Removal of Nickel ions from Aqueous Solutions on Packed bed of Zeolite NaX

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Zeolite X, a synthetic zeolite, is investigated for its ability to remove nickel (II) from aqueous solution. Batch tests were conducted to find out optimum pH and equilibrium isotherm. It is observed that the optimum pH for the adsorption of nickel (II) on zeolite X is 5 and the adsorption kinetics for nickel adsorption fits well with Langmuir isotherm with an uptake value of 39 mg Ni (II)/g zeolite X. The ability of zeolite X to adsorb nickel in a packed column was investigated, as well. The experiments were conducted to study the effect of important design parameters such as bed height, flow rate and influent concentration. Results shows that the nickel uptake increases with increasing flow rate and influent concentration. High removal capacities up to 96% were recorded at high flow rate, bed depth and influent concentration. The Bohart-Adams and Thomas adsorption model were employed to determine characteristic parameters such as N (saturation concentration, mg/l) and qe (maximum solid phase concentration of solute, mg/g), useful for process design.

1. Introduction

In order to preserve the ecology of aqueous environment the introduction of pollutants must be carefully controlled. Toxic metals like cadmium, lead, mercury, chromium, nickel and copper are inorganic pollutants which are harmful for the environment as well as human health. The affect of acute nickel poisoning in humans causes serious problems like high blood pressure, kidney damage, red blood cells (Axtell et. al., 2003). The removal of toxic metals from aqueous pollution source is not only of the benefit to the environment but recovery makes economical sense to commercial concerns such as the metallurgical and electronic industries (Gupta et. al., 2003). The removal of heavy metal ions from effluent of the industries is done by many established technologies such as chemical precipitation, electrolytic recovery, membrane separation, ion exchange and evaporation (Zhao and Duncan, 1998). These technologies are not economically feasible for their relative high cost, and also produce high sludge at the end, therefore there is a need to look for some more alternatives which not only have low cost but also highly efficient. A number of conventional technologies have been considered for treatment of wastewater contaminated with metal ions. Among them, adsorption is found to be the most effective method. Commercial activated carbon is regarded as the most effective material for controlling the metal ions load. However, due to its high cost and 10-15% loss during regeneration, unconventional adsorbents like sand, alumina, silica, zeolite etc. have attracted the attention of several investigations and adsorption characteristics and have been widely investigated for the removal of metal ions (Bailey et. al., 1998; Babel and Kurniawan, 2003). The unique property of ion-exchange capability to preferentially remove unwanted heavy metals, of
zeolites makes it favorable for wastewater treatment (Grant, 1987). Adsorption on zeolite X although is not only economically good but also have highly efficient. Therefore, it is a suitable candidate for the adsorption of nickel from effluent of industries containing nickel as waste. The objective of the present work is to examine the adsorption of nickel on zeolite X beads in a column and to describe the kinetics of metal removal by the adsorption column using Adams-Bohart (1920) and Thomas (1948) model by varying operating parameters e.g. flow rate, bed depth and inlet metal ion concentration, and to see how these influence the characteristic parameters of both the models.

2. Materials And Methods

2.1 Nickel and ZeoliteX solutions
Nickel stock solutions were prepared from UV Spectroscopy reference solutions for nickel. To make the stock solutions, 447.9 mg of nickel sulphate (NiSO₄·6H₂O) was added in 1000 ml distilled water to make 100 mg/l solution. The analysis of nickel ions concentration in water was done using DMG method at 445 mµ, providing a path of 2.5 cm. Zeolite X used in this study was (CDH Ltd., India) in the form of cylindrical beads has the unit cell composition Na₈(AlO₂)₆(SiO₂)₁₁ which has a CEC value of 5.42 meq/g for heavy metal ion removal. The homoionic sodium form was obtained by contacting zeolite three times with 1 mol/1 solution of NaCl at 298 K followed by washing with deionized water. Washed Zeolite was oven dried at 373 K and stored over saturated ammonium chloride in dessicator.

2.2 Batch pH and isotherm studies
Batch pH studies were conducted by shaking 200 ml of metal solution containing approximately 50 mg/l of cadmium with 1 g of zeolite X for 3 h, over a range of initial pH values from 2 to 6 in increments of 1. The pH of the nickel stock solution was adjusted by using acetic acid and sodium acetate. The final pH of the reaction mixture was recorded. The experiments were repeated and mean values were used in the analysis of the data. An optimum pH was selected for further studies. After determining the optimum pH, isotherm studies were conducted at room temperature (298 K) by varying the nickel concentration in water. Representative concentration of nickel (10, 20, 30, ..., 100 mg/l) were used in the experiments. 1 g of zeolite X was mixed in 200 ml of nickel solution for 2-3 hours. The initial pH of the metal solutions was adjusted to an optimum value of 5.0 with acetic acid and sodium acetate. The nickel concentration at the end of the study was determined after filtering the samples. The experiments were repeated for duplicate values.

