Preparation of Functionalized Hybrid Membranes Cured at Different Temperatures and Their Adsorptions for Lead(II)

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A series of functionalized hybrid membranes cured at different temperatures were synthesized *via* sol-gel process, in which the $-NH_2$ groups were grafted on the molecular chains by the functionalization of Si-OH groups in silicone with the -OH groups in the PVA chains. FTIR spectra confirmed the existence of functionalized groups in the molecular chains. Thermogravimetric analysis and DSC revealed that the thermal stability of these hybrid membranes could arrive at 240 °C and their degradation temperatures were located within the temperature range of 220-275 °C. Adsorption experiments demonstrated that these hybrid membranes could be used to adsorb lead(II) from water, indicating promising applications in wastewater treatment. Meanwhile, it was confirmed that the curing temperature had some effects on lead(II) adsorption on these hybrid membranes. Moreover, it was found that lead(II) adsorption on these hybrid membranes increased not only with an increase in the initial concentration of solution, but also increased with the elevated solution temperature. The upward trend in lead(II) adsorption capacity with the increasing solution temperature reveals that lead(II) adsorption on these hybrid membranes was a spontaneous process. These findings are very meaningful in the removal of lead(II) from lead(II) containing water using these functionalized hybrid membrane as efficient adsorbents.

Keywords: Hybrid membrane, Adsorption, Lead(II) ions, Curing temperature.

INTRODUCTION

With the rapid development of IT and other electrical industry, leaded materials have been widely applied in household appliances, such as PC and lead-acid rechargeable batteries. The contamination caused by the spent leaded residues has become serious[1-4]. The removal of lead(II) from lead(II)-containing water thus catches much public attention. Consequently, removing lead(II) from the spent device and wastewater is significantly important and highly needed.

To eliminate or reduce lead(II) pollution from the lead(II) containing water or aqueous media, many effective methods are newly developed[1-4]. Among these, adsorption using functionalized hybrid materials or polymers as effective adsorbents has captured much interest[4,5]. However, the reuse of these functionalized adsorbents especially the powder-type ones encounters some technique problems, such as small size of the particle and frangibility of the used materials, which block their further applications in industry. Interestingly, the membrane-type adsorbents indicates more advantage than those powder-type ones. Therefore, the study of membrane-type adsorbents becomes increasingly attractive.

Recently, much effort was made to develop hybrid materials and the related membranes as adsorbents for the removal of heavy-metal ions from aqueous media[3,4,6]. These hybrid adsorbents revealed better adsorption properties for heavy-metal ions in aqueous solution than the commonly used ones. Our continuing interest in these hybrid adsorbents drives us to do more job. Consequently, the objective of this work is to: (1) develop a new type of functionalized hybrid membranes as adsorbents, in which the silica was incorporated to promote their thermal stabilities, (2) examine the effect of curing temperature on the adsorption of lead(II) on these functionalized hybrid membrane.

EXPERIMENTAL

3-Aminopropyl trimethoxysilane (APTMS, purity ≥ 95 %) was purchased from Jiangsu Chenguang Coincident Dose Co., Ltd. (Danyang City, China) and used without further purification. Poly(vinyl alcohol) (PVA, MW: 10000) was purchased from Shanghai Chemical Reagent Co., Ltd. (Shanghai city, China) and used as received. Other reagents were of analytical grade and used as received.

Membrane preparation: The preparation of functionalized hybrid membranes used in this case was presented in a previous article[7]. For the convenience of study, the procedure was described briefly as follows:

First, APTMS (about 3 g) was mixed with a 5 % (weight percentage) aqueous PVA solution (about 60 g) and stirred violently for an additional 1 h to produce the coating solution of hybrid precursor *via* sol-gel process. Subsequently, the previously-prepared coating solution of hybrid precursor was coated on a Teflon plate and air-dried at room temperature for an additional 12 h to obtain the preproduction substance of hybrid membranes. Finally, the preproduction substance of hybrid membrane was cured at different temperatures for 24 h to achieve the final samples (the hybrid membranes cured at 40, 60, 80 and 100 °C were labeled as samples A-D, respectively).

Sample characterizations: FT-IR spectra of products were obtained by using a Shimadzu FTIR-8400S Fourier transform infrared spectrometer in the region of 4000-400 cm^{-1}.

Thermogravimetric analysis (TGA) thermal analysis of the above-prepared samples were measured using a Netzsch STA 409 PC/PG thermogravimetry analyzer, under a nitrogen flow using a heating rate of 10 (°C min^{-1}) from room temperature to 500 °C.

Adsorption experiment: To examine the effect of curing temperature on the adsorption of lead(II) on these hybrid membranes in an aqueous solution, the adsorption experiments were performed at pH 4 by titration.

Procedure can be described briefly as follows: About 1 g of sample was immersed in a 0.01 mol/L aqueous $Pb(NO_3)_2$ solution at pH 4 for 24 h. Subsequently, it was taken out and washed with deionized water. An EDTA solution (0.01mol/L) was used to determine the concentration of lead(II) ions in the remaining solution by titrimetric analysis.

The adsorption capacity ($q_{Pb^{2+}}$) of lead(II) ions onto these samples was calculated using eqn. 1:

$$q_{Pb^{2+}} = \frac{(C_0 - C_R)V}{W} \qquad (1)$$

where V is the volume of the aqueous $Pb(NO_3)_2$ solution (L), C_0 and C_R are the concentrations of the initial and remaining $Pb(NO_3)_2$ (mmol/g), respectively and W is the weight of the tested sample (g).

RESULTS AND DISCUSSION

Membrane preparation: The coating solution of hybrid precursor for samples A-D was obtained *via* sol-gel process, in which the -OH groups in PVA chains and the Si-OH groups in the molecular chains of APTMS will conduct the cross-linking reaction to form the O-Si-O linkage in aqueous PVA solution. Such crosslinking of functionalized groups will increase the thermal stability of the previously-prepared hybrid precursor and the related hybrid membranes. The membrane-type samples A-D can thus be obtained by casting the coating solution of hybrid precursor on a Teflon plate and a subsequent curing process at different temperatures. Because the functionalized groups existed in the molecular chains of APTMS are the -NH$_2$ groups, the related hybrid membranes thus contain -NH$_2$ groups. Therefore, the functionalized hybrid membranes

containing -NH$_2$ groups cured at different temperatures could be synthesized *via* sol-gel process. Since samples A-D emerged as membrane-type species, we thus named them as hybrid membrane adsorbents.

FTIR spectra: Fig. 1 showed the large band at near 3400 cm^{-1} was in the range of stretching vibration from -NH and -OH groups. The absorption peaks at around 3000 cm^{-1} could be ascribed to the C-H stretching and C-H bending vibration of CH$_3$ and CH$_2$ groups, respectively. The strong peak at 1100-1050 cm^{-1} can be ascribed to the overlapping of Si-O-Si, Si-O-C and C-O-C stretching vibration[8].
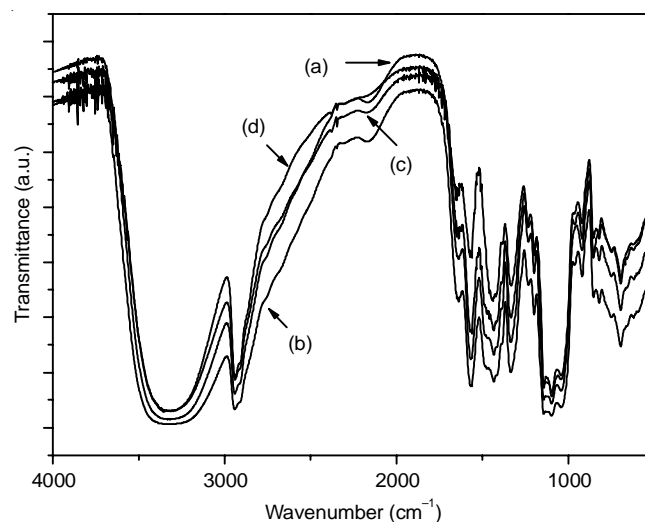

Fig. 1. Curves (a-d) denoted the FTIR spectra of samples A-D, respectively

By comparison the curves (a-d) in Fig. 1, it can be noted that their change trends were similar, demonstrating that the curing temperature did not destroy the functionalized groups in the molecular chains, *i.e.*, the -NH$_2$ groups keep intact as the samples were cured at different temperatures. Due to the existence of -NH$_2$ groups in the prepared hybrid membranes, they can be used to adsorb lead(II) from aqueous solution.

Thermogravimetric analyses: Thermal stability is vital importance for the utilization of hybrid membranes in some harsh environments such as higher temperature or oxidative atmosphere. To explore the thermal stability of samples A-D, TGA thermal analysis was conducted and shows in Fig. 2(a). Meanwhile, the thermal analysis data of samples A-D in TGA curves were analyzed and is listed in Table-1.

