Jurnal Teknologi

Full paper

Poly(*N*-isopropylacrylamide-co-acrylic acid) Hydrogel and Its Thermo-responsive Properties for Polymer Enhanced Ultrafiltration

J. J. Chen, A. L. Ahmad, B. S. Ooi*

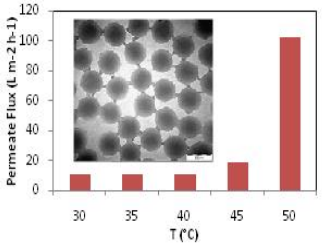
School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri Ampangan 14300, NibongTebal, Pulau Pinang, Malaysia

*Corresponding author: chobs@eng.usm.my

Article history

Received :15 September 2013
Received in revised form :
17 November 2013
Accepted :15 January 2014

Graphical abstract



Abstract

Poly(*N*-isopropylacrylamide-co-acrylic acid) hydrogel with thermo-responsive properties has been successfully synthesized. The hydrogel functional groups, volume phase transition (VPT) temperature and hydrodynamic size were altered upon copper ion adsorption indicated that the copper ion adsorption had disturbed the hydrogen bonding between the water molecule and the amine/ carboxylic groups present in the hydrogel matrix. It also demonstrates that internal adsorption also play important roles that enhance the copper ion removal. The adsorption process is more favourable at low temperature while the separation process should be carried out at higher temperature to mitigate fouling phenomenon. The hydrophobic behaviour of the hydrogel at temperature higher than the VPT value could minimize its interactions with the hydrophilic membrane.

Keywords: Hydrogel; polymer enhanced ultrafiltration; thermoresponsive; fouling

■1.0 INTRODUCTION

Ultrafiltration (UF) is a type of membrane separation processes which is efficient for wastewater purification in terms of rejection and permeate flux. However, molecular weight of metal ions such as Cu(II) cations are relatively low to be retained by UF membranes with pore sizes in the range of 0.1–0.01 µm. Therefore, to overcome this urgent deficiency, a combination of metal-polymer complexation and UF was first proposed by Alan S. Micheals in 1968. A type of polymer with metal-binding ability is used to complex with metal ions. Metal ions are usually bound by functional groups of polymers such as carboxylic (COOH) and amine (NH) groups through physisorption, ion exchange or chemisorption mechanisms. The molecular weight and size of metal-polymer complexes are large enough to be retained by UF membrane. This combination process is usually known as polymer-enhanced ultrafiltration (PEUF) [1-6].

Nevertheless, the major drawback behind most PEUF studies is the high tendency of large metal-polymer complexes to cause fouling which could further lead to the occurrence of concentration polarization (CP) onto active layer of UF membrane [3-6]. In the previous PEUF studies, several water-soluble polymers (WSP) have been utilized as metal-binding agent especially polyethyleneimine (PEI) where its viability to retain copper in PEUF had been confirmed. Cañizares *et al.* (2002) applied PEI as metal-chelating polymer for binding Cu(II). The permeate flux and rejection were reported as 78.3 L $m^{-2}h^{-1}$ and 94%, respectively at 25°C, pH 5.75 and transmembrane pressure (ΔP) of 5 bars by using ceramic membrane (MWCO = 10 kDa) [6]. Camarillo *et al.* (2010) compared the performance of Cu(II) removal from aqueous nitrate solution by PEUF with electrodeposition. They used poly(acrylic acid) sodium salt (PAANa) as metal-binding polymer in PEUF. The highest permeate flux was more than 180 L $m^{-2}h^{-1}$ at pH 7.7 at 50°C and rejection of 97%was achieved at pH 5.5, 50°C [7]. Camarillo *et al.* (2012) had also selected PEI as copper-binding polymer in their PEUF study. The highest permeate flux was found to be 78.3 L $m^{-2}h^{-1}$ at pH 4, 25°C and ΔP of 3 bars and the rejection was higher than 90% by using ceramic membrane (MWCO = 15 kDa). They also discovered that at pH 4, the permeate flux increased with increasing temperature until 50°C [3]. On the other hand, Llanos *et al.* (2008) had utilized partially ethoxylated PEI (PEPEI) as copper-binding WSP. The permeate flux obtained was higher than 90 L $m^{-2}h^{-1}$ at 25°C and it increased up to above 200 L $m^{-2}h^{-1}$ at 50°C, at pH 6. The maximum rejection of 97% was also reported at pH 6, 50°C [8].

