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Hybrid membrane adsorbents: preparation and their adsorptions for copper(II) ions

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ABSTRACT

A new type of hybrid membrane adsorbents was prepared via a sol–gel reaction. As typical examples, the adsorption performances of samples D and E for copper(II) ions were investigated. TGA measurement showed that the thermal stability of these hybrid membrane adsorbents could exceed 240˚C. DSC thermal analysis displayed that the incorporation of 3-aminopropyl triethoxysilane (APTES) into 3-methacrcypropyl trimethoxysilane (MPTMS) did not result in larger transformation of crystallization in these samples. Adsorption experiments confirmed that the adsorption of copper(II) ions onto the samples D and E followed the Langmuir isotherm model, suggested that such adsorption was Langmuir monolayer adsorption. The negative Gibbs free energy values further demonstrated that copper(II) adsorption onto these hybrid membrane adsorbents was spontaneous in nature. The desorption experiment revealed that these samples could be effectively regenerated via aqueous HCl solution as a desorbent. These findings imply that these hybrid membranes are promising adsorbents in the separation and recovery of copper(II) ions from the copper-curing wastewater or the contaminated water.

Keywords: Hybrid membrane; Adsorbent; Adsorption; Copper(II); Water treatment

1. Introduction

With the wide applications of copperware and coppered materials in industry and household appliances, water contamination caused by toxic copper(II) ions has become increasingly serious [1–4]. Currently, it is well accepted that toxic copper(II) ions cannot be effectively biodegraded in nature, and are easily accumulated in the human body and other organisms. Its toxic effect will induce some diseases in the human body. It was reported [5] that an excess intake of Cu^{2+} ions by humans will cause gastrointestinal distress, even liver or kidney damage. Consequently, removing copper(II) ions from the spent coppered residues and the contaminated water has significant importance, since it has attracted much public attention in recent years.

To remove or delete the toxic copper(II) ions from the spent coppered residues and the contaminated water, many innovative techniques have been newly proposed [6–10]. Among them, adsorption using functionalized hybrid materials or the related hybrid membranes as adsorbents is considered as one of the most effective methods [6–10]. This is because copper(II)

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ions can be chemically bonded by inorganic/organic hybrid matrices to produce the complex species. However, the use of these functionalized hybrid materials also confronts some technique problems, such as frangibility of the materials used and recovery problem of tiny particle size, which has blocked their further applications in industrial processes. Thus, adsorption using the functionalized hybrid membranes as solid adsorbents becomes more and more attractive.

Recently, much effort was made to prepare the functionalized hybrid materials and the related hybrid membranes used as adsorbents for the removal of toxic copper(II) ions from aqueous solutions [9,11–13]. Our continuing interest in these solid hybrid adsorbents makes us to do more. Therefore, to develop a new type of membrane-type hybrid adsorbent for the removal of copper(II) ions from water, herein, a novel route for the preparation of hybrid membrane adsorbents via a sol–gel reaction will be reported and their adsorption performances for copper(II) ions are detected. Compared with the previous articles [11–13], the particularity of this new route is that (1) the hybrid adsorbent was shaped as membrane-type form, which is different from the conventional particle-type adsorbents; and (2) the functionalized groups (–NH_2) were incorporated into the hybrid membrane adsorbents via a sol–gel reaction between PVA and silicone containing the amino groups (–NH_2). Moreover, their adsorption properties for copper(II) ions were examined as a typical model for the removal of toxic heavy-metal ions from water.

2. Experimental

2.1. Materials

3-Methacrcypropyl trimethoxysilane [MPTMS, $CH_2{=}C(CH_3)COOC_3H_6Si(OCH_3)_3$] and 3-aminopropyl triethoxysilane [APTES, $H_2\,N(CH_2)_3Si(OC_2H_5)_3$] were purchased from Jiangsu Chenguang Coincident Dose Co. Ltd. (Danyang City, China) and was used without further purification. Poly(vinyl alcohol) (PVA, DP: 1750) 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.

