**Supporting Material**

Preparation of chitosan graft benzo-15-crown-5/non-woven fabric composite membrane for enhanced Pd2+ adsorptive separation

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## *1. Adsorption kinetics of CTS-g-B15C5/NWF composite membrane for Pd2+*

The dynamic adsorption data at different initial concentrations of Pd2+ were depicted in Fig. S1. As shown in Fig. S1, the adsorption amount (*Q*t) increased significantly at the first stage of 60 min, then it reached a plateau after 90 min. The equilibrium adsorption amount (*Q*e) increased with increase of initial concentrations of Pd2+, and the maximum *Q*e was up to 29.1 mg·g−1. The adsorption amount for Pd2+ by various materials was compared in Table S1. It can be found that the maximum adsorption amount of the crown ether functionalized CTS composite membrane was similar to the crown ether functionalized crosslinked chitosan reported by Wang’s group [1, 2].



**Fig. S1.** Adsorption dynamics of Pd2+ on CTS-*g*-B15C5/NWF composite membrane at different initial concentration of Pd2+: (a), 10 mg·L-1; (b), 20 mg·L-1; (c), 30 mg·L-1; (d), 40 mg·L-1.

Table S1. Comparison of the maximum adsorption amount of Pd2+ by various materials

|  |  |  |  |
| --- | --- | --- | --- |
| Adsorbents | Separation  method | Adsorption  amount  (mg·g−1) | Ref. |
| Ethylenediamine immobilized  lignophenol gel | Adsorption | 25.3 | [3] |
| Bayberry tannin immobilized  collagen fiber | Membrane filtration | 22.7 | [4] |
| Crosslinked chitosan with  benzo-15-crown-5 | Adsorption | 38.7 | [1] |
| Crosslinked chitosan with  benzo-18-crown-6 | Adsorption | 33.2 | [1] |
| N-secondary amino-type  benzo-21-crown 7 chitosan | Adsorption | 37.2 | [2] |
| Dithiodiglycolamide  impregnated XAD-16 beads | Adsorption | 29.0 | [5] |
| 5-tert-butyl-2-hydroxybenzaldehyde thiosemicarbazone immobilized mesoporous silica | Adsorption | 171.6 | [6] |
| CTS-*g*-B15C5/NWF composite membrane | Membrane filtration | 29.1 | This work |

To study the adsorption mechanism, the pseudo-first-order (Eq. S1) and pseudo-second-order adsorption (Eq. S2) kinetic models have been developed to describe the adsorption process as shown in Fig. S2 (a) and (b), and the parameters were shown in Table S2. It can be found that the pseudo-first-order model presented a higher value of *R*2 than that of the pseudo-second-order. The calculated *Q*e was in consistent with the actual values from experiments. The results indicated that the adsorption kinetic model of pseudo-first-order was more appropriate for the adsorption process of Pd2+ than that of pseudo-second-order.

 (S1)

 (S2)

where *k*1 (min-1) and *k*2 (mg·g-1·min-1) are the rate constant of the pseudo-first-order and the pseudo-second-order models. *Q*e and *Q*tare the adsorption amount (mg·g-1) at equilibrium and at time *t* (min), respectively.



(a)



(b)

**Fig. S2**. Fitted results of adsorption kinetics. (a) pseudo-first-order adsorption kinetic model, (b) pseudo- second-order adsorption kinetic model.

**Table S2.** The fitting parameters of adsorption kinetic models

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Initial cont. Of Pd2+  (mg·L-1) | Pseudo-first-order | | | | Pseudo-second-order | | |
| *k*1 (×10-2)  (min-1) | *Q*e  (mg·g-1) | *R*2 | *k*2 (×10-3)  (g·mg-1·min-1) | | *Q*e  (mg·g-1) | *R*2 | |
| 10 | 1.77 | 22.08 | 0.9807 | 0.88 | | 25.22 | 0.9433 | |
| 20 | 2.49 | 23.19 | 0.9942 | 1.36 | | 25.67 | 0.9597 | |
| 30 | 3.40 | 26.36 | 0.9936 | 1.81 | | 28.63 | 0.9588 | |
| 40 | 4.39 | 28.69 | 0.9943 | 2.32 | | 30.75 | 0.9654 | |

## *2 Adsorption thermodynamics of CTS-g-B15C5/NWF composite membrane for Pd2+*

In order to further illustrate the adsorption process, thermodynamic parameters, such as ∆*G*o, ∆*H*o, and ∆*S*o, were calculated from equilibrium constant (*K*) of thermodynamic as Eq. (S3) and Eq. (S4):

 (S3)

 (S4)

where ∆*G*o is the changes of standard Gibbs free energy. *K* is obtained by plotting ln(*Q*/*C*e) against *C*e and extrapolating to zero *Q* [7]. ∆*H*o (standard enthalpy) and ∆*S*o (standard entropy) are determined from the slope and the intercept of the regression line of ln*K* ~ 1/*T* as shown in Fig. S3. The values of these thermodynamic parameters were summarized in Table S3. As shown in Table S3, the values of ∆*G*o at different temperature were all negative, which indicates a spontaneous complexing process. This means that the adsorption of Pd2+ ions on the CTS-*g*-B15C5/NWF composite membrane was spontaneous and the crown ether-Pd2+ complexes were formed. In addition, the positive value of *∆H*o indicates an endothermic nature for the formation of crown ether-Pd2+ complexes.



**Fig. S3.** The plot of ln*K* versus 1/*T* for adsorption thermodynamic study of Pd2+ ions on the composite membrane

**Table S3.** Thermodynamic parameters for adsorption of Pd2+ on the composite membrane at different temperature

|  |  |  |  |
| --- | --- | --- | --- |
| *T* (K) | Δ*G*°(kJ·mol­-1) | Δ*H*°(kJ·mol­-1) | Δ*S*°(kJ·(mol·K)-1) |
| 298 | -3.18 |  |  |
| 308 | -3.52 | 7.04 | 0.03 |
| 318 | -3.87 |  |  |

**Reference**

(1) Peng, C.; Wang, Y.; Tang, Y. (1998) Synthesis of crosslinked chitosan‐crown ethers and evaluation of these products as adsorbents for metal ions. *Journal of Applied Polymer Science*, 70(3): 501-506.

(2) Tang, X.H.; Tan, S.Y.; Wang, Y.T. (2002) Study of the synthesis of chitosan derivatives containing benzo‐21‐crown‐7 and their adsorption properties for metal ions. *Journal of Applied Polymer Science*, 83(9): 1886-1891.

(3) Parajuli, D.; Inoue, K.; Kawakita, H.; Ohto, K. (2008) Recovery of precious metals using lignophenol compounds. *Minerals Engineering*, 21(1): 61-64.

(4) Ma, H.; Liao, X.; Xin, L.; Shi, B.I. (2006) Recovery of platinum(IV) and palladium(II) by bayberry tannin immobilized collagen fiber membrane from water solution. *Journal of Membrane Science*, 278(1): 373-380.

(5) Kanagare, A.B.; Singh, K.K.; Bairwa, K.; Ruhela, R.; Shinde, V.; Kumar, M.; Singh, A. (2016) Dithiodiglycolamide impregnated XAD-16 beads for separation and recovery of palladium from acidic waste. *Journal of Environmental Chemical Engineering*, 4(3): 3357-3363.

(6) Awual, M.R.; Hasan, M.M.; Naushad, M.; Shiwaku, H.; Yaita, T. (2015) Preparation of new class composite adsorbent for enhanced palladium (II) detection and recovery. *Sensors and Actuators B: Chemical*, 209: 790-797.

(7) Yan, F.; Liu, H.; Pei, H.; Li, J.; Cui, Z.; He, B. (2017) Polyvinyl alcohol-graft-benzo-15-crown-5 ether for lithium isotopes separation by liquid–solid extraction. *Journal of Radioanalytical and Nuclear Chemistry*, 311(3): 2061-2068.