TABLE-1
THERMAL ANALYSIS DATA OF SAMPLES A, B, C AND D
OBTAINED FROM THE TGA CURVES

Sample	T_{d5} (ºC)	T_{d20} (ºC)	R_{500} (wt %)
A	117.0	257.3	30.9
B	113.8	255.8	24.1
C	116.9	256.1	10.4
D	111.5	255.5	29.6

It can be found in Fig. 2(a) that for samples A-D, three main degradation steps are easily found and the first degradation temperature was larger than 240 °C. This trend suggests that the thermal stability of samples A-D could reach 240 °C. In addition, it can also be found that for the individual sample,
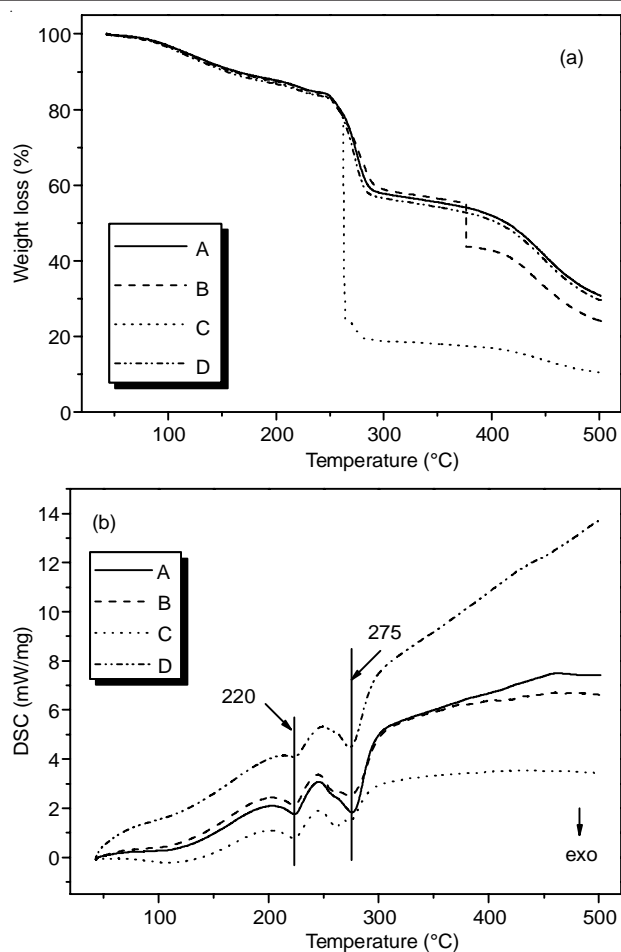
Fig. 2. TGA and DSC curves of samples A-D

indicates a decrease and then increase change trend. Among them sample C had the lowest residual weight (wt %), suggesting that sample C decomposed relatively full, which is consistent with the trend in its lower degradation temperature. The reason can be ascribed to the formation of organic and inorganic moieties in the functionalized hybrid matrix.

DSC analysis: To further examine the degradation behaviours of the previously-prepared samples A-D, DSC measurement was conducted and the associated curves are presented in Fig. 2(b).

It can be seen in Fig. 2(b) that for samples A to D, different amounts of exothermic peaks were observed in the DSC curves. For sample A and D, two strong exothermic peaks were observed in the DSC curves, which mainly centered at around 220 and 275 °C (Table-2). However, for sample B and C, three exothermic peaks were detected in the DSC curves, they are also situated at the temperature range of 220-275 °C (Table-2). This result reveals that the exothermic peaks of samples A-D are mainly located within the range of 220-275 °C and the degradation reaction are occurred in this temperature range, demonstrates that curing temperature did not change the molecular structure of hybrid membranes. The reason can be assigned to the harmonization of organic and inorganic moieties in the hybrid matrix.

TABLE-2
EXOTHERMIC PEAKS OF SAMPLES A, B, C
AND D OBTAINED FROM THE DSC CURVES

Sample	First (°C)	Second (°C)	Third (°C)
A	220	275	-
B	220	257	275
C	220	261	275
D	220	275	-

Adsorption capacity of lead(II) ions: Adsorption of heavy-metal ions using adsorbents is considered as one of the most effective methods to remove environmental pollutants from aqueous media[9,10]. To investigate their adsorption behaviours of the previously-prepared hybrid membranes cured at different temperatures for lead(II), adsorption experiments of samples A-D were performed. The main influencing factors, such as initial concentration of solution and solution temperature, were examined.