2.3 Column studies
Column studies were conducted using a Perspex column with an inner diameter of 2.44 cm and a length of 30 cm. The column was packed up to 5 and 8 cm of zeolite, i.e. 15 and 22 g of zeolite X was in the column; the calculated bed volume was 0.52. At the bottom of the column, a 0.5 mm stainless sieve was attached followed by a layer of glass beads of diameter of 2 mm in order to provide a uniform inlet flow of the solution into the column (Fig. 1). The approximate influent concentration and flow rate of the cadmium solution were 50, 75 and 100 mg/l and 20, 30, and 40 ml/min, respectively. Samples were collected at regular intervals of time, filtered and stored for analysis. Column studies were terminated when the column reached exhaustion. In all experiments pH of the inlet solution was maintained at 5 and pH of the effluent was also measured for certain column studies.
3. Results And Discussion

3.1 Batch pH and isotherm studies
The removal of nickel by adsorption on zeolite X was found to increase with increase in pH (2.5) values. On further increase in the pH beyond 5, adsorption capacity was found to be constant. The plot of pH versus zeolite uptake capacity (Fig. 2) has one inflection points at pH 5, where the maximum uptake of nickel ion per gram zeolite X take place. It can be seen from the Fig 2 that the removal of nickel is dependent on the pH of the solution. At low pH the nickel ion uptake is relatively small. Mineral acids affect the structure of zeolites and the extent of damage to their structure depends on the pH of the acids. In fact, pH less than 4.5 is not recommended for zeolites (Ahmed and Keane, 1998). The loss in removal capacity at lower pH can therefore be ascribed to the collapse of the structure of zeolites. Isotherm experiments were carried out at an optimum initial pH of 5.0. The adsorption data was fitted to the Freundlich, i.e., \( q = Kc^{1/n} \), and the Langmuir, i.e., \( C/q = C/q_m + 1/bq_m \) models using the non-linear regression analysis. It was found that the adsorption data obtained was best described by the Langmuir isotherm model. Fig. 3 shows the Langmuir model plot for nickel adsorption on zeolite X. The Langmuir isotherm can be used to calculate the theoretical adsorption capacity of zeolite X for nickel. The value of Langmuir constants \( q_m \) and b from Fig. 3 are found to be 39.06 mg nickel(II)/gm zeolite X and 0.7265 l/mg nickel.

3.2 Column experiments
3.2.1 Effect of flow rate
The effect of flow rate on the adsorption of nickel ions was studied by varying flow rates at a fixed bed height of 5 cm, inlet nickel pH of 5.0 and inlet concentration of 50 mg/l. Breakthrough curves for adsorption of Ni on the zeolite X at different flow rates are shown in Fig. 4. In general, the breakthrough curves became steeeper and the breakthrough time decreased with increasing flow rate. This behavior may be due to insufficient residence time of the solute in the column and diffusion limitations of the solute into the pores of the sorbent at higher flow rates (Ko, 2000). Even though more shortened mass transfer zone (usually preferable) was observed at the highest flow rate, the total metal removal percentage and the metal uptake were actually observed maximum at the low flow rate (20ml/min).
3.2.2 Effect of inlet metal ion concentration on breakthrough time
When the inlet metal ion concentration is increased for the same flow rate the effect is a decrease in the breakthrough time. Fig. 5a shows the removal breakthrough curves obtained by changing inlet flow concentration from 50 to 100 mg/l at 20 ml/min. Since the lower concentration gradient causes a slower transport due to decreased diffusion coefficient or mass transfer coefficient. The breakpoint time decreases with increasing inlet concentration as both the binding sites and ion exchange sites become quickly saturated. It can be seen that the change in the breakpoint time is somewhat in the same ratio as it change in the inlet concentration.

3.2.3 Effect of bed height
Fig. 5b shows the breakthrough curves for adsorption of nickel on fixed beds of zeolite X at different bed heights. In order to yield different bed heights, 15 and 22 g of zeolite X were added to produce 5 and 8 cm, respectively. The uptake of nickel also increased with an increase in bed height. The reason behind increase in the uptake capacity of nickel ions as bed height increases is availability of more binding sites for sorption, which also resulted in a broadened mass transfer zone.
3.3 Model parameter estimation

3.3.1 Calculation of parameters of Adam-Bohart Model

Adams-Bohart model (Bohart and Adams, 1920; Oulman, 1980): Adam-Bohart model is applied to the experimental data for the description of the initial part of the breakthrough curve. The Adams-Bohart equation is as follows:

$$\ln \frac{C}{C_0} = K_{AB}C_s f - K_{AB}N \frac{H}{U_o}$$  \hspace{1cm} (1)

Adams-Bohart model was applied to the experimental data for varying flow rates, bed depths and inlet concentrations. A linear relationship between in $C/C_0$ and time is obtained for the relative concentration up to $C/C_0=0.5$ and thus the value of $N$ and $k_{AB}$ were calculated as intercept and slope of the line. On applying these values of $N$ and $k_{AB}$ in eq. (1) it can be seen that the predicted values of $C/C_0$ agrees well up to $C/C_0=0.1$ to $0.3$ (Fig. 4) with the experimental breakthrough data for flow rates of 30 and 40 ml/min but for low flow rates it is good only up to $C/C_0=0.05$ (Fig.4). Fig 5a gives that Adams-Bohart model predicts theoretical value of $C/C_0$ for low concentration very well and the diversion increases as the inlet concentration increases. The same trend is there as one increases the bed depth Fig 5b. Thus large discrepancies are there as one goes for increased inlet concentration and bed depth. Respective values of $N_0$ and $k_{AB}$ for different flow rates, heights and inlet concentrations are given in Table 1. The value of kinetic coefficient are influenced by flow rate and it increase with increase in flow rate at bed depth of 5 cm and inlet concentration of 50 mg/l. One can see that the value of $N$ increases and then slightly decrease for higher flow rates for all inlet concentrations. Maximum percentage removal at these conditions is 91 %.

3.3.2 Calculation of parameters of Thomas Model

The linearized form of the Thomas model is as follows (Chu, 2004; Aksu and Gonen, 2003):

$$\left[ \ln \left( \frac{C}{C_0} - 1 \right) \right] = k_{TH}q_{w}W - k_{TH}C_f$$  \hspace{1cm} (2)

where $V_{ef} = Q,t$, $k_{TH}$ is the kinetic coefficient and $q_w$ is the adsorption capacity of the bed. The column data is fitted to the Thomas model and found to be good in predicting the value of $C/C_0$ for the whole length of the breakthrough curve. From Fig. 5c, it can be seen that the theoretical data agrees well with the experimental data for almost the whole range of $C/C_0$. The value of $k_{TH}$ and $q_w$ are given in Table 1. From the data it can be interpreted that as the flow rate increase values of $k_{TH}$ and $q_w$ increase. From the trend of $q_w$ it can be easily interpreted that the overall value is higher at high bed depth, flow rate and inlet concentration with a maximum value being 37.02 mg nickel/ g zeolite X and a percentage removal value of 96 % at bed depth of 8 cm, flow rate of 40 ml/min and inlet concentration of 100 mg/l.

4. Conclusions

Zeolite X was investigated for its ability to remove nickel (II) from aqueous solution. Both batch and column tests were conducted to find out optimum pH and equilibrium isotherm. The experiments were conducted to study the effect of important design parameters such as bed height, flow rate and influent concentration. It was observed that the optimum pH for the adsorption of nickel (II) on zeolite X is 5 and the adsorption kinetics for nickel adsorption fits well with Langmuir isotherm with an uptake value of 39 mg Ni (II)/g zeolite X. It was observed that the nickel uptake increases with increasing flow rate and influent
concentration. High removal capacities up to 96% were recorded at high flow rate, bed depth and influent concentration. The Thomas model and Adam-Bohart model were used to fit the column data and it was observed that the Thomas model was found to be effective over the whole range of $C/C_0$ whereas the data upto 30-40% was found fitted in case of Adam-Bohart model.

Table 1. Predicted parameters from the Adams-Bohart model and Thomas model for adsorption of nickel on fixed beds of zeolite NaX

<table>
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<tr>
<th>H (cm)</th>
<th>Q (ml/min)</th>
<th>$C_0$ (mg/l)</th>
<th>$k_{AB} \times 10^4$ (l/mg.min)</th>
<th>N (mg/l)</th>
<th>$k_Th$ (ml/mg/min)</th>
<th>$q_0$ (mg/g zeolite X)</th>
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Fig. 6. Comparison of experimental and predicted breakthrough curves obtained at different (a) flow rates, (b) inlet metal ion concentration and (c) bed depths according to Thomas model.
5. References

Grant, D. C., 1987, Removal of strontium and cesium on natural Zeolites, Environ. Prog. 6, 104.