2.2. Preparation of the hybrid membrane adsorbents

The preparation of the hybrid membrane adsorbents could be described briefly as follows. First, 40 g PVA was dissolved in deionized water to produce the 5% aqueous PVA solution. Second, proper amount of MPTMS and APTES (the mass ratio of MPTMS and APTES in the samples A–E was 4:0, 4:1, 4:2, 4:4, and 0:4, respectively) was dissolved in a DMF solution (20 mL) and stirred for additional 2 h to prepare the hybrid precursor. Subsequently, the previously produced hybrid precursor was added into the above-prepared aqueous PVA solution and was stirred vigorously at room temperature for additional 24 h to fabricate the coating solution of PVA-based hybrid membranes. Third, the coating solution of PVA-based hybrid membranes was aged for 24 h and then cast onto a Teflon plate, air-dried at room temperature for additional 24 h. To clean the unreacted materials and other impurity, the hybrid membrane was rinsed with methanol for three times and dried at 60℃ for additional 12 h. The hybrid membrane adsorbents (labeled as samples A–E, respectively) could thus be obtained. To increase the membrane thickness, this step might be repeated several times.

2.3. Sample characterizations

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) thermal analyses of the samples were measured with a Netzsch STA 409 PC/PG thermogravimetry analyzer under a nitrogen flow at a heating rate of 20℃/min from room temperature to 500℃.

2.4. Adsorption experiments

Adsorption experiments for copper(II) ions removal were established in a way as described in our previous publications [11–13], in which the copper(II) ions were used as the adsorption medium. The adsorption capacity of copper(II) ions ($q_{Cu^{2+}}$) was determined by titrimetric analysis. To decrease the testing errors, the final results were the mean values of thrice testing. The $q_{Cu^{2+}}$ value was calculated with Eq. (1):

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

where, V is the volume of the aqueous $Cu(NO_3)_2$ solution (mL); C_0 (mol/dm^3) and C_R are the concentrations of the initial and remaining $Cu(NO_3)_2$ (mol/dm^3), respectively; and W is the weight of the examined sample (g).

To determine the optimal pH scale for copper(II) adsorption onto the samples A–E, the initial pH of the solution was first examined, in which the pH value of the solution was adjusted with 0.01 mol/L aqueous NaOH or HCl solution. For the adsorption kinetic studies, the samples were immersed in a 0.1 mol/dm^3 aqueous $Cu(NO_3)_2$ solution for different adsorption times. Meanwhile, the adsorption isotherm was obtained through changes in the initial concentration, which ranged from 0.01 to 1.0 mol/dm^3, for 24 h.

Moreover, the desorption efficiency (%) of samples A–D was measured by titrimetric analysis with aqueous HCl, HNO_3, or H_2SO_4 solution (0.1 mol/dm^3) as the desorbent.

3. Results and discussion

3.1. Preparation of the hybrid membrane adsorbents

The coating solution for the PVA-based hybrid membranes was prepared by the hydrolysis and condensation of –OH groups in PVA, $[CH_2CH(OH)]_n$, with the functionalized Si–OH groups in the hybrid precursor via a sol–gel process, in which both the MPTMS and the APTES conducted the alcoholysis and condensation reaction to fabricate the hybrid precursor via an Si–O–Si linkage between the Si–OH groups from the MPTMS and APTES. Subsequently, the hybrid membrane adsorbent could be obtained via casting the cross-linked mixed solution on the Teflon plate and air-dried process.

Considering the above-prepared membranes contained the inorganic ingredient Si, we thus categorized them as inorganic–organic hybrid membranes.

Notice that, in this new route, the functionalized groups (i.e. $–NH_2$ groups) were directly incorporated into the hybrid membranes via a sol–gel process. Meanwhile, inorganic ingredient Si was also introduced into these hybrid membranes during the formation of membranes, thus it will conduce to an increase in the thermal stability of the previously prepared hybrid membrane adsorbents as expected.

3.2. TGA study

To examine the thermal stability of the prepared samples A–E, TGA measurement was conducted. The related curves are presented in Fig. 1. Meanwhile, the thermal analysis data from these curves are tabulated in Table 1.

As presented in Fig. 1, it is interesting to find that for samples A–E, their change trends in weight loss (%) were similar, and two degradation stages could be observed. Accompanying these degradation steps, several exothermic peaks were found in the DSC curves of samples A–E (see Fig. 2). The first weight loss below 300℃ was the evaporation of solvents and the degradation of organic compositions in the samples. The second weight loss higher than 300℃ was the further degradation of functionalized groups and the formation of the hybrid network between the organic and inorganic moieties.

