



Studies on Novel Zwitterionic Hybrid Membranes: Adsorption Kinetic Models for Cobalt(II) Removal

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A zwitterionic hybrid membrane was prepared *via* the ring-opening of 1,3-propanesultone with the amine groups in the chains of 3-aminopropyl trimethoxysilane and a subsequent sol-gel process. Its adsorption performances for cobalt(II) removal were examined. On the basis of adsorption capacity of cobalt(II) ions on contact time, two-parameter kinetic equations were determined to evaluate the adaptivity of the fitted model. It was found that the adsorption of cobalt(II) ions on the prepared hybrid membrane fitted well with the Lagergren pseudo-second order model. The measurement of intraparticle diffusion confirmed that the adsorption of cobalt(II) ions on the hybrid membrane didn't only governed by intraparticle diffusion. Elovich model evidences that chemisorption didn't occur during the period of cobalt(II) removal. These findings are very useful in the removal of cobalt(II) ions from the stimulated radioactive wastewater and can be potentially used to dispose the radionuclide from the spent radioactive wastewater.

Keywords: Hybrid membrane, Adsorption, Cobalt(II), Kinetic model, Radionuclide.

INTRODUCTION

Radioactive wastewater contains various radionuclides, such as strontium (^{90}Sr), cobalt (^{60}Co) and cesium (^{137}Cs). These radionuclides are harmful to various organisms and the surroundings inhabited^{1,2}. Especially, the nuclear accident at the Fukushima Daiichi Nuclear Power Plant (Japan) has caused great panic among the inhabitants in the region and worried the people around the world³⁻⁵. Thus how to delete or remove the radionuclides from the spent radioactive wastewater attracts much public attention. Among these radionuclides, cobalt (^{60}Co) is one of the major radioactive pollutants and its amount is larger than the others^{6,7}. Consequently, the removal of cobalt(II) from the spent radioactive wastewater is significantly important and highly needed.

To decrease or remove the pollution caused by cobalt(II) ions, various innovative methods are proposed^{1,2,5-7}. Among these, membrane adsorption exhibited obvious advantages over others^{5,8,9}. This is because the radioactive pollutants in the aqueous solution can be adsorbed to the surface of the membrane, meanwhile the waste water can easily permeate through the membrane pore to the other side. Thus membrane adsorption and separation operating can be conducted simultaneously *via* one operating step. As a result, the separation efficiency of membranes can be highly lifted. However, membrane adsorption also encounters some technique difficulties,

such as the selectivity of the produced membranes, membrane fouling and adsorptive mechanism of different types of ionic groups. Especially, the adsorptive mechanism of membranes containing various ionic groups cannot be extensively understood. Their applications for cobalt(II) removal in industrial processes are thus blocked. Therefore the previous study on membrane adsorption for cobalt(II) removal is insufficient and further investigation is essential.

Recently, a series of hybrid membranes are prepared in our laboratory¹⁰⁻¹². These hybrid membranes used as adsorbents have revealed some excellent adsorption properties for heavy-metal ions in aqueous solution. It is believed that these hybrid membranes can also be extended to the field of radionuclide removal from the spent radioactive wastewater. Our interest in the treatment of radioactive wastewater drives us to do more. Consequently, the objective of this study is to evaluate the most suitable adsorption kinetic models for cobalt(II) removal from the stimulated radioactive wastewater.

EXPERIMENTAL

3-Aminopropyl trimethoxysilane (APTMS, purity $\geq 95\%$) was purchased from Jiangsu Chenguang Coincident Dose Co., Ltd. (Danyang City, China) and used without further purification. Poly(vinyl alcohol) (PVA) was purchased from Shanghai Chemical Reagent Co., Ltd. (Shanghai city, China) and used

as received. 1,3-Propanesultone, cobalt(II) chloride (CoCl_2) and other reagents were of analytical grade and used as received.

Membrane preparation: The preparation of zwitter ionic hybrid membrane was performed using the reaction product of 3-aminopropyl trimethoxysilane (APTMS) and 1,3-propane sultone as a hybrid precursor of sol-gel process. The preparation procedure can be described as follows. First, APTMS (about 2g) and 1,3-propanesultone (about 0.5 g) were dissolved in a DMF solution at room temperature and stirred for 2 h to prepare the hybrid precursor. Second, the above-prepared hybrid precursor was added dropwise into 3 % poly(vinyl alcohol) aqueous solution (about 40 g) and stirred for additional 4 h. Subsequently, it was aged for additional 1 h to obtain the coating solution. The coating solution for membrane preparation was thus produced.

