Adsorptive removal of Ni(II) ions from aqueous solution by PVDF/Gemini-ATP hybrid membrane

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Abstract. As a highly hydrophilic fibrillar mineral in nature, attapulgite (ATP) is a promising new additive for preparation of ultrafiltration (UF) hybrid membrane. In this work, ATP particles, which were grafted with a new Gemini surfactant of Ethyl Stearate-di(octadecyl dimethyl ammonium chloride) to detach the crystal bundles to single crystal and enhance the uniform dispersion in an organic polymer matrix, were incorporated into poly(vinylidene fluoride) (PVDF) matrix, and PVDF/Gemini-ATP hybrid membranes for adsorptive removal of Ni(II) ions from aqueous solution were prepared via a phase inversion method. Chemical composition, crystalization and morphology of the modified ATP were characterized by Fourier transform infrared spectroscopy (FTIR), Transmission electron microscope (TEM) and X-ray diffraction (XRD), respectively. The morphology of the hybrid membrane was characterized by Scanning electron microscopy (SEM), the performance of permeability, hydrophilicity and adsorption of Ni(II) ions were studied, and the adsorption kinetics of the PVDF/ATP hybrid membranes were particular concerned. The results showed that the hybrid membrane displayed a good thermal stability and hydrophilicity. Comparing with PVDF membrane, the hybrid membrane possessed good adsorption capacity for Ni(II) ions, and the adsorption kinetics fit well with Lagergren second-order equation.

Keywords: PVDF; attapulgite; hybrid membrane; Gemini surfactant; adsorption; Ni(II)

1. Introduction

Nickel is one of the most toxic metals. Most pollutant of nickel in environment come from the mining and smelting of nickel ore, the production and processing course of alloy steel, the discharge of smoke from coal and oil burned, the process of nickel plating (Fan *et al.* 2008, 2009, Dumrul *et al.* 2011, Cayllahua and Torem 2011). A number of different technologies, such as membrane filtration (Vatanpour *et al.* 2012, Malamis *et al.* 2011) coagulation and precipitation (Charerntanyarak 1999), ion exchange (Vinodh *et al.* 2011), adsorption (Chauhan *et al.* 2009, Faghihian *et al.* 2014, El-Mallah and Hassouba 2014) and so on have been applied for the sequestering of heavy metal ions from wastewater. Among the above methods, the most promising process for the removal of Ni(II) ions from wastewater is adsorption and membrane filtration.

Attapulgite (ATP) is a kind of crystalloid hydrous magnesium-aluminum silicate mineral,

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having special layer structure, chain structure and good colloidal properties such as specific features in dispersion, high adsorbing and de-coloring capabilities. In recent years, as a naturally cheap absorbent clay mineral with exchangeable cations and reactive-OH groups on its surface, ATP has been intensively used as an adsorbent in the removal of heavy metal ions and organic contaminants. Nonetheless, it generally possesses poor sorption capacity and selectivities in aqueous solution. In order to enhance its adsorption capacity, ATP has recently been widely treated with some reagents, such as 2,2-bis (hydroxymethyl) propionic acid (Liu and Wang 2007) NaCl solution and so on.

Catalytic activity and physico-chemical properties of ATP can be improved to different degrees by progressive acid treatment, thermal treatment and organic modification, which results in the enhancement of surface area and porosity, or introduce some functional groups. Among those methods, the organic modification is useful process to change the properties of ATP (Pushpaletha and Lalithambika 2011, Liu *et al.* 2014, Huang *et al.* 2008).

In recent years, Gemini surfactant has become the focus in the field of colloid and interface chemistry as a result of its outstanding surface activity, based on its molecule structure with double hydrophile groups, double lipophile groups, and joint space group to break through that of traditional surfactant (Menger and Keiper 2000, Honglu and Guomei 2008). The structure of Gemini surfactant is a dimer which joins two single alkyl chain single head group of ordinary ionic surfactant head groups imposes a bond together through a spacer group. Exactly, the molecules possess, in sequence, a long hydrocarbon chain, an ionic group, a rigid spacer, a second ionic group, and another hydrocarbon tail (Zana 2002).

The morphology of the arrangements of Gemini monomers in polar solvent may be of four different types depending on the structure of the molecule and its orientation (Shown as Fig. 1) (Menger and Keiper 2000). The long hydrocarbon chain tends to increase the surface activity. But increasing hydrophobicity may make the molecule insoluble, whereas increasing hydrophilicity of the head group may impart solubility in water. Hydrophilic groups in the spacer also increase the aqueous solubility. Increase in carbon number in the nonpolar chain increases both lipophilicity and surface activity with decrease in critical micellar concentration.

The available research results indicate that membrane technologies are increasingly used in water treatment because of their high space utilization and guarantee of treated water quality. Poly(vinylidene fluoride) (PVDF) is a representative membrane material with excellent thermo-
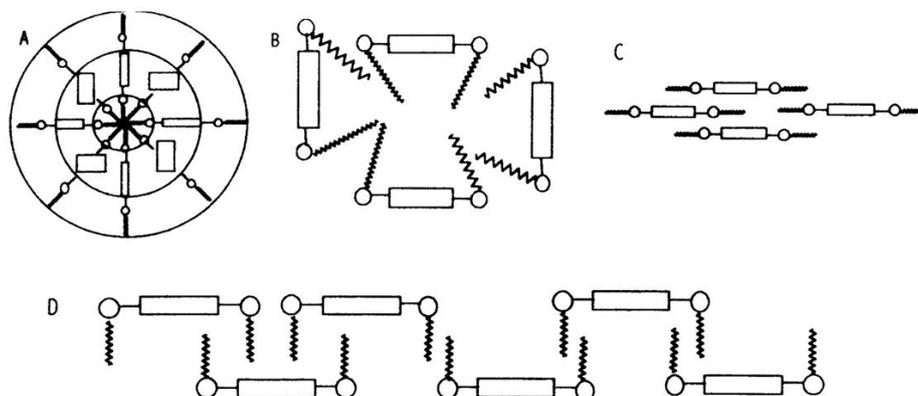

Fig. 1 Possible morphology of Gemini surfactants

stability, strong chemical inertness, high mechanical strength, and great insulating performance (Palmarin and Young 2016, Zhang *et al.* 2014).

In this work, a new kind of modified ATP (Gemini-ATP) was prepared by grafting ethyl stearate-di(octadecyl dimethyl ammonium chloride) onto the ATP treated with acid (a-ATP) to improve the adsorption capacity for heavy metal ions. Amphiphilic surfactant modified inorganic material, an organic hydrophobic group to improve-inorganic interface compatibility, while the hydrophilic head groups to provide better external hydrophilic. It plays an important role in this study With the Gemini-ATP as adsorbent, PVDF as matrix, PVDF/Gemini-ATP hybrid membrane for adsorptive removal of heavy metal ions from aqueous solution was prepared. The adsorption performance for Ni(II) ions and the adsorption thermodynamics and kinetics of the hybrid membrane were evaluated.

2. Experimental

2.1 Materials and reagents

ATP, provided by JiangSuXuYuan halt non-metallic mining Ltd., treated by acid activation with the average diameter of 500 meshes. It was dried in vacuum at 100°C for 24 h before used. Ethyl Stearate-di(octadecyl dimethyl ammonium chloride) was purchased from TianJing Chemical Technology Ltd. of Henan Province. PVDF powder was obtained from Elf Atochem, UK. All other chemicals used in this work were of analytical grade as received.

2.2 Preparation of hybrid membrane

Prepared of Gemini-ATP

9.0 g a-ATP were divided into three, successively added 4%, 6%, 8% Gemini surfactant, respectively. Samples were added into 100 mL water in a 250 mL flask, the mixture was then dispersed with ultrasonic vibrations for 40 min and refluxed for 2 h under stirring with a magnetic stirrer at 70°C. After the reaction, the ATP immobilized with the Gemini surfactant centrifuged and the precipitate was dispersed into 100 mL ethanol with ultrasonic vibrations for 30 min until
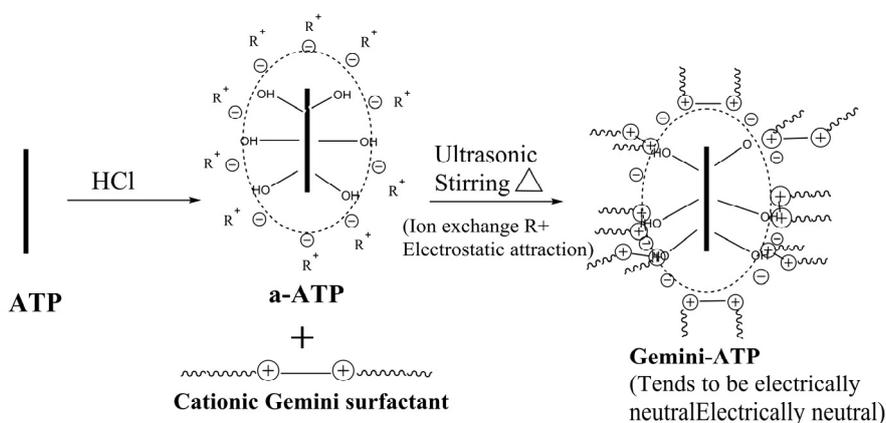
Scheme 1. Schematic illustration of the surface modification of attapulgite (ATP) by Gemini

the pH was neutral. The product was dried 24 h in a desiccator at 90°C. Then the 4%, 6%, 8% Gemini-ATP were obtained. The steps related to the surface grafting of APT are illustrated in Scheme 1. Since the electrostatic attraction after maintaining electrical neutrality, such Gemini surfactant hydrophilic head groups exposed to the outer surface of the ATP.

Preparation of PVDF/Gemini-ATP membrane

Casting solutions were prepared by dissolving PVDF in DMF, and the total PVDF concentration in casting solutions is fixed at 15wt%. Then Different levels of Gemini-ATP were added into the solvent. In order to achieve better functional results, 1wt% of ATP was selected according to the study reported previously. All the mass weight of PEG was fixed at 8% solution quality. In addition, the casting solution of pure PVDF was prepared by dissolving 15wt% PVDF in 85wt% DMF. The samples were refluxed for 4h under stirring with a magnetic stirrer at 70°C in a 250 mL flask. After the reaction, releasing the bubbles in reduced pressure (-50 kPa) for 20 min. Finally, the casting solutions were cast at 20°C on glass plates, the homogeneous solutions was spread into liquid film with a scraping membrane rods (350 μm), and immersed in a coagulation bath of water at 20°C immediately. Subsequently, the products were peeled off and subsequently soaked in deionized water for 3 days to remove residual solvent. After dried in a desiccator, the formed membranes were used for characterization and testing.

2.3 Adsorption properties

The simulated wastewater was obtained in a 1L flasks, which contained pH = 3 and 200 mg/L aqueous solutions of Ni(II) ions. 0.2 g adsorbent (ATP samples or membranes) was added into 50 mL Ni(II) ions solution and then shocked in shaker at fixed temperatures. The amount of the adsorbed Ni(II) ions was indicated from the absorbance intensity at 534 nm recorded on a UV–vis spectrometer (TU-1901, Japan). The reported data were the average value of triplicate samples.

2.4 Analysis and characterization

Bruker Tensor37 infrared spectrometer was used for the FT-IR spectroscopy analysis. XRD was performed using a Bruker Axs D8 system with Cu Kα radiation, operated at 50 kV and 80 mA over the range $5° < 2\theta < 40°$. The morphologies of the ATP and o-ATP were recorded with a Hitachi H-7650 transmission electron microscope (TEM). The PVDF membranes were assessed morphologically using a Hitachi S-4800 FE-SEM.

Pure water flux of PVDF membranes were measured by a cross flow filtration system (Laboratory homemade). The measuring protocol was as follows:

In the first 1 h, the membrane was compacted at 0.2 MPa to diminish the compaction effect and obtain the stable flux, and then the flux was measured at 0.1 MPa. Water flux reported in this work was the final steady flux. The water flux was calculated using the following equation.

$$J = \frac{V}{t \cdot m} \tag{1}$$

Where J was the flux for pure water (L/m^2·h), V was the volume for permeate water (L), m was the effective membrane area (m^2), and t was the permeation time (h), respectively.

In this study, dynamic contact angle analyzer (DSA100) was used to test a variety of flat membrane contact angle.

3. Results and discussion

3.1 Characterization of the Gemini grafted ATP

3.1.1 Surface composition and crystal structure of the Gemini-ATP

The FTIR spectra of ATP before and after modification were shown in Fig. 2. The absorption spectra of a-ATP (see Fig. 2(b)) retain almost all of the features of the bare ATP. While the peak for a-ATP at 1462 cm^{-1} of Carbonate group fade obviously. It showed that the carbonate impurity in ATP reduction.

Peak at 1640 cm^{-1} for ATP belongs to the flexural vibration band of coordinated water and absorbed water molecular. After the modification of Gemini onto the surfaces of ATP (see Fig. 2(c)), the disappearance of the characteristic band at about 3619 cm^{-1} showed that high molecular weight organic group replaces ATP inorganic cations (Li *et al*. 2011). Adsorption peaks at 2925 cm^{-1} and at 2854 cm^{-1} due to asymmetric and symmetric C-H stretching modes. The C = O

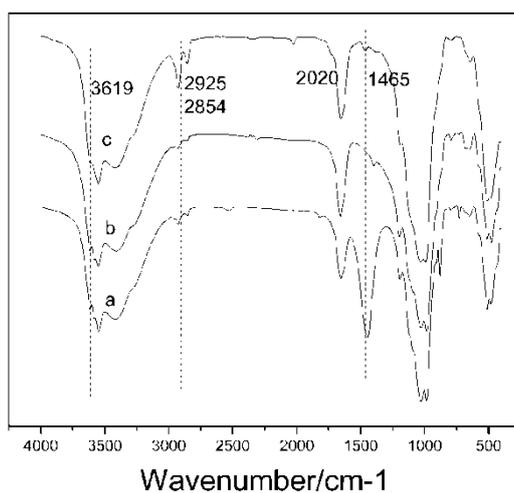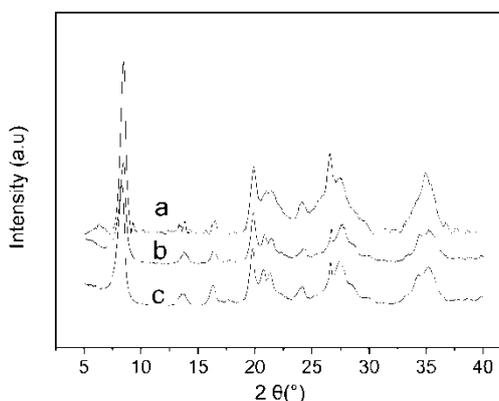
Fig. 2 FT-IR spectra of ATP: (a) ATP; (b) a-ATP; (c) o-ATP

Fig. 3 XRD patterns of modified ATP

stretching peak is observed at 1726 cm^{-1}, and a band at 1465 cm^{-1} due to H-C-H scissoring of Quaternary ammonium salt. It showed the Gemini surfactant had been successfully grafted from the surfaces of the ATP nano-fibrillar clay by the proposed method.

The XRD patterns of the three kinds of ATP were given in Fig. 3. It can be clearly seen that crystallinity decreased in a-ATP and Gemini-ATP compared to that of natural ATP, indicating that important reactions occurred at the ATP surface. There was no change of the XRD patterns of the a-ATP after surface modifications with the Gemini Surfactant. It could be concluded that the Gemini was grafted from the surfaces of the nanofibril clay by the proposed method and it had no effect on the crystal structure of the nanofibril.

The different modification ATP TEM photographs can be seen from the Fig. 4. It can be clearly observed that the surface morphology of natural ATP changed evidently after modification. The bare ATP (see Fig. 4(a)) evenly dispersed, showed loose aggregates and clear fibrous structure (see Fig. 4(a)) with a diameter of about 20 nm and about 500 nm in length. The shaded associated impurities disappear after acid treatment (see Fig. 4(b)). Acid treatment increased the active site of ATP, the surface charge distribution became uneven. After modification, the M-ATP shows compact aggregates (see Fig. 4(c)) and a larger diameter of about 40 nm (see Fig. 4(c)), also increasing the ratio of surface area, to some extent, increased the ATP reunion, which could be attributed to the adherence of ATP caused by the Gemini surfactant. It could be concluded that the grafting of the Gemini had markedly improved the dispersibility of the nanofibrillar clay in solvents.

3.1.2 Adsorption properties

The adsorption capacities of the three temperatures towards Ni(II) ions were summarized in Table 1. It was found that the negative ΔH^0 described the adsorption process of Ni(II) ions is an
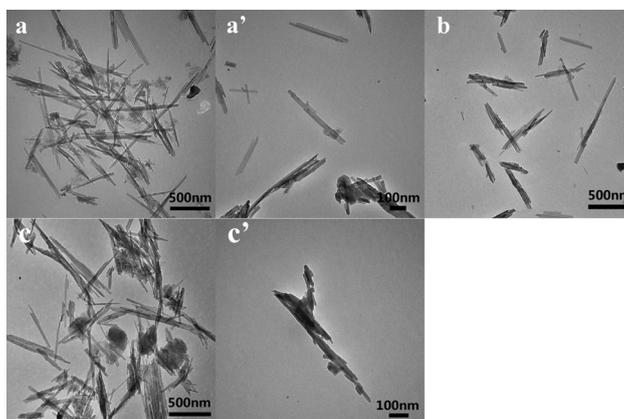

Fig. 4 TEM photographs of modified ATP: (a)ATP; (a') enlarged ATP; (b) a-ATP;
(c) Gemini-ATP; (c') enlarged Gemini-ATP

Table 1 The Ni(II) ions adsorption thermodynamic parameters

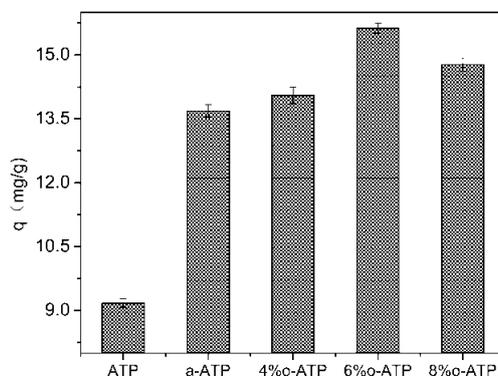| C_0 (mg/L)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol·K)	ΔG (kJ/mol)			R^2
			298.15 K	308.15 K	318.15 K	
200	-2.3242	-14.363	-0.3591	-0.5026	-0.6448	0.9827

Fig. 5 Ni(II) ions adsorption of the modified ATP

exothermic reaction. The negative ΔS^0 indicated that the reaction is a process of entropy reduction, and the degree of chaos of the solid-liquid interface was reduced in the adsorption process. ΔG is negative, indicating ATP to Ni(II) ions adsorption can occur spontaneously (Argun *et al.* 2007).

The adsorption capacity of the different modification ATP was shown in Fig. 5. It was found that the a-ATP and o-ATP had the higher adsorption capacities for Ni(II) ions. Furthermore, the o-ATP had the highest adsorption capacities for Ni(II). In addition, among the different levels of ATP, the adsorption capacities of the 4% o-ATP and 8% o-ATP were lower slightly than the 6% o-ATP because the groups containing N element were enshrouded with the long chain macromolecules, which is hydrophobic. However, the amido and hydroxyl groups of the Gemini surfactant had the decent complexation abilities towards the heavy metal ions. And the o-ATP had faster sedimentation rate than the A-ATP which is an advantage in production or application.

3.2 Membrane performance

3.2.1 Morphology of the hybrid membrane

The surface and cross-sectional morphologies of the PVDF/ATP hybrid membranes were characterized using SEM (see Fig. 6) (Hashim *et al.* 2009, Zhao *et al.* 2008) The Figs. 6(a1)-(a4) show that the pure PVDF membrane and the PVDF/ATP membranes exhibited similar smooth surface morphologies. However, additional pores can clearly be observed on the membrane surface with increasing ATP in the matrix. All of the membranes showed the typical asymmetrical structure consisting of a skin layer as the selective layer and a thick finger-like sub-layer (see Figs. 6(b1)-(b2)). The low viscosity of the doping ATP enhanced the phase separation, and instantaneous de-mixing occurs, leading to a porous skin-layer and finger-like pores in the sublayer. Unlike the membrane without additives, the presence of ATP in the solution promotes the diffusion of water to the PVDF due to the good affinity between them. In case of Gemini-ATP, finger-like pores are seen to grow from the top surface almost to the bottom surface. On the one hand, the Gemini-ATP amphiphilic additives may exacerbate the formation of finger-like pores by enhancing the water diffusion rate. On the other hand, with increasing the compatibility between the organic solvent and ATP, the smaller isolated pores conquered the interface tension barrier and were gradually connected together to form the long finger-like pores through the cross section. As shown in Fig. 6(b2), large slanting macro-voids and a porous top layer were observed. The inner spongy porous structure of the sample is shown in Figs. 6(c1)-(c4). The rod-like ATP was evenly dispersed in the
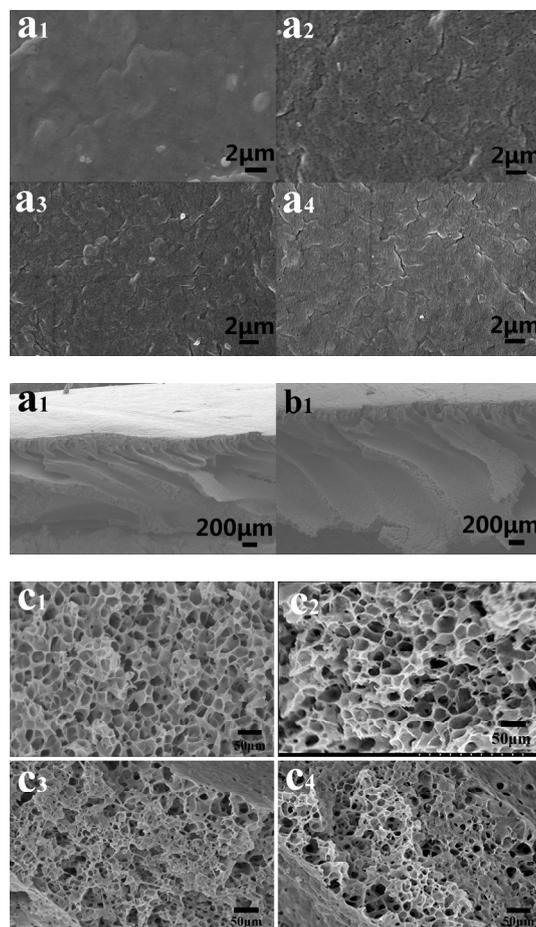
Fig. 6 SEM images of the bottom surface, cross-section and inner porous structure of the prepared membranes: (a1) PVDF; (a2) PVDF/ATP; (a3) PVDF/a-ATP; (a4) PVDF/Gemini-ATP; (b1) PVDF; (b2) PVDF/Gemini-ATP; (c1) PVDF; (c2) PVDF/ATP; (c3) PVDF/a-ATP; (c4) PVDF/Gemini-ATP

polymer matrix, resulting in no obvious agglomeration in the hybrid membrane. However, With the ATP added, the inner spongy porous was enlarged to some extent, which was apparently beneficial to the enhancement of the membrane properties.

3.2.2 The FTIR-ATR spectrum of membranes

The FTIR-ATR spectrum of the PVDF and the nanoclay composites can be seen in Fig. 7. Peaks at 840 cm^{-1} and 879 cm^{-1} were α-crystal and β-crystal of PVDF, respectively. Bands of 1176–1273 cm^{-1} are ascribed to C-F stretching. The peak at 1670 cm^{-1} represented a typical carbonyl (C = O) stretching vibration, which confirmed the Gemini in the matrix, and the absorption peaks at 1406 cm^{-1} and 2978 cm^{-1} were due to C-H deformation and C-H stretching. The new peak at 987 cm^{-1} (Si = Si stretching) showed much more significantly with the increase of modified ATP, implying the successful attachment of additives and PVDF membrane (Yeow *et al*. 2005, Zhang 2014, Hester 2002).
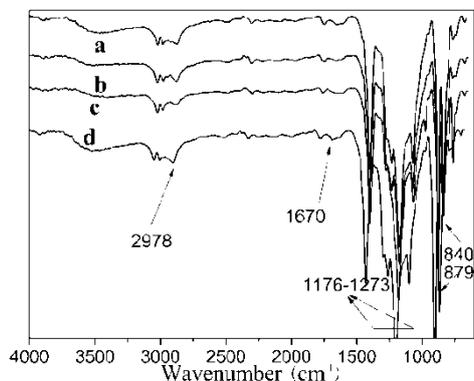
Fig. 7 FTIR-ATR spectra of PVDF membranes: (a) PVDF; (b) PVDF/1%ATP;
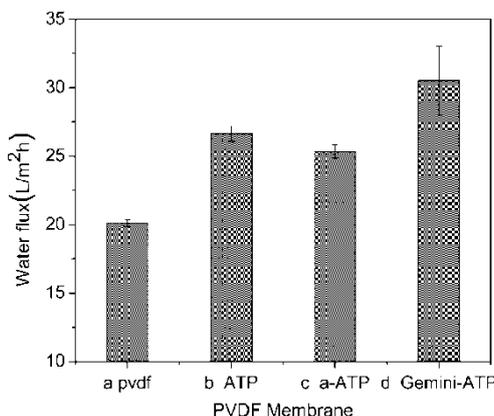(c) PVDF/1%a-ATP; (d) PVDF/1%Gemini-ATP

Fig. 8 Water flux of various membranes at 0.1 MPa

3.2.3 Permeability of membranes

Permeability of membranes was measured by pure water flux (Wang *et al*. 1999) as can be seen in Fig. 8. Water flux reflects the pore size, pore size distribution and morphologies of the membranes. All of the modified membranes with higher additions exhibited a higher water flux than that of the pure PVDF membrane. Water flux of the o-ATP/PVDF sample attained a maximum value of 60.51 $L/(m^2 \cdot h)$, while the pure PVDF membrane shows the lower flux of 40.11 $L/m^2 \cdot h$. It can be explained as follows. Incorporation of mineral ATP enhanced the hydrophilicity of the membranes from 74.4° to 64.3° (Table 2), which improved the water permeation to a certain extent. And o-ATP/PVDF has sufficient finger-like pores through the cross section and porous bottom surface.

Table 2 Contact angle of PVDF/ATP hybrid membranes

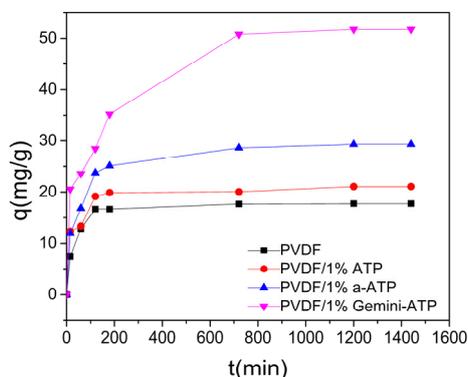|	PVDF	PVDF/1%ATP	PVDF/1%a-ATP	PVDF/1%Gemini-ATP
Contact angle (°)	70.1	64.3	70.5	74.4

Fig. 9 Effect of contact time on the removal of heavy metals

3.2.4 Effects of adsorption time

In an attempt to present the kinetic equation representing adsorption of heavy metals on membranes, the kinetic parameters for the adsorption process were studied for contact time ranging between 1 and 1600 min. To establish an appropriate contact time between the different PVDF membrane and Ni(II) solution, adsorption capacities of metal ion were measured as a function of time (Fig. 9). The Process of PVDF, ATP/PVDF and a-ATP/PVDF showed an increasing trend up to a reaction time of 3h beyond which adsorption appeared to have approached equilibrium. After 3 h, the adsorption capacity of Ni(II) by PVDF/1% Gemini-ATP was still increasing. The others became constant. After 13 h, all got equilibrium. Obviously, the rate of uptake of heavy metals by o-ATP/PVDF was faster than pure PVDF.

3.2.5 Adsorption kinetic model

Adsorption is a physical-chemical process that the mass transfers a solute (adsorbate) from the fluid phase to the adsorbent surface. A study of kinetics of adsorption is desirable as it provides information about the mechanism of adsorption, which is important for efficiency of the process (Salehi *et al.* 2012, Ricordel *et al.* 2001, Liu 2009, Li *et al.* 2007)

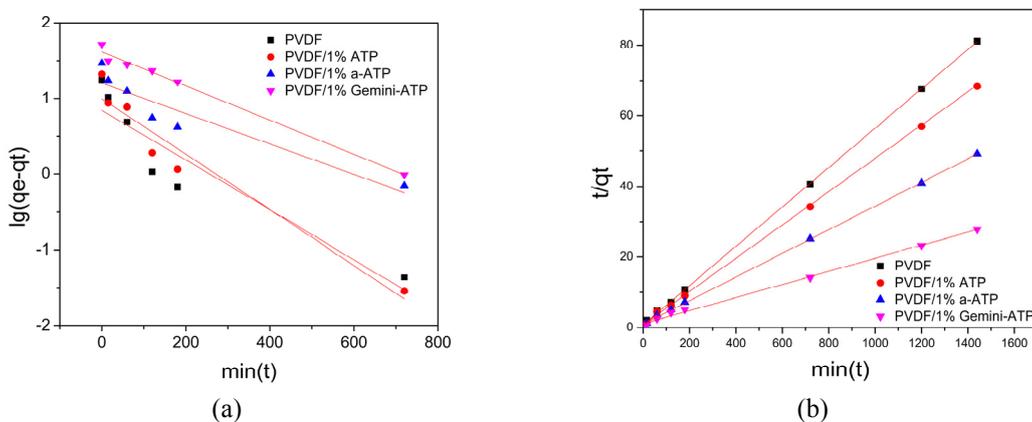(a)   (b)

Fig. 10 Pseudo-first-order kinetic (a) and Pseudo-second-order kinetic; (b) for adsorption of Ni(II)

Table 3 Adsorption kinetic parameters of Ni(II) on PVDF membranes

Sample	q_e exp(mg g^{-1})	Pseudo-first-order kinetic			Pseudo-second-order kinetic		
		q_e, cal(mg g^{-1})	k_1 (min^{-1})	R^2	q_e, cal(mg g^{-1})	k_2 (min^{-1})	R^2
PVDF	17.748	6.932	0.00758	0.8361	17.934	0.00427	0.9998
PVDF/1%ATP	21.051	9.853	0.00845	0.9329	21.204	0.00288	0.9993
PVDF/1%a-ATP	29.297	15.909	0.00463	0.8666	29.833	0.00127	0.9994
PVDF/1% Gemini-ATP	51.734	41.498	0.00520	0.9877	53.908	0.00032	0.9955

Two kinds of kinetic models were used to test the experimental data. These are Lagergren-first-order equation and second-order equation.

Lagergren-pseudo-first-order equation is the most popular kinetics equation. The form is

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{2}$$

Where q_t is the amount of adsorption time t (min) (mg/g); k_1 the rate constant of the equation (l/min); q_e is the amount of adsorption equilibrium (mg/g). And the adsorption rate constant, k_1, can be determined experimentally by plotting of $\ln(q_e - q_t)$ against t.

The pseudo-second-order equation is in the following form

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{3}$$

Where k_2 is the rate constant of the second-order equation (g/mg/min); q_t the amount of adsorption time t (min)(mg/g); q_e is the amount of adsorption equilibrium (mg/g).

The plots, slop of the plots and intercepts of curves were used to determine the constant k1 and k_2, capacity q_e and the corresponding linear regression correlation coefficient R values (Table 3). The calculated (cal) value of q_e from the pseudo-first-order kinetics model was dramatically lower than the experimental (exp) value. However, the linearized pseudo-second-order kinetics model (Fig. 10 and Table 3), provided much better R^2 values (all values greater than or equal to 0.99) than those for the first-order model, and the calculated values closely approximate the measured experimental values. As a result, the sorption system appears to follow pseudo-second-order reaction kinetics. The first and pseudo-second-order kinetics rate constants for the adsorption of Ni(II) ions on membrane were k_1 = 7.58, 8.45, 4.63 and 5.20×10^{-3} min^{-1}, respectively. And k_2 = 4.27, 2.88, 1.27 and 0.32×10^{-3} min^{-1}, respectively.

4. Conclusions

We have described the fabrication of a new functionalized Adsorbent, in which Gemini modified ATP is grafted into the internal of PVDF ultrafiltration membrane, and the effects of ATP additive were studied. First, SEM images, XRD patterns, and FTIR spectra confirmed that the Gemini was grafted from the surfaces of the nanofibril clay by the proposed method and it had no effect on the crystal structure of the nanofibril. Also, the ATP itself has a certain adsorption

properties, and 6% Gemini grafted ATP had the highest adsorption capacities for Ni(II) and faster sedimentation rate in the solution. Furthermore, the Surfactant Gemini achieved a more uniform presence of additives in the polymer matrix than that of the natural ATP such that the hybrid membranes exhibited better performance not only in microstructure and hydrophilicity but also in thermal stability, permeation and adsorption properties. The surface and cross-section of the nanocomposite membranes characterized by SEM indicated that greater amount of additives promoted the formation of smaller size pores and finger-like pores. Most importantly, the filtration experiments and adsorption experiments demonstrated that novel hybrid membranes showed excellent pure water filtration and successfully adsorbed Ni(II) ions capacity. The adsorption kinetics of M-ATP fitted a pseudo-second-order kinetic model, therefore chemisorption contributes mainly to Ni(II) adsorption. All of these results show that Gemini-ATP is a favorable additive for fabrication of ultrafiltration membranes.

Acknowledgments

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