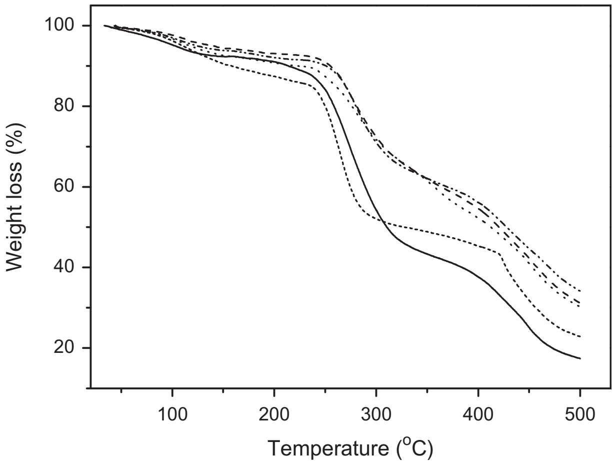

Fig. 1. TGA curves of samples A (—), B (dash line), C (dash dot dot line), D (dot line), and E (short dash line).

Table 1
Thermal analysis data of samples A–E from the TGA curves

Sample	T_{d10} (°C)	T_{d20} (°C)	R_{500} (wt%)
A	213.92	258.53	17.41
B	255.07	280.72	31.15
C	250.74	279.97	34.13
D	223.63	276.30	30.27
E	158.03	249.72	22.87

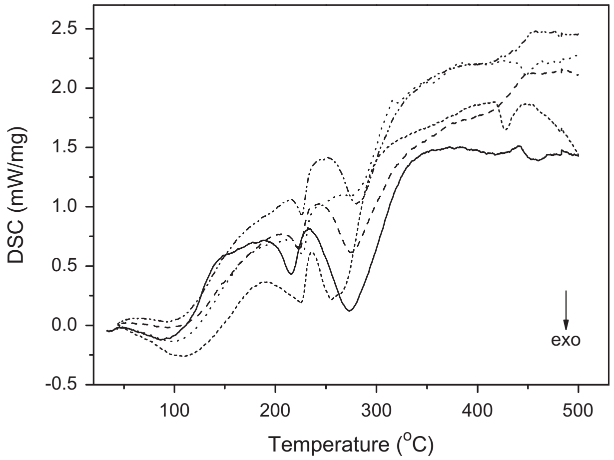

Fig. 2. DSC curves of samples A (—), B (dash line), C (dash dot dot line) D (dot line), and E (short dash line).

Moreover, it is shown in Fig. 1 that the degradation temperatures at the weight loss of 10 and 20% (T_{d10} and T_{d20}, respectively) displayed the similar change trends: it increased from sample A to B and reached the maximal value; subsequently, it decreased from sample C to E. Such change trends suggested that proper addition of APTES into the MPTMS can increase the thermal stability of the prepared hybrid membranes. But excess incorporation of APTES into the MPTMS will decrease their thermal stability. These results demonstrate that the thermal stability of hybrid membrane adsorbents can be adjusted via the addition of APTES into the MPTMS. Furthermore, it is also shown in Fig. 1 that the weight loss (%) of the samples A–E rapidly increased as it was larger than 85% (the degradation temperature was around 240℃ at this point). This outcome implied that the degradation step was accelerated when the sintering temperature was elevated to some extent. The reason can be ascribed to the degradation of organic ingredients and partial dissociation of functionalized groups in the relatively high-temperature conditions.

Moreover, it can be noted in Fig. 1 that for samples A–E, the residue at 500℃ (R_{500}, wt%) showed a similar change trend to those of T_{d10} and T_{d20} (cf. Table 1). However, the position of maximal value of residue was moved to sample C, which was inconsistent with the mass ratio of APTES and MPTMS into the hybrid membrane adsorbent as the theoretical estimation. This trend revealed that the amount of residue in the hybrid matrix possibly depended on the molecular structure of silicone and the partition of functionalized groups.

On the basis of the previous findings, it can be reasoned out that the thermal stability and amount of residue in the hybrid membrane adsorbents could be artificially adjusted via the proper addition of inorganic species into the hybrid precursor.

3.3. DSC thermal analysis

Presently, it is well accepted [14] that DSC thermal analysis is a helpful tool to detect the glass transition temperature (T_g) and the crystallization transformation temperature (T_c) of a material via the measurement of the position of endothermic or exothermic peak in the DSC curves. To determine the glass transition temperature and the crystallization transformation of samples A–E, DSC thermal analysis was carried out and the related DSC curves are depicted in Fig. 2. Meanwhile, the temperature of exothermic peak in the DSC curves is listed in Table 2.

