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Self-assembly functionalized membranes with chitosan microsphere/polyacrylic acid layers and its application for metal ion removal

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Abstract Multilayer composite membranes with high removal capability for metal ion were prepared using electrostatic self-assembly (ESA) technique. Especially, self-assembled multilayer of chitosan microspheres and PAA were formed onto charged surface of polyacrylonitrile (PAN) membranes. It was confirmed that the alternate multilayer of chitosan and PAA were deposited on the base membrane surface. The formation of the ESA layer-by-layer of chitosan/PAA or chitosan microspheres/PAA onto the base membrane surface functionally equipped the membrane with removal capability for Cu^{2+}. Especially, membranes with chitosan microspheres/PAA ESA layers on the surface showed relatively higher adsorption capability as compared with membranes with chitosan/PAA ESA layers. Besides, the influence of the pH of metal ion solution on the metal ion adsorption property of ESA modified membrane was investigated. It was proposed that the layer-by-layer self-assembled deposition of chitosan microspheres would be a new approach to functionalize membrane with high adsorption capability for metal ions.

Introduction

With the development of modern industries, the demand for wastewater treatment has been increasing drastically. Especially, as the existence of heavy metal ions, such as copper, nickel, chromium, zinc, mercury, and cadmium, in excess by even a few ppm in water may be toxic to living species [1]. Thus, the metallic ions in waste water should be seriously treated before disposed into the environment. Various processes such as membrane process [2, 3], adsorption-extracted procedures [4, 5], biological treatment [6, 7] have been widely developed and used for removing ionized metals effectively. Considering the effectiveness and environmentally friendliness with some other factors, biopolymers having abundant free hydroxyl, amino, and other active functional groups used as adsorbent for water treatment have received particular attention. Among the mostly used biopolymers, chitosan [8–11], poly-β-(1 → 4)-2-amino-2-deoxy-D-glucose, has been identified as an attractive option in the field of wastewater treatment because of its unique properties, such as low cost and polyelectrolyte containing a high amount of amino and hydroxyl functional groups, cationicity which makes it reactive for chelation with metal cations in near-neutral solution. The removal of heavy metal ions by chitosan was first reported by Muzzarelli [12], after which the application of chitosan and its derivation for chelating with metal ions were widely studied and developed. Especially, chitosan microsphere [13, 14] has received particular attention because of its efficient loading process ability and fast loading process. Assembled alginate/chitosan (ALG/CHI) micro-shells were prepared for removal of organic pollutants, and compared with conventional polyelectrolyte $(PSS/PAH)_5$ shells [15]. It was shown that the $(ALG/CHI)_5$ shells expressed stronger adsorption capacity and faster adsorption rate for pollutant loading. So it was proposed to be a more efficient and economic purification system for removal of persistent pollutants from wastewater.

On the other hand, Decher et al. [16] developed electrostatic self-assembly (ESA) method which could form multiple-electrolyte layers onto charged substrate. Due to the electrostatic interaction between positively and negatively

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charged groups of electrolytes, the ESA method could be applied for the preparation of functional membrane with electrolyte multilayer. It was proposed that a membrane with multiple electrolyte layers on the surface could be used for the water treatment along with various applications [17]. Lu et al. [18] reported that alternating adsorption of polyanions and polycations on porous supports was applied to prepare ion-selective nanofiltration membrane and the resultant membrane showed high rejection for Mg^{2+} along with considerable selectivity for Na^+/Mg^{2+} and Na^+/Ca^{2+}. Because of the high loading capability of polyelectrolyte layers onto charged substrate surface, it would be able to prepare separation membranes with high adsorption capability for metal ions by introducing multiple-layers of chitosan or chitosan microsphere onto charged membrane surface via ESA technique. The modified membrane is expected to concentrate metal ions in wastewater and lower their concentration for sewage disposal.

It was known that membranes with multilayer polyelectrolyte layers were developed for the separation of ions [19, 20]. For instance, from the research of Hong et al. [19], nanofiltration membranes with multilayer polyelectrolyte layers were developed for the separation of fluoride from other monovalent anions, simple layer-by-layer deposition of bilayer poly(styrene sulfonate) (PSS)/poly(diallyldimethylammonium chloride) (PDADMAC) exhibited considerable selectivity for fluoride. But to the knowledge of the authors, there has been few research of ESA layers composed of microsphere that can be used for metal ion removal application.

As chitosan has excellent chelating effect on the abundant free-hydroxyl groups and amino groups, and has been proved to be able to remove metal ions efficiently. In the present study, we alternately deposited cationic chitosan microspheres and PAA onto charged PAN membrane and the properties of the resultant membranes were investigated. Fourier transform infrared (FT-IR) was used to confirm the deposition of the ESA layers onto charged base membrane surface, while atom force microscope (AFM) was applied to observe the surface morphology of membrane before and after the ESA modification treatment. Because copper is extensively used in paper board mills, plating baths, fertilizer industry, etc., it is proved to be toxic to human beings (leading to liver damages) and aquatic organisms [21, 22]. So here we have chosen Cu^{2+} as target metal ion for studying the removal capability of the resultant membranes having layer-by-layer chitosan microspheres/PAA on the surface.

Experimental

Materials

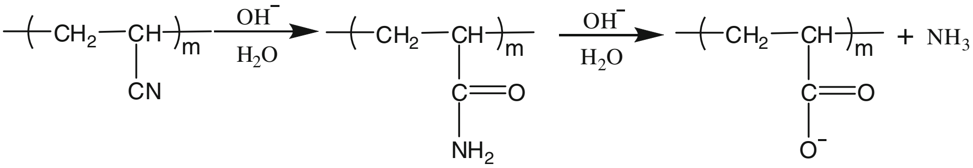
Chitosan with deacetylation of about 78.8% was supplied by Funakoshico, ltd. (Japan), poly(acrylic acid) (PAA, $M_w = 25{,}000$ g/mol) and polyoxyethylene Sorbitan Monooleate (Polysorbate 80) were purchased from Nakarai Tesque (Japan). Acrylonitrile (AN) and dimethyl sulfoxide (DMSO) were distilled under reduced pressure before use and were used for polymerization of membrane material. Deionized water with a resistivity of about 18.2 mΩ cm^{-1} was used throughout the study. The desired pH of the solution was adjusted by diluted aqueous solution of acetic acid and sodium acetate. Potassium hydroxide, acetic acid, and sodium acetate and all the other reagents were of reagent grade and were used without further purification.

Preparation and characterization of charged base membrane

PAN membrane, which was used as the base membrane for ESA treatment, was prepared by phase-inversion method as previously reported [23]. In the present study, the membrane surface was then treated with 2 M KOH solution for certain hours to obtain negatively charged PAN base membrane according to the chemical reaction indicated by the following scheme (Scheme 1). The treated membranes were then washed intensively by deionized water for 24 h for the following use.

A Prestige-21 spectrophotometer (Shimadzu, Japan) was used for fourier transform infrared (FT-IR) analysis on chemical composition of membrane surface before and after KOH treatment. Water contact angle on the surface was measured by using dropmaster DM100 (Kyowa interface science Co., Ltd). Water droplet with 2 µL was deposited on the membrane surface using a contact angle goniometer for each measurement at ambient temperature about 25 °C. For each membrane, five drops were analyzed and the obtained values of contact angles were on standard deviation.

Tensile strength of the resultant membranes was measured using a Strograph-M1 (Toyo Seiki, Japan) and was



Scheme 1 Chemical reaction of PAN treated by alkali solution

calculated by the following equation: $\sigma t = \frac{p}{b \times d}$. Here, σt (MPa) is the tensile strength; p (N) is the maximum load, and b is the width of sample of 13.000 mm, while d is the membrane thickness of 0.128 mm.

The permeability of membrane was evaluated via the water flux by using an ultrafiltration cell (Amicon 8010, 50 mL volume). The water flux was defined as the water permeating unit area membrane during unit time (s), the effective membrane area for the permeation experiment was 1.45×10^{-3} m^2.

Preparation of chitosan microspheres

Chitosan microspheres were prepared according a modification method reported in the literature [24]. Chitosan (50 mg) was dissolved in an aqueous solution of acetic acid (2 wt%) and was stirred for 2 h. Then, 20 mL polysorbate 80 was added slowly and the mixture solution was treated with ultrasonication for 30 min. A solution of sodium sulfate, Na_2SO_4 (10 wt%), was added during stirring and then the solution became turbid. After the addition of sodium sulfate, ultrasonication was resumed for another 20 min. Then, the microspheres were purified by centrifugation for 10 min at 3000 rpm and the obtained sediment was then suspended in water. Finally, the purified microspheres were freeze dried for further use.

Formation of ESA multilayer on charged PAN base membrane

The formation of ESA multilayer was carried out as follows: PAN membrane treated by KOH solution was first immersed into the aqueous solution of chitosan or chitosan microspheres with a concentration of 2 g/L and then removed from the solution, the loosely bound chitosan or microspheres on the membrane was washed out with water. The membrane with chitosan (chitosan microspheres) layer was then immersed into the solution of PAA 2 g/L. The deposition procedure was repeated to form alternate ESA layers onto the charged base membrane surface.

In order to confirm the construction of ESA multilayer on charged substrate surface, FT-IR and AFM (Nanopics 1000, Seiko Instruments, Inc.) measurement were carried out. Furthermore, the metal ion removal properties of the modified membranes were evaluated by absorption experiments. The experimental procedure was carried out as follows: immersing the sample membranes into 2 ppm copper ion solution for 40 min and then, the original and residual ion concentrations remained in the ion solution were measured by atomic absorption spectrophotometer (AA-6300, Shimadzu Ins.). The metal ion adsorption capacity (10^{-6}g/g-membrane) was defined as the amount of Cu^{2+} (g) adsorbed by unit weight of membrane (g).

Results and discussion

Surface treatment of the base membrane

In order to convert the CN groups to negatively charged COO^- group on the PAN membrane surface, the chemical reaction illustrated by Scheme 1 was performed using KOH solution. The FT-IR measurement was carried out in order to study the chemical composition of the PAN membrane surface before and after the KOH treatment. As shown by Fig. 1, it was found that compared with original PAN membrane, in the spectrum of the PAN membrane treated by KOH for 24 h, the characteristic absorption peak for the CN group at about 2300 cm^{-1} became weaker while the characteristic peak assigned to carboxyl group in the range from 2800 to 3700 cm^{-1} appeared stronger. Especially, the band at 1700 cm^{-1} assigned to the carbonyl group from COO^- existed in the FT-IR spectrum. So, it was concluded that the PAN membrane surface was negatively charged due to the formation of carboxyl groups resulting from the KOH treatment. Properties of membranes treated by KOH for various time were studied and the results are represented in Table 1. The values of the contact angle of the treated membranes decreased from

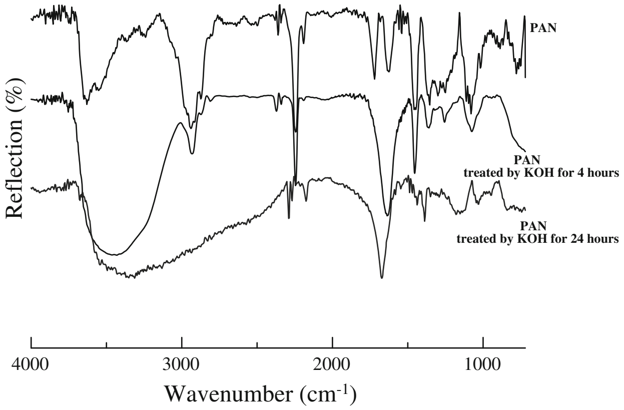


Fig. 1 FT-IR spectra of PAN original membrane and membrane treated by KOH

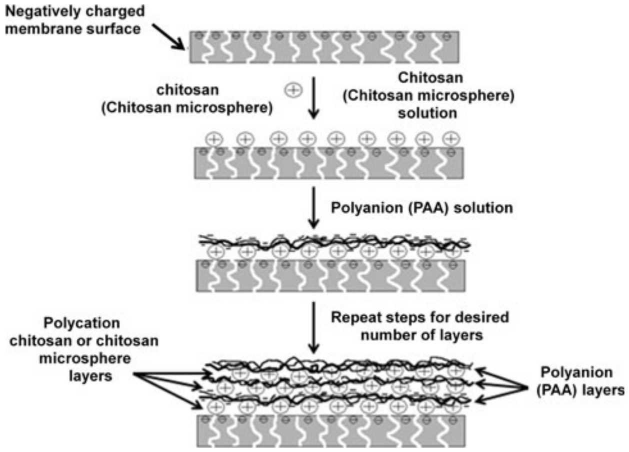
Table 1 Properties of membrane treated by KOH for different time

Treatment time (h)	Tensile strength (MPa)	Contact angle (°)	Water flux (10^{-4}g/m^{2}s)
0	0.94	63.1	1.23
1	1.63	56.4	1.42
2	1.57	49.6	1.17
4	1.40	40.3	1.12
6	1.27	33.8	1.03
24	1.22	19.1	0.98

63.1° to 19.1° as the treatment time increased from 0 to 24 h, suggesting the enhancement of hydrophilic property of membrane surface due to the existence of carboxylic groups on membrane surface and the increasing amount with the longer treatment time. However, the tensile strength of the resultant membranes decreased from 1.63 to 1.22 MPa and the water flux decreased from 1.42 to 0.98×10^{-4}g/m^{2}s as the KOH treatment was prolonged from 1 to 24 h. It means that the 24-h treatment caused membrane and its permeability to become weaker. Considering the tensile strength and the application for separation, membranes treated by KOH for 4 h were used as the charged substrate for the further ESA modification.

Formation of the ESA multilayer of chitosan/PAA

As the surface of the treated PAN membrane was negatively charged due to the KOH treatment, positively charged chitosan and negatively charged PAA were alternatively coated to form self-assembled layers onto the charged PAN membrane (Scheme 2). Also, chitosan polycation microspheres cross-liked by sulfate groups were used instead of chitosan to form electrostatically self-assembled layers onto the negatively charged base membrane. The deposition process of the alternate formation of chitosan or chitosan microspheres and PAA layers was repeated four times. In Scheme 2, for the first step, the cationic chitosan or chitosan microspheres electrostatically interacted with the negatively charged groups on the base membrane surface. The membrane surface was then positively charged due to the deposition of chitosan or chitosan microspheres. Then, for the second step, PAA was deposited over the first layer of chitosan or chitosan microspheres due to the electrostatic interaction between amino groups of the chitosan and carboxyl groups of the PAA. These steps were repeated to form multiple ESA layers on the base membrane surface.



Scheme 2 Illustration images of layer-by-layer assembling of chitosan/PAA and chitosan microsphere/PAA layers onto charged base membrane

Characterization of membrane with ESA multilayer

The surface of membrane having alternate ESA multilayer was investigated using reflection FT-IR spectroscopy. The results are shown as Fig. 2a, b for PAN/chitoan/PAA system and PAN/chitosan microspheres/PAA system, respectively. It was found that the characteristic band of CN group from the charged PAN base membrane at about 2300 cm^{-1} became weaker due to the deposition of ESA layers of chitosan or chitosan microgel and PAA. In addition, the characteristic band at about 1170 cm^{-1} corresponding to the primary alcoholic group of chitosan at the C-6 position and the peak at about 1400 cm^{-1} assigned to the stretching vibration of amide band from chitosan appeared in the spectra, especially for cycled 1 and 3, for which the surface was terminated with chitosan layer or chitosan microspheres layer. In the cases of cycle 2 and 4 for surfaces terminated with PAA layer, similar spectra with PAA were observed and it was believed to be resulted by the coverage of PAA on membrane surface. It was also

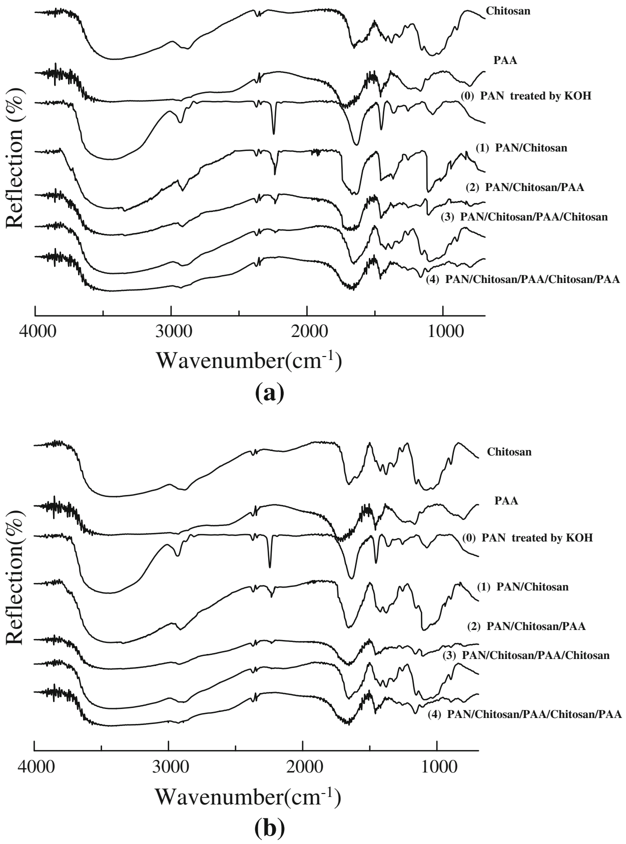


Fig. 2 FT-IR spectra of membranes with self-assembled layers. **a** PAN/chitosan/PAA system, **b** PAN/Chitosan microsphere/PAA system

noticed that the characteristic peak from chitosan became weaker while the peak in the range of about 2500 to 3750 cm^{-1} from the PAA layer became stronger, proving that the PAA layer covered the chitosan or chitosan microspheres layers on the surface. The upper change repeated alternately along with the alternate deposition of chitosan (chitosan microspheres) layers and PAA layers onto charged PAN membrane as revealed by IR spectrum. These spectral changes proved the successful formation of alternate chitosan or chitosan microspheres layers and PAA layers onto charged PAN membrane surface. Furthermore, the obvious difference between the IR spectrum of PAN/Chitosan/PAA system and PAN/Chitosan microspheres/PAA system was observed in comparison of (a) and (b). For the PAN/Chitosan microspheres/PAA system, the disappearance of the peak of the CN group from the charged PAN base membrane was drastic due to the coverage of the ESA layers.

Furthermore, we examined the surface morphology of the base membrane and membranes with ESA multilayer by using AFM. The AFM pictures of the membrane surfaces covered with different number of ESA layers are shown in Fig. 3. After the PAN membrane was treated by KOH solution, the membrane surface became rougher than that of the untreated membrane. After the chitosan or chitosan microspheres and PAA layers were alternately deposited on the base membrane, the surface covered with chitosan microspheres was much rougher than that of membrane terminated with chitosan layers. It was observed that there were some tops having grain shapes appearing on the membrane surface for the PAN/Chitosan microspheres/PAA system.

Surface roughness of the chitosan microspheres/PAA membranes was represented in Fig. 4. As shown in Fig. 4, the surface roughness of −1 and 0, which referred to membranes before and after NaOH treatment, indicated that the membrane surface became rougher due the existence of hydrophilic carboxyl groups resulting from NaOH treatment. It was also apparent that the surface morphology was dramatically altered by the formation of the chitosan microspheres/PAA ESA multilayer. While the corresponding surface roughness values were 8.0, 23.1, 15.0, 39.9, and 36.4 nm for the chitosan microspheres/PAA membranes with cycle layers of 0, 1, 2, 3, and, 4, respectively. However, much less change in the surface roughness was observed for the membrane with chitosan/PAA ESA layers. The values of the surface roughness were 8.0, 8.6, 9.0, 12.2, and 13,7 nm for the cycled layers of 0, 1, 2, 3, and 4, respectively. Therefore, the introduction of the chitosan microspheres for the ESA multilayer could be effective for roughening base membrane surface. Therefore, this approach could be attractive in the uses of adsorption of such metal ions.

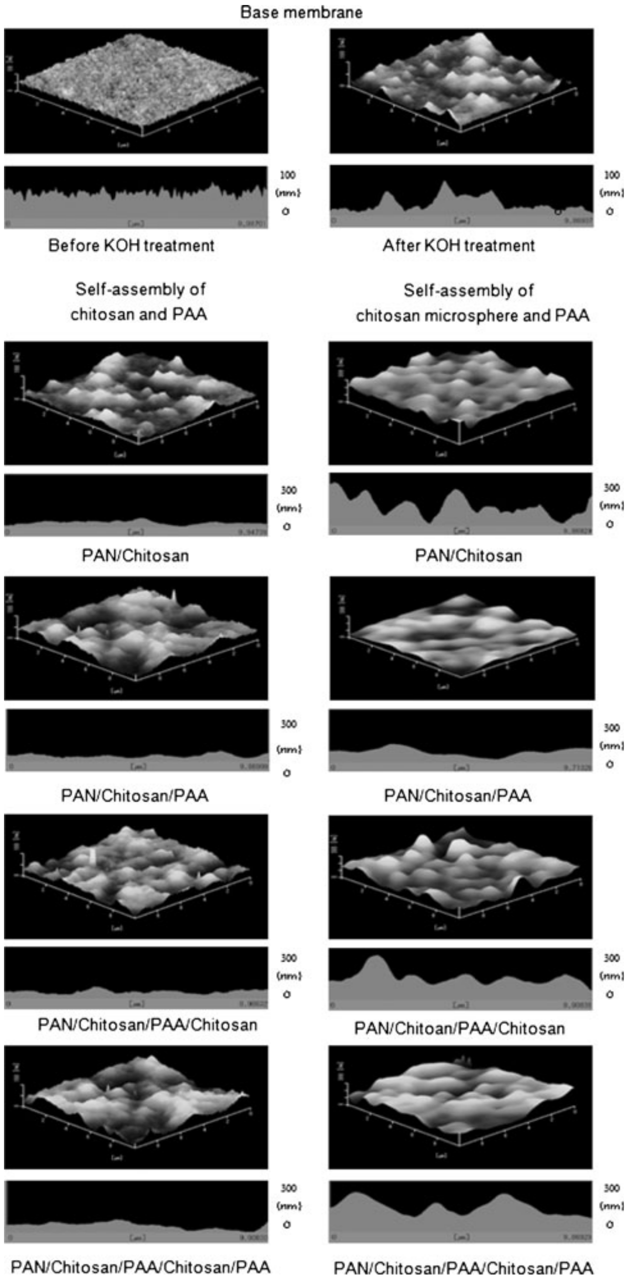


Fig. 3 AFM images of PAN/Chitosan/PAA system and PAN/Chitosan microsphere/PAA system

Adsorption capability for copper ion

It was known that chitosan could be applied for adsorption of metal ions since the amino group is capable of binding metal ions and served as coordination sites [25, 26]. For example, Juang et al. [25] reported high selectivity for Cu^{2+} ion was observed by chitosan adsorbents. Chang et al. [27] found that the chitosan-modified microsphere showed the largest equilibrium adsorption capacity at pH 5.5. Therefore, in the present work, we studied the binding capability for Cu^{2+} ion of the resultant membrane at

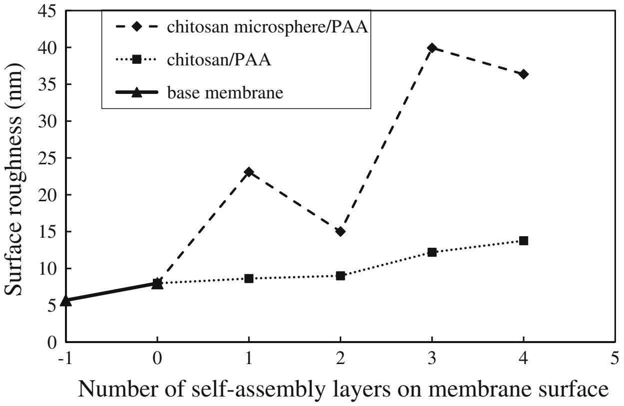


Fig. 4 The influence of numbers of self-assembled layers on membrane surface on the surface roughness for the two systems

various pHs. Here, the pH of the Cu^{2+} ion solution was adjusted using buffer solution of 0.2 mol/L CH_3COOH and 0.2 mol/L CH_3COONa.

Figures 5 and 6 show the effect of the pH of Cu^{2+} ion solution on the Cu^{2+} adsorption of resultant membranes with Chitosan/PAA and Chitosan microspheres/PAA ESA multiple-layers, respectively. The adsorption amounts of the Cu^{2+} ion were plotted at the cycle number for the ESA multilayer formation. The odd lines were for the chitosan or chitosan microspheres layers exposed on the membrane surface outmost and evens were for PAA layers on the outmost. It could be seen that when the adsorption was carried out at pH 3, membranes terminated with PAA layers showed higher adsorption capacity rather than those with terminal chitosan or chitosan microspheres layers. But with the increase of the pH, the change regulation could not be seen at pH 7 in both (a) and (b) systems. In the case of the chitosan microspheres/PAA system, the vales of the adsorption capacity were significantly decreased to be in the range of about 50 ppm/g-membrane. However, at pHs 5 and 6, the values of the adsorption capacity increased with the increase of the cycled number of the ESA operation and then ranged from about 200 to 240 ppm/g-membrane. It was thought that the adsorption capacity of resultant membrane depended on the isoelectric point of chitosan, which was at about 6.3 [28]. At lower pH, the protonation of amine groups of chitosan could occur, while at higher pH the group behaves as non-protonated group. However, the binding ability of chitosan for copper ions is mainly due to the amine groups which serve as coordination sites for the sequestration of copper ion [29], at lower pH, most of the amine groups in the chitosan segments protonated and were not available for copper uptake, thus the values of the adsorption capacity decreased with decreasing pH. So the resultant membranes showed a tendency with low adsorption capacity for Cu^{2+} ion at low pH region. But, at pH 7, the adsorption capacity became dramatically low relative to those at pHs 5 and 6 for the chitosan microspheres/PAA system. It was considered that, at higher pH, the destruction of the self-assembled layers might have occurred since the chitosan layers on membrane surface behaved as non-charged forms. Especially the chitosan microspheres/PAA system demonstrated low adsorption at pH 7. This meant that the increase of the solution pH restrained the coordination of Cu^{2+} ions, which was induced by the destruction of the ESA multilayer at pH 7. However, at pH 5 and 6, partial amino group remained on the protonation form which was favorable for the stability of chitosan or chitosan microspheres layers on resultant membranes. Also, Fig. 7 was plotted for comparing the adsorption capacity of resultant membranes with chitosan/PAA ESA layers and chitosan microspheres/PAA ESA layers. It can be seen that the adsorption capacity of membranes functionalized with chitosan microspheres/PAA ESA layers at pH6 was several times higher than that of membranes modified with chitosan/PAA ESA layers. So it was suggested that the ESA multilayer of chitosan microspheres/PAA onto charged

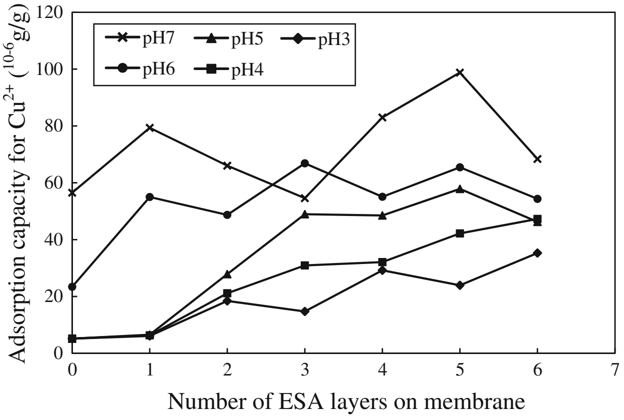


Fig. 5 Effect of the copper solution pH on the adsorption capacity of the resultant membranes of PAN/chitosan/PAA system

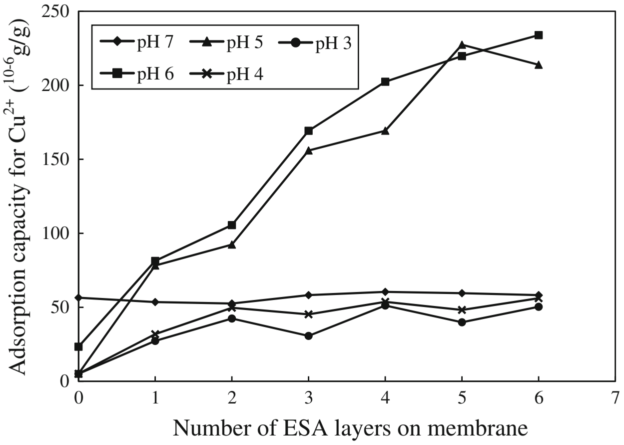


Fig. 6 Effect of the copper solution pH on the adsorption capacity of the resultant membranes of PAN/chitosan microsphere/PAA system

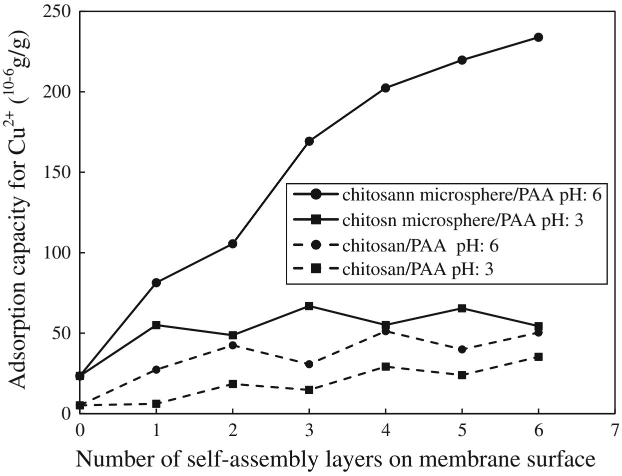


Fig. 7 Comparison of the adsorption capacity for Cu^{2+} of the two kinds of resultant membranes

substrate prepared in the present paper showed great potential in functioning membranes with high removal capability of heavy metal ions.

Conclusions

In the present work, successful research was performed using deposited chitosan or chitosan microspheres layers and PAA onto the charged PAN membrane surface using ESA technique. The Cu^{2+} ions could be adsorbed on the ESA multilayer membranes. Especially the membranes with chitosan microspheres and PAA alternate layers on the surface showed high adsorption capacity for Cu^{2+} ion for about 200–240 ppm/g membrane. Therefore, such membrane has bright prospects for the purification of wastewater along with application for separation process. Also it was proposed that introducing ESA multilayer of chitosan microspheres onto membrane surface could be a very promising way for preparing functional membranes with excellent metal binding capacity. Further work would appear in near future.

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