To obtain a hybrid membrane, the above-prepared coating solution was spread on a glass plate and air dried for 24 h at room temperature. Subsequently, the hybrid membrane was dried at 60 °C for additional 24 h. The hybrid membrane for cobalt(II) removal could thus be achieved.

Adsorption experiment: The adsorption capacity (q_t) of cobalt(II) ions on the previously prepared hybrid membrane can be calculated using eqn. 1:

$$q_t = \frac{(C_0 - C_R)V}{W} \quad (1)$$

where V is the volume of aqueous CoCl_2 solution (mL), C_0 and C_R are the concentration of initial and remaining CoCl_2 (mol/L), respectively; W is the weight of hybrid membrane (g).

RESULTS AND DISCUSSION

Membrane preparation: The coating solution for the hybrid membrane was obtained *via* sol-gel process, in which the ring-opening reaction of 1,3-propanesultone with the $-\text{NH}_2$ groups in the chains of APTMS was conducted. As a result, the $-\text{N}^+$ - and $-\text{SO}_3^-$ - groups were produced in the molecular chains of hybrid precursor. Due to the molecular chains simultaneously contain anionic and cationic groups, we thus named it as zwitterionic hybrid membrane. The hybrid membrane was obtained *via* the incorporation of hybrid precursor into the aqueous poly(vinyl alcohol) solution and a subsequent drying step. Such incorporation could not destroy the structure of ionic groups, *i.e.* the ionic groups kept intact during the membrane preparation. Therefore the ionic groups can perform the subsequent adsorption experiment.

Adsorption capacity versus contact time: The adsorption capacity of cobalt(II) ions on the prepared hybrid membrane *versus* contact time (t) is presented in Fig. 1.

From Fig. 1, it is interesting to find that the adsorption capacity of cobalt(II) ions increased with the elapsed contact time and reached an equilibrium state as the contact time is larger than 120 min. Consequently, the saturation adsorption time was 120 min. After this time, the adsorption cannot be continually performed. Moreover, to obtain the best fitting adsorption kinetic model, these adsorption data were analyzed using three typical two-parameter kinetic equations, such as Lagergren kinetic model, intraparticle diffusion and Elovich

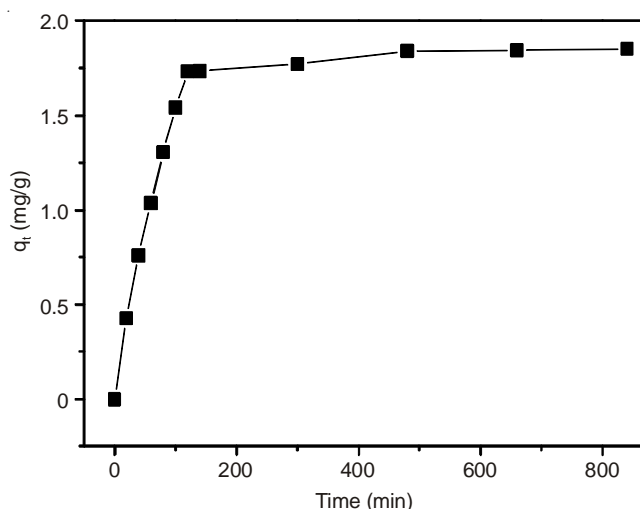


Fig. 1. Plot of adsorption capacity of cobalt(II) ions *versus* contact time

equations, in which the adjusted linear regression (R^2_{adj}) was used to evaluate which model fitting better or worse.

Kinetic model

Lagergren kinetic model: Lagergren kinetic model is a powerful method to assess the adsorption performances of a solid-state adsorbent. Typically, Lagergren pseudo-first order and pseudo-second order kinetic models can be linearly expressed as eqns. 2b and 3b, respectively^{13,14}.

$$q_t = q_e (1 - e^{-k_1 t}) \quad (2a)$$

$$\text{or} \quad \ln(q_e - q_t) = \ln q_e - k_1 t \quad (2b)$$

$$q_t = \frac{q_e^2 k_2 t}{(1 + q_e k_2 t)} \quad (3a)$$

$$\text{or} \quad \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3b)$$

where k_1 (h^{-1}) and k_2 ($\text{g h}^{-1} \text{mmol}^{-1}$) are the rate constant of pseudo-first order and pseudo-second order kinetic model, respectively; q_t and q_e (mg/g) are the adsorption capacity of metal ions (Me^{2+}) at time t (h) and at equilibrium state, respectively.

Fig. 2(a) and 2(b) presents the Lagergren pseudo-first order and pseudo-second order kinetic models for cobalt(II) removal. Table-1 summarizes the related kinetic parameters.

