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Facile preparation of P84® polyimide affinity membrane with high adsorption of bilirubin

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ABSTRACT

In this work, polyimide (P84®) affinity membranes are prepared with P84® and different additive by facile phase inversion method. Polyethyleneimine containing numerous amino groups is grafted on the membrane for further amidation reaction with bilirubin carboxyl group. Organic additive polyvinylpyrrolidone and inorganic additive $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ nanoparticles are introduced to improve membrane performance. Effect of polymide concentration and additive content on the adsorption of bilirubin are investigated in detail. The morphology and structure of the membrane are characterized by scanning electron microscopy and atomic force microscopy. The results show that the polyimide affinity membrane prepared with 14 wt.% polyimide and 5 wt.% PVP has a significant effect on the specific adsorption of bilirubin. During the dynamic adsorption process, the P84® affinity membrane showed high bilirubin adsorption of 4.4 mg/g.

Keywords: Polyimide; Bilirubin; Polyethyleneimine; Adsorption; Affinity membrane

1. Introduction

Affinity separation is a powerful tool in the field of biomedical engineering. Materials with high hydrophilicity, high specific binding capacity, low nonspecific protein adsorption, good chemical, and solvent resistance are necessary for the affinity separation [1]. A lot of synthetic polymers such as ethylene vinyl alcohol, cellulose acetate, and polyvinylidene fluoride (PVDF) are modified to improve the separation performance [2–4]. Polyimide is widely studied to prepare separation membrane especially solvent resistance nanofiltration membranes because it has excellent permselectivity, solvent resistance, and chemical stability. The performance of polyimide membrane can be improved further because it can be crosslinked with polyamines or polyalcohols [5,6]. Polyethyleneimine (PEI) can be used to modify reactive polymer with carboxyl group and prepare nanofiltration membrane for its polycationic structure and abundant amino group [7,8]. It can carry amidation reaction with the polyimide main chain that forms a hydrophilic, crosslinked, and positively charged membrane [9]. Polyvinylpyrrolidone (PVP) with excellent hydrophilicity, compatibility with polymer, and low toxicity is a widely used polymer additive and utilized to control the ultrafiltration and microfiltration membrane structure [10,11]. It has no covalent bonds between the polymer and additive and is well soluble in water. So, PVP plays the role of pore former during the membrane synthesis by phase inversion [12]. $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF) nanoparticle has been used as inorganic additive in the preparation of polyether sulfone/LSCF membrane and solvent-resistant cellulose acetate/LSCF nanofiltration membrane because the hydrophilic inorganic additive can improve the permselectivity and mechanical strength of the membrane [13,14].

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Bilirubin is formed by the breakdown of red blood cells in the body. High levels of bilirubin can lead to jaundice and permanent damage to brain [15]. Hyperbilirubinemia treated with hemoperfusion is a promising method with the circulation of blood through an extracorporeal unit which needs an adsorbent system like affinity membrane. The removal of toxins such as bilirubin from blood is an important corporeal therapy of disease [16]. Affinity membrane with functional sites can be used as the adsorbent and it also owns large surface area, short diffusion path, and low-pressure drop compared with fixed bed chromatography. Shi et al. [17] reported a Lysine-attached anodic aluminum oxide (AAO)-silica affinity membrane for bilirubin removal. The polytetrafluoroethylene (PTFE) microporous membranes is also modified with CB F3GA and albumin for removal of bilirubin [18,19].

In this work, polyimide P84® with reactive main chain is chosen for the affinity membrane material and fabricated with facile phase inversion method. Branched PEI with much amino groups was used to improve the affinity capacity and crosslink the polymer chains. Different additives are investigated to improve the membrane performance. The membrane is also studied with the characterization of scanning electron microscopy (SEM) and atomic force microscopy (AFM).

2. Experimental

2.1. Preparation and characterization of polyimide membrane

Polyimide (P84®, HP Polymer Inc., Lenzing, Austria, Mw: 25,000) is used as the membrane material while additive is added into the casting solution to adjust the membrane structure and adsorption capacity. The membrane is prepared with phase inversion method with N,N-dimethylacetamide (DMAc) used as solvent and water as non-solvent. Additive is added into the polyimide/DMAc solution to improve the membrane performance when needed. The membranes are cast with the suspension on a horizontal glass plate with a glass blade. After evaporation for 10 s in the air, the membranes were precipitated by immersing them in a water bath at room temperature (about 25°C). The membranes prepared have to be rinsed before crosslinking with branched PEI (Mw: 10,000) which also provides numerous amino group as binding site. PVP (K30) is used as organic additive while LSCF nanoparticles with a mean diameter of 500 nm are used as inorganic additive. The characteristic of inorganic additive LSCF is described in our previous work [13]. The prepared affinity membrane are tested with SEM (FEI Nova NanoSEM 450) and AFM (Dimension ICON, Bruker, US) to determine the morphology of the membrane.

2.2. Static adsorption experiments

Ten milligrams of bilirubin is added in 10 mL NaOH solution (0.1 M) to get clear solution. To keep constant pH of the alkaline bilirubin solution, 20 mL phosphate buffer (0.2 M, pH 7.4) is added into the solution then diluted to 100 mL to form the bilirubin testing solution with a bilirubin concentration of 0.1 mg/mL. The solution is kept in dark place before utilization. The concentration of bilirubin is tested at 440 nm with UV-vis spectrometer. Dry polyimide membrane sheet with 20 mg is immersed in 10 mL bilirubin buffered solution in a cuvette with a cover under the seal of aluminum foil. The adsorption sample and the control sample without affinity membrane are incubated at 25°C and vibrated at 170 rpm using a constant temperature water bath shaker (SHA-A, Saidelis, Tianjin, China) for 2 h. The adsorption capacity of the affinity membrane q (mg/g dry membrane) is defined as the weight of bilirubin adsorbed on the unit mass of membrane and calculated by the concentration difference between the reference sample and adsorption sample according to Eq. (1).

$$q = \frac{\left(C_0 - C_t\right)V}{W} \tag{1}$$

where C_0 (mg/mL) is the concentration of reference sample while C_t (mg/mL) is concentration of the adsorption sample. V (mL) is the volume of bilirubin solution and W (g) is the weight of the dry membrane.

2.3. Dynamic adsorption experiment

The dynamic adsorption performance of the polyimide affinity membrane was performed in a dead-end filtration apparatus with an effective membrane area of 38 cm^2 at 25°C. The buffered bilirubin solution (prepared as above description) is 100 mL with a concentration of 0.1 mg/mL and is pressed with a peristaltic pump (Baoding Longer Precision Pump Co., China) to permeate through the membrane with a rate of 1 mL/min. The permeate sample is tested with UV-vis spectrometer at 440 nm every 5 mL. The bilirubin concentrations ratio is determined as the collected permeate C (mg/mL) divided by the feed concentration C_0 (mg/mL). The bilirubin removal content (mg) is calculated by bilirubin filtration content minus the permeate volume integration of the bilirubin concentration in the permeate curve. The membrane dynamic adsorption capacity q_d is calculated by the bilirubin permeate content divided by dry membrane weight (mg).

3. Results and discussion

3.1. Effect of polymer concentration on the membrane performance

The polyimide membrane prepared with different polymer concentration are characterized with SEM and the top-surface morphology are shown in Fig. 1. With the magnification of 5,000, all the membranes show a uniform top surface without defects. The membrane with 14% polyimide has obvious pores in the membrane surface. When the polymer concentration is lower than 12%, the viscosity of the casting solution is too low to prepare the membrane with enough mechanical strength.

The increase of polymer concentration in the casting solution will lead to a high polymer concentration in the membrane interface with the less porous top layer. As shown in Fig. 2, all the membranes show uniform finger-like pores with a dense skin layer which can provide enough space for the adsorption of bilirubin. When the polymer concentration is low, the skin layer shows numerous

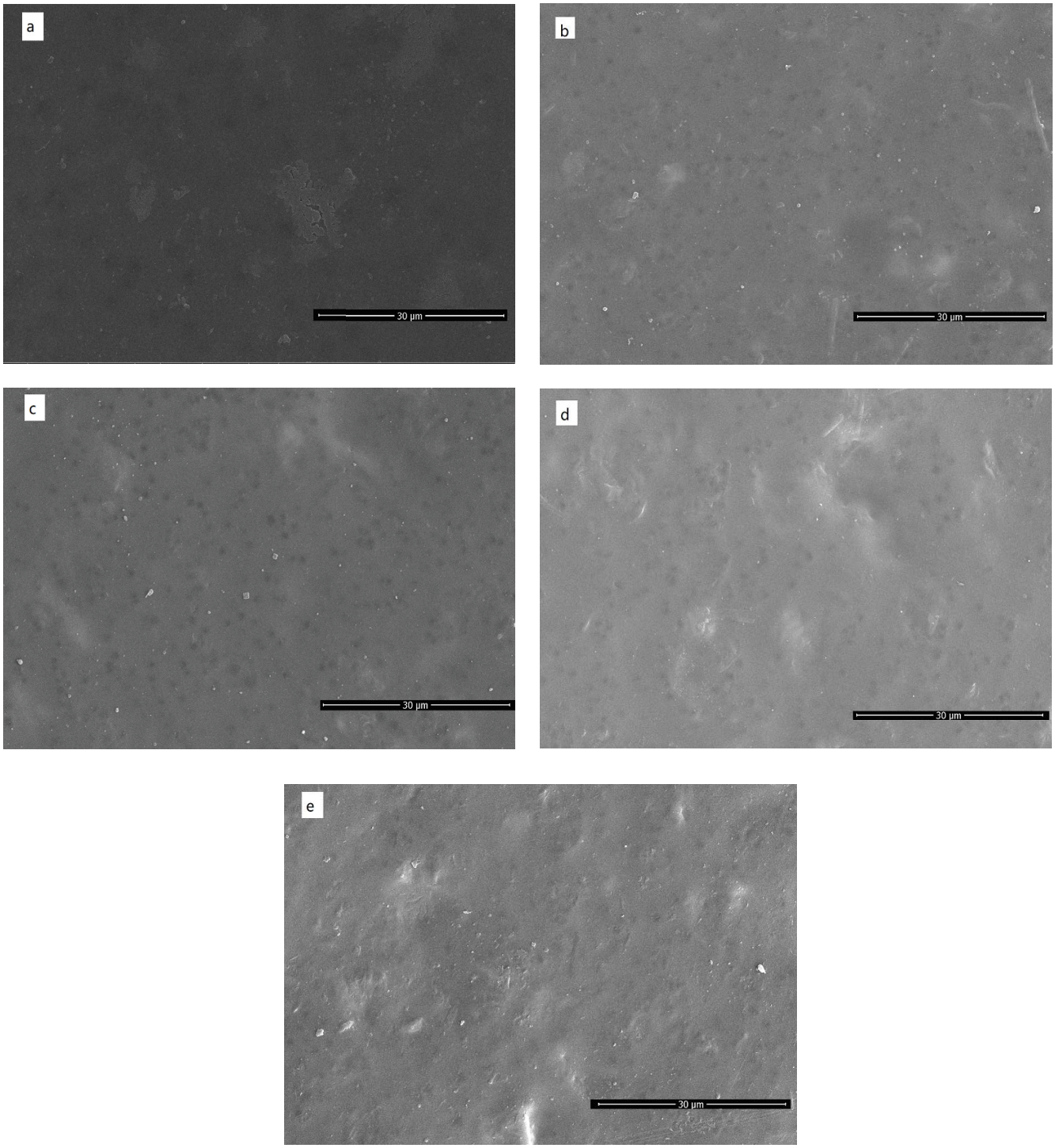

Fig. 1. Top surface morphology of polyimide membranes with different polymer content (a) 12%, (b) 13%, (c) 14%, (d) 15%, and (e) 16%.

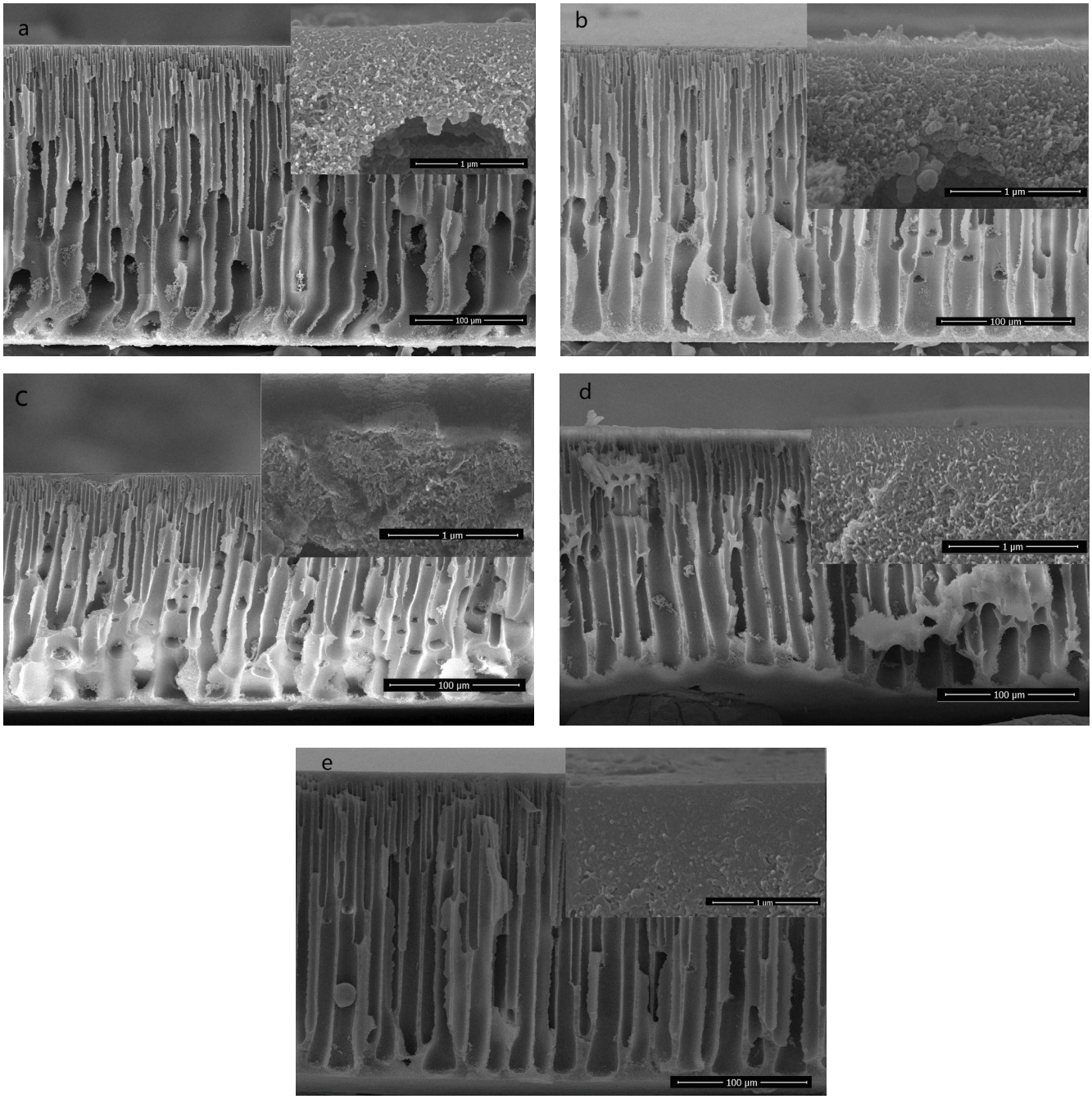

Fig. 2. Cross-section morphology of the polyimide membranes with different polymer contents (the insets are the morphologies of the skin layer with a magnification of 100,000, (a) 12 wt.%, (b) 13 wt.%, (c) 14 wt.%, (d) 15 wt.%, and (e) 16 wt.%.

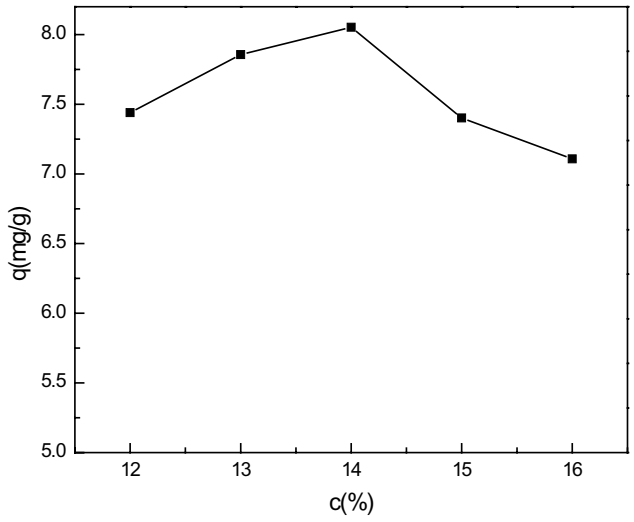

Fig. 3. Effect of polyimide concentration on the bilirubin adsorption.

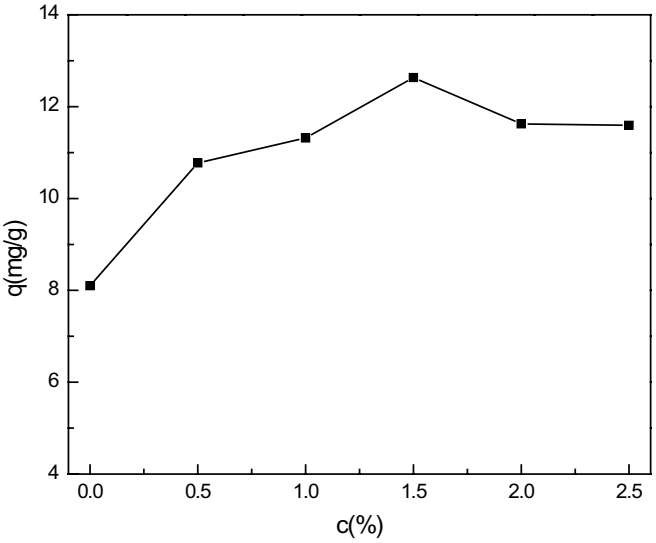

Fig. 4. Effect of PEI concentration on the adsorption capacity of affinity membrane.

pores with uniform structure as shown in the insets of the pictures. However, when the polymer concentration is up to 16 wt.%, the skin layer is too dense for the adsorption of bilirubin.

Effect of polyimide concentration on the adsorption of bilirubin to the affinity membrane is shown in Fig. 3. As seen from the figure, the adsorption capacity of the membrane increases first then declines after the polymer concentration exceeds 14 wt.% which is consistent with the structure of the membrane. Higher polymer concentration will induce denser skin layer and lower porosity which decreases the adsorption space for bilirubin. So in the next research work, polyimide concentration is fixed on 14 wt.% to optimize the membrane performance.

PEI with a lot of amino groups can provide ligands of the bilirubin adsorption because the amino groups have strong electrostatic interaction with negatively charged bilirubin molecules even at moderately alkaline media. Polyimide can easily react with PEI to form a modified polyimide membrane with numerous amino group in the surface and pores. In this work, prepared polyimide membranes are immersed in PEI/water solution with different concentrations at 50°C for 30 min for the graft of PEI. As shown in Fig. 4, the affinity membranes show improved bilirubin adsorption. When the PEI concentration exceeds 1.5 wt.%, the adsorption capacity decreases a little which may be induced by the membrane pores blocked by too much PEI polymer in the skin layer. In further research, 1.5 wt.% PEI is used to cross-link the affinity membranes with different additives.

PVP is a water soluble polymer additive that can improve the porosity of the membrane because it can be washed out by water during a solvent exchange in a water bath. With the polyimide concentration fixed 14 wt.%, different contents of PVP are added in the casting solution to improve the membrane performance. As shown in Fig. 5, at the magnification of 200,000, the membrane surfaces are all very smooth and dense.

As shown in Fig. 6, the skin layer of the membranes become denser and thicker sponge-like pores when more PVP is introduced in the casting solution. The big finger-like cavities in the skin layer disappear which can be attributed to the delayed phase inversion when hydrophilic and viscous PVP is moving into the water bath. The PVP can form a lot of interconnected micropores in the polymer matrix which is positive to the adsorption space of bilirubin.

The bilirubin removal efficiency of the polyimide affinity membrane is improved obviously with the increase of PVP content as shown in Fig. 7. The membrane is very dense especially in the skin layer and the increase of PVP content will form straight-through pores and high porosity. When the PVP content is 5 wt.% at 25°C, the adsorption capacity is up to 15.1 mg/g which is about three times the lysine-attached anodic aluminum oxide–silica affinity membrane [17]. Higher PVP content may increase the adsorption capacity. In order to keep fine mechanical strength of the membrane, PVP content was not increased further.

The LSCF nanoparticles are introduced into the membrane matrix to improve membrane performance. As shown in Fig. 8, the membrane surface is very dense and defect-free with some small protuberance which should be the inorganic nanoparticles encapsulated in the polymer matrix. Because the polymer matrix and the nanoparticles are all very hydrophilic and compatible, particle aggregation is not dominant as shown in the surface of the membrane.

Because LSCF is hydrophilic inorganic additive that causes instantaneous phase inverse. The addition of LSCF does not change the finger-like pore structure of the polyimide membrane as shown in Fig. 9. The good compatibility between the polymer and inorganic additive will decrease the agglomeration in the polymer matrix. As the increase of LSCF content, more, and more nanoparticles disperse uniformly in the membrane pores which is positive to the membrane porosity.

Effect of LSCF content on the performance of the polyimide affinity membrane is investigated. The hydrophilic LSCF

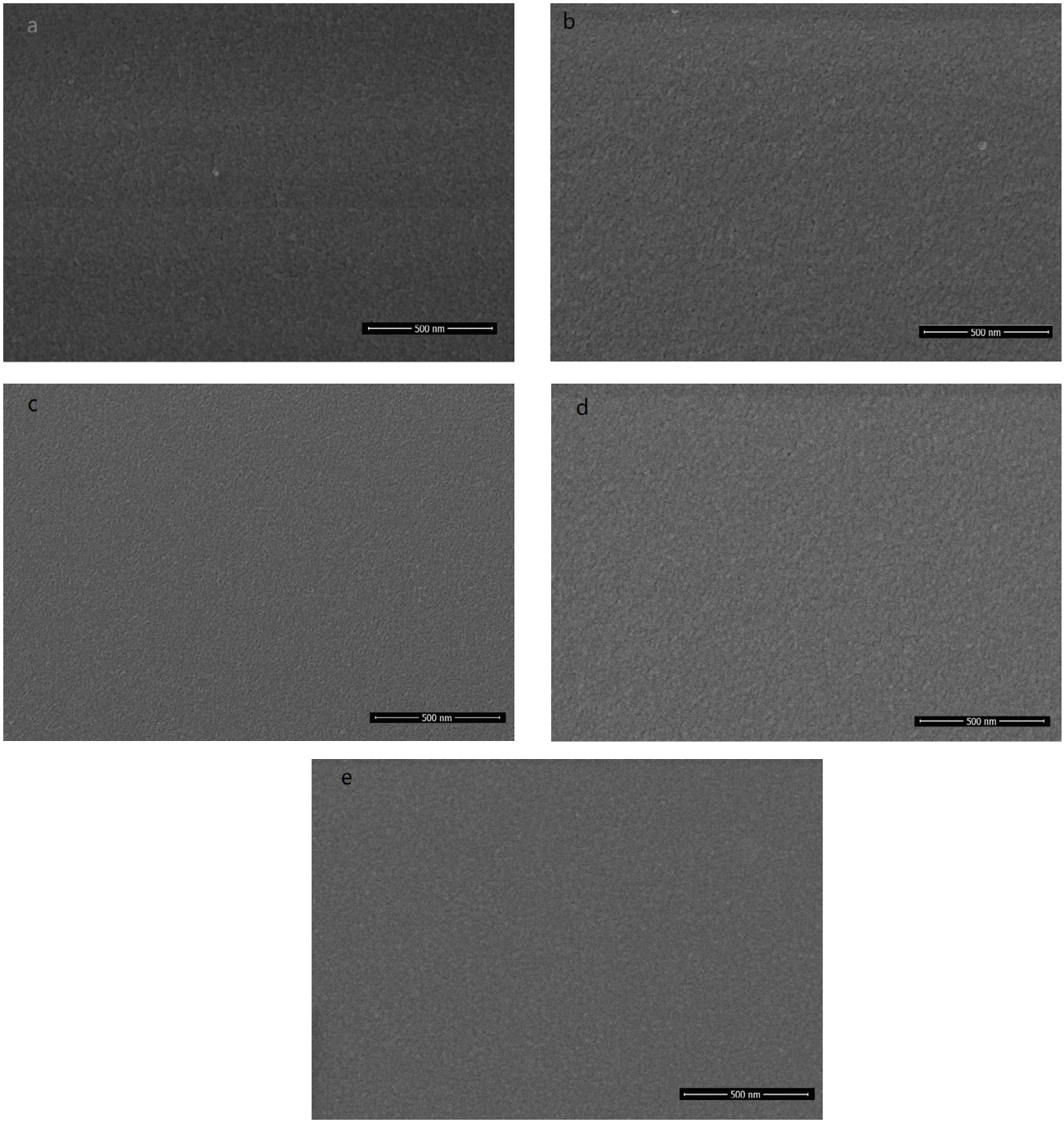

Fig. 5. Top surface morphology of the polyimide membranes with different PVP contents (a) 1 wt.%, (b) 2 wt.%, (c) 3 wt.%, (d) 4 wt.%, and (e) 5 wt.%.

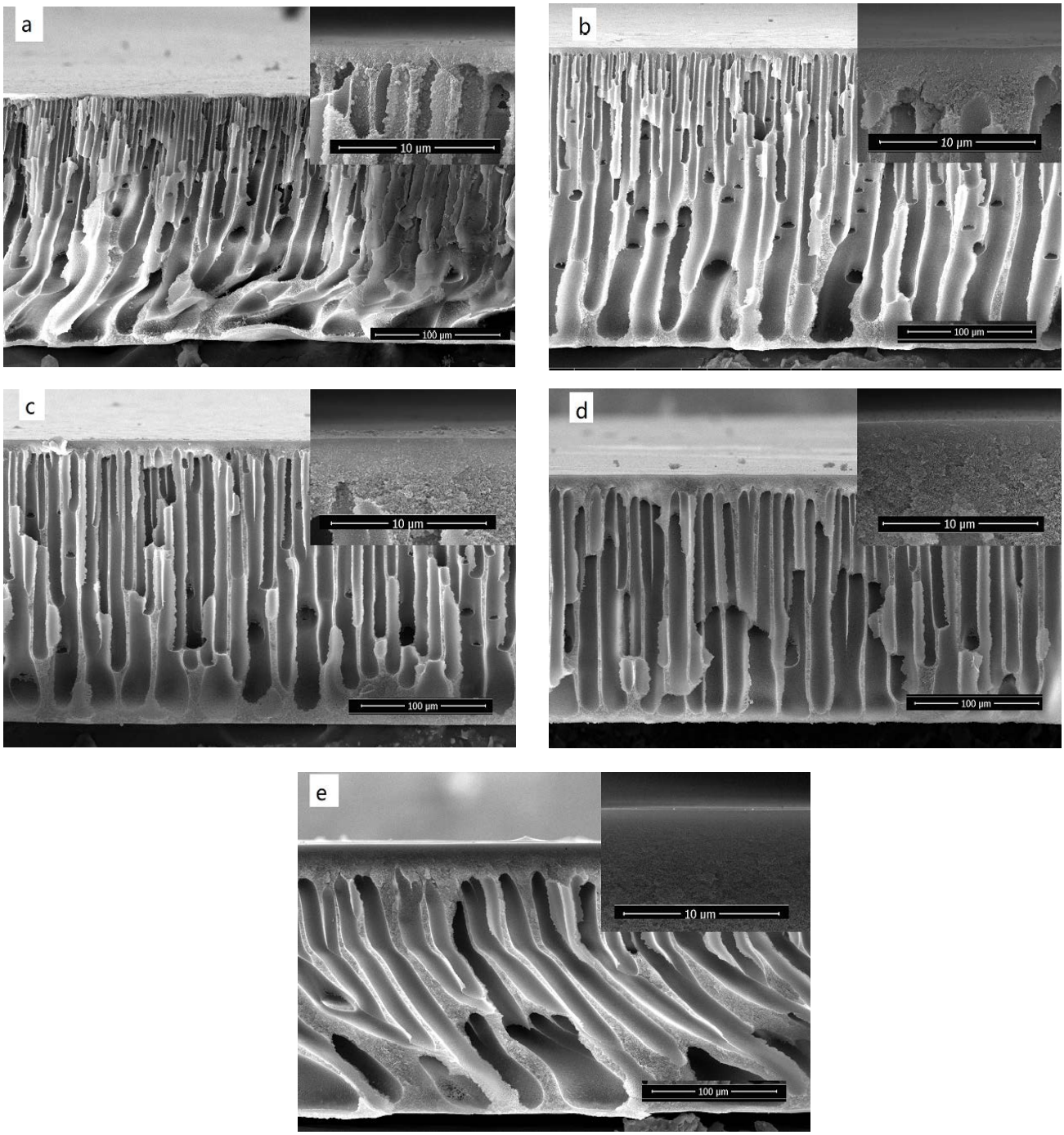

Fig. 6. Cross-section morphology of the polyimide membranes skin layer with different PVP contents (the insets are the morphologies of the skin layer with a magnification of 10,000 (a) 1 wt.%, (b) 2 wt.%, (c) 3 wt.%, (d) 4 wt.%, and (e) 5 wt.%.

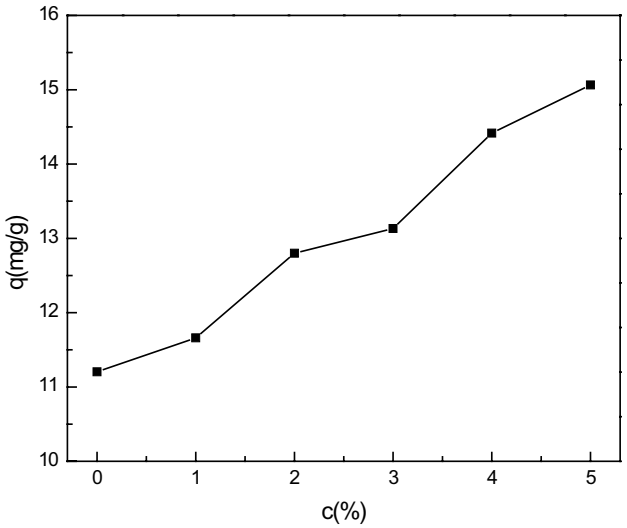

Fig. 7. Effect of PVP content on the adsorption capacity of the affinity membrane.

is embedded in the polymer matrix firmly and the exposed part of the particle will improve the ligands of the adsorption because the surface of LSCF nanoparticles has a lot of –OH groups. As shown in Fig. 10, with the increase of LSCF content, the bilirubin adsorption is increased gradually. When the LSCF content is above 3 wt.%, further increase of LSCF content did not increase the adsorption capacity may be caused by fewer membrane pores at higher LSCF content as shown in Fig. 9.

3.2. Characterization of the membrane surface with optimized additive content

AFM images of membranes prepared with or without additive are shown in Fig. 11 with a scanning area of 5 μm × 5 μm. The root mean square roughness (R_q) and arithmetical mean height roughness (R_a) are also shown in the images. As shown in the pictures, pure polyimide membrane has a relatively rough surface with some peaks in the surface which demonstrates the excellent compatibility of the two polymers. When 5 wt.% PVP is added in the casting solution,

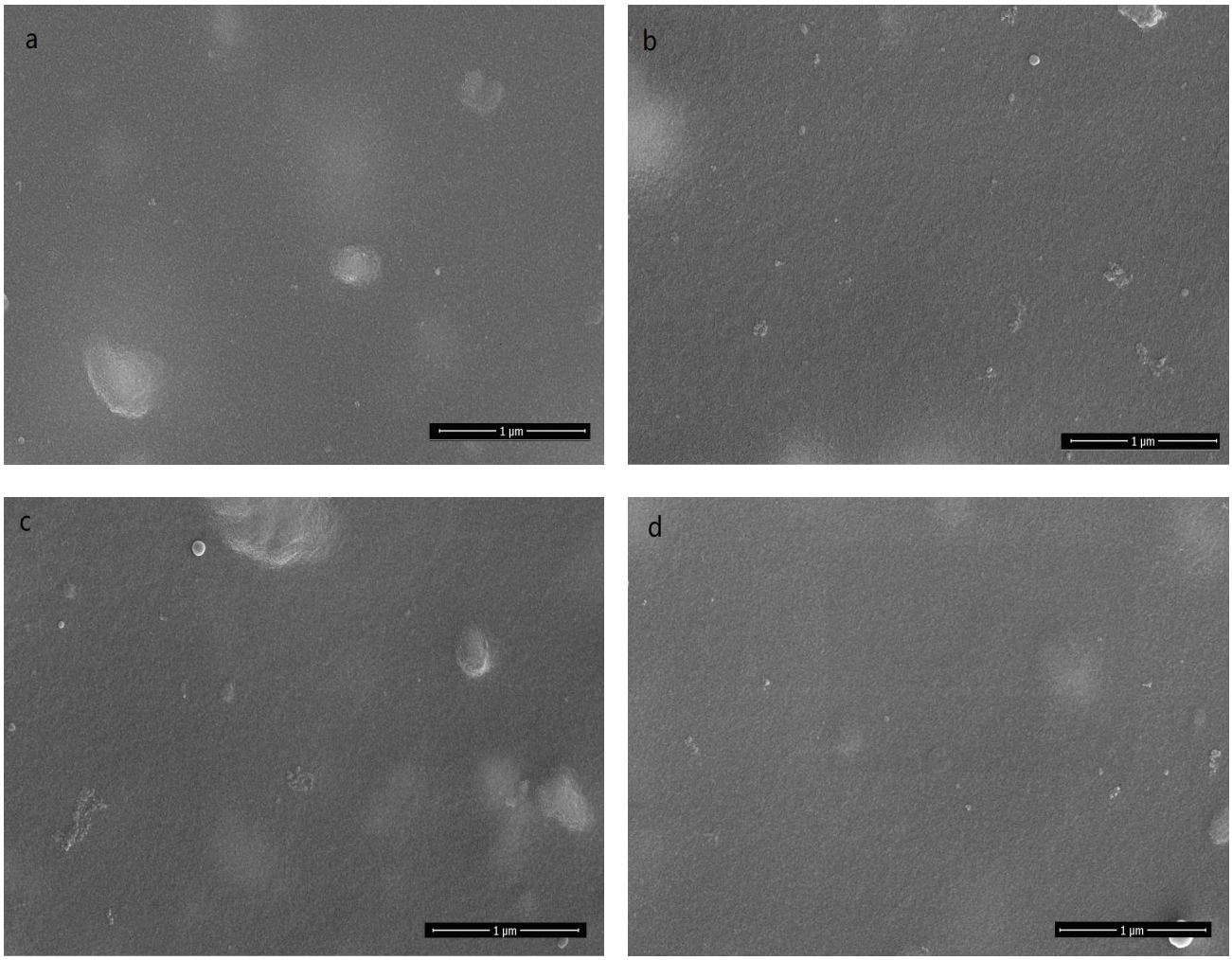

Fig. 8. Top surface morphology of polyimide membranes with different LSCF contents (a) 1 wt.%, (b) 2 wt.%, (c) 3 wt.%, and (d) 4 wt.%.

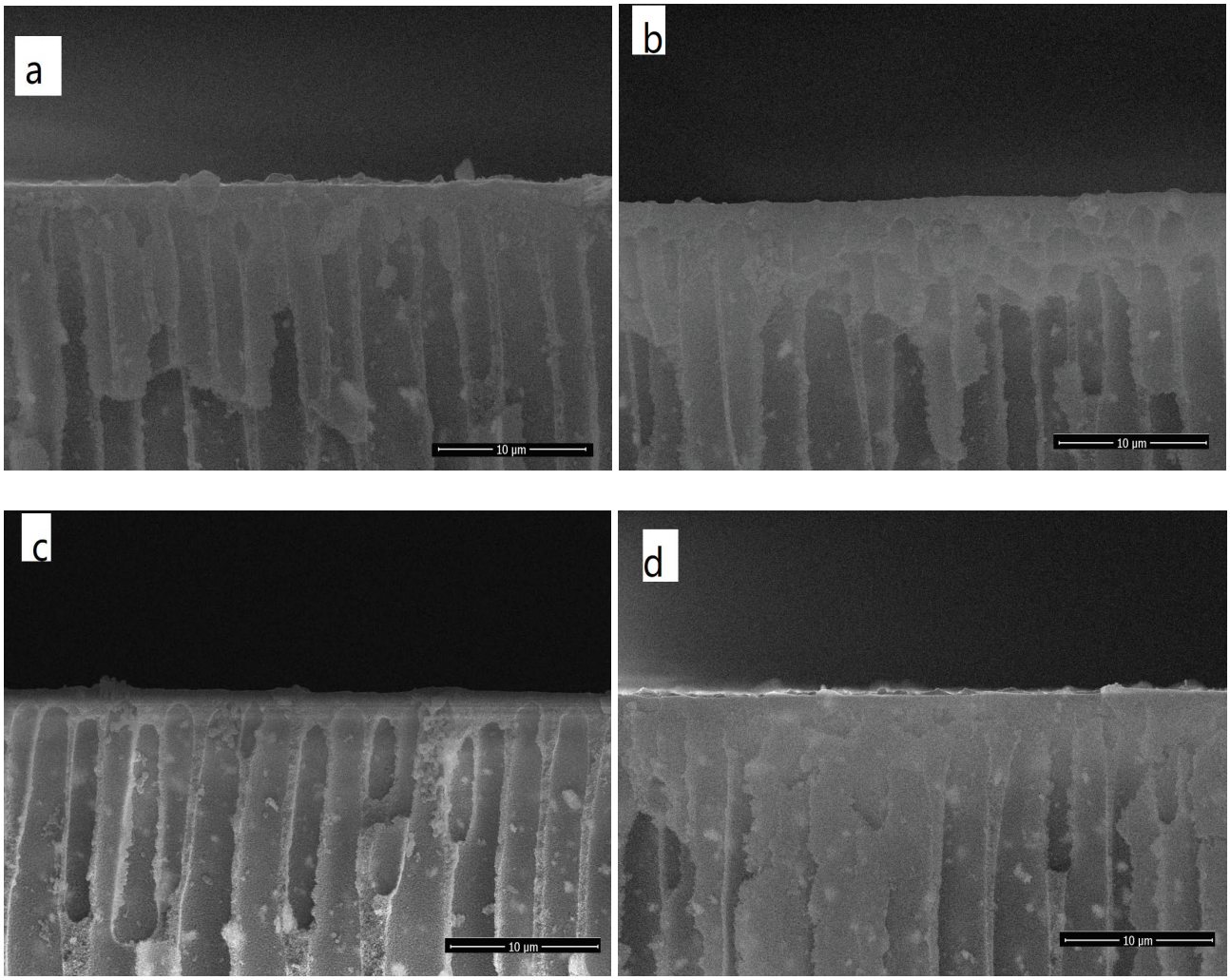

Fig. 9. Cross-section morphology of polyimide membranes with different LSCF content (a) 1 wt.%, (b) 2 wt.%, (c) 3 wt.%, and (d) 4 wt.%.

the membrane surface becomes very smooth. Because of the agglomeration of the inorganic nanoparticles, some big protuberances occur in the membrane surface when LSCF is used as inorganic additive which is in consistent with the SEM images in Fig. 8 and improves the membrane roughness obviously.

3.3. Bilirubin removal during dynamic adsorption

The affinity membranes can overcome the diffusion limitations of adsorbents by membrane filtration. To evaluate the bilirubin dynamic adsorption, 100 mL bilirubin solution (0.1 mg/mL) was filtrated with the membrane. As shown in Fig. 12, the ratio between permeate and feed concentrations C/C_0 is plotted as a function of the permeate volume every 5 mL. The ratio is increased gradually with the permeate volume and become a platform at last during filtration. After adsorption equilibrium, the membrane dynamic adsorption capacity (q_d) is determined as 4.4 mg/g which is similar with the q_d (4.7 mg/g) of cellulose acetate/PEI membrane [3].

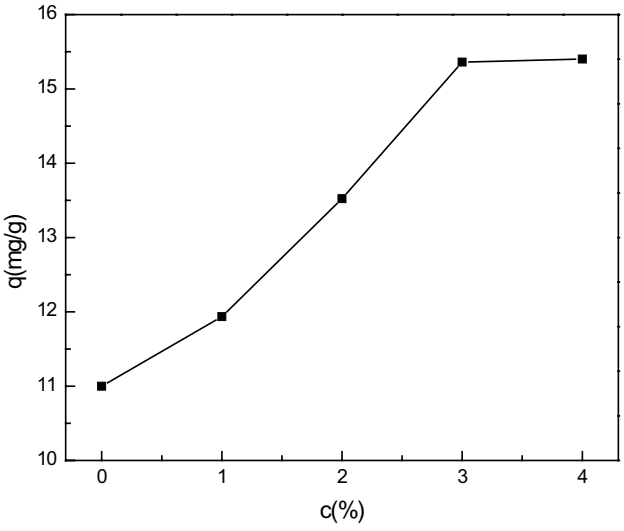

Fig. 10. Effect of LSCF content on the adsorption capacity of the affinity membrane.

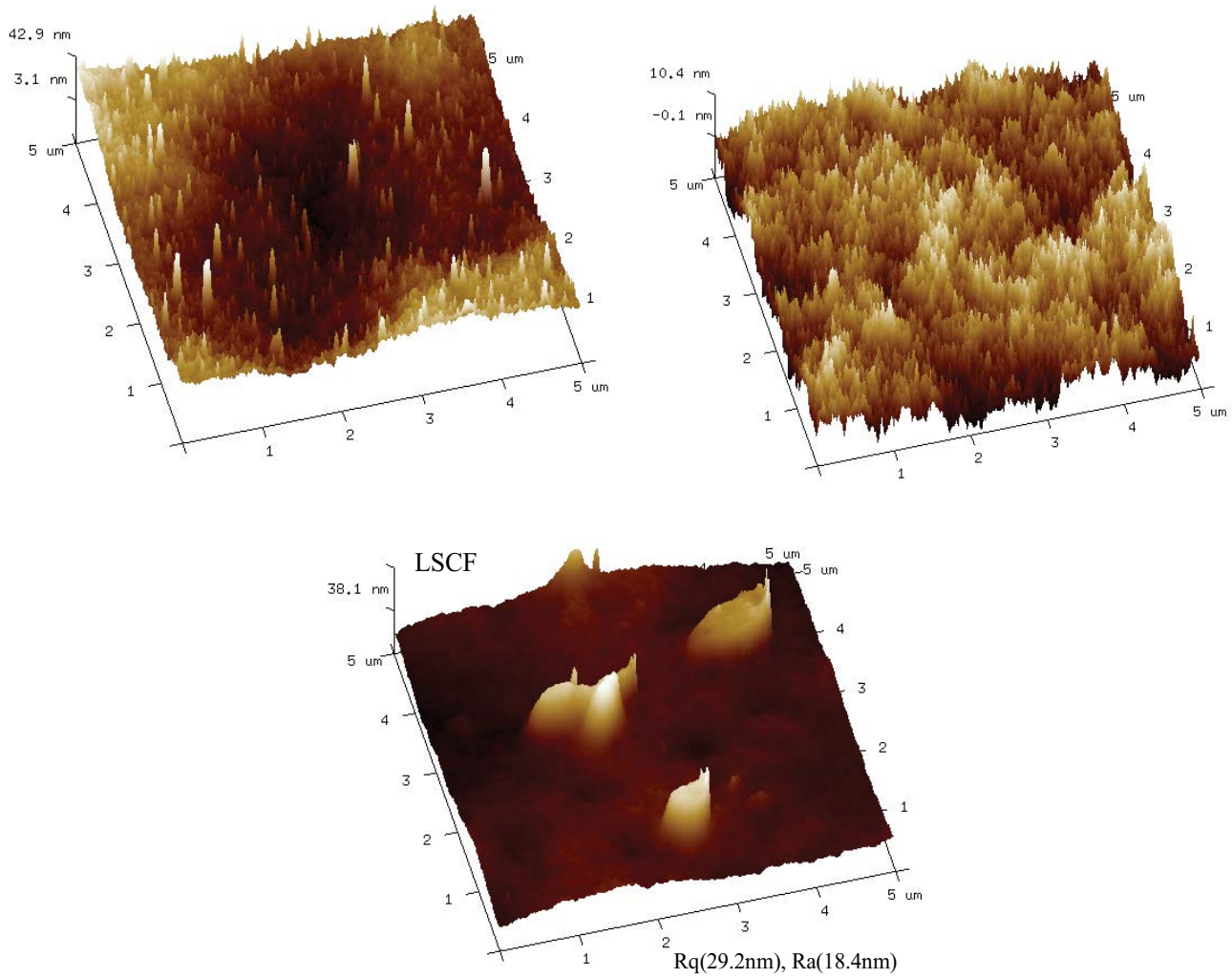

Fig. 11. AFM images of the polyimide membrane (no additive, bare polyimide membrane; PVP, membrane with 5 wt.% PVP; LSCF, membrane with 4 wt.% LSCF).

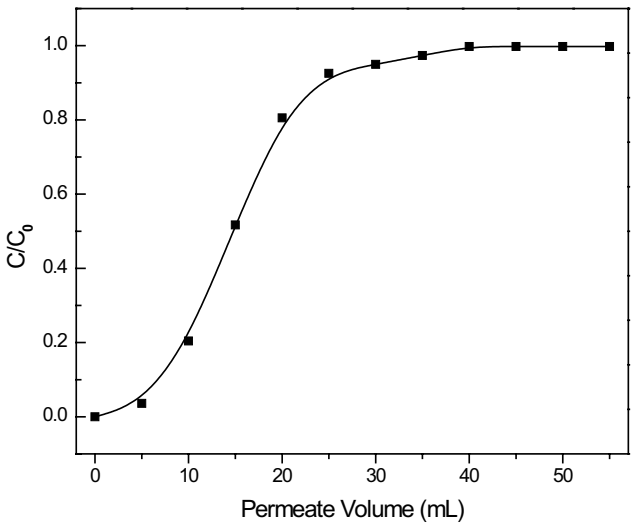

Fig. 12. Dynamic adsorption for bilirubin of P84® membrane.

4. Conclusions

In this work, polyimide membranes with PEI modification are used to prepare affinity membrane and the resultant membrane with numerous ligands provides a lot of active sites for the adsorption of bilirubin. Both organic additive and inorganic additive can change the membrane morphology and result in an enhanced bilirubin adsorption capacity. When the bilirubin concentration is 0.1 mg/mL, the adsorption capacity of the affinity membrane is up to 15.1 mg/g at 25°C at optimal preparation parameters. The dynamic adsorption capacity of the P84® membrane with 5 wt.% PVP is 4.4 mg/g at 25°C.

Acknowledgments

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