Kinetics and Equilibrium of Cobalt Ion Adsorption on Cross-Linked Polyethylenimine Membrane

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ABSTRACT: The kinetics and equilibrium of cobalt ion adsorption on crosslinked polyethylenimine (PEI) membrane were studied by the spectroscopic method in terms of time, cobalt ion concentration, and temperature. It was found that the adsorption of cobalt ion on crosslinked PEI membrane obeyed the pseudofirst-order kinetic model and the equilibrium adsorption amount of cobalt ion on crosslinked PEI membrane was closely related to the initial cobalt ion concentration. The equilibrium adsorption amount increased with the decrease of temperature and obeyed a Langmuir isotherm to give the equilibrium constant for the adsorption of cobalt ion on crosslinked PEI membrane under various temperatures. Based on Van't Hoff equation the enthalpy and entropy of the adsorption of cobalt ion on crosslinked PEI membrane were determined to be -12.9 kJ mol^{-1} and -107 J mol^{-1} K^{-1}, respectively. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 1964–1967, 2007

Key words: polyethylenimine; cobalt ion; adsorption; kinetics; thermodynamics

INTRODUCTION

Heavy metal ions in wastewater generated from various industries have a significant impact on human health and the environment. Adsorption is one of the methods commonly used to remove heavy ions from industrial effluent.[1,2] Many types of adsorbents including activated carbon, oxide minerals, as well as polymer materials have been used to absorb metal ions from various aqueous solutions. Among them, polymer materials play an important role in adsorption of metal ions because of their superior properties. The groups including carboxylate, hydroxyl, sulfate, phosphate, amide, and amino groups in the polymer materials are found to be responsible for metal sorption.[3]

Polyethylenimine (PEI) is well known for its metal chelation potentialities. The high proportion of amino groups in PEI has been found to provide novel binding properties for metal ions like cobalt, zinc, chromium ions, and thus a number of studies using PEI have been conducted.[4] The adsorption and inhibitive effect of water-soluble PEI on copper ions was demonstrated by Schweinsberg et al.[5] PEI was investigated as a complexing agent in a laboratory pilot, which lead to high rejection of nickel, even in the presence of salts such as NaCl or NaNO₃.[6]

However, PEI is a hydrophilic polymer and dissolves in water, therefore, it cannot be used repeatedly and effectively in water treatment. Saegusa prepared crosslinked PEI membrane and found that the membrane showed a high adsorption capacity for Cu²⁺ ions, and high Cu²⁺/Ca²⁺ selectivity.[7] Recently, Liu et al. found that the adsorption of zinc ions on PEI membrane obeys Langmuir isotherm.[8]

The adsorption behavior of cobalt ions on crosslinked PEI membrane is important for water treatment and other areas, therefore, PEI was crosslinked by polyepichlorohydrin (PECH) and crosslinked PEI membrane was prepared according to Ref. 7. The aim of this work is to study the adsorption kinetics and equilibrium of cobalt ion on crosslinked PEI membrane. Several models such as pseudofirst-order equation were tested to describe the kinetic adsorption process and the adsorption isotherm results were analyzed by the Langmuir model to obtain the adsorption equilibrium constant.

EXPERIMENTAL

Materials

Polyethyleneimine ($M_n = \sim 6 \times 10^4$, 50% aqueous solution) was obtained from Aldrich. PECH ($M_n = \sim 1.2 \times 10^5$) was supplied by Wuhan Chem., and dissolved in benzene, then purified by precipitation using

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methanol. Cobalt chloride was of analytical pure, supplied by Shanghai Hengxin Chem.

Preparation of crosslinked PEI membrane

A solution of PEI and PECH (PEI/PECH molar ratio = 1.2/1, 3 g in total) in DMF (40 mL) was heated to 60°C slowly to prevent gelation, and stirred for 3–4 h. The hot solution was casted on a glass plate and crosslinked at 100°C for 3 h, followed by drying under vacuum for 20 h to afford the transparent membrane. Based on the density of the polymer ($\sim$ 1 g cm^{-3}) the thickness of the resulting membrane was calculated to be 50 μm.

Adsorption experiments

All experiments were carried out in a thermostated bath. A crosslinked PEI membrane was immersed into an aqueous CoCl$_2$ solution at various temperatures, and then the membrane was taken out at an appropriate time interval. The cobalt ion concentration in the aqueous solution was determined by the spectroscopic method. The adsorption amount of cobalt ion on crosslinked PEI membrane was calculated from the difference of the cobalt ion concentration in the aqueous solution before and after adsorption.