As shown in Fig. 2, the DSC curves of samples A–E indicated different change tendencies. For example, for samples B and C, their change trends in the exothermic and endothermic peaks were identical and three exothermic and two endothermic peaks were detected. In contrast, for samples A, D, and E, their change trends in the exothermic and endothermic peaks were similar, and four exothermic and two endothermic peaks were spotted.

It was reported [15] that, in DSC curves, single or multiple endothermic peaks were the crystal melting, whereas the exothermic peak can be considered as the crystallization. On the basis of this result, it can be deduced that the glass transition temperature (T_g) of samples A–E was 92.09, 106.75, 92.82, 101.16, and 109.96℃, respectively (cf. Table 2). In addition, it can be found that the first crystallization temperatures (T_{c1}'s; i.e. the second exothermic peak) of samples A–E were positioned at 222.20, 224.47, 226.03, 226.73, and 225.29℃, respectively; which showed a slight increase in the crystallization temperature as the incorporation of APTES into the MPTMS. Moreover, it can also be found that the second crystallization temperatures (T_{c2}'s; i.e. the third exothermic peak) were situated at 273.29, 276.92, 280.22, 274.02, and 255.09℃, respectively; it showed a first upward and then a downward trend. These findings suggested that the incorporation

Table 2
Temperatures of exothermic peak (ºC) for samples A–E from the DSC curves

Sample	First	Second	Third	Fourth
A	92.09	222.20	273.29	452.73 (broader)
B	106.75 (weaker)	224.47	276.92	–
C	92.82 (weaker)	226.03	280.22	–
D	101.16	226.73	274.02 (weaker)	448.30
E	109.96	225.29	255.09	426.84

of APTES into the MPTMS did not result in larger transformation of crystallization in these samples. The reason can be assigned to the Si–O–Si linkage between the Si–OH groups from the MPTMS and the APTES in the hybrid precursor was a sol–gel process, which does not change the molecular structure of hybrid matrix. Accordingly, it does not cause the transformation of crystallization in these samples.

3.4. Adsorption of the copper(II) ions

To understand the effect of silicone addition on the adsorption of copper(II) ions onto the previously prepared hybrid membrane adsorbents, adsorption experiments of samples A–E for copper(II) ions under the static condition were performed and are given in Fig. 3. It is interesting to find that the adsorption capacity of copper(II) ions onto the samples A–E increased from sample A to E, i.e. it increased with the elevated amount of APTES into the MPTMS. This result suggests that the addition of the APTES into the hybrid membrane adsorbents favored the adsorption of copper(II) onto them. The reason can be ascribed to the existence of $-NH_2$ groups into the molecular chains of APTES. Considering samples D and E (i.e. the original membrane) indicated relatively larger adsorption capacity for copper(II) ions in this case, for the convenience of copper(II) adsorption study, the adsorption behavior of samples D and E for copper(II) ions was, therefore, selected as a typical example to examine the adsorption performances of copper(II) on the prepared hybrid membrane adsorbents. Some chief influencing factors, such as the initial pH, contact time and initial solution concentration, were examined. Meanwhile, based on the adsorption data, the corresponding thermodynamic parameter, Gibbs free energy (ΔG) was calculated. To further examine the adsorption mechanism of the copper(II) ions on these hybrid membrane adsorbents, the experimental data were correlated with the Langmuir and Freundlich two-parameter isotherm equations.

3.4.1. Effect of the initial pH

The initial pH of the solution had marked influence on the adsorption of heavy metal ions onto the adsorbents; this was because the metal ions could be deposited in the solution for the pH value of solution was elevated to higher than 7. To obtain the optimal pH value for copper(II) adsorption onto samples D and E, the pH in the range of 1–5 at a concentration of 0.03 mol/dm^3 for 24 h was selected to examine the effect of the initial pH on copper(II) adsorption. The obtained experimental results are illustrated in Fig. 4.

As shown in Fig. 4, it can be found that the adsorption capacity of copper(II) ions onto samples D and E increased with the elevated initial pH and reached its highest value at around pH 4.37. On the basis of this finding, aqueous $Cu(NO_3)_2$ solution at pH 4.37 was thus chosen as the adsorption medium to explore the adsorption behaviors of copper(II) ions onto the previously prepared hybrid membrane adsorbents, i.e. samples D and E.