In the present study, polymeric hydrogel known as; poly(*N*-isopropylacrylamide-co-acrylic acid) (PNIPAM-co-AA) was synthesized and applied in the PEUF process as Cu(II) adsorbent. The carboxylic groups of AA moieties in PNIPAM-co-AA are capable of forming complexes with divalent Cu(II) cations. The thermo-responsiveness of this cross-linked PNIPAM-co-AA hydrogel and its high affinity towards Cu(II) were expected to enhance the Cu(II) binding and permeate flux

[7-11]. The study on the surface interaction of the hydrogel with membrane at different temperature is important to minimize the fouling tendency of the adsorbent.

2.0 EXPERIMENTAL

2.1 Reagents and Solutions

Monomer *N*-isopropylacrylamide (NIPAM) ($C_6H_{11}NO$), crosslinker, N,N'-methylene-bis-acrylamide (MBA) ($C_7H_{10}N_2O_2$) (~99%;), acrylic acid (AA) ($C_3H_4O_2$) were purchased from Sigma Aldrich. Ammonium persulfate (APS) and sodium dodecyl sulfate (SDS) were obtained from Merck. Copper sulphate ($CuSO_4{\cdot}5H_2O$) purchased from Sigma Aldrich is used in this study as the heavy metal source by dissolving it in deionized water. All chemicals are of analytical grade. Cellulose acetate (CA) UF membranes, (MWCO=20k) were purchased from General Osmonics.

2.2 Experimental Procedures

PNIPAM-co-AA hydrogels were prepared using emulsion polymerization method in a 250 mL three-necked flask equipped with a nitrogen gas inlet, a thermometer, and a condenser. NIPAM monomer (2.8 g), AA monomer (30 mol%), MBA (0.25 g) as cross-linker and surfactant SDS (0.039 g) were dissolved in deionized water (170 mL). The mixture solution was stirred in the three-necked flask at 350 rpm and it was heated to 70°C in water bath. Nitrogen gas was purged into the solution for 30 min to remove the dissolved oxygen. Then, the initiator, APS (0.11 g) dissolved in 30 mL deionized water was added to the solution to initiate the polymerization. The polymerization process proceeded for 4 h at 70°C. The core-shell PNIPAM-co-AA hydrogels were then purified by filtering through cellulose acetate UF membranes (MWCO = 20 k) for several cycles with pure water. The final hydogel solution obtained was centrifuged and redispersed in deionized water.

2.3 Hydrogel Characterization

2.3.1 Fourier Transform Infrared Spectroscopy (FT-IR) Analysis

FT-IR spectra of the pure and Cu^{2+} loaded PNIPAM-co-AA hydrogels in powder form were obtained after air-drying the solutions. The functional groups of the dried hydrogels were characterized using Fourier transform infrared spectroscope (Nicolet iS10 FT-IR spectrometer, USA) in the range of 4000–500 cm^{-1} with ATR technique.

2.3.2 Dynamic Light Scattering (DLS)

A dynamic light-scattering apparatus (Malvern Zetasizer 1000) equipped with a helium-neon laser (λ = 633 nm) with detector placed at 90° was used to investigate the swelling and shrinking behaviours of the PNIPAM-co-AA hydrogels. The hydrodynamic diameters (D_h) of the hydrogel particles were measured at temperatures from 25 to 50°C.

2.3.3 Transmission Electronic Microscopy (TEM)

Morphological observations of the hydrogels were carried out using a JEOL transmission electron microscope (TEM, JEOL JEM-200CX) at 100 kV. A few droplets of the samples were spread onto the surface of a 300-mesh copper grid and were allowed to dry for 30 minutes. The dried specimen was clamped onto a TEM specimen rod, inserted into the sample chamber for observation.

2.3.4 Polymer Enhanced Ultrafiltration

100 mL of PNIPAM-co-AA hydrogel solutions were mixed into 400 mL of copper (II) solutions with to make up final solution of 0.5 mg Cu^{2+}/mg polymer. The mixture solutions were kept stirring at 350 rpm. The pH of the solutions were adjusted to pH 5 and were kept stirring at different temperatures to study the effects of temperatures towards the permeate fluxes and copper (II) rejections. The ultrafiltration processes were conducted in a cross-flow (total recirculation) mode where permeate and retentate were streamed back to feed solution to maintain the steady state operation. Cellulose acetate ultrafiltration membranes (GE Osmonics YMCQSP3001) with 20 kDa molecular weight cut-off were used in the experiments. The ultrafiltrations were performed under pressure difference, ΔP, of 1.5 bars.