RESULTS AND DISCUSSION

Adsorption kinetics

As PEI is a hydrophilic polymer, crosslinking of PEI can provide an insoluble and swellable membrane to remove metal ions from wastewater. Crosslinked PEI membrane was prepared from DMF solution of PEI and PECH by casting and heating under nitrogen due to the reaction between secondary amino groups in PEI and chloromethyl groups in PECH [eq. (1)]. Crosslinked PEI membrane was extracted in methanol and benzene for a period of 48 h, respectively, to remove uncross-linked molecules. From the same weight of crosslinked PEI membrane before and after extraction, it indicated that almost all of the PEI and PECH molecules have been crosslinked.
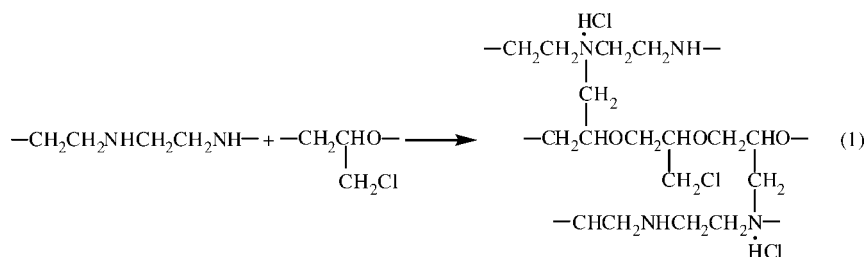
Cobalt ions were incorporated into the crosslinked PEI membrane by immersing the membrane in an aqueous cobalt chloride solution. The change of the adsorption amount of cobalt ion on crosslinked PEI membrane (q_t) with time was shown in Figure 1. It was revealed that the adsorption was rapid in the first 10 min and reached its equilibrium after $\sim$ 460 min under 60°C and then remained constant. The adsorption kinetics of cobalt ions on crosslinked PEI membrane is comparable to porous adsorbents such as activated carbon and resin, thus indicating that diffusion may be an important parameter in the adsorption process. It was also found that the cobalt ion concentration had a great effect on the equilibrium adsorption. The equilibrium adsorption amount of cobalt ion on crosslinked PEI membrane increased with the increase of the cobalt ion concentration. During the adsorption process, cobalt ion penetrated into the crosslinked PEI membrane and bound with the amino groups in PEI, resulting in the gradual increase of the adsorption amount. Finally, the

adsorption reached its equilibrium and equilibrium adsorption amount was obtained.

To examine the controlling mechanism of the adsorption process, such as mass transfer and chemical reaction, two models were used to test the experimental data.

A simple kinetic analysis of adsorption is the rate-controlled pseudofirst-order equation in the following form [eq. (2)][9]:

$$\mathrm{d}_{q_t}/\mathrm{d}t = k_1(q_e - q_t) \tag{2}$$

where k_1 is the rate constant of pseudofirst-order adsorption, q_e (mg/g) denotes the adsorption amount at equilibrium.

After definite integration by applying the initial conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, eq. (2) becomes

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{3}$$
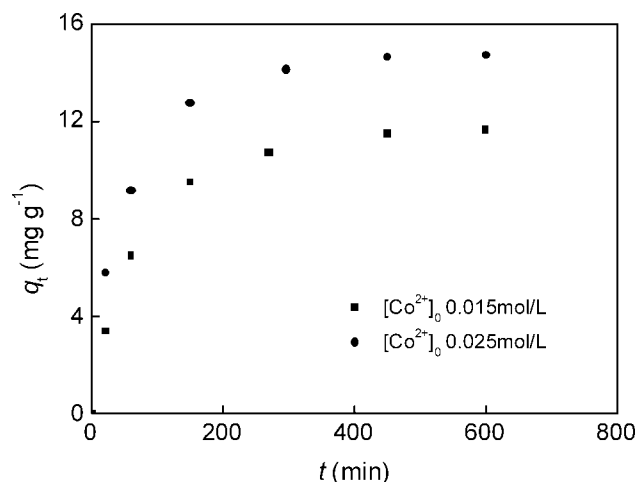
Figure 1 Change of the adsorption amount of cobalt ion on crosslinked PEI membrane (q_t) with time under 60°C.

Based on the Fickian diffusion law, the adsorption amount as a function of time by diffusion-controlled dynamics can be given as[1,4]

$$q_t = 2C_0 S\sqrt{Dt/\pi} \qquad (4)$$

where C_0 is the initial ion concentration in the bulk solution, D is the diffusion coefficient, and S is the specific surface area of crosslinked PEI membrane.