It should be emphasized that the pH of the residual solution may vary with the change in the adsorption capacity of copper(II) ions during the course of adsorption. However, such change in the pH value of the residual solution is a continue process with the

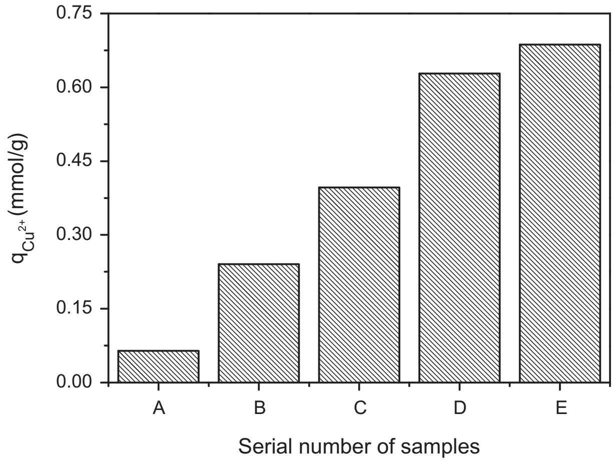

Fig. 3. The adsorption capacity of copper(II) on the prepared samples A–E.

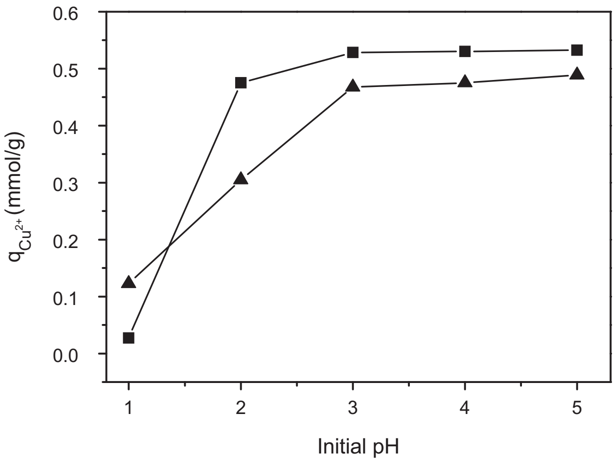

Fig. 4. Initial pH vs. the adsorption capacity of copper(II) ions on samples D (solid uptriangle) and E (solid square).

elapsed time. Consequently, it is hard to precisely determine the pH value in a continue process. Meanwhile, it is unnecessary to record these data. Because the adsorption experiment in this case was conducted in a static condition. The change of the residual solution pH during the course of adsorption was slight. Thus, it has little effect on the adsorption capacity of copper(II) ions. For these reasons, the change of the residual solution pH during the course of adsorption was not recorded in this manuscript.

3.4.2. Adsorption capacity vs. contact time

The adsorption capacity of copper(II) ions onto samples D and E vs. the contact time t in the time range of 0–24 h was conducted and is presented in Fig. 5.

As shown in Fig. 5, the adsorption capacity of copper(II) ions onto samples D and E rises with the elapsed contact time. However, it can be noted that although the adsorption capacity of copper(II) ions onto sample E is larger than that onto sample D, and the time for copper(II) adsorption reached to the equilibrium state is different. For example, for sample E (i.e. the original membrane), the time to the equilibrium state was about 3 h. But the equilibrium time of sample D was decreased to near 2 h. Compared with the original membrane adsorbent E, it indicates that the incorporation of the MPTMS into the hybrid membrane adsorbents had decreased the adsorption capacity of copper(II) ions, but it shortened the adsorption time of copper(II) ions. This result implies that both the adsorption equilibrium time and the adsorption capacity of copper(II) ions onto these hybrid membrane adsorbents can be artificially adjusted by the hybridization of different hybrid precursors.

3.4.3. Adsorption isotherms

The adsorption isotherms can be obtained through the dependency of adsorption capacity of copper(II) ions on the initial solution concentration. As a typical example, the adsorption isotherm of copper(II) ions onto samples D and E was measured and is presented in Fig. 6.

