Application of a novel quaternized ammonium poly(vinyl alcohol)-based hybrid anion exchange membrane for the removal of Cr(VI) from wastewater

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ABSTRACT

Two quaternized ammonium poly(vinyl alcohol) (QPVA)-based hybrid anion exchange membranes were successfully fabricated by using sol–gel method. The mass ratios of QPVA aqueous solution to polydimethyl allyl chloride (PDADMAC) aqueous solution were 4:1 and 2:1, then 10 wt% tetraethyl orthosilicate (TEOS) was added. The obtained membranes were separately designated as QPVA/0.25PDADMAC/0.1TEOSm and QPVA/0.5PDADMAC/0.1TEOSm. The properties for the adsorption removal of Cr(VI) and the effect on the Cr(VI) saturation adsorption amount and removal rate were investigated. Results indicated the adsorption was an exothermal reaction. Thus, low temperature was beneficial for the removal of Cr(VI). Optimal removal of Cr(VI) was achieved using the QPVA/0.5PDADMAC/0.1TEOSm membrane at a pH value of 2. Dynamic simulation was carried out simultaneously to determine if particle diffusion was the sole contributor for the adsorption rate, which was in accordance with the Langmuir isotherm adsorption model. Furthermore, the static adsorption amount (Q_0) was 61.77 mg/g, and the efficiency of recycling the hybrid membranes was higher than 90%. Scanning electron microscopy (SEM) characterization showed the surface and the cross-section tightened after the Cr(VI) adsorption, thereby demonstrating the potential application of these hybrid membranes for Cr(VI) removal.

Key words | adsorption isotherm model, dynamics simulation, influence factor studies, novel hybrid anion exchange membrane, the adsorptive removal of Cr(VI)

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INTRODUCTION

Cr(VI) is a primary pollutant with a toxicity 100 times higher than Cr(III). Cr(VI) poses great danger to human health, and long-term exposure to this metal may induce cancer. Moreover, Cr(VI) does not self-degrade under normal conditions (Lucía *et al.* 2013). The current methods for the removal of Cr(VI) have mainly involved chemical chelating adsorption (An *et al.* 2011), ion exchange adsorption (Abo-Farha *et al.* 2009), biological adsorption (Chen & Wang 2006), reverse osmosis, electrodialysis (Liu *et al.* 2008; Akrama & Andrew 2012), and so on.

The novel polyethylene glycol methyl acrylate vinyl imidazole copolymer microspheres have been prepared for Cr(VI) adsorption (Uğuzdoğan *et al.* 2010). The highest Cr(VI) removal rate was obtained at pH 2. Moreover, the initial Cr(VI) concentration of 3,000 mg/L produced the highest adsorption amount of 108.7 mg/L. Another new type of polyethylene glycol methyl acrylate vinyl imidazole copolymer microspheres was fabricated to trap Cr(VI) ions (Jayalakshmi *et al.* 2012). Their results showed the highest removal rate of Cr(VI) was 98.3% by using a CA/EPES (80/20 wt%) hybrid membrane. Several conductive polymers could effectively eliminate some heavy metal ions in aqueous solutions (Ansari & Fahim 2007; Ansari & Delava 2008). Hena (2010) prepared a functional adsorbent via the combination of 3-methyl thiophene polymer and chitosan surface. The results revealed that acidic environment and high temperature facilitated the removal of Cr(VI), indicating an endothermic reaction. Furthermore, the adsorbent could be recycled by alkali treatment, which was basically in accordance with the Langmuir isotherm model. The catalytic electrode materials were produced by coating monolayer carbon nanoparticles on a stainless-steel mesh to eliminate Cr(VI) ions from aqueous solution by an electrochemical method (Liu *et al.* 2011). The optimal

