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Preparation of an anion exchange resin/PES blend flat sheet membrane and its application in the enrichment of bromine from aqueous solution

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ABSTRACT

In this study, an anion exchange resin/polyethersulfone (PES) blend flat sheet membrane was prepared, using anion exchange resin 201×7 as function particle and PES as matrix material. The highlight of this membrane is to combine strong enrichment of bromine by resin and stable mechanical properties by PES, obtaining a new material with stronger practicability than traditional materials. The membrane adsorbents were characterized by scanning electron microscope (SEM), nitrogen adsorption (Brunauer, Emmett and Teller) and Fourier transform infrared spectroscopy. The batch adsorption experiments demonstrated that the membrane effectively enriched bromine in a wide optimal pH ranging from 3 to 9. The adsorption equilibrium could be established in 2 h, and the maximum adsorption capacity was 145.35 mg/g. The adsorption data were well described by the pseudo-second-order rate model and the Langmuir isotherm model. The adsorption process was endothermic and spontaneous. In addition, the effects of coexisting anions on the adsorption capacity declined with the following order: $SO_4^{2-} > Cl^- > NO_3^-$. The membrane saturated by bromine could be easily regenerated using trisodium citrate dehydrate (1 mol/L) with a high recovery rate of 97.77%. Compared with other adsorbents, the resin/PES membrane shows high adsorption capacity.

Keywords: Resin/PES blend membrane; Bromine; Adsorption; Enrichment

1. Introduction

Bromine is the element that was first discovered and separated from seawater. Natural bromine is mainly present in seawater, subsurface brine, salt lake brine and sediment rock salt mine in the paleoocean [1]. About 99% of the bromine exists in seawater on Earth, so it is also known as "marine element". Bromine belongs to the large abundance of trace elements; its content in seawater is about 65 mg/L. As a member of the halogen group, bromine evaporates readily at room temperature from liquid to a red vapor with a strong pungent odor resembling chlorine [2]. As an important chemical raw material, bromine forms easily soluble compounds [3]. It has been widely used in the fields of flame retardants, pesticides (mostly methylbromide and bromoxynil), bromobutyl rubber, mercury adsorbent, drilling fluids and water treatment. Bromine is also used in the production of photographic materials, dyes, perfumes, pharmaceutical, etc. From 2015 annual report of Israel Chemicals Limited (Israel), according to the consumption composition to the current end user, application distribution of bromine could be divided into five areas shown in Fig. 1. A wide variety of bromides derived from it have a special value in the development of the national economy. It is of great practical value to achieve the enrichment of bromine from seawater [4–6].

The industrial production of bromine began in the 19th century. Various methods, such as steam distillation, air stripping, ion-exchange adsorption and membrane separation have been used to separate and extract bromine [7–10]. With the improvement of the production technology, the steam distillation method and the air stripping method are

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relatively mature, and they have been widely used in both China and foreign countries. The annual bromine output of the USA and Israel are more than 55 million tons, ranking in the top two of the word. And China ranks the third place with an annual output of 16 million tons [11–13].

Ion-exchange resin is a new method for extracting bromine, emerging in 1950s. This method has advantages of convenient operation, relatively low-cost, low energy consumption, high stability, easy regeneration, etc. [14]. The properties of strong basic anion resin are the core of this method. According to reports, Amerliye IRA-400 and Dowex-1 from the USA, Deacidite FF from England and Duolite-A-42 from France have better effect on the extraction of bromine with the exchange capacity of 6.23 equivalents. Former Soviet Union reported that AB-17 resin can extract bromine up to nearly 100% extraction rate [15]. In China, the Salt Research and Industry Institute in Tianjin used 717 (now called 201×7) resin for extracting bromine from bittern and low concentration brine in laboratory and industrial test in 1967 [16]. Bi [17] investigated the effect of extracting bromine from bittern with D201BR resin. Zhu [8] researched the capacity of 201×7 resin to extract bromine from brine and gas-field water in Sichuan, providing rational technical criteria. Zhang [18,19] studied adsorption kinetics and thermodynamics behavior of 201×7 resin in the process of extracting bromine, using materials of concentrated seawater after desalination. Liu et al. [20] studied the capacity of D301 macroporous resin to extract bromine in concentrated seawater system. Meanwhile, a variety of process parameters in adsorption were optimized.

As the particle size of the resin sorbent is small, additional separation unit becomes necessary. It is inconvenient to use resin directly in aqueous solution. Due to the poor industrial operability of ion-exchange resin method, it has not yet achieved industrial application. Moreover, this method also has other drawbacks, such as short operating cycles, long cleaning time for column, etc. To overcome shortages, we developed a research idea of combination of both the resin and membrane to achieve better enrichment of bromine. The new flat sheet membrane would have good affinity of bromine. It would also have basic advantages of membrane such as separation of suspended solids and so on.

In the present study, a new blend flat sheet membrane, made with polyethersulfone (PES) as matrix material and strong basic anion exchange resin 201×7 as function particle, was successfully prepared. The key membrane properties and batch adsorption experiments were evaluated. The adsorption isotherm data were measured and the thermodynamic property changes were calculated. The dynamic and thermodynamic behavior of bromine adsorption from aqueous solution with 201×7 strong basic anion exchange resin/PES membrane was researched. The aim of this work was to obtain a highly performed anion exchange resin/PES blend membrane which has higher extraction efficiency, less pollution to bromine, easier application and longer lifetime in the adsorption process and the subsequent recycling.