TABLE-I
LAGERGREIN KINETIC PARAMETERS
FOR COBALT(II) REMOVAL

Pseudo-first order model			Pseudo-second order model		
k_1	q_e	R^2_{adj}	k_2	q_e	R^2_{adj}
0.0111	1.204	0.948	0.0122	1.968	0.995

As shown in Table-1, it can be found that the adjusted linear regression coefficient (R^2_{adj}) of Lagergren pseudo-second order model fitted better than that of pseudo-first one. This finding reveals that the Lagergren pseudo-second order kinetic model can be used to describe the adsorption behaviours of cobalt(II) on the prepared hybrid membrane. Such trend is similar to the result reported in an article¹⁵, in which a poly(vinyl alcohol) (PVA)/chitosan magnetic composite was used to

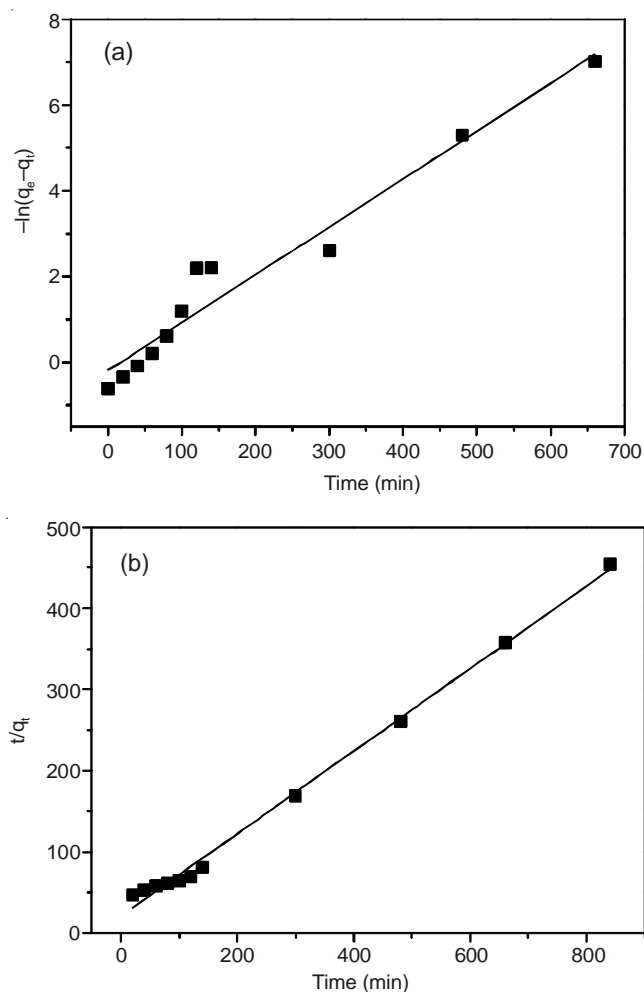


Fig. 2. Lagergren kinetic model for cobalt(II) removal, (a) pseudo-first order, (b) pseudo-second order

remove the Co^{2+} from radioactive wastewater, the adsorption process also followed the Lagergren pseudo-second order kinetic model.

Intraparticle diffusion model: It is reported^{16,17} that when metal ions are adsorbed by an adsorbent, the transport property of metal ions from the solution to the interface can be described *via* intraparticle diffusion model. The intraparticle diffusion model can be expressed as eqn. 4.

$$q_t = x_i + k_p t^{0.5} \quad (4)$$

where q_t (mg/g) is the adsorbed amount at time t (h), k_p ($\text{mg g}^{-1} \text{h}^{-1/2}$) is the intraparticle diffusion rate constant and x_i (mg/g) is the intercept of straight line, which is related to the boundary layer thickness.

Some authors proposed^{16,17} that if the plot of q_t versus $t^{0.5}$ gives a straight line, the adsorption process is solely controlled by intraparticle diffusion. In contrast, if the linear fitting exhibit multi-linear curves, two or more steps will influence the adsorption process.