parameters for the highest Cr(VI) removal rate were a pH of 4, a voltage of 2.5 V, and an electrolyte concentration of 10 mg/L. X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) characterization confirmed the removal mechanism: Cr(VI) is initially reduced to Cr (III) on the cathode and then Cr(III) ions are adsorbed on the surface of the monolayer carbon nanoparticles. At pH 4, the removal rate of Cr(VI) was 99.9%, and the total removal rate of Cr(VI) was 96.9%. When combining ion exchange and electrode ionization to treat Cr(VI)-containing wastewater, the removal rate of Cr(VI) ions could reach as high as 98.5% (Lucía *et al.* 2013). At pH 2, the highest removal rate of Cr(VI) was 24.1%, and the concentration of Cr(VI)-containing wastewater was 250 mg/L utilizing *Bacillus thuringiensis* biosorption to remove Cr(VI) ions from aqueous solution (Şahin & Öztürk 2005).

The current techniques for the treatment of Cr(VI) in aqueous solutions are limited by several drawbacks, such as poor selective adsorption performance, secondary pollution after adsorption, a complex preparation process, and high energy consumption. Compared with traditional chemical adsorption, the main advantage of an anion exchange membrane in eliminating Cr(VI) ions is that it does not cause secondary pollution. This work employed an environmentally friendly method to fabricate a novel organic–inorganic anion exchange membrane of quaternary ammonium melt polyvinyl alcohol (QPVA)/polydimethyl diallyl ammonium chloride (PDADMAC)/tetraethyl orthosilicate (TEOS). The properties of the anion exchange membrane for the removal of Cr(VI) were also investigated.

EXPERIMENTAL

Materials

Potassium dichromate and sulfuric acid were obtained from Wuxi Ruiyun Chemical Co., Ltd. Diphenylcarbazide and acetone were purchased from Ling Feng Shanghai Chemical Reagent Co., Ltd. Phosphoric acid and hydrochloric acid were supplied by Shanghai Yanchen Chemical Enterprise Co., Ltd and Shuangshuang Chemical Co., Ltd, respectively. All chemicals were of analytical grade.

Hybrid membrane preparation

A sufficient amount of QPVA was added to deionized water, and the mixture was continuously stirred until swelling. The 10 wt% casting solution was obtained after sufficient

dissolution of QPVA as the temperature gradually increased to 80 °C. Likewise, 8 wt% PDADMAC casting solution was prepared by dissolving PDADMAC in deionized water with magnetic stirring at room temperature. Both of the solutions were mixed on the basis of their mass ratio marked as QPVA/χPDADMAC (where χ is the mass ratio of PDADMAC and QPVA casting solutions with values of 0, 25%, 50%), while keeping the total mass fixed at 20 g. Subsequently, the pH of the mixture was adjusted to 3 by the addition of 0.1 mol/L HCl. TEOS (0.2 g) was added dropwise to the mixture under magnetic stirring for 1 h at 30 °C. Through ultrasonic deaeration, the mixture became an apparent sol–gel solution. A given volume of mixture was poured onto a homemade mould and dried. In the end, hybrid anion-exchange membranes with varying intensities were produced. The hybrid membranes were immersed into a 5 wt% glutaraldehyde/acetone solution and cross-linked at 30 °C, pH 5 for 5 h. The cross-linking solution absorbed on their surfaces was removed and they were immersed into 1 mol/L NaOH solution for 24 h to obtain the alkaline membranes. Subsequently, the membranes had another round of immersion, this time in deionized water for another 24 h for the subsequent tests.

Experimental methods

Determination of Cr(VI) concentration

According to the national standard GB7467-87 of the diphenylcarbazide spectrophotometric method, the accurate weight of 0.2829 ± 0.0001 g $K_2Cr_2O_7$ was dried at 110 °C for 2 h in a 100 mL beaker, dissolved with distilled water and transferred to a 1,000 mL volumetric flask. The Cr(VI) standard store solution was obtained with the Cr(VI) concentration of 0.1 mg/mL, which must be used immediately before its removal application.

Approximately 0.05 g of the hybrid membrane was placed in 40 mL of simulated Cr(VI)-containing wastewater under constant temperature. After being magnetically stirred for a certain period of time, the initial and equilibrium Cr(VI) ion concentration, which were marked as C_0 and C_e, were determined using a UV752N UV-Vis light spectrophotometer at 540 nm wavelength (Shang 1987).