As shown in Fig. 6, it can be noted that the adsorption capacity of copper(II) ions onto samples D and E rised with the elevated initial solution concentration. However, by comparison of the adsorption capacity of copper(II) ions onto samples D and E, it can also be noted that the $q_{Cu^{2+}}$ value of sample E (i.e. the original membrane) is larger than that of sample D. This finding indicates that the incorporation of the MPTMS into the hybrid membrane adsorbents did not help to increase the adsorption capacity of copper(II) ions onto the hybrid membranes. Such result implies that the adsorption capacity of copper(II) ions onto these hybrid membrane adsorbents can be artificially controlled by the hybridization of different species.

3.4.4. Adsorption mechanism

Presently, it is well accepted that both the Langmuir and Freundlich isotherm equations are two helpful tools to examine the adsorption behaviors of metal ions on the interface of a solid material. The Langmuir isotherm equation is based on monolayer

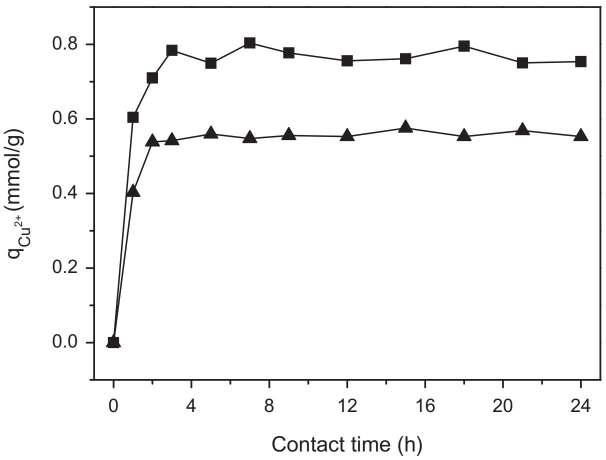

Fig. 5. Adsorption capacity of copper(II) ions on samples D (solid uptriangle) and E (solid square) vs. contact time.

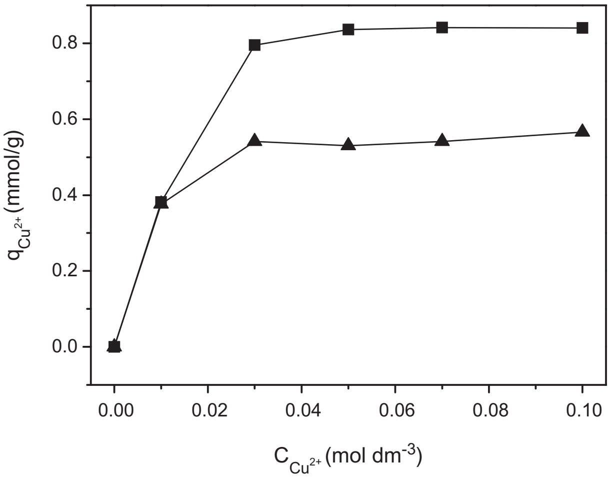

Fig. 6. Adsorption capacity of copper(II) ions on samples D (solid uptriangle) and E (solid square) vs. concentration.

adsorption onto the active reaction sites of the adsorbent and can be expressed as Eq. (2) [16–18]:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m b} \tag{2}$$

where q_e is the adsorption capacity (mmol/g) of the metal ions in the equilibrium state, C_e is the equilibrium concentration (mol/dm^3) of metal ions in the liquid phases. Q_m (mmol/g) and b (dm^3/mol) are Langmuir constants, which can be calculated from the intercept and slope of the linear plot based on C_e/q_e vs. C_e.

Generally, the Freundlich isotherm equation was considered as the adsorption occurred on a heterogeneous surface with uniform energy; it can be linearly expressed with Eq. (3b) [16–18]:

$$q_e = k_F C_e^{\frac{1}{n}} \tag{3a}$$

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \tag{3b}$$

where k_F [(mmol/g) (mol/dm^3)$^{-1/n}$] and n are the Freundlich constants, they can be calculated from the slope and intercept of the linear plot according to log q_e vs. log C_e.

Fig. 7(a) and (b) presents the Langmuir and Freundlich adsorption isotherm of copper(II) ions. On the basis of Fig. 7(a) and (b), the Langmuir and Freundlich isotherm parameters were calculated and are tabulated in Table 3. As shown in Table 3, it can be found that the experimental data fit well with the Langmuir isotherm equation (R^2 > 0.999). In contrast, these data fit worse with the Freundlich isotherm equation (R^2 < 0.940). Such observation evidences that copper(II) adsorption onto these hybrid membrane adsorbents was the Langmuir monolayer adsorption rather than the heterogeneous surface adsorption.