The adsorption of cobalt ion on crosslinked PEI membrane may be considered to consist of two processes: (1) the transport of cobalt ion from the bulk solution to the cross-linked PEI membrane, (2) the attachment of cobalt ion to the amino groups in crosslinked PEI membrane. The experimental data were fitted by the pseudofirst-order equation and diffusion-controlled model, and the results were shown in Figure 2. It was found that the
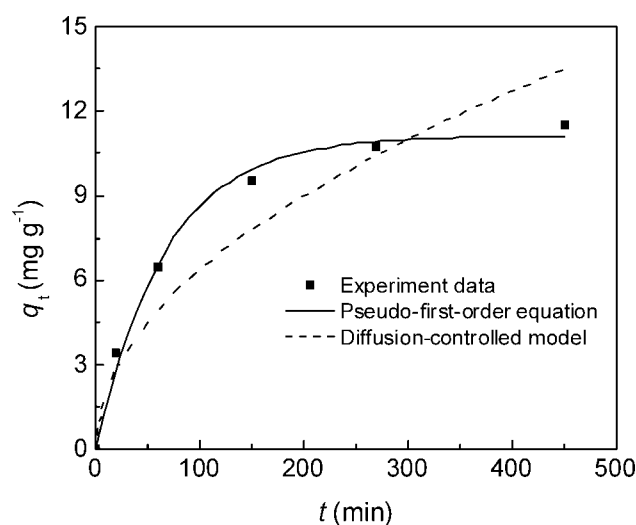

Figure 2 Test of the pseudofirst-order equation and diffusion-controlled model for the adsorption of cobalt ion on crosslinked PEI membrane. (60°C, $[Co^{2+}]_0 = 0.015$ mol L^{-1}).
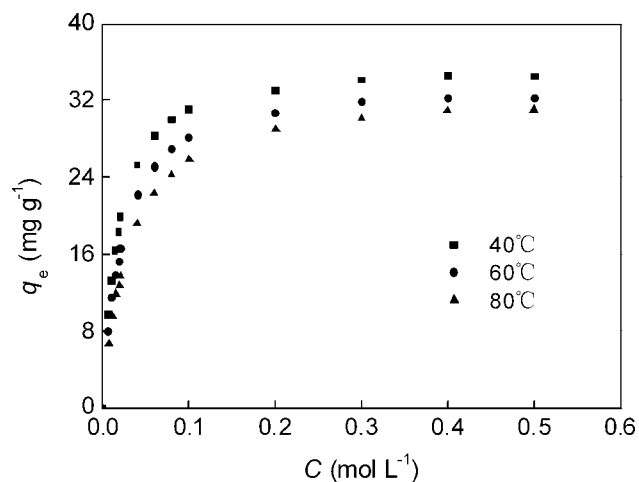
Figure 3 Sorption isotherm of cobalt ion on crosslinked PEI membrane under various temperatures.

adsorption of cobalt ion on crosslinked PEI membrane obeyed the pseudofirst-order kinetic model ($R^2 = 0.993$) and there were some deviations between the experimental data and the diffusion-controlled model ($R^2 = 0.905$), which indicated that the adsorption was the rate-controlled process other than the diffusion-controlled process. According to pseudofirst-order equation, when the initial cobalt ion concentration was 0.015 mol L^{-1} and 0.025 mol L^{-1} the rate constants (k_1) were determined to be 1.48×10^{-2} g mg^{-1} min^{-1} and 1.90×10^{-2} g mg^{-1} min^{-1}, respectively, indicating that the rate constant increased with the increase of the cobalt ion concentration.

Adsorption isotherm

The adsorption capacity of cobalt ion on crosslinked PEI membrane was investigated over a wide range of cobalt ion concentrations. Figure 3 presented the equilibrium adsorption amount under various equilibrium cobalt ion concentrations in the solution. It was found
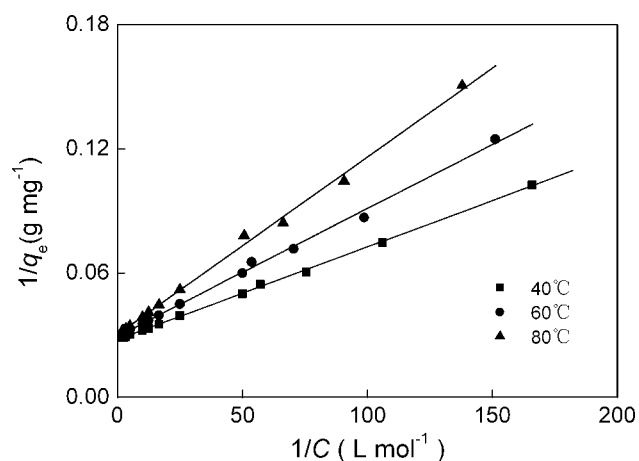

Figure 4 Relation between $1/q_e$ and $1/C$.

TABLE I
Parameters from Modeling the Cobalt ion Adsorption Using the Langmuir Model

T (°C)	R^2	K_a (L mol^{-1})	q_{max} (mg g^{-1})
40	0.9981	62.0	36
60	0.9881	47.4	34
80	0.9864	35.4	33

that the equilibrium adsorption amount increased with the increase of cobalt ion concentration and decreased with the increase of temperature.