Standard curve of the linear fitting of the concentration and absorbance of chromium-containing wastewater

First, 0, 0.5, 2, 6, 8, and 10 mL of 1 μg/mL Cr(VI) standard solutions were added to individual 50 mL colorimetric tubes. The solutions were diluted to 50 mL using deionized

water. Afterwards, 0.5 mL of concentrated H_2SO_4, 0.5 mL of diluted H_3PO_4, and 2 mL of diphenylcarbazide/acetone/water solution were added to the colorimetric tubes. After stirring for 5–10 min, the absorbance of the solutions was obtained to prepare the standard curve of Cr(VI) and the linear fitting equation obtained was $Y = 0.81648X + 0.00104$. The concentration of Cr(VI) was predicted after measuring the absorbance of the simulated chromium-containing wastewater.

Effects of temperature on Cr(VI) removal

To investigate the effects of temperature on the removal rate of Cr(VI) ions, the equilibrium adsorption capacity, equilibrium adsorption time, and removal efficiency of 0.05 g of the hybrid membrane were determined in 40 mL and 50 mg/L of Cr(VI)-containing simulated wastewater at 10, 20, 30, 40, and 50 °C, respectively.

Effect of type of anion exchange membrane on the adsorption and removal performance of the Cr(VI) ions and its kinetics fitting

To investigate the effect of different types of ion-exchange membranes (QPVAm, QPVA/0.25PDADMAC/0.1TEOSm, and QPVA/0.5PDADMAC/0.1TEOSm) on the adsorption removal of Cr(VI), 0.05 g of three types of membranes were employed to treat 40 mL and 50 mg/L of Cr(VI)-containing simulated wastewater at 20 °C, respectively. The adsorption capacity and Cr(VI) removal rate were measured after a given time interval. The typical membrane QPVA/0.5PDADMAC/0.1TEOSm was used to study the kinetics of the adsorption process.

Effect of pH on Cr(VI) removal

The pH value of the simulated wastewater was adjusted using 0.1 mol/L HCl and 0.1 mol/L NaOH aqueous solutions. The saturated adsorption capacity and the equilibrium adsorption rate were determined at 20 °C.

Effect of different initial concentrations of simulated wastewater on Cr(VI) removal and its adsorption model fitting

Approximately 40 mL of simulated wastewater (pH 2) with different initial concentrations of 50, 65, 75, 85, and 100 mg/L were used. 0.05 g of the QPVA/0.5PDADMAC/0.1TEOSm hybrid membrane was added to the above wastewater separately at 20 °C to reach equilibrium concentration. Langmuir isotherm adsorption model fitting was performed.

Recyclability of the anion exchange membrane

The saturated adsorption membranes were placed in 0.1 mol/L of NaOH aqueous solution for recovery, and the hybrid membrane was recycled after being washed and dried.

Morphology of the micro-membrane before and after adsorption

The surface and cross-section morphologies of the QPVAm, QPVA/0.25PDADMAC/0.1TEOSm, QPVA/0.5PDADMAC/0.1TEOSm membranes were characterized by SEM (QUANTA200, USA). The morphology of QPVA/0.5PDADMAC/0.1TEOSm before and after adsorption was also characterized.

Functional groups determination of the micro-membrane by Fourier transform infrared (FTIR)

The functional groups of the micro-membrane were determined using Fourier transform infrared (FTIR) spectroscopy (NEXUS-670 spectrophotometer) over a wave number range of 400–600 cm^{-1}.

Calculation formulas

Equilibrium adsorption quantity was calculated according to Equation (1), the removal efficiency percentage was calculated according to Equation (2), and the Langmuir adsorption isotherm model fitting was calculated according to Equation (3)

$$Q_e = \frac{(C_0 - C_e)V}{M} \qquad (1)$$

$$A_\% = \frac{C_0 - C_e}{C_0} \times 100\% \qquad (2)$$

Langmuir formula $\frac{C_e}{Q_e} = \frac{1}{Q_e}C_e + \frac{1}{Q_0}b$ $\qquad (3)$

where Q_e is the equilibrium adsorption quantity (mg/g), C_0 is the initial concentration of Cr(VI)-containing wastewater (mg/L), C_e is the equilibrium concentration of Cr(VI)-containing wastewater (mg/L), V is the volume of

Cr(VI)-containing wastewater (L), M is the quality of the hybrid membrane (g), $A_\%$ is the removal efficiency of Cr(VI), and Q_0 is the static adsorption capacity.