Adsorption capacity of lead(II) ions *versus* initial concentration of solution: To study the adsorption behaviours of lead(II) on the previously-prepared hybrid membranes, the adsorption capacity of lead(II) on samples A-D in different concentrations of solution was determined and presented in Fig. 3.

From Fig. 3, it can be seen that for the individual sample, the adsorption capacity of lead(II) all increased with an increase in the initial concentration of solution. However, considering samples A-D, different change trends were observed. For example, the adsorption capacity of lead(II) on samples A-D indicated increased with the elevated curing temperature from sample A to D as the initial concentration of solution was lower than 0.02 mol/L, which indicated an upward trend as the curing temperature was elevated. In contrast, such trend was changed as sample C > A > B > D as the initial concentration of solution
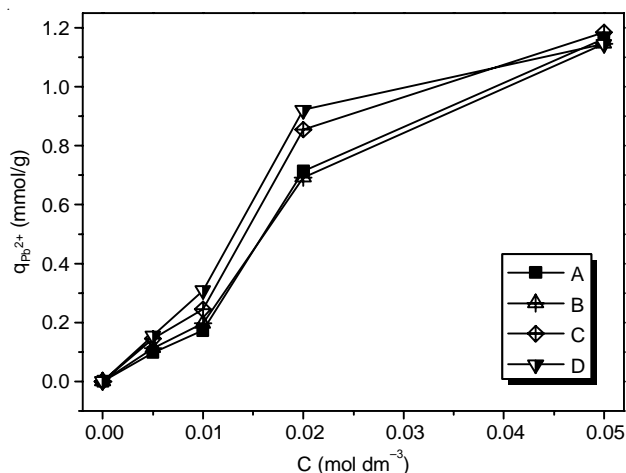
its degradation curve in weight loss (%) indicated different change trends and two sharp degradation stages were detected for samples B and C. For example, for sample B, a sharp degradation stage was observed as the temperature was larger than 380 °C. Meanwhile, for sample C, the temperature of sharp degradation stage was decreased to near 250 °C. Considering sample D, such sharp degradation stage was disappeared and indicated the same change trend as that of sample A. By comparison the degradation temperature, it can be noted that sample C is easily decomposed. This phenomenon demonstrates that the curing temperature plays an important role on the structural formation of hybrid membranes. The theoretical explanation to this phenomenon can be seen as follows. The decomposition of functionalized groups might be responsible such trends as the degradation temperature was elevated. In addition, the further formation of hybrid matrix would also be the mainly influencing factors.

Moreover, it is interesting to find that the temperature of degradation (T_d) at 5, 20 % weight loss (*i.e.*, T_{d5} and T_{d20}) shows the similar change trends, they centered at near 114 and 255 °C, respectively (Table-1). Meanwhile, it can also be found that the weight loss (%) sharply decreased when the T_d value was larger than the T_{d20}, suggesting that the decomposition of functionalized groups has been accelerated.

Furthermore, it can be observed that the residual weight (wt %) at 500 °C (R_{500}) are located at 30.9, 24.1, 10.4 and 29.6 % for samples A to D, respectively (Table-1), which

Fig. 3. Lead(II) adsorption capacity *versus* initial concentration of solution

was larger than 0.02 mol/L. These findings demonstrated that curing temperature of hybrid membranes has some effects on their adsorptions for lead(II).

The reason can be assigned to the effect of lead(II) on the functionalized groups. At lower initial concentration of solution, due to the existence of water, the complex of amino group in the hybrid membranes with lead(II) will dominate the adsorption of lead(II) on them. In contrast, at higher initial concentration of solution, the amount of water becomes less. Thus molecular structure of hybrid membranes will also partly impact the lead(II) on the functionalized hybrid membranes. Thus it will influence the adsorption capacity of lead(II) on samples A-D. Among samples A-D, sample C had the lowest residual weight (wt %) at 500 °C (Table-1). Accordingly, sample C had the most amount of silica. Due to its porous nature of silica, it will favor the adsorption capacity of lead(II) at higher initial concentration of solution.