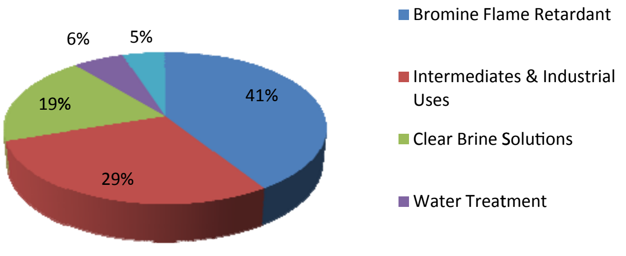

Fig. 1. The application distribution of bromine from 2015 annual report of Israel Chemicals Limited.

2. Experimental setup

2.1. Materials

Basic anion exchange resin (201×7) used in this study was supplied by Tianjin Nankai Hecheng Science & Technology Co., Ltd. (China). *N*,*N*-Dimethylacetamide (DMAc) used as the polymer solvent was supplied by Sinopharm Chemical Reagent Co., Ltd. (China). PES used as the membrane material was supplied by Yuyao Hechang Plastic Co., Ltd. (Yuyao City, Zhejiang Province, China). Sodium bromide, potassium nitrate, potassium chloride, sodium hydroxide and hydrochloric acid from Sinopharm Chemical Reagent Co., Ltd. (China) were used. All the medicals used were of analytical grade unless otherwise stated.

2.2. Pretreatment of anion exchange resin

The basic parameters of strong basic anion resin 201×7 are presented in Table 1. The structure of the newborn resin is unstable, which would stabilize only after repeated transition. Moreover, the samples often contain mechanical impurities, and the ion species also differ from different technology. Therefore, the resin must pass through a pretreatment process before directly used for analysis and determination [21]. The details of pretreatment are as follows. First, newborn resins were washed with deionized (DI) water for three times, and then immersed in DI water in 24 h. Second, hydrochloric acid was added to immerse the above resins in 12 h. The resins were then washed by DI water to pH 6.5–7.5. Finally, the above resins were immersed in sodium hydroxide in 12 h, and then washed by DI water to pH 5.5–6.5. After pretreatment, the resins were dried in air to a constant weight. They were then ground into fine particles by a gas type pulverizer (FDV, Taiwan) and used for the subsequent experiments.

Table 1
Basic parameters of strong basic anion resin 201×7

Item	Specification
Matrix structure	Styrene–DVB
Functionality	$-N^+(CH_3)_3$
Total exchange capacity (mmol/g) (dry)	≥3.6
Moisture content (%)	42–48
pH range	1–14

2.3. Determination method of bromine from aqueous solution

The ion selectivity electrode method was employed to measure concentrations of bromine from aqueous solution. The operating parameters were established as follows. The volume ratio between ionic strength adjustment buffer and the sample solution is 1:4, consistent temperature, mixing with uniform velocity and the response time is 1.0 min. Bromine can be determined in the range from 0.0004 to 7.9904 mg/L.

2.4. Preparation of anion exchange resin/PES blend membrane

The flat sheet membranes were carried out by phase inversion via immersion precipitation technique. Different amounts of anion exchange resins prepared above were added into blend homogeneous solution consisting of a mixture of PES and DMAc. The mixture was placed on a magnetic stirrer at 50°C for 24 h so that the resin particles could be homogeneously distributed in the solution. For the preparation of flat sheet membranes the solution was sprinkled and cast using a home-made casting glass rod on a glass plate. Then, the membrane was immediately moved into the DI water bath for immersion precipitation at room temperature. The non-solvent was DI water. The membranes were immersing in DI water for 24 h so that the remaining solvent would be thoroughly removed from the membrane. After casting, the membranes were dried in air at room temperature. The pure PES membrane (labeled as N0) was also prepared on the same condition with the exception of adding anion exchange resin.

2.5. Characterization of anion exchange resin/PES blend membrane

The surface morphology and cross-section structure were characterized by using a scanning electron microscope (SEM; TM3000, Japan). The membranes were cut into pieces of small sizes. These pieces were frozen in liquid nitrogen and fractured in order to visualize the cross-section areas. The fractured membranes were dried in air and sputter coated with aurum for producing electric conductivity.

Brunauer, Emmett and Teller (BET) nitrogen adsorption experiments were carried out in a specific surface area and pore-size analyzer (NOVA 2200e, Quantachrome, USA) at liquid nitrogen temperature and at relative pressures (P/P_0) ranging from 0.001 to 1.0. P_0 is a saturate pressure at ambient condition. Parameters of specific surface area and pore distribution were analyzed based on the BET and Barrett, Joyner and Halenda (BJH) models [22–24].

Fourier transform infrared spectroscopy (FTIR) was used to elucidate the interaction of the anion exchange resin/PES blend membrane with bromine. The spectra were collected by a Tensor27 spectrometer (Germany) within the range of wave number of 400–4,000 cm^{-1}. The samples were first mixed with KBr. Then the resulting mixture was pressed at 10 ton for 5 min. Sixteen scans and 4 cm^{-1} resolution were applied in recording the spectra. The background obtained from scan of pure KBr was automatically subtracted from the sample spectra. All spectra were plotted using the same scale on the absorbance axis.

2.6. Static adsorption study

Bromine adsorption by the anion exchange resin/PES blend membrane was carried out in the static mode. The bromide solution employed in the experiments was prepared by dissolving sodium bromide in DI water. All the sorption experiments were conducted by adding the membrane into airtight bottles containing the bromide solution.