RESULTS AND DISCUSSION

Influence of temperature on the removal of Cr(VI) by hybrid membrane

Equilibrium adsorption time, equilibrium adsorption quantity, and removal rate of Cr(VI) of the QPVA/0.25PDADMAC/0.1TEOSm membrane were determined at 10, 20, 30, 40, and 50 °C, respectively. The results are shown in Table 1. The testing conditions were as previously described.

As shown in Table 1, the equilibrium adsorption capacity and the removal rate of Cr(VI) in simulated wastewater for the QPVA/0.25PDADMAC/0.1TEOSm membrane decreased with temperature ramping. Results indicated that the Cr(VI) removal was an exothermal reaction. Low temperature promoted the removal of Cr(VI), and this finding was in agreement with the reported results (Gode & Pehlivan 2006). Moreover, the significant equilibrium adsorption time of this kind of anion exchange membrane decreased with increasing temperature. This decrease indicated that high temperature accelerated the exchange adsorption between membranes and Cr(VI). Two reasons for this decrease may be summarized as follows. First, the chain segment structure of the polymer became relatively loose with increasing temperature. This change accelerated the exchange between quaternary ammonium groups of functions and chromium ions. Second, temperature increasing accelerated the ion motion while reducing its contact time with the functional quaternary ammonium groups. The stability of the equilibrium adsorption capacity and Cr(VI) removal rate between 30 and 50 °C could be
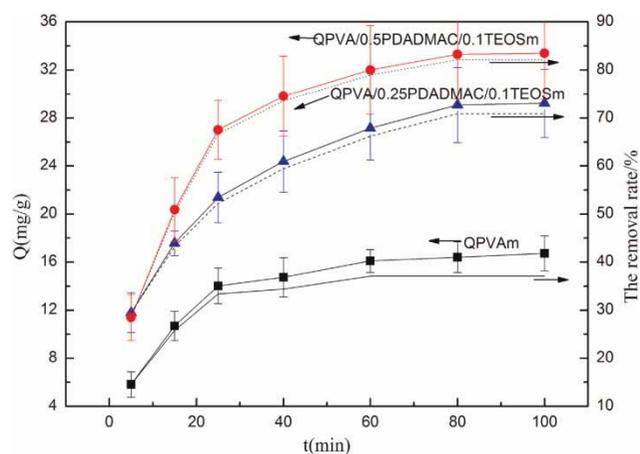
attributed to the effect of the amount of quaternary ammonium groups in the functional anion exchange membrane on the exchange number with the chromium ion. In other words, the exchange adsorption of chromium ion in this temperature range was related to the number of quaternary ammonium groups in the functional membrane directly. As a result, high temperature was favorable only for the reduction of the equilibrium adsorption time but not for the removal of Cr(VI) ions.

Influence of the type of anion exchange membrane on the adsorption and removal of chromium ion and its kinetics fitting

The examination method was used as previously described. Solid lines in Figure 1 represent the adsorption of chromium ion by the three membranes, while the dotted lines represent the removal rate of chromium ion. According to Figure 1, it is shown that both the adsorption amount and Cr(VI) removal rate were low when the QPVAm membrane was used. Moreover, the equilibrium adsorption time reached as long as 60 min, indicating the poor performance of the QPVA membrane. There were two main reasons: first, the number of quaternary ammonium functional groups was less than that of the hybrid membrane; second, the closely packed structure of the membrane was not favorable for the diffusion of Cr(VI) ions. In contrast, the other two membranes (QPVA/0.25PDADMAC/0.1TEOSm, QPVA/0.5PDADMAC/0.1TEOSm) with loosely packed structures were used for the Cr(VI) removal application. As a result, the highest adsorption amount and removal rate could reach 33.3874 mg/g and 82.1282%, respectively.