Equilibrium data were fitted with the rearranged Langmuir adsorption isotherm which is given as[4]

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{K_a q_{max} C} \tag{5}$$

where q_{max} is the maximum adsorption amount (mg g^{-1}), C(mol L^{-1}) is the equilibrium concentration of cobalt ion in the solution, and K_a is the adsorption equilibrium constant (L mol^{-1}). By fitting the experimental data to the linear form of $1/q_e$ versus $1/C$ (Fig. 4), the model parameters were calculated and given in Table I.

Based on the correlation coefficient (R^2), the adsorption isotherms were well described by the Langmuir equation under various temperatures. The adsorption equilibrium constant (K_a) and the maximum adsorption amount (q_{max}) under 60°C were calculated to be 47.4 L mol^{-1} and 34 mg g^{-1}, respectively. It was also found that both K_a and q_{max} decreased with the increase of temperature and the adsorption order was consistent with the order of the affinity constants (K_a) listed in Table I.

Thermodynamic parameters

Thermodynamic parameters were estimated for the temperature dependence of adsorption equilibrium constants using the van't Hoff equation.[10]

$$\ln K_a = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{6}$$

where R and T are the gas constant and absolute temperature, respectively.

A plot of $\ln K_a$ versus $1/T$ (Fig. 5) was linear with gradient ($-\Delta H/R$) and intercept ($\Delta S/R$). Therefore, the enthalpy (ΔH) and entropy (ΔS) were calculated to be -12.9 kJ mol^{-1} and -107 J mol^{-1} K^{-1} from eq. (6), respectively. The negative enthalpy indicated that the adsorption of cobalt ion on crosslinked PEI membrane was exothermic. The negative entropy indicated that
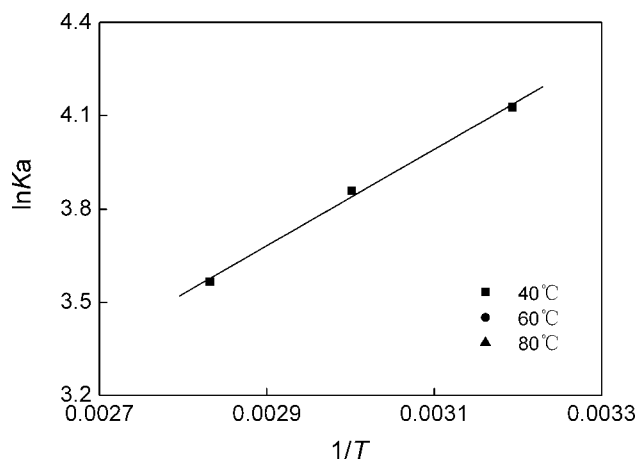

Figure 5 Relation between $\ln K_a$ and $1/T$.

the disturbance in the system decreased during the adsorption process.

CONCLUSIONS

Crosslinking of PEI can provide an insoluble membrane to remove cobalt ion from the aqueous solution. The adsorption of cobalt ion on crosslinked PEI membrane was rapid in the first 10 min and finally reached its equilibrium. The adsorption of cobalt ion on crosslinked PEI membrane obeyed the pseudofirst-order kinetic model. Langmuir model showed a well fit to the experimental data. The enthalpy and entropy of the adsorption indicated that the adsorption of cobalt ion on crosslinked PEI membrane was exothermic and the disturbance in the system decreased during the adsorption process.

References

1. Deng, S. B.; Ting, Y. P. Water Res 2005, 39, 2167.
2. Ghoul, M.; Bacquet, M.; Morcellet, M. Water Res 2003, 37, 729.
3. Justi, K.; Laranjeira, M.; Neves, A.; Mangrich, A.; Favere, V. Polymer 2004, 45, 6285.
4. Zhang, X.; Bai, R. J Colloid Interf Sci 2003, 264, 30.
5. Schweinsberg, D. P.; Hope, G. A.; Trueman, A.; Otieno-Alego, V. Corrosion Sci 1996, 38, 587.
6. Baticle, P.; Kiefer, C.; Lakhchaf, N.; Leclerc, O.; Persin, M.; Sarrazin, J. Sep Purif Technol 2000, 18, 195.
7. Saegusa, T.; Yamada, A.; Kobayashi, S. J Appl Polym Sci 1979, 23, 2343.
8. Liu, Y. L.; Shen, S. G.; Fan, H. M.; Chen, Z. W. Tech Equip Environ Pollution Control 2003, 4, 56.
9. Ho, Y. S.; Mckay, G. Water Res 2000, 34, 735.
10. Angove, M. J.; Johnson, B. B.; Wells, J. D. J Colloid Interf Sci 1998, 204, 93.