Adsorption capacity of lead(II) ions *versus* solution temperature: It is well accepted that adsorption of an adsorbent for a species in water possibly is an endothermic or exothermic process, which is highly affected by temperature. To determine the impact of solution temperature on lead(II) adsorption, adsorption experiment at different solution temperatures for lead(II) was performed (Fig. 4).
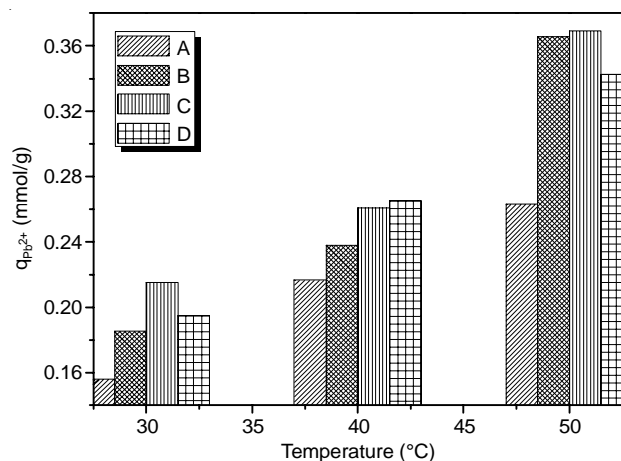

Fig. 4. Lead(II) adsorption capacity *versus* solution temperature. The samples were immersed in 0.01 mol/L aqueous Pb(NO₃)₂ solution for 24 h

It can be seen that the adsorption capacity of lead(II) on the individual sample all increased with the elevated solution temperature, suggesting that lead(II) adsorption on these hybrid membranes was an endothermic and a spontaneous process. By comparison the adsorption capacity of lead(II) on samples A-D at the fixed temperature, it can be observed that their change trends are different. For example, at 30 °C, the adsorption capacity of lead(II) followed such trend: sample A < B < D < C, *i.e.*, sample C had the largest adsorption capacity of lead(II), such change trend is disagreement with the elevated curing temperature from sample A to D. At 50 °C, the adsorption capacity of lead(II) followed the following trend: sample A < D < B < C, *i.e.*, sample C also had the largest adsorption capacity of lead(II), such tendency is also inconsistent with the elevated curing temperature from sample A to D. However, at 40 °C, the change trend in the adsorption capacity of lead(II) is consistent with the elevated curing temperature from sample A to D. This finding evidences the effect of curing temperature on lead(II) adsorption on the prepared hybrid membranes, demonstrating that lead(II) adsorption on the prepared hybrid membranes could be artificially controlled *via* the adjustment of curing temperature.

Conclusion

Novel functionalized hybrid membranes containing -NH₂ groups were prepared and their adsorptions for lead(II) from aqueous solution were examined. It was found that lead(II) adsorption on these hybrid membranes was an endothermic and a spontaneous process. Meanwhile, it was also found that the curing temperature had some impacts on the adsorption properties of functionalized hybrid membranes, indicating that the adsorption properties of hybrid membranes can be artificially controlled *via* the modification of curing temperature.

REFERENCES

1. K.R.A. Sidhaarth and J. Jeyanthi, *Asian J. Chem.*, **25**, 9920 (2013).
2. M.R. Awual, M. Ismael, T. Yaita, S.A. El-Safty, H. Shiwaku, Y. Okamoto and S. Suzuki, *Chem. Eng. J.*, **222**, 67 (2013).
3. X. Wang, W.X. Zhang, J.S. Liu and L.L. Wu, *Asian J. Chem.*, **25**, 6575 (2013).
4. J.S. Liu and X. Wang, The *Sci. World J.*, Article ID 897159 (2013).
5. K.-H. Kim, A.A. Keller and J.-K. Yang, *Colloids Surf. A*, **425**, 6 (2013).
6. Q. Dong, J.S. Liu, L. Song and G. Shao, *J. Hazard. Mater.*, 186, 1335 (2011).
7. J.S. Liu, L.L. Wu and X.H. Chen, *Desalin. Water Treat.*, doi:10.1080/19443994.2014.898000.
8. C.M. Wu, T.W. Xu and W.H. Yang, *J. Solid State Chem.*, **177**, 1660 (2004).
9. D.H.K. Reddy, K. Seshaiah, A.V.R. Reddy, M.M. Rao and M.C. Wang, *J. Hazard. Mater.*, **174**, 831 (2010).
10. A.A. Atia, A.M. Donia and A.M. Yousif, *Sep. Purif. Technol.*, **61**, 348 (2008).