Table 1 │ Adsorption and removal of Cr(VI) by QPVA/PDADMAC/0.25/0.1TEOSm at different temperatures

Temperature (°C)	Equilibrium adsorption time (min)	Equilibrium absorption capacity (mg/g)	Removal rate (%)
10	90	29.7156	72.575
20	75	29.0726	70.8603
30	65	26.8680	64.9814
40	50	26.8951	65.9612
50	30	26.9273	65.1395

Figure 1 │ Adsorption time and adsorption quantity diagram of chromium ion using the three membranes.

The main diffusion theories for the removal of Cr(VI) by ion exchange method usually involves membrane diffusion, particle diffusion, and chemical reaction (Ma *et al.* 2006). The kinetic process of the adsorption using the QPVA/0.5PDADMAC/0.1TEOSm membrane was carried out according to Equations (4)–(6)

Membrane diffusion: $\ln(1 - F) = -kt$ (4)

Particle diffusion: $1 - 3(1 - F)^{2/3} + 2(1 - F) = kt$ (5)

Chemical reaction: $1 - (1 - F)^{1/3} = kt$ (6)

Q_t is the adsorption amount when response time is t, Q_e is the equilibrium adsorption capacity, and K is the diffusion coefficient at 20 °C; $F = Q_t/Q_e$.

The kinetic results are shown in Figure 2. According to the particle diffusion theory, the linear fitting correlation coefficient R was 0.98472, which demonstrated that the Cr(VI) adsorption rate using the QPVA/0.5PDADMAC/0.1TEOSm membrane was dependent on particle diffusion.

Effect of pH on Cr(VI) removal

The results of the effect of pH on Cr(VI) removal are shown in Figure 3 and the detailed operations are as described above.

As shown in Figure 3, both the equilibrium adsorption amount and removal rate using QPVA/0.5PDADMAC/0.1TEOSm decreased with increasing pH. pH values between 2 and 4 were favorable for the removal of Cr(VI) ions. However, when pH was higher than 6, the removal
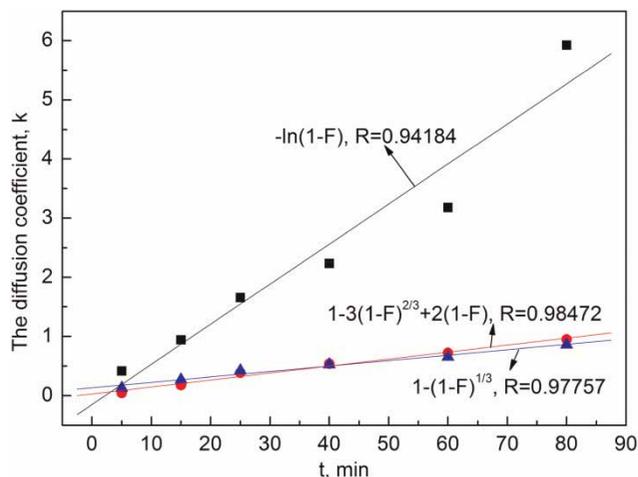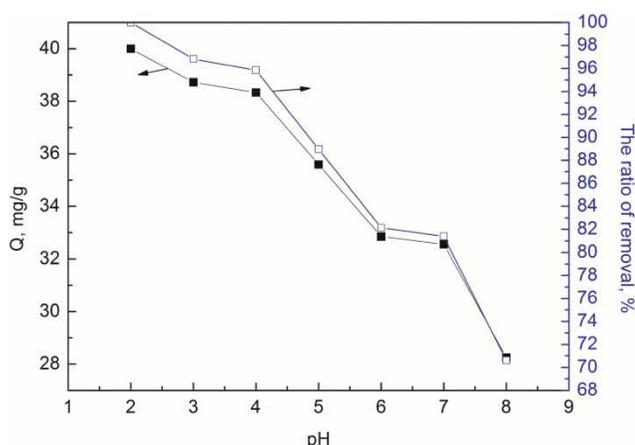

