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Adsorption Behaviour of Co(II) from Aqueous Solutions onto D113-III Resin

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In this study, the adsorption and desorption properties of Co(II) on D113-III resin have been studied. The different variables affecting the adsorption capacity such as pH of the solution, temperature and contact time have been investigated, which indicate that D113-III resin could adsorb Co(II) effectively from aqueous solution. The results show that the optimal adsorption condition of D113-III resin for Co(II) is achieved at pH = 6.5. The maximum saturated adsorption capacity of Co(II) is 192.1 mg g^{-1} D113-III resin at 298 K. The thermodynamic parameters such as ΔG^o which were all negative and ΔH^o which was positive, indicated that the adsorption of Co(II) ion onto D113-III resin was spontaneous and endothermic, respectively. Positive ΔS^o value of Co(II) adsorption process indicates an irregular increase of the randomness at the D113-III resin-solution interface during adsorption. Adsorption isotherms correlated well with the Langmuir model. Experimental data were also evaluated to find out kinetic characteristics of the adsorption process. Desorption studies revealed that Co(II) ion could be eluted effectively by using the 0.25-1.0 mol L^{-1} HCl solution. Thomas model was applied to experimental data to predict the breakthrough curves and to determine the characteristics parameters of the column useful for process design.

Keywords: D113-III resin, Co(II), Adsorption, Thermodynamics, Adsorption isotherm.

INTRODUCTION

Cobalt, which is one of the most important non-ferrous metals, has been drawn more and more attention because of the wide range of applications that utilize the element in huge quantities[1]. Cobalt and its compounds have been found a variety of applications especially in rechargeable batteries, super-alloys[2], colours/pigments[3], catalysts and hard materials carbides. However, cobalt present in industrial wastewaters can also produce a variety of undesirable effects on environment and human beings. Exposure to cobalt can induce harmful health effects including asthma, pneumonia, wheezing, allergies[4,5] and cancer[6] as well as DNA damage[7]. Therefore, recovery of cobalt ion is extremely important, not only from the view of their limited resource availability, but also for the reduction of their quantum for disposal as wastes which are harmful to humans.

Different methods which have been proposed for the recovery of cobalt suffer from major drawbacks, such as coprecipitation[8], solvent extraction[9], electrochemical deposition[10], membrane extraction[11,12]. These range from large secondary wastes, solvent losses, complex equipment and bulky design, which translate to an inability to effectively remove low concentrations of cobalt at acceptable costs. Compared with those methods, solid phase extraction is more effective. Various solid phase extraction materials including activated carbon[13], C_{18}-bonded silica gel[14], modified chromosorb[15] and resins[16,17] have been used for the removal of cobalt. Of all the above solid phase extractants, resins are the most widely used absorbents. The reasons for widespread application of resins are their inherent advantages. Resins which can exchange their mobile ions to ions of equal charge from the surrounding medium are more effective and environmentally friendly. D113-III resin is a polymeric material containing a functional group (-COOH), which has not only proton that can exchange with cation, but also oxygen atom that can coordinate directly with metal ions. D113-III has high stability and reusability and also the adsorption capacity of this material is much higher than the paper reported before[16,17]. Therefore, D113-III resin can be widely used in the preconcentrate, concentrate and recover of cobalt.

In this work, the adsorption and desorption of Co(II) ion by D113-III resin using batch and column methods was investigated. Some factors affecting adsorption, such as initial pH of solution, contact time and temperature were examined. Kinetics and isotherm adsorption experiments were carried out. Thermodynamic parameters of adsorption for Co(II) ion were calculated. Thomas model was applied to experimental data obtained from column experiments. The experimental results may provide important information for the removal of Co(II) from aqueous solutions in the environmental protection.