3.0 RESULTS AND DISCUSSION

3.1 Hydrogel Synthesis and Characterization

The presence of AA in the co-polymeric PNIPAM-co-AA hydrogels were confirmed by the appearance of the bands with characteristic peaks at around 1709–1712 cm^{-1} contributed by the carbonyl (C=O) stretching of carboxylic (-COOH) groups in AA moieties. After Cu^{2+} adsorption, the intensity of these characteristic peaks had reduced due to the chemical reaction as shown in Figure 1. This elucidated that Cu^{2+} had bound with the AA moieties of these hydrogels which supports that AA moieties are responsible for the Cu^{2+} adsorption within the hydrogels [10-11].

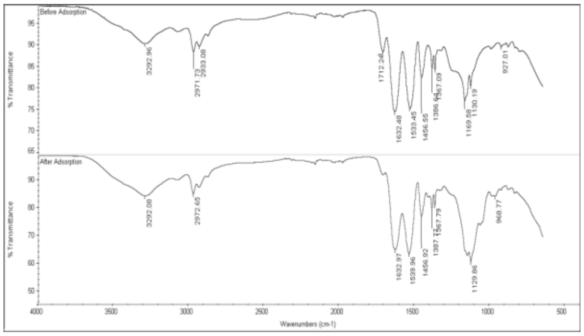


Figure 1 FTIR spectrum of PNIPAM-co-AA hydrogels before and after Cu^{2+} adsorption

3.2 TEM Images on Hydrogel Size

Figure 2 shows the TEM images of PNIPAM-co-AA hydrogel particles which exhibit nearly perfect spherical shape. The average particle diameter for the hydrogel was observed to be around 370 nm in a stable colloidal suspension and become 440 nm after Cu^{2+} adsorption indicated that Cu^{2+} adsorption also occurred in the internal structure through diffusion.

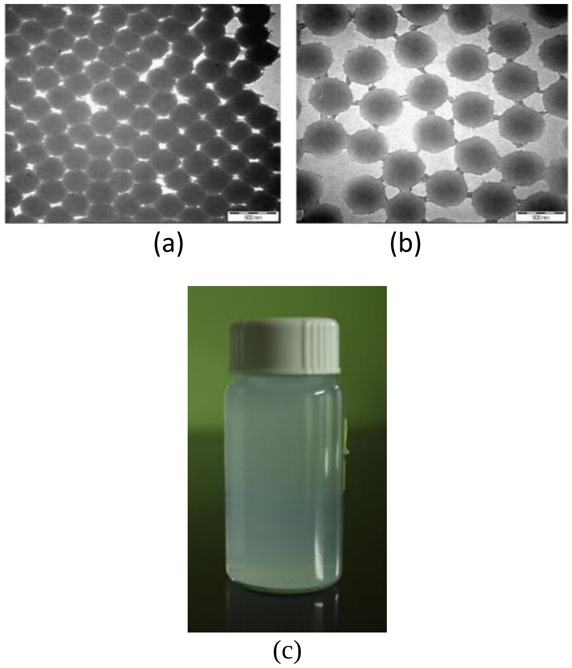


Figure 2 TEM image of PNIPAM-co-AA hydrogel before (a) and after (b) Cu^{2+} adsorption, (c) particle suspension

3.3 Thermoresponsive of PNIPAM-co-AA Hydrogel

The thermal sensitivities of the PNIPAM and PNIPAM-co-AA hydrogels before and after Cu^{2+} adsorption were characterized by using dynamic light scattering (DLS) technique. The change in hydrodynamic diameter, D_h was determined within the temperature range of 25–50°C. Figure 3 shows the temperature-induced volume phase transition (VPT) curves of PNIPAM before and after Cu^{2+} adsorption.

The D_h of the hydrogel decreased with the increase in temperature from 25 to 50ºC. However, volume phase transition temperature (VPTT) for PNIPAM-co-AA was found to be around 33ºC. At temperature below the VPTT, the spherical hydrogel networks were solvated by hydrogen bonding between water molecules and the NIPAM/AA moieties. Above the VPTT, the hydrogel particles undergo volume phase transition from swollen to the collapsed (dehydrated) globule conformation [12-20].

After the Cu^{2+} adsorption, the VPTT of the copper-loaded hydrogels shifted from 33 to 29°C. The decrease in VPTT indicated that the Cu^{2+} ions had diffused into the hydrogel interior cross-linked networks (or matrices) and bound with the carboxylates (-COO^-) of AA and carbonyls (-C=O) of NIPAM moieties to reduce the water-associated hydrogen bonds. Hence, less heat energy required to dissociate the hydrogen bonds formed between water molecules and the functional groups[10-12]. Above these shifted VPTT, D_h of the Cu^{2+} loaded hydrogels decreased in relatively slower rate with increasing temperature compared to the pristine hydrogel. The core-size temperatures in which hydrogel networks were fully collapsed had also increased significantly from 40 to 46 °C.