Figure 3 | Effect of pH on adsorption capacity and removal rate of chromium ions.

rate of Cr(VI) ions decreased significantly. The existing forms of Cr(VI) ions in alkaline simulated wastewater were responsible for this decrease. Under acidic conditions, the ratio of the QPVA/0.5PDADMAC/0.1TEOSm membrane to Cr(VI) ($HCrO_4^-$ and $Cr_2O_7^{2-}$) was 1:1 (Li *et al.* 2008). However, the ratio was 1:2 under alkaline conditions (CrO_4^{2-}). Furthermore, an increase in pH led to the simultaneous occurrence of adsorption and desorption in the ion exchange process, which in turn reduced the removal efficiency of the chromium ions.

Influence of different initial concentrations on the adsorption and removal of chromium ions and Langmuir adsorption model fitting

The results of the analysis are shown in Figure 4. The obtained linear fitting formula is $Y = 0.01619X + 0.0073$. The static adsorption amount (Q_0) was 61.77 mg/g, and
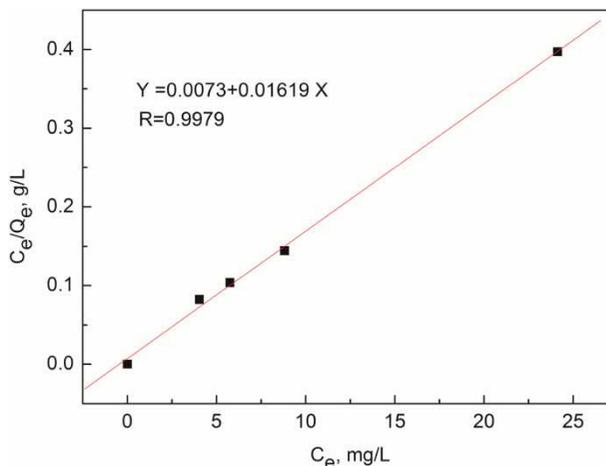

Figure 2 | Linear fitting of three kinds of moving boundary model.

Figure 4 | Adsorption isotherm of Cr(VI) using the hybrid membrane at 20 °C.

Table 2 | Comparative data on the repeated adsorption of chromium ions using the membrane

| Membrane type	Saturated adsorption quantity for the first time (mg/g)	Saturated adsorption quantity for the second time (mg/g)	Balance the removal rate for the first time (%)	Balance the removal rate for the second time (%)	Effective rate (%)
QPVA/ 0.25PDADMAC/ 0.1TEOSm	29.2183	25.9534	70.8602	64.8834	91.5654
QPVA/0.5PDADMAC/ 0.1TEOSm	32.8513	30.6957	82.1282	76.7392	93.4383

the linear coefficient (R) was 0.9979, which basically confirmed that the adsorption procedure was in agreement with the Langmuir adsorption isotherm model.

Recoverability of the anion exchange membrane

As shown in Table 2, the results show that the hybrid membranes can have repeated use, due to the total effective rate of these two kinds of hybrid membranes reuse being above 90%.

Functional group determination of the QPVA/ 0.5PDADMAC/0.1TEOSm by FTIR

Compared with QPVAm, the characteristic absorption peak of hydroxyl groups on the chain of QPVA/0.5PDADMAC/ 0.1TEOSm was relatively weaker at 3,400 cm^{-1}, as shown in Figure 5. Such a phenomenon could be attributed to the sol–gel structure formed in QPVA on the addition of TEOS. Particularly, a new peak attributed to the Si–O bonds emerged at 1,000 cm^{-1}. Because of the synergic effect of Si–O and C–O
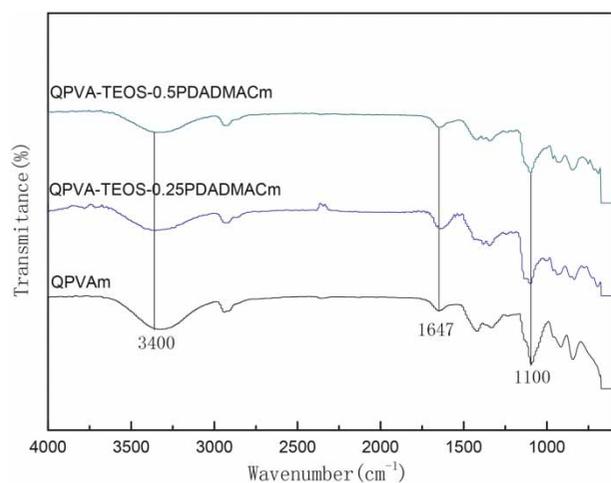
Figure 5 | Functional groups determination of the QPVA/0.5PDADMAC/0.1TEOSm by FTIR.