EXPERIMENTAL

The metal ions were determined with Shimadzu UV-2550 UV-visible spectrophotometer. The resin dosage was measured by electronic balance of Sartorius BS224S. Mettler Toledo delta 320 pH meter was used for measuring pH of solutions. The sample was shaking in the DSHZ-300A and THZ-C-1 shaking machine at constant temperature. The water used in the present work was purified within Molresearch analysis-type ultra-pure water machine.

The D113-III resin was supplied by Jiangsu Suqing Co., Ltd. The standard stock solutions were prepared by dissolving an appropriate amount of $CoSO_4{\cdot}7H_2O$. HOAc-NaOAc buffer solution (pH 3.50-6.50) and HCl-hexamethylenetetramine buffer solutions (pH 6 and 6.5) were prepared from the HOAc, NaOAc, HCl and hexamethylenetetramine ($C_6H_{12}N_4$) solutions. The chromophoric reagent of 0.1 % 4-(2-pyridylazo)resorcinol (PAR) solution was obtained by dissolving 0.1000 g PAR powder into 100 mL 95 % ethanol solution. All other chemicals were of analytical grade and purified water was used.

Batch studies: Experiments were run in a certain range of pH, temperature and contact time as well as adsorption isotherms. The operation for the recovery of Co(II) is usually carried out in batch vessels and glass columns.

Batch adsorption experiments were conducted by placing a desired amount of treated D113-III resin in 100 mL conical flasks containing various concentrations of metal ions solution (30 mL). The sample pH was adjusted to the desired value with HOAc-NaOAc and HCl-$C_6H_{12}N_4$ buffer solution. The flasks were agitating at 100 rpm in a DSHZ-300A temperature constant shaking machine until to reach the equilibrium. Aliquot samples were taken from the flask at appropriate time intervals as necessary. The residual concentration of the metal ions in the aqueous phases was determined at 580 nm by Shimadzu UV-2550 UV-visible spectrophotometer. The adsorption capacity (Q) was calculated with the following formula:

$$Q = \frac{C_o - C_e}{W} V \qquad (1)$$

The distribution coefficient (D) of Co(II) ion between the aqueous phase and the solid phase can be directly obtained by using:

$$D = \frac{C_o - C_e}{C_e} \times \frac{V}{W} \qquad (2)$$

where C_o (mg mL^{-1}) and C_e (mg mL^{-1}) are the initial and equilibrium concentrations of Co(II) ion in solution, respectively. V/W is the ratio of the volume of metal solution (mL) to the amount of Co(II) (g) in a batch.

Desorption studies: Desorption of metal ions was performed by mixing D113-III resin-metal complexes and HCl eluent solutions of different concentrations and stirring at 100 rpm for 24 h at 298 K. The final metal ion concentrations in the aqueous phase were similarly analyzed as the described above. The desorption ratio (E) was calculated as follows:

$$E\,(\%) = \frac{C_d V_d}{(C_o - C_e)V} \times 100\ \% \qquad (3)$$

where E is the desorption ratio; C_d is the concentration of the solutes in the desorption solutions; V_d is the volume of the desorption solution; and C_o, C_e and V are the same as defined above.

Column studies: The dynamic adsorption curve was applied to experimental data to predict the breakthrough curve and to determine the characteristic parameters of the column. Dynamic adsorption and desorption experiments were carried out on glass columns (4.5 mm × 235 mm) which was wet-packed with the selected resin (0.15 g, dry weight). The packed length of resin bed was 7.4 cm. Sample solution of which the initiate concentration is 0.1mg mL^{-1} flowed through the glass column and the Co(II) solution at the outlet of the column were collected at regular time intervals and the concentration of Co(II) was measured using a UV-visible spectrophotometer at 580 nm.

RESULTS AND DISCUSSION

Influence of pH on the distribution coefficient for Co(II): The influence of pH on the adsorption behavior of D113-III resin for Co(II) in two buffer solutions is illustrated in Fig. 1. The uptake of Co(II) as a function of hydrogen ion concentration was studied in HOAc-NaOAc medium (pH 3.50-6.50) for an initial concentration of Co(II) ion (0.3333 mg mL^{-1}) at 298 K, 100 rpm. Fig. 1 shows that the distribution coefficient for Co(II) ion is the highest when pH value is 6.50 in the HOAc-NaOAc medium and decreases by lowering pH under the experimental conditions. The reduced cobalt uptake at the lower pH is proposed to be associated with the higher affinity of hydrogen ion toward the resins[18,19]. The competition existed between H^+ and Co(II) ion for adsorption sites decreases the adsorption capacity. However, the Co(II) ion was prone to deposit at higher pH values[20]. Due to the stronger buffer action of HCl-$C_6H_{12}N_4$ medium in high pH, the experiment was also carried out in HCl-$C_6H_{12}N_4$ medium (pH 6 and 6.5) under the same condition. From Fig. 1, it can be found that the uptake of Co(II) in HCl-$C_6H_{12}N_4$ medium is higher than that in HOAc-

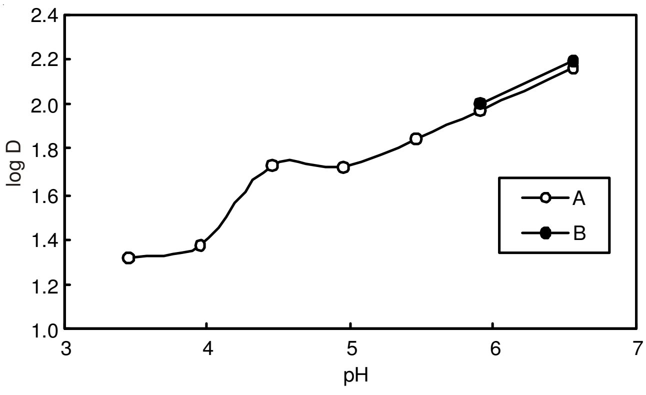

Fig. 1. Influence of pH on the distribution coefficient of Co(II) in the buffer solutions of A (HOAc-NaOAc) and B (HCl-$C_6H_{12}N_4$). Initial concentration of Co(II) ion (0.3333 mg mL^{-1}), resin (20 mg), batch volume (30 mL), rpm (100), temperature 298 K

NaOAc medium. Therefore, all the following experiments were performed at the optimum pH of 6.5 in the HCl-$C_6H_{12}N_4$ system.

Thermodynamic parameters: The effect of temperature on the adsorption of Co(II) ion on the D113-III resin in aqueous solution has been examined at 298, 308 and 318 K. Standard free energy change (ΔG^0), standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0) such thermodynamic parameters were calculated by using the following eqn.[21,22].

$$\log D = \frac{\Delta S^0}{2.303\ R} - \frac{\Delta H^0}{2.303\ RT} \qquad (4)$$

$$\Delta G^0 = \Delta H^0 - \Delta S^0 T \qquad (5)$$

where R is the gas constant (8.314 J (mol K)$^{-1}$) and T is the absolute temperature. The plot of log D *versus* 1/T gives the straight line from which ΔH^0 and ΔS^0 were calculated. Then the free energy variation, ΔG^0, is obtained from eqn. 5. The free energy variation, ΔG^0, is the fundamental criterion of spontaneity. The negative ΔG^0 values at given temperatures indicate the spontaneous nature of the adsorption and confirm the feasibility of the adsorption process. The free energy variation (negative values) increases (from -13.61 to -14.73 kJ mol^{-1}) with an increasing temperature from 298 to 318 K, which clearly shows that the process is favorable at higher temperature. The magnitude of adsorption free energy (ΔG^0) ranging from -13.61 to -14.73 kJ mol^{-1} suggests that the adsorption can be considered as a physical one[23]. The positive value of ΔH^0 reveals the endothermic type of the adsorption process. Positive ΔS^0 value of Co(II) adsorption process indicates an irregular increase of the randomness at the D113-III resin-solution interface during adsorption[24].