Furthermore, it was reported [16–18] that for the Langmuir isotherm model, the separation factor or equilibrium parameter (R_L) could be used to further determine the favourability of adsorption. When the R_L value is within $0 < R_L < 1$, it is favorable the adsorption of metals on an adsorbent. In contrast, it is unfavorable in its adsorption. The related R_L value can be calculated with Eq. (4) [16–18]:

$$R_L = \frac{1}{(1 + bC_0)} \tag{4}$$

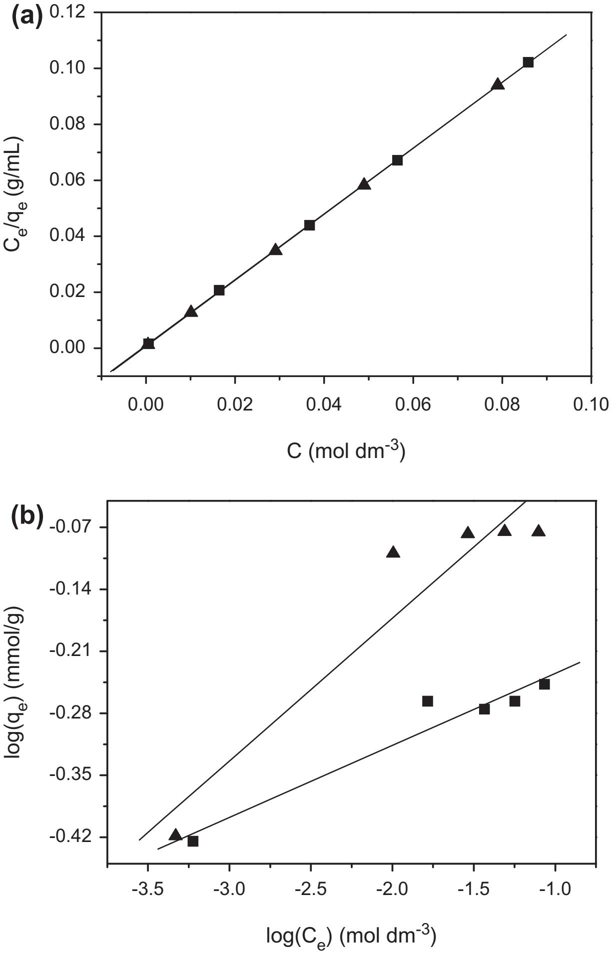

Fig. 7. Adsorption isotherm of copper(II) ions on samples D (solid square) and E (solid uptriangle): (a) Langmuir model and (b) Freundlich model.

where C_0 (mol/dm^3) is the initial solution concentration and b is the Langmuir equilibrium constant (dm^3/mol).

Table 4 summarizes the calculated R_L values. As shown in Table 4, it can be seen that the R_L values of samples D and E were all within $0 < R_L < 1$; this trend suggested that copper(II) ions' adsorption onto these hybrid membrane adsorbents was favorable. Such result can be further confirmed by the calculation of ΔG as discussed later. This finding confirmed that these samples are promising adsorbents for copper(II) ions' removal from the wastewater or the contaminated water.

3.4.5. Gibbs free energy

Thermodynamic parameter, ΔG, is a useful tool to determine the adsorption performances of heavy metal

Table 3
Langmuir and Freundlich isotherm parameters for copper(II) adsorption

	Langmuir			Freundlich		
Sample	Q_m (mmol/g)	b (dm^3/mol)	R^2	k_F [(mmol/g) $(mol/dm^3)^{-1/n}$]	n	R^2
D	0.850	1236.722	0.999	0.702	12.295	0.937
E	0.847	1866.580	0.999	1.411	6.205	0.900

Table 4
The calculated R_L values based on the Langmuir isotherm constant

	R_L value	
C_0 (mol/dm^3)	D	E
0.01	0.07481	0.05085
0.03	0.02625	0.01754
0.05	0.01591	0.0106
0.07	0.01142	0.0076
0.1	0.00802	0.00533

ions on a solid-state adsorbent. Presently, it was reported [19,20] that for the Langmuir adsorption process, the ΔG value can be calculated with Eq. (5):

$$\Delta G = -RT \ln b \tag{5}$$

Where, R is the gas constant (8.314 J/mol K), and T is the absolute temperature (K).