bonds, their characteristic absorption peak around 1,100 cm^{-1} was markedly different from that of QPVAm. Futhermore, the peaks of quaternary ammonium groups at 1,647 cm^{-1} were all present in the three membranes, which might be due to the combined effect of PDADMAC and the cations of QPVA. However, the peaks of QPVA/0.25PDADMAC/0.1TEOSm were the strongest, indicating that it has a comparatively high ionic exchange capacity.

Morphology analyses of membranes

The surfaces ($\times 4,000$) and cross-sections ($\times 2,400$) of the three hybrid membranes were observed by SEM, and the types of potential elements could be further identified and confirmed by the energy spectrum analyses.

Figure 6 distinctly depicts the appearances of the three hybrid alkaline membranes, that is, QPVAm (Type A), QPVA/0.25PDADMAC/0.1TEOSm (Type B), and QPVA/ 0.5PDADMAC/0.1TEOSm (Type C). Numbers 1 and 2 represent the surface and the cross-section images, respectively. A1 and A2 were compact without the obvious existence of pores and channels, and the white matter present indicates the grafting of the quaternary ammonium groups on PVA. B1 and B2 had 'orange peel-like' tissues, unlike the smooth surfaces of A1. This observation was caused by the diversity of the compatibility between PDADMAC cation polymer and QPVA, which contributes to the microphase separation on the surfaces. Despite their fracture surfaces being dense, a decent quantity of PDADMAC was constrained into the sol–gel structure. C1 and C2 had similar surfaces vis-à-vis those of B1 and B2, but their cross-sections exhibited a 'honeycomb' appearance. This was caused by the excess PDADMAC cation polymer, which brings about the deterioration of the compatibility, and the distinct phase separation that decreases the barrier property of the membranes. The morphologies of QPVA/0.5PDADMAC/ 0.1TEOSm before and after Cr(VI) ion adsorption were also characterized and were marked as D1 and D2.
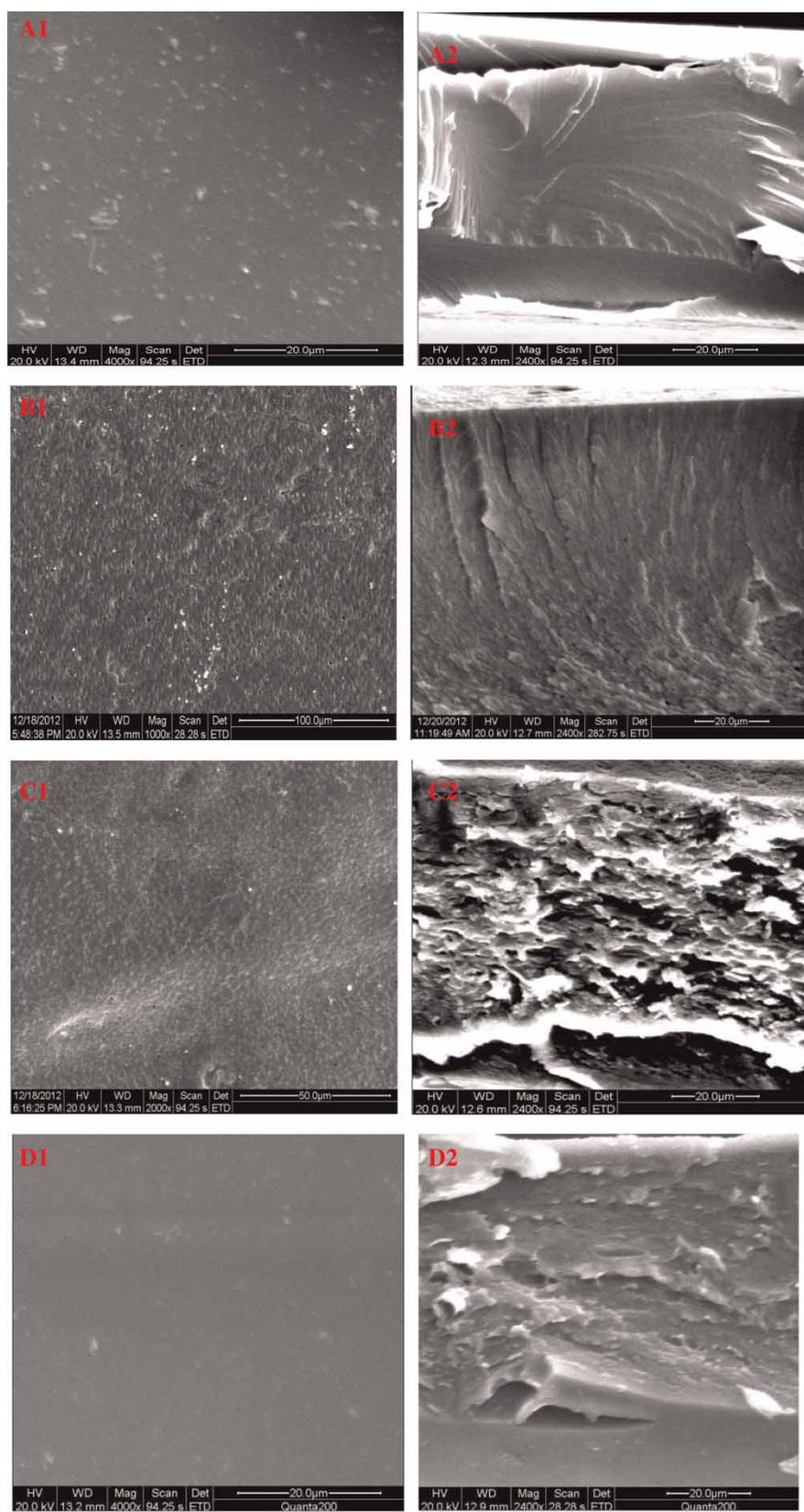
Figure 6 | Surface and cross-section morphology of different membranes.

Saturation of the microporous structure was observed after the adsorption of Cr(VI) ions, indicating that Cr(VI) ions were sufficiently adsorbed.

CONCLUSIONS

1. Anion hybrid membranes (QPVA/0.25PDADMAC/0.1 TEOSm and QPVA/0.5PDADMAC/0.1TEOSm) for the adsorption removal of Cr(VI) were successfully prepared.

2. The process of exchange adsorption and removal of chromium ions by functional groups in this kind of hybrid membrane is an exothermic reaction.

3. The as-prepared QPVA/0.5PDADMAC/0.1TEOSm membrane with microporous structure has excellent adsorption ability for the removal of Cr(VI) ions. The kinetic fitting results show that particle diffusion has an important function during the adsorption process.

4. The pH value of the simulated wastewater significantly affects the existing forms of Cr(VI). At pH 2, Cr(VI), which exists as $HCrO_4^-$ and $Cr_2O_7^{2-}$, is conveniently removed by the hybrid anion membrane.

5. The adsorption process at 20 °C is in agreement with the Langmuir adsorption isotherm model. The static adsorption amount is 61.77 mg/g.

6. The prepared hybrid membrane is recyclable. The recovery coefficient may reach as high as 90%.

7. The microstructures of QPVA/0.5PDADMAC/0.1TEOSm densify after adsorption.

ACKNOWLEDGEMENTS

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