The intraparticle diffusion model of cobalt(II) adsorption on the hybrid membrane is given in Fig. 3. From Fig. 3, it can be detected that the intraparticle diffusion curve didn't exhibit a straight line. Three straight lines (*i.e.* in the range of 0-20, 20-120 and larger 120 min) were clearly detected, suggesting that the adsorption of cobalt(II) ions on the hybrid membrane didn't governed by intraparticle diffusion, more adsorption

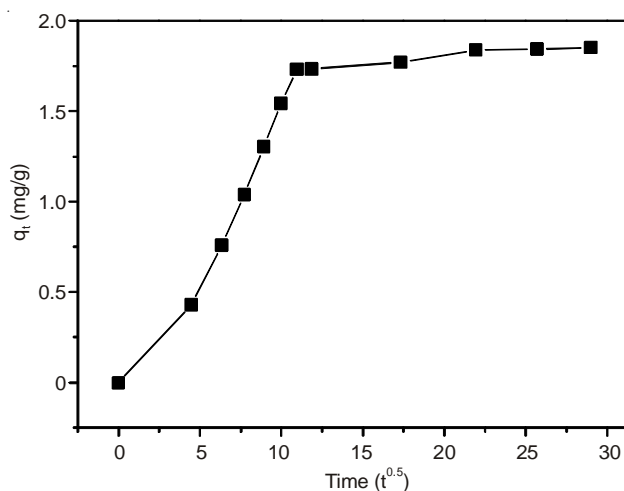


Fig. 3. Intraparticle diffusion model for cobalt(II) removal

steps might be involved. Such three adsorption steps are consistent with the result reported in an article¹⁵, in which a poly(vinyl alcohol) (PVA)/chitosan magnetic composite was used to remove the Co^{2+} from radioactive wastewater, the intraparticle diffusion model was also divided into three straight lines. In present case, the first step can be ascribed to the surface adsorption, which derived from the electrostatic attraction effect of $-\text{SO}_3^-$ groups from the hybrid membrane and cobalt(II) ions in the aqueous solution. Since the electric effect from the ionic groups and cobalt(II) ions dominated the starting period, such adsorption was rapidly. The second line is the intraparticle diffusion process. Because the straight lines did not go through the origin, demonstrating that the effect of boundary layer thickness on the adsorption cobalt(II) ions cannot be ignored. The third line might be related to the adsorption of membrane pore. As hybrid membrane is porous structure. The impact from the pore size of hybrid membrane on cobalt(II) adsorption cannot be ignored.

Elovich model: It is reported¹⁸⁻²⁰ that Elovich equation is mainly used in the kinetic study of chemisorption of gases on the solid surface. Presently, it was proposed¹⁸ that such equation can be used to study the liquid-state sorption and linearly expressed as eqn. 5:

$$q_t = a + b \ln(t) \quad (5)$$

where a (mmol g^{-1}) and b are the Elovich parameters, which can be obtained from the intercept and slope of straight line.

Elovich model for cobalt(II) adsorption on the prepared hybrid membrane was performed and is illustrated in Fig. 4.

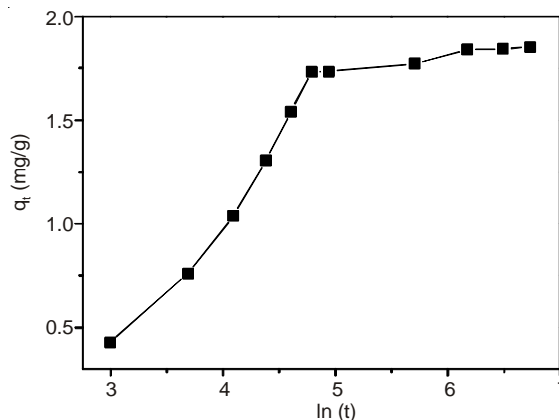


Fig. 4. Elovich model for cobalt(II) removal

As shown in Fig. 4, it can be observed that the curve didn't exhibit a straight line and two adsorption steps were involved. Such trend suggests that cobalt(II) adsorption on the prepared hybrid membrane could not be described using the Elovich model. This finding demonstrates that the effect of chemical adsorption between the active sites on membrane surface and cobalt(II) ions in the solution didn't occur during the adsorption process. Such result further confirmed that the effect of electrostatic attraction from the ionic groups and cobalt(II) ions was one of the major dominating factors.

Conclusions

In this study, a novel zwitterionic hybrid membrane was used as an adsorbent to remove cobalt(II) ions from the stimulated radioactive wastewater. The following results were obtained.

- It was observed that the adsorption of cobalt(II) ions on the hybrid membrane followed the Lagergren pseudo-second order model.
- Intraparticle diffusion model confirmed that the adsorption of cobalt(II) ions on the hybrid membrane didn't uniquely controlled by intraparticle diffusion, three adsorption steps were involved.
- Elovich model revealed that chemisorption had little effect on the adsorption of cobalt(II) ions on the prepared hybrid membrane. The electrostatic attraction effect from the ionic groups and cobalt(II) ions was one of the dominating factors.

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