The ΔG values for the copper(II) adsorption on samples D and E were calculated and are tabulated in Table 5. As listed in Table 5, the ΔG values were all negative for samples D and E. This result demonstrates that copper(II) adsorption onto these hybrid membrane adsorbents was spontaneous in nature, which further corroborated the findings obtained from R_L values.

3.4.6. Surface appearance

To further confirm the adsorption of copper(II) ions onto the previously prepared hybrid membrane adsorbents, the comparison of the surface appearance of the adsorbed sample with the original one was performed. As a typical example, the surface appearance of the original sample D and the adsorbed one is presented in Fig. 8.

It can be found that the surface color of the original sample D is transparent (left in Fig. 8). In contrast, the surface color of the adsorbed sample D changes into dark green (right in Fig. 8). This change in the surface color of the adsorbed sample D demonstrates that copper(II) ions had been adsorbed on the surface of the examined hybrid membrane D. Consequently, it can be concluded that these hybrid membranes are promising adsorbents for the treatment of copper-curing wastewater.

Table 5
The calculated ΔG values of samples D and E at 25℃

Sample	Temperature (K)	ln b	ΔG (kJ/mol)
D	298.15	7.120	−17.649
E	298.15	7.531	−18.670

For comparison, Table 6 lists the maximum capacity, Q_m obtained from the samples D and E with those of other adsorbents reported in the literature [2,9,21–23]. Obviously, the adsorption copper(II) ions on these samples was satisfactory, i.e. the hybrid adsorbents prepared in our case have an advantage over other different types of sorbents reported in literature for copper(II) removal. Consequently, it can be concluded that these hybrid membranes are promising adsorbents for the removal of copper(II) ions from water.

Fig. 8. The surface color of the original sample D (left) and the adsorbed sample D (right), respectively.

Table 6
A comparison of Q_m obtained from samples D and E with those of different types of sorbents reported in references

Adsorbent type	Q_m (mg/g)	References
Graphene oxide/Fe_3O_4	18.26	[2]
Hybrid adsorbent	25.16	[9]
Activated nylon-based membrane	10.79	[21]
Carboxymethyl-β-cyclodextrin modified Fe_3O_4 nanoparticles	47.2	[22]
Negatively charged silica-based hybrid copolymers	11.88 (0.187 mmol/g)	[23]
Hybrid membrane adsorbents	54.01 (0.85 mmol/g)	this work

Table 7
Desorption efficiency of samples D and E for copper(II) ions in various desorbents

Sample	Desorbent	Desorption time (*h*)	Efficiency (%)
D	HCl	2	94.505
	HNO_3	2	79.675
	H_2SO_4	2	81.775
E	HCl	2	94.13
	HNO_3	2	90.63
	H_2SO_4	2	94.35

3.5. Desorption experiment

It is well-known that regeneration and recovery of spent adsorbents and metals, respectively, are of vital importance for the industrial applications of solid-state adsorbents [24,25]. For such purpose, desorption experiment in various desorbents was performed and the related data are listed in Table 7.

It can be noted that the desorption efficiency (%) of samples D and E with aqueous HCl solution as a desorbent could reach around 94%. This outcome reveals that the adsorbed samples D and E could be effectively regenerated using aqueous HCl solution as a desorbent. It demonstrated their potential applications in the regeneration or removal of copper(II) ions from the copper-curing wastewater or the polluted water.

4. Conclusions

A series of hybrid membrane adsorbents containing $–NH_2$ groups were prepared via a sol–gel process. TGA and DSC thermal analyses revealed that these hybrid membrane adsorbents had higher thermal stability. Adsorption measurements demonstrated that the adsorption capacity of copper(II) ions onto these hybrid membrane adsorbents can be artificially controlled by the adjustment of different hybrid precursors. It was confirmed that copper(II) adsorption onto samples D and E followed the Langmuir isotherm equation. The negative ΔG values suggested that copper(II) adsorption onto these hybrid membrane adsorbents was spontaneous in nature. Desorption experiment confirmed that the adsorbed copper(II) ions could be effectively regenerated using various desorbents and the desorption efficiency (%) of aqueous HCl solution could arrive at near 94%.

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