Adsorption isotherm: Langmuir[25] and Freundlich[26] models are the most frequently employed models which have been published in the literature to describe experimental data of adsorption isotherms. In this work, both models were applied to describe the relationship between the amount of Co(II) ion adsorbed and its equilibrium concentration in solution at three temperature (298, 308 and 318 K). Langmuir isotherm is based on the assumption that all adsorption sites on a structurally homogeneous adsorbent are identical and energetically equivalent. The basic idea behind the Langmuir model is the coverage of the surface by a monomolecularic layer. Theoretically, the adsorbent has a finite capacity for the adsorbate. Therefore, when no further adsorption can take place, the adsorption capacity is reached. The Langmuir and Freundlich parameters for the adsorption of Co(II) are calculated by the following equations.

Langmuir isotherm[25]

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{bQ_m} \qquad (6)$$

where Q_e is the equilibrium Co(II) ion concentration on the adsorbent (mg g^{-1}), C_e is the equilibrium Co(II) ion concentration in solution (mg mL^{-1}), Q_m is the monolayer capacity of the adsorbent (mg g^{-1}), b is the Langmuir constant and related to the free energy of adsorption.

The Freundlich isotherm is a specific case of the Langmuir model that describes adsorption based on heterogeneous surface energy. The energy varies with surface coverage a result of different adsorption.

Freundlich isotherm[26]

$$\log Q_e = \log k_f + \frac{1}{n}\log C_e \qquad (7)$$

where K_f is Freundlich constant and n(dimensionless) is the heterogeneity factor.

Langmuir plots are shown in Fig. 2 and Freundlich plots are shown in Fig. 3. On the comparison of the R^2 values, higher R^2 values ($R^2_{298\ K} = 0.9892$, $R^2_{308\ K} = 0.997$, $R^2_{318\ K} = 0.9949$) were obtained from Langmuir model for Co(II) than from the Freundlich model ($R^2_{298\ K} = 0.9559$, $R^2_{308\ K} = 0.9868$, $R^2_{318\ K} = 0.9877$). It is concluded that in the case for the adsorption of Co(II) to D113-III resin Langmuir model represents a better fit to the experimental data than Freundlich model. Langmuir model assumes that the adsorption is localized in a monolayer and there is no interaction between the adsorbate molecules. This indicates that the adsorption of Co(II) by D113-III resin is monolayer-type.

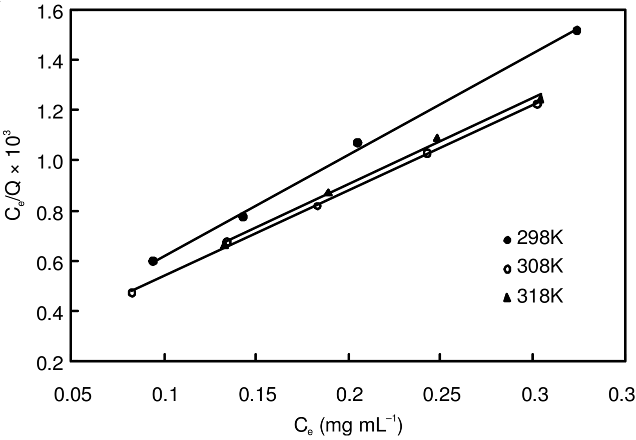

Fig. 2. Langmuir plots for adsorption of Co(II) by D113-III resin. Resin (15 mg), batch volume (30 mL), rpm (100)