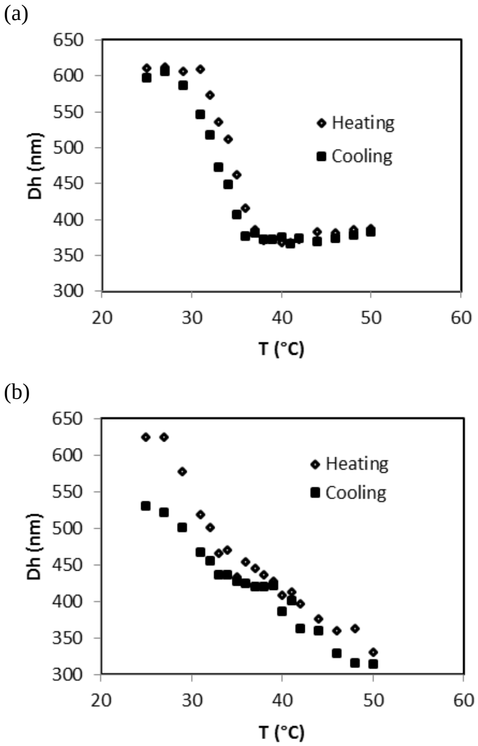


Figure 3 Thermoresponsive of hydrogel (a) without and (b) with copper loading

3.4 Performance Evaluation of Polymer-enhanced Ultrafiltration (PEUF)

After adsorption, transmembrane pressure of 1.5 bars was exerted on the solution separated by a hydrophilic CA membrane. The flux was found to be quite constant (10.75–10.38 L $m^{-2}h^{-1}$) in the temperature range of 30 to 40°C. However, as the solution temperature was increased to 45°C, the permeate flux was slightly raised from 10.38 to 18.81 L $m^{-2}h^{-1}$ and increased dramatically to 101.98 L $m^{-2}h^{-1}$ at 50°C (Figure 4). This can be explained in term of the thermo-responsiveness of the hydrogels. The copper-hydrogel complex particles reached their core-size in which they are fully dehydrated at around 46°C. The sharp increases in permeate flux at higher temperature of 50°C were also reported by Camarillo *et al.* (2012)[3] and Llanos *et al.* (2008) using PEI and PEPEI as copper-binding polymer, respectively [21].

Below this temperature, the unlinked hydroxyl (-OH) groups of the cellulose acetate (CA) membrane tend to form hydrogen bonds with the carboxylic and amine groups of hydrogels [3-4, 21-23]. The hydrogels were then being attracted and accumulated on the membrane surface, consequently causing fouling phenomenon which resulted in lower permeate flux [23-24]. At above 46°C, the copper loaded hydrogels were reaching dehydrated state and become hydrophobic. Less surface interactions between the CA membrane and collapsed hydrogel were expected. The increase in flux was mainly governed by two reasons; 1) the breakdown of the hydrogen bonds between membrane and the hydrophobic hydrogels which reduced the pore blocking for the permeation of solvent [25-27]; 2) water released from the shrunken hydrogels helped enhance the solvent flow through the membrane as explained earlier based on the feed solution without presence of polymeric hydrogels.

In term of rejection, the system has better copper ion rejection percentage at lower temperature which is around 92-95% from 30 to 40 °C. As temperature increased from 40 to 45°C, rejection dropped from 94.73 to 77.45% and dropped drastically to 28.91% when the temperature further increased to 50°C. This phenomenon shows that the rejection is not favourable at higher temperature and it is most likely due to the changes of physical properties of hydrogel. At higher temperature, the collapse structure exert diffusional problem for the copper to diffuse into the hydrogel matrix thus reduced its active site for copper ion adsorption. Besides, the hydrogel tends to precipitate at higher temperature which further inhibits the adsorption process. This phenomenon can be proven through the AFM images (Figure 5) of surface hydrogel. It was found that at higher temperature, the hydrogels tends to agglomerate and lumps on the membrane surface as discussed earlier.