Solution pH is one of the most important parameters affecting the adsorption process. To investigate the effect of initial pH of the aqueous phase, the experiments were performed by adjusting the initial pH with 1 M HCl or NaOH. The membrane with the same weight was added into the bromide solution. The mixtures were shaken by a rotary shaker with a speed of 200 rpm for 1 h. All the experiments were controlled at 298 ± 0.5 K.

The adsorption isotherm for the anion exchange resin/PES blend membrane was obtained by incubating the same amount of membrane with different bromide concentrations and followed in time to obtain the equilibrium adsorption as a function of the equilibrium concentration. The pH of bromine solution was controlled at 6–7, which was selected based on the pH effect study. The other procedure was same to the pH effect experiments. In addition, contact time and temperature on adsorption of bromide were studied.

The effect of coexisting ions (Cl^-, SO_4^{2-} and NO_3^-) on the adsorption was performed by varying the concentrations of NaCl, Na_2SO_4 and $NaNO_3$ from 20 to 800 mg/L at an initial Br^- concentration of 40 mg/L.

All batch experiments were conducted in duplicate under the same conditions and the relative error between duplicates was less than 5%. The results are reported as mean values.

2.7. Desorption studies

The adsorbent that was used for the adsorption of bromide was separated from solution (initial Br^- concentration was 130 mg/L) by filtration and dried at 50°C. 0.1 g adsorbent was agitated with 50 mL different eluting reagents, for example, NaOH, KNO_3 and $C_6H_5Na_3O_7$ for 2 h, at 25°C.

3. Results and discussion

3.1. Preparation of anion exchange resin/PES blend membrane

The compositions of the casting solution are shown in Table 2. In preliminary study, it was expected that a high amount of anion exchange resins in the membrane would be favorable to

Table 2
Compositions of the casting solution

Membrane	Casting solution compositions (wt%)		
	PES	DMAc	201×7
N0	12	88	0
N5	12	83	5
N7	12	81	7
N10	12	78	10
N13	12	75	13
N15	12	73	15

the adsorption of bromide onto the blend membrane. However, we found that the casting solution became like slurry when too many resin particles were added. It was found to be difficult to get a homogeneous and flexible membrane when weight percentage of resin was higher than 15%. Therefore, the PES concentration was around 12% in the casting solution.

3.2. Membrane characterization

An important parameter for the preparation of PES/anion exchange resin membranes is the amount of resins incorporated into the polymeric matrix. By increasing of the resin loading, the amount of adsorptive sites increases and a higher bromine adsorption capacity is expected. The morphologies of the blend membranes prepared with different loading capacities of 201×7 anion exchange resin are shown in Fig. 2.

The SEM images demonstrate that the bottom surface is denser and tougher than the top surface, which results from the resin particles loading in the membrane matrix. As depicted in Fig. 2, the surface structures of the membranes are significantly affected by the presence of the resin particles. The micrograph of N0 indicates that there are fewer pores in the top surface of the pure PES membrane than the resin blend membranes. With an increase in resin content in the casting solution, the roughness and porosity of the surface increased dramatically, which leads to the apparent enhancement of the adsorption capability. For low loading content, the resin particles are homogeneously dispersed in the PES membrane matrix and therefore the membrane is expected to have optimum morphology for bromide adsorption. The resin particles can hardly fall out in the reaction under the protection of polymer membrane matrix. Because of this porous structure, the diffusion resistances of bromide ions moving into membrane decreased, so that the adsorption performance improves significantly. However, a further increase in the resin content leads to agglomeration, which restricts the resin loading to 15%.

The cross-section SEM images of the membranes in Fig. 2 show that, the membranes exhibit a structure with finger-like macrovoids through the whole thickness. With an increase in resin content, these finger-like macrovoids gradually become smaller. During formation of the membrane, too many resin particles limit the space expansion of large cavity in the phase separation process. Furthermore, if the resin content grows too high, the low adhesion between the resins and the polymeric matrix can cause the resins falling out during the bromide adsorption experiments.

Membrane N5 and N15 were analyzed as representative by BET analysis in order to further characterize the nanoscale pore structure of the membrane. Nitrogen adsorption/desorption isotherm and the corresponding pores-size distribution curve (inset) from adsorption branch using BJH method of the two membranes are, respectively, shown in Fig. 3. The type of the adsorption and desorption isothermal curves is the combination of Type II and Type IV isotherms [25]. As can be seen, membranes N5 and N15 have the same isotherm type, while N15 has higher adsorption quantity. At $P/P_0 > 0.90$, due to capillary condensation of liquid nitrogen in the macropores at its saturation point, a large increase in volume (the take-off on the curve) is observed, which indicates that there is a large amount of macropores in the as-received samples [26]. Kaneko [27] stated that the adsorption isotherm near $P/P_0 = 1$ provided important information concerning macropores. Furthermore, N15 has relatively larger average pore width and exhibits higher BET surface area of 6.413 m^2/g than N5 found to be 4.884 m^2/g. All of these observations in BET results were also evidenced in the SEM images.

The compounds of PES, 201×7 anion exchange resin and N15 membrane were characterized by FTIR spectroscopy (Fig. 4). The peak at 3,300–3,500 cm^{-1} found in both anion exchange resin and membrane can be assigned to the presence of –NH. The peak at 1,296 cm^{-1} found in both PES and membrane can be attributed to the stretching vibration of functional group C–O. The characteristic peaks at 1,149 and 1,105 cm^{-1} (S=O) are found in both PES and membrane but not observed in anion exchange resin. The peak at 1,010 cm^{-1} found in both PES and membrane is the characteristic band of C–O–C. Therefore, it could be confirmed that the structure of our synthetic membrane contains the functional groups of both PES and 201×7 anion exchange. As the membrane authentically contained resin particles, it showed good adsorption properties.

4. Membrane performance

4.1. Influence of pH on the adsorption of bromine

Fig. 5 shows the effect of pH on the bromide adsorption onto the anion exchange resin/PES blend membrane. Under the initial pH ranging from 3 to 9, most of the bromide could be adsorbed with an initial solution concentration of 130 mg/L. This result indicates that the blend membrane can be used for bromide adsorption in a wide pH range. The optimal pH with a wide range is of importance in the application.

When pH is higher than 9, the adsorption of bromide onto the anion exchange resin/PES blend membrane decreases significantly. That decrease can be attributed to the increase in the concentration of competing hydroxyl ions at higher pH. It can be found that the membrane has a certain buffering effect, thus no pH adjustment is needed. Therefore, the bromine solution with initial pH = 6 was used in the subsequent experiments.

4.2. Effect of contact time and adsorption kinetics

The kinetics of bromine adsorption is required for selecting the optimum operating conditions for a full-scale batch adsorption process. As shown in Fig. 6, most of bromide adsorption on the anion exchange resin/PES blend membrane rapidly occurs with increasing reaction time, and then further increases in contact time do not enhance the adsorption capacity significantly. Even though equilibrium is reached in 60 min at the stated conditions, the batch adsorption tests were run for 2 h to ensure complete equilibration.

Pseudo-first-order rate model [28] and pseudo-second-order rate model [29] were employed to investigate the adsorption kinetic mechanism by fitting the experimental data obtained from batch experiments, expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{1}$$

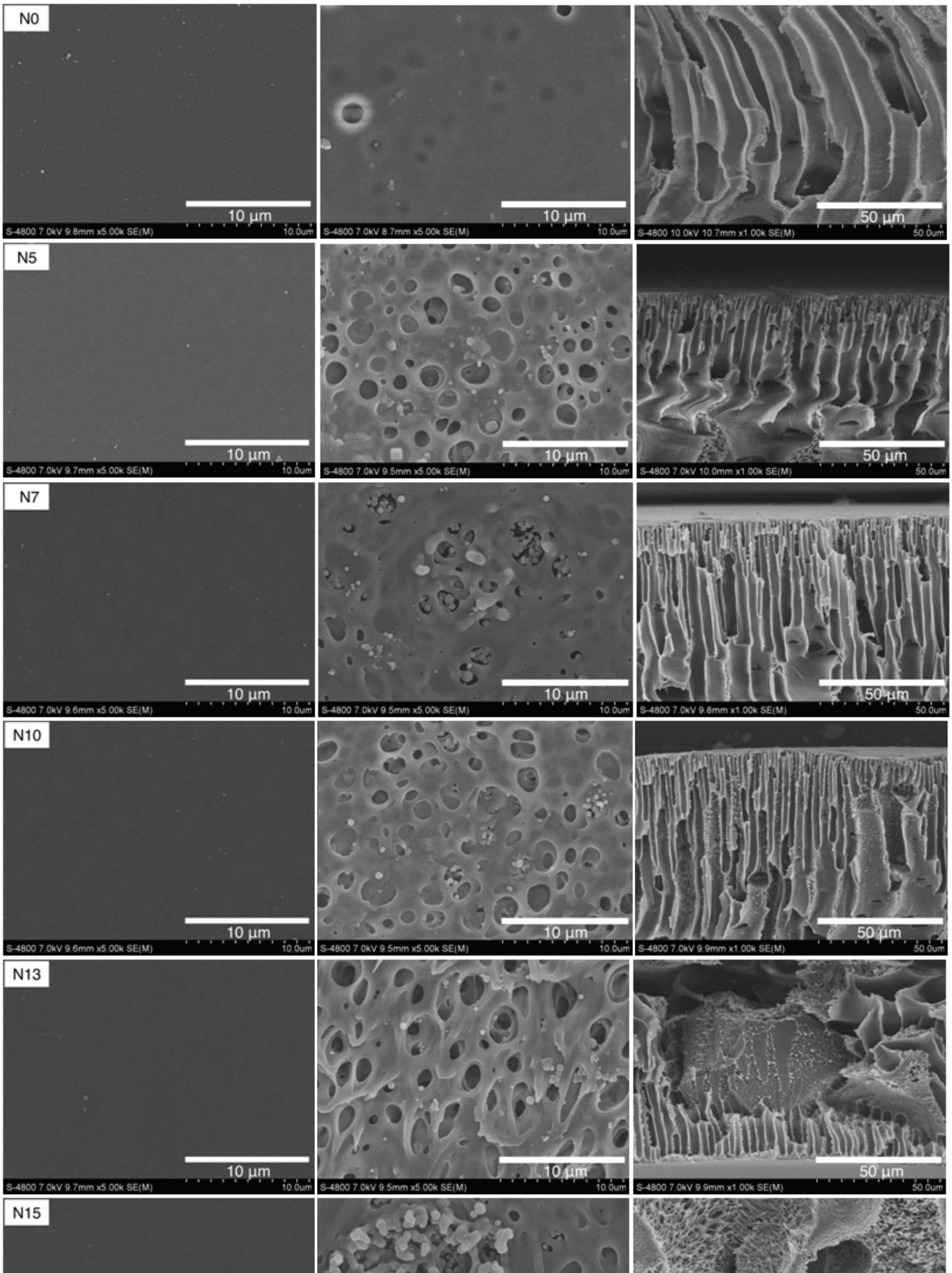

Fig. 2. SEM images of bottom surface, top surface and cross-section morphology: N0, N5, N7, N10, N13 and N15.

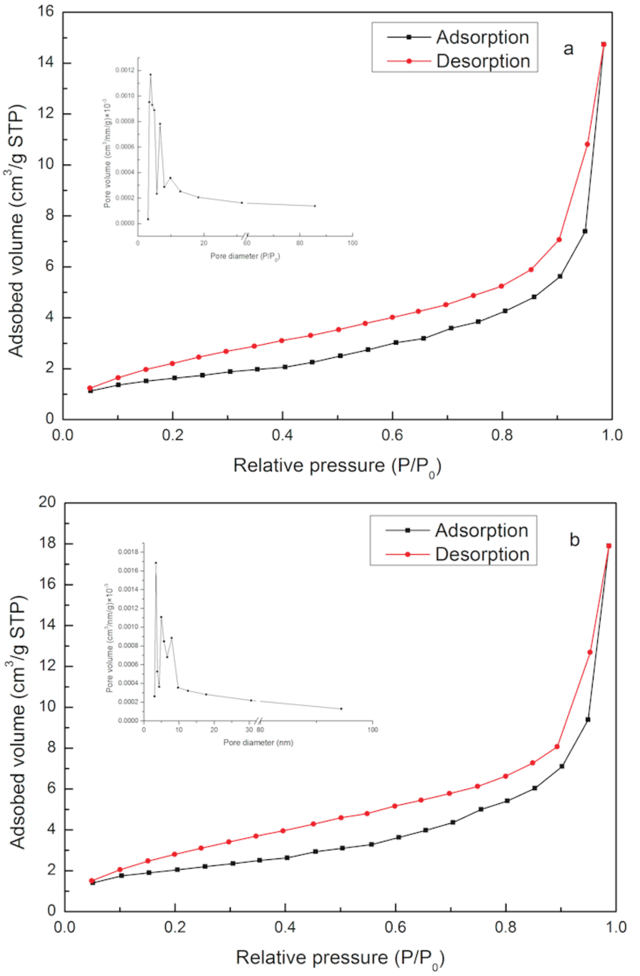

Fig. 3. Nitrogen adsorption–desorption isotherm of the prepared membrane. (a) N5 and (b) N15. Inset: corresponding pore-size distribution curve determined from the N_2-adsorption isotherm.

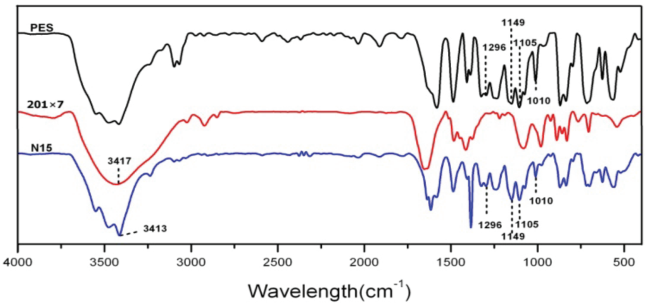

Fig. 4. FTIR spectra of (1) PES, (2) 201×7 anion exchange resin, and (3) N15 membrane.

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{2}$$

where k_1 and k_2 are rate constants for the pseudo-first-order (1/min) and the pseudo-second-order adsorption [g/(mg·h)], respectively, while q_t and q_e are the amounts of bromine adsorbed (mg/g) at time t and at equilibrium, respectively.

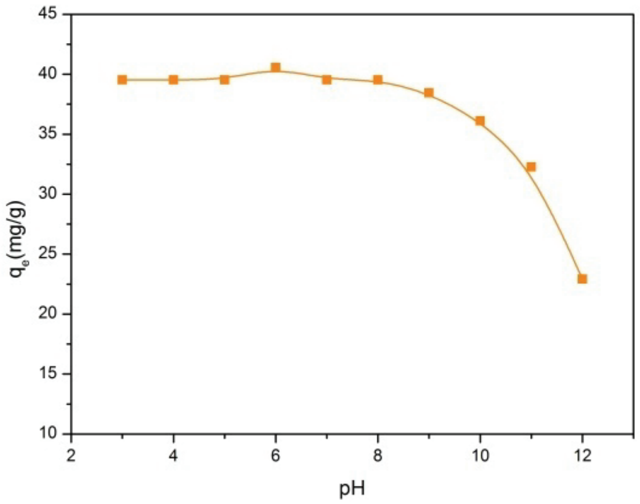

Fig. 5. Effect of initial pH on the adsorption of bromide on the anion exchange resin/PES membrane. Initial concentration of Br ion 130 mg/L, amount of N15 sorbent 0.1 g, temperature 25°C, and shaking time 2 h.

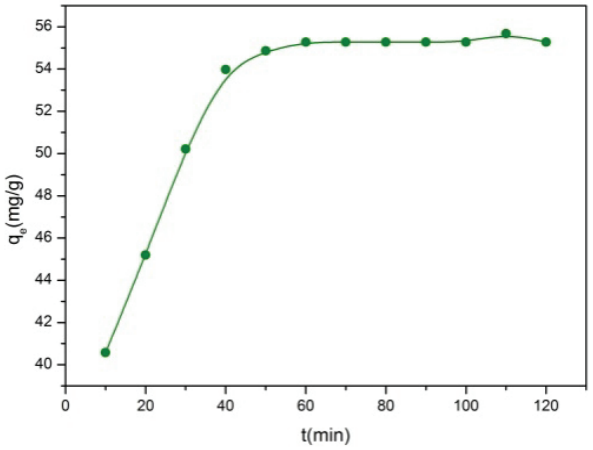

Fig. 6. Effect of contact time on the adsorption of bromide. Initial concentration of Br ion 130 mg/L, amount of N15 sorbent 0.1 g, temperature 25°C, and solution pH 6.

Plots of q_t against t for pseudo-first-order and pseudo-second-order models are shown in Fig. 7 and the related parameters in Table 3. It can be found that the correlation coefficients (R^2) value of pseudo-second-order rate model is 0.999 which is higher than that of pseudo-first-order rate model 0.955. In addition, the adsorption capacity calculated by pseudo-second-order rate model is 57.47 mg/g which is close to the experimental one. As discussed above, we can draw a conclusion that the adsorption kinetics date can be well described by the pseudo-second-order rate model.

4.2.1. *Effect of initial concentration of bromine and adsorption isotherm models*

The adsorption isotherm indicates how the adsorbates interact with adsorbents. It is basically important to describe

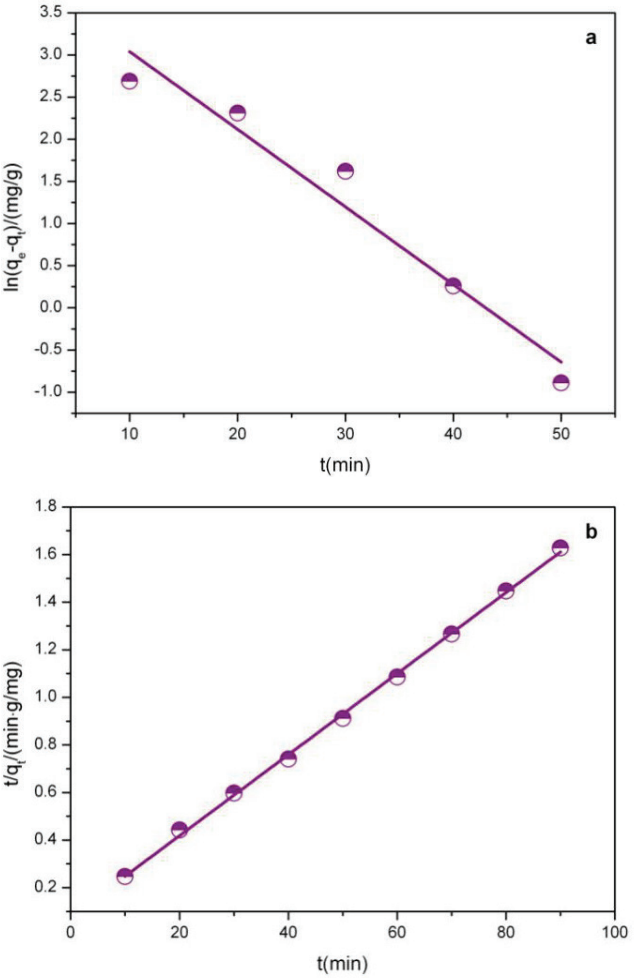

Fig. 7. Pseudo-first-order (a) and pseudo-second-order (b) kinetic models for Br adsorption on the anion exchange resin/PES blend membrane. Initial concentration of Br ion 130 mg/L, amount of N15 sorbent 0.1 g, temperature 25°C, and solution pH 6.

Table 3
Adsorption kinetic parameters obtained by different models

q_e exp (mg/g)	First-order kinetic model			Second-order kinetic model		
	q_e (mg/g)	k_1 (min^{-1})	R^2	q_e (mg/g)	k_2 (g/mg min)	R^2
55.67	52.40	0.092	0.955	57.47	0.0047	0.999

how the adsorption molecules distributed between the liquid and the solid phase when the adsorption process reaches equilibrium, which will give some valuable information to optimize the design of new adsorption systems [30,31]. The experimental data were analyzed using the Langmuir and Freundlich isotherm models. The isotherm diagrams are presented in Fig. 8.

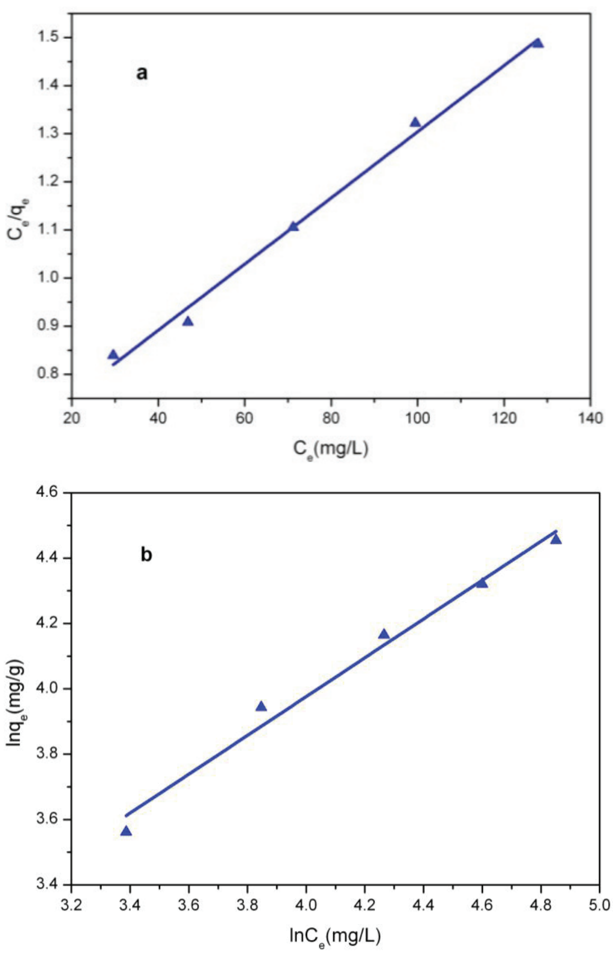

Fig. 8. Adsorption isotherms of Langmuir (a) and Freundlich (b). Amount of N15 sorbent 0.1 g, temperature 25°C, solution pH 6, and shaking time 2 h.

The Langmuir isotherm (Eq. (3)) assumes monolayer coverage of the adsorption surface and no interaction among adjacent adsorbed molecules [32]:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \tag{3}$$

where q_e and C_e are the equilibrium adsorption amounts (mg/g) and the equilibrium concentration of bromide in solution (mg/L) respectively, q_m is the maximum bromide adsorption capacity (mg/g) and K_L is the Langmuir constant which is related to the strength of adsorption.

The Freundlich equation (Eq. (4)) is derived to model multilayer adsorption and adsorption on heterogeneous surfaces.

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{4}$$

where K_f and $1/n$ are the constants related to the adsorption capacity and the adsorption intensity. The experimental data for the isotherm modeling were the equilibrium data acquired from isothermal adsorption experiment at 298 K.

The fitted parameter values and the correlation coefficient values in Table 4 show that the Langmuir model has better correlation over the whole concentration range than the Freundlich model. The maximum adsorption capacity obtained from the Langmuir isotherm is close to the experimental data, which implied the adsorption of bromine onto the PES/anion exchange resin membrane was more applicable for the Langmuir linear model.

4.2.2. The influence of adsorption temperature and the determination of thermodynamic parameters

The adsorption isotherms at different temperatures are presented in Fig. 9. It was observed that the adsorption capacity increased apparently with the adsorption temperature gone up, thus suggesting that the adsorption reaction was an endothermic reaction. It was proved that the temperature could influence the reaction rate.

The change of Gibbs free energy (ΔG) can be calculated according to the following equation [33]:

$$\begin{aligned} \Delta G &= -RT\ln K \\ K &= 1/K_L \end{aligned} \tag{5}$$

where ΔG is free energy (J/mol), R is gas constant which values 8.314 J/mol·K, T is absolute temperature (K), K is adsorption equilibrium constant (mL/mg), K_L is 0.0112 mg/mL (25°C).

From the experimental data, it can be found that the ΔG value is negative, which indicates that the adsorbate tends to be adsorbed from solution to the membrane surface. It can also be inferred that the adsorption process is spontaneous.

Table 4
The parameters of Langmuir and Freundlich isotherm models

T (°C)	Langmuir			Freundlich		
	q_m (mg/g)	K_L	R^2	K_f	N	R^2
25	145.349	0.0112	0.992	4.954	1.683	0.979

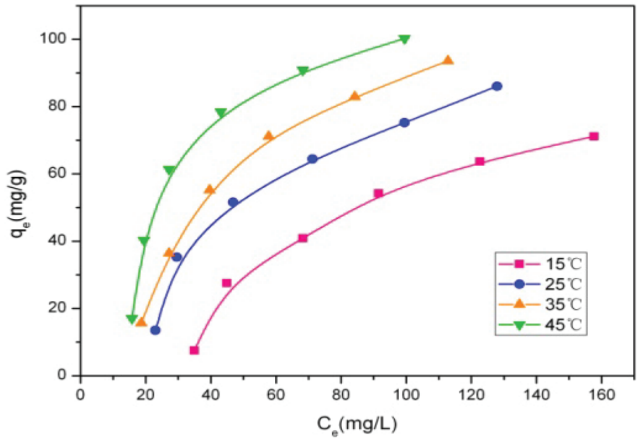

Fig. 9. Effect of adsorption temperature on the adsorption of bromide. Initial concentration of Br ion 130 mg/L, amount of N15 sorbent 0.1 g, solution pH 6, and shaking time 2 h.

4.2.3. Effect of coexisting anions

To evaluate the selective adsorption of the blend membrane toward bromide, a batch of competitive adsorption experiments were conducted. The effect of different ions (Cl^-, SO_4^{2-} and NO_3^-) on the adsorption of bromide onto the blend membrane is shown in Fig. 10, where it can be easily found that the adsorption performance exhibited negative trends in the presence of all counterions. However, the blend membrane shows greater preference and higher selectivity for Br^- compared with other anions. Referring to the figure, SO_4^{2-} exerts the strongest competition for the active sites of the resin during the adsorption process, while Cl^- and NO_3^- have weaker competition. The effect of monovalent ion on bromide adsorption is superior to bivalent ion. Each type anion causes the decrease in the uptake of bromide on membrane to a certain extent. This can be explained by the fact that the competition between each type anion for the adsorption active sites of membrane surface. It is also observed from Fig. 10 that the selectivity order of the membrane is $Br^- > SO_4^{2-} > Cl^- > NO_3^-$. This is approximately consistent with the affinities between anions and adsorption active sites of strong alkali anion resin. Some research results also showed bromide adsorption was affected by the chloride, sulfate and water alkalinity [34,35].

4.2.4. Desorption and regeneration

Desorption studies help to elucidate the mechanism and recovery of the adsorbent. It can be easily seen from Table 5

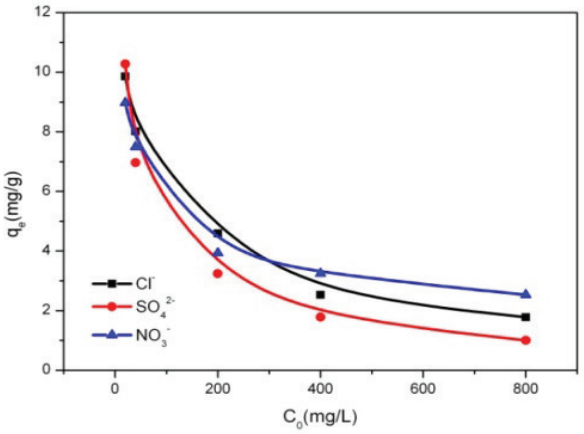

Fig. 10. Effect of coexisting ions on the adsorption of bromide. Initial concentration of Br ion 40 mg/L, coexisting ions initial concentration 20–800 mg/L, amount of N15 sorbent 0.1 g, temperature 25°C, solution pH 6, and shaking time 2 h.

Table 5
Elution of anion exchange resin/PES membrane by NaOH, KNO_3 and $C_6H_5Na_3O_7$

Elution agent (1 mol/L)	Capacity of adsorption (mg/g)	Capacity of desorption (mg/g)	Desorption (%)
NaOH	55.67	41.58	74.69
KNO_3	55.67	46.01	82.63
$C_6H_5Na_3O_7$	55.67	54.43	97.77

Table 6
Comparison of resin/PES membrane with other sorbents for bromine adsorption

Sorbent	q_m	Conditions					Reference
		C_0 (Br$^-$)	*T* (°C)	Adsorption time	Adsorption dosage	pH	
D201	0.104 g/mL	130 mg/L	25	60 min	0.2 mL		36
201×7	2.489 mg/mL	130 mg/L	45	90 min		3.05	37
Calcined LDH	133.3 mg/g	40 mg/L	35	4 h	0.2 g	6–7	38
Lanthanum-modified chitosan	3.230 mg/g	100 mg/L	10–20		1.0 g	5	39
	0.669 mg/g	65 mg/L	10–20		1.0 g	5	
Resin/PES membrane	145.4 mg/g	130 mg/L	25	60 min	0.1 g	6	Present study

that sodium citrate (1 mol/L) is highly efficient desorbent, enabling the recovery of 97.77% of bromine. The percentage elution of bromine from the anion exchange resin/PES membrane can be calculated by Eq. (6):

$$\mathrm{E}(\%) = \frac{N_1}{N_2} \times 100 \tag{6}$$

where E is desorption efficiency, N_1 is amount of bromine desorbed to desorption solution and N_2 is amount of bromine adsorbed on membrane.

To evaluate the reusability of the membrane after regeneration, repeated use several times in adsorption–elution processes showed no change in the sorption capacity. Therefore, these results demonstrated that the membrane could be reused after regeneration.

4.2.5. Comparison of bromine adsorption on resin/PES membrane with other sorbents

The value of maximum sorption capacity (q_m) obtained from Langmuir model is of importance to identify which sorbent shows the highest sorption capacity and is useful in scale-up considerations. As is showed in Table 6, the adsorption capacity of bromine on anion exchange resin/PES membrane is compared with those other types of sorbents reported in some works [36–39]. Although it is difficult to compare resin/PES membrane with other sorbents directly because of the maximum adsorption capacities obtained under different experimental conditions, the membrane shows a relatively high sorption capacity and short equilibrium time. The shorter time needed to reach equilibrium for resin/PES membrane is significant to diminish the size of adsorption facilities.

5. Conclusion

An anion exchange resin/PES blend membrane was successfully prepared by phase inversion process for adsorptive enrichment of bromine from aqueous solution, which has the advantages of both membrane and adsorbent. The SEM studies showed that an increase in content of resin 201×7 leads to an increase in surface porosity of the resin/PES blend membrane. According to the BET nitrogen adsorption experiments, the average pore width, surface area and adsorption quantity of membrane increased significantly with an increase of resin content. The FTIR data indicated that the resin/PES membrane showed good adsorption properties by authentically containing resin particles. The batch adsorption studies demonstrated that the blend membrane can be used for efficient adsorption of bromine in a wide pH range, and the optimal pH is from 3 to 9. The kinetics adsorption experiment revealed that the adsorption equilibrium can be obtained within 60 min, and pseudo-second-order rate model can well fit the experimental data. The Langmuir isotherm described the adsorption data better than the Freundlich isotherm, and the maximum bromine adsorption capacity calculated by Langmuir equation was 145.35 mg/g. Thermodynamic parameters suggested that the adsorption process was spontaneous in nature. The effects of coexisting anions on the adsorption capacity declined with the following order: $\mathrm{Br}^- > \mathrm{SO}_4^{2-} > \mathrm{Cl}^- > \mathrm{NO}_3^-$. The blend membrane can be regenerated using sodium citrate (1 mol/L) with a high recovery rate of 97.77%. All of these indicate that the anion exchange resin/PES blend membrane has higher enrichment efficiency and stronger operability in the adsorption process.

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