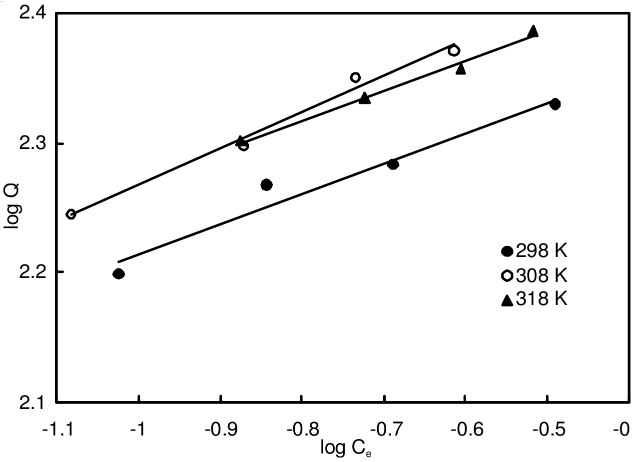

Fig. 3. Freundlich plots for adsorption of Co(II) by D113-III resin. Resin (15 mg), batch volume (30 mL), rpm (100)

Influence of contact time and adsorption kinetics: The adsorption kinetics of Co(II) on the D113-III resin at initial concentration of 20 mg/60 mL were studied as a function of contact time. Fig. 4 showed that the removal amount of metal ions increased rapidly during the few hours due to the existence of greater number of resin sites available for metal ions adsorption and then increased slowly until the equilibrium state was reached within 12 h. As can be seen from Fig. 4, an increase in the temperature deals induced an increase in the capacity of Co(II) adsorption, which meant that the adsorption process was an endothermic process. The maximum adsorption capacity of Co(II) is 180.9 mg g^{-1} at 298 K, 205.4 mg g^{-1} at 308 K and 214.8 mg g^{-1} at 318 K, respectively. This value of uptake by the resin is relatively higher than the value reported earlier[16,17].

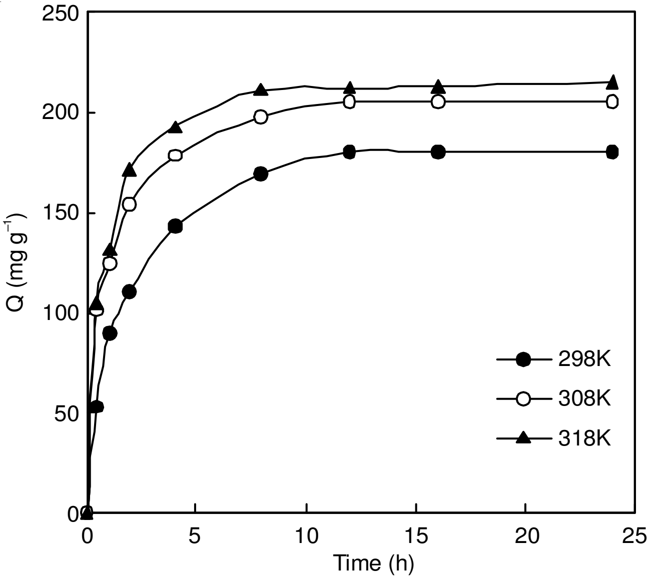

Fig. 4 . Effect of contact time on adsorption of Co(II) by D113-III resin. Initial concentration of Co(II) ion (0.3333 mg mL^{-1}), resin (40.0 mg), batch volume (60 mL), rpm (100)

According to Brykina method[27], the adsorption rate constant k can be calculated from:

$$-\ln(1-F) = kt \tag{8}$$

where F is the fractional attainment of equilibrium ($F = Q_t/Q_e$), Q_t (mg g^{-1}) and Q_e (mg g^{-1}) are the adsorption amounts at certain time and at equilibrium time, respectively. The experimental results accorded with the equation and a straight line was obtained by plotting -ln(1-F) *vs.* t. Therefore, the adsorption rate constant (k) can be found from the slope of the straight line. The correlation coefficient (R^2) was obtained from the linear fitting. The calculated adsorption rate constants (k) are $k_{298\,K} = 6.22 \times 10^{-5}$ s^{-1}, $k_{308\,K} = 8.29 \times 10^{-5}$ s^{-1}, $k_{318\,K} = 1.22 \times 10^{-4}$ s^{-1}. According to Boyd's liquid film spreading equation, it can be deduced from the linear relationship between -ln(1-F) and t, that liquid film spreading is the predominant step of the sorption process[28]. The results demonstrate how efficient the resin is in recovering Co(II) from low concertration solution.

Elution and regeneration: Whether an adsorbent is economically attractive in removal of metal ions from aqueous solution depends not only on the adsorptive capacity, but also on how well the adsorbent can be regenerated again. Therefore, metal ions adsorbed should be easily desorbed under suitable conditions. In this work, desorption of the adsorbed Co(II) ion from D113-III resin were studied. The results are shown in Fig. 5. As can be seen from the figure, maximum recovery of Co(II), at 100 %, was achieved with 0.25 mol L^{-1} HCl solution, 0.50 mol L^{-1} HCl solution, 0.75 mol L^{-1} HCl solution and 1.0 mol L^{-1} HCl solution under the experimental condition. These results suggest that Co(II) adsorbed by D113-III resin can easily be desorbed, which indicates that the resin can be employed repeatedly in Co(II) adsorption.

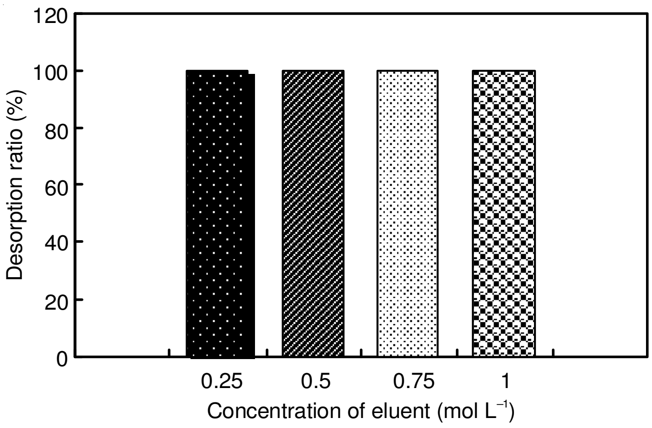

Fig. 5. Desorption of Co(II) from D113-III resin by HCl in varying concentrations. Resin (20 mg), batch volume (30 mL), rpm (100), temperature. 298 K

Dynamic adsorption curve: Batch experimental data are often difficult to apply directly to the fixed-bed sorption because isotherms are unable to give accurate data for a dynamically operated column. The fixed-bed column operation allows more efficient utilization of the adsorptive capacity than the batch process. Therefore, Co(II) adsorption onto D113-III resin was carried out by means of the dynamic method to determine the breakthrough curves of Co(II). Total adsorbed Co(II) quantity (Q_c) in the column for a given feed concentration and flow rate is calculated from equation[29].

$$Q_c = Q_o \frac{V_e(C_o - C_e)}{m} dV_e \tag{10}$$

where C_o and C_e are metal ion concentrations in the influent and effluent (mg mL^{-1}), respectively, m the total mass of the sorbent loaded in the column (g) and V_e is the volume of metal solution passed through the column (mL). The capacity value Q_c was obtained by graphical integration as 201.3 mg g^{-1}. Successful design of a column adsorption process requires prediction of the concentration *vs.* time profile or breakthrough curve for the effluent. The maximum sorption capacity of D113-III resin is also in design. Traditionally, Thomas model is used to fulfill the purpose. The model has the following equation[30].

$$\frac{C_e}{C_o} = \frac{1}{1 + \exp[K_T(Q_T m - C_o V_e)/q]} \tag{11}$$

where K_T [mL (min mg)$^{-1}$] is the Thomas rate constant, θ (mL min^{-1}) is the volumetric flow rate and Q_T is the theoretical maximum sorption capacity value (mg g^{-1}). The linearized form of the Thomas model is as follows:

$$\ln\left(\frac{C_o}{C_e}\right) - 1 = \frac{K_T Q_T m}{\theta} - \frac{K_T C_o}{q} V_e \tag{12}$$

The kinetic coefficient K_T and the adsorption capacity of the bed Q_T can be determined from a plot of ln [$(C_o/C_e)^{-1}$] *vs.* t at a certain flow rate. Thomas equation coefficients for Co(II) adsorption were $K_T = 6.3 \times 10^{-2}$ [mL (mg min)$^{-1}$] and Q_T = 209.8 mg g^{-1}, respectively. Theoretical predictions based on the model parameters were compared with the observed data as shown in Fig. 6.

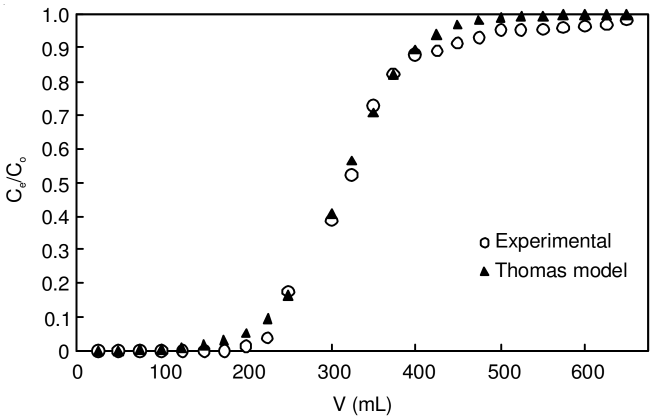

Fig. 6. Experimental and predicted breakthrough curves using the Thomas model for Co(II)

Thomas model was found in a relatively good fitness with breakthrough curves for sorption of Co(II) on D113-III resin with a R^2 value 0.9813. In addition, theoretical maximum adsorption capacity value Q_T was close to the experimental one Q_C. Therefore, it can be concluded that the experimental data fitted well to the Thomas model, which indicates that this model was successfully used for the prediction of the breakthrough curves and can be employed to determine the characteristics parameters of the column process design.

IR spectra: From the experimental results above, the functional groups of D113-III, CO, C-OH and Co(II) were supposed to form bonds. To identify the possibility of Co(II) bonding to resin, IR spectra were obtained for D113 resin before and after Co(II) adsorption. It should be noticed that the bands at 3430 and 3426 cm^{-1} are stretching vibrations of the hydroxyl groups, 1718 and 1716 cm^{-1} is an indication of the presence of C=O bond. It was found that the characteristic absorption peak of the bond C=O (1718 cm^{-1}) became weak and the new peaks 1566 and 1013 cm^{-1} formed after Co(II) ion adsorption. The characteristic peak of the hydroxyl groups shifts from 3430 to 3426 cm^{-1}. These results indicates that the coordination bonds are formed between oxygen atoms and Co(II) and H of C-OH is exchanged with the formation of a complex compound.

Conclusions

- Cobalt(II) can be optimally adsorbed on D113-III resin in the HOAc-NaOAc and HCl-$C_6H_{12}N_4$ system at the pH of 6.50. The statically saturated sorption capacity is 192.1 mg g^{-1} resin at 298 K. The Co(II) adsorbed on D113-III resin can be effectively eluted with 0.25 mol L^{-1} HCl.
- The adsorption behaviors fulfill the Langmuir isotherm. The adsorption rate constant under experiment is $k_{298\,K} = 6.22 \times 10^{-5}\ s^{-1}$.
- Thermodynamic parameters, ΔG^o, ΔH^o and ΔS^o, on the adsorption for Co(II) indicate that the adsorption process is spontaneous, endothermic.
- Thomas model is applied to predict the breakthrough curves and to determine the column kinetic parameters. The capacity values are obtained as 201 mg g^{-1} resin using this model.

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