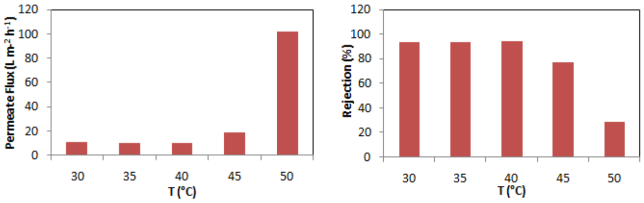


Figure 4 Temperature effect on the permeate flux and rejection of PEUF

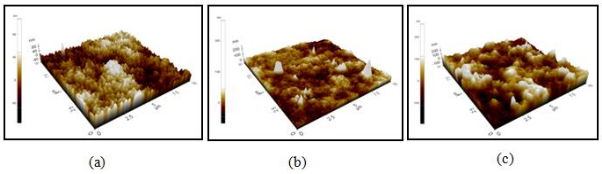


Figure 5 AFM images of hydrogel deposited on membrane at different temperature (a) 30ºC, (b) 40ºC and (c) 50ºC

■4.0 CONCLUSION

PNIPAM-co-Acrylic acid hydrogel has been successfully synthesized using emulsion polymerization method. It possess the desired thermoresponsive properties with VPT temperature around 33°C and hydrodynamic size of 370 nm. The hydrogel could adsorb copper ion readily, however, copper loaded hydrogel shows both chemical and physical properties changes. The hydrodynamic diameter of copper loaded hydrogel increased to 440 nm indicated that adsorption do take place within the polymer matrix. The thermoresponsive property of the hydrogel has significant effect on the PEUF process due to the hydrophilic-hydrophobic interactions between the membrane surface and the hydrogel. High permeate flux of more than 100 L $m^{-2}h^{-1}$ can only be achieved at higher temperature of 50°C. However, the rejection declined significantly at temperature higher than 40°C. Hence, the optimum temperature having both high permeate flux and rejection was not attainable in the study. As a result, this suggests that adsorption is more favorable at lower temperature but PEUF should be carried out at higher temperature to mitigate its fouling tendency on hydrophilic membrane.

Acknowledgement

The authors are grateful to the financial support provided by USM Membrane Science and Technology Cluster, MoHE Fundamental Research Grant (FRGS) (305/PJKIMIA/6071252) and Ministry of Higher Education (MyMaster).

References

[1] Memorial Tributes. 2008. *National Academy of Engineering*. 12.
[2] M. Almutairi, R. W. Lovitt. 2012. *Inter. J. Chem. Environ. Eng.* 3(2): 15–25.
[3] R. Camarillo, Á. Pérez, P. Caῆizares, A. de Lucas. 2012. *Desalination*. 286: 193–199.
[4] H. Zerze, B. Karagoz, H. O. Ozbelge, N. Bicak, N. Aydogan, L. Yilmaz. 2013. *Desalination*. 310: 158–168.
[5] M. Palencia, B. L. Rivas, E. Pereira. 2009. *J. Membr. Sci*. 345: 191–200.
[6] P. Caῆizares, Á. Pérez, R. Camarillo. 2002. *Desalination*. 144: 279–285.
[7] R. Camarillo, J. Llanos, L. García-Fernández, Á. Pérez, P. Caῆizares. 2010. *Sep. Purif. Technol*. 70: 320–328.
[8] J. Llanos, Á. Pérez, P. Caῆizares. 2008. *J. Membr. Sci*. 323: 28–36.
[9] M. J. Snowden, B. Z. Chowdhry, B. Vincent, G. E. Morris. 1996. *J. Chem. Soc. Faraday Trans*. 92(24): 5013–5016.
[10] G. E. Morris, B. Vincent, M. J. Snowden. 1997. *J. Colloid. Inter. Sci*. 190: 198–205.
[11] A. Burmistrova, M. Richter, M. Eisele, C. Uzum, R.V. Klitzing. 2011. *Polymers*. 3: 1575–1590.
[12] Y. P. Hou, A. R. Matthews, A. M. Smitherman, A. S. Bulick, M. S. Hahn, H. J. Hou, A. Han, M. A. Grunlan. 2008. *Biomater*. 29: 3175–3184.
[13] M. Constantin, M. Cristea, P. Ascenzi, G. Fundueanu. 2011. *Expr. Polym. Lett.* 5(10): 839–848.
[14] G. E. Morris, B. Vincent, M. J. Snowden. 1997. *Progr. Colloid. Polym. Sci*. 105: 16–22.
[15] S. Sun, J. Hu, H. Tang, P.Y. Wu. 2011. *Chem. Phys.* 13, 5061 – 5067
[16] J.X. Yang, Y. Fang, C.L. Bai, