94.05%, 96.99% and 94.44% for iron concentrations of 50, 100 and 150 mg L^{-1}, respectively. The subsequent increase in time had no effect on iron adsorption. Therefore, the maximum contact time of 20 min is adequate to achieve the reaction at equilibrium.

3.2. Effect of pH

The studies were made to evaluate the effect of pH on the adsorption of Fe (III) from the aqueous feed solutions with a fixed quantity of resin. The pH of the solution was adjusted by the addition of NaOH. The results shows that the adsorption of iron decrease with the increase in equilibrium pH of the solution. At equilibrium near to pH 1.0, the maximum adsorption of iron 87.45% e 87.17% was found from the solution containing iron 50 e 100 mg/L, respectively. For the 150 mg/L concentration, maximum adsorption was observed at pH 2.0. At higher pH, the adsorption of iron was found low due to the formation of insoluble iron oxyhydroxides [3,6,7].

3.3. Effect of resin dose

The effect of resin dose on adsorption of iron from the aqueous feed containing Fe (III) at pH 1.0 was studied keeping retention time for mixing at 20 min. Resin dose was varied from 0.2 to 0.6 g in 50 mL solution. The results indicate the increase in adsorption of Fe (III) with increase in resin mass. In higher concentration an increase in surface area of resin automatically enhances the rate of adsorption reaction. The total adsorption of Fe (III) was found with resin dose of 0.6 g resin. The resin dose has shown negligible effect on 50 mg L^{-1} of Fe (III).

3.4. Effect of Agitation

The effect of stirring speed of the Fe (III) solution was investigated with agitation speed between 150 and 250 rpm at pH 1.0 with the resin amount of 0.6 g. Most of the results show that while stirring speed of the solution increases the adsorption of Fe (III) has increased. However, a

small reduction in the amount removed was observed at a concentration of 50mg/L.

3.5. Effect of contact time

Adsorption of Fe (III) with respect to the effect of time was studied within the range of 1 – 250 min. The initial concentration of Fe (III) was fixed at 150 mg L^{-1}, resin mass of 0.6 g, stirring speed of 250 rpm, contact time of 20 min and pH solution of 1.0 were used. The adsorption profile at different time intervals has been presented in Fig. 1. A rapid initial absorption of 80.93% was observed in 5 minutes of contact, while 94.08% of the adsorption occurred in the first 10 minutes of the contact period. The maximum percentage removal of Fe (III) was 99.11% at 50 min. The rapid initial uptake of the metal ions onto the adsorbent is due to the increased in the concentration gradient between the adsorbate in solution and adsorbate in adsorbent as this will result in the increased in the number of vacant sites available for adsorption [3]. Consequently, the adsorption rate of the metal ions decreased with increased of contact time, as a smaller number of vacant sites will be made available on the surface of the adsorbent. After a certain point of contact (20 min), it reached the equilibrium where there was no significant change in the concentration of the metal ions in the solution as the available adsorption sites are occupied by the metal ions [8].
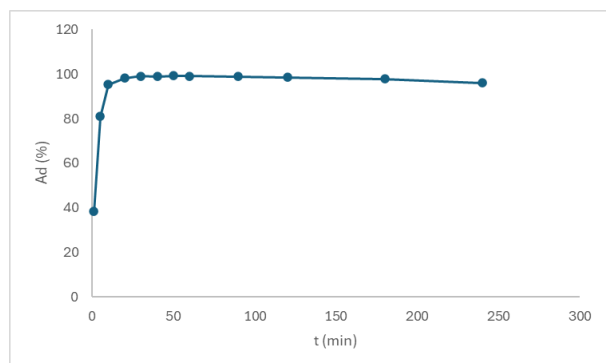

Fig. 1. Effect of contact time on Fe (III) removal by cationic resin. [Fe (III)] = 150 mg L^{-1}, pH = 1.0, stirring speed = 250 rpm, stirring time = 20 min and resin mass dosage = 0.6 g.

3.6. Kinetics of adsorption

The kinetic tests for Fe (III) adsorption were carried out within the time interval of 1 – 60 min. The mechanism of the adsorption process was determined using the pseudo-first order and pseudo-second order model. The plots of pseudo-first order and pseudo-second order model for Fe (III) adsorption were obtained. The adsorption kinetic parameters were calculated from the linear plots of log (q_e - q_t) vs. t and t/q_e vs. t, respectively. Results obtained showed that the adsorption process was fast, and the sorption equilibrium was achieved at 60 min for the iron ions.
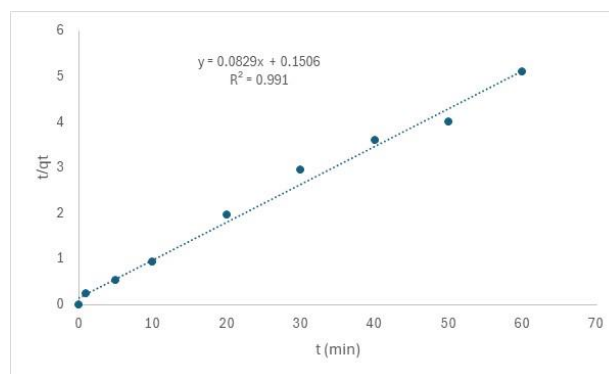

Fig. 2. Fitting of pseudo-second order rate for Fe (III) adsorption onto Amberlite IR-120 resin.

The pseudo-first order model considers that the rate of adsorption site occupation is proportional to the number of unoccupied sites [2, 8 – 10]. It is given by the equation:

$$Log\ (q_e - q_t) = logq_e - (k_1t)/2.303 \qquad (3)$$

where q_e and q_t are the amount of metal ions adsorbed (mg g^{-1}) onto the cationic resin mass at equilibrium and at any time t, k_1 (min^{-1}) is the rate constant of pseudo-first order model and t is the time (min). Pseudo-second order model model is given by the equation:

$$t/qt = (1/(k_2q_e^2)) + t/q_e \qquad (4)$$

where k_2 is the equilibrium rate constant of pseudo-second order model (g mg^{-1} min^{-1}). Pseudo-second order model assures that the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites [2, 7, 11]. The correlation coefficient (R^2) values of the pseudo-first order model was 0.6868 for Fe (III) adsorption, while pseudo-second order model correlation coefficient (R^2) value was 0.9913 (Fig. 2). The

theorical k_2 value calculated was 0.0456 g mg^{-1} min^{-1}. The experimental q_e value (11.80 mg g^{-1}) showed good correlation with the calculated value (12.06 mg g^{-1}) from pseudo-second order model. The calculated error between the experimental and theoretical value of q_e was 2.22%. Therefore, it can be concluded that the pseudo-second order model was better in describing the adsorption kinetics compared to the pseudo-first order model.

4. Conclusions

The test results were evaluated, and it can be concluded that the ideal parameters for iron adsorption are to use 0.6 g of cationic resin in a volume of 50 mL (maintaining a constant mass/volume ratio even after adding NaOH to control the pH), with the pH of the sample close to 1.0, and stirring speed at 250 rpm for mixing time of 20 minutes. Equilibrium of metal ion removal was achieved at 240 min. The use of optimized conditions resulted in adsorption of approximately 99 % of Fe (III) ions from the aqueous solution. Kinetics of adsorption followed the pseudo second order model. Studies involving the application of the Langmuir isotherm model to describe the adsorption mechanism will be evaluated to calculate the maximum iron adsorption capacity on the adsorbent. Iron adsorption in the presence of other metal species such as Al, Ca, Mg, Mn and Na will also be evaluated, as well as ion exchange resin recovery studies (desorption experiments). Finally, the aim is to evaluate the applicability of the ion exchange resin in a flotation effluent sample with a view to reusing the water in the reverse flotation of the iron ore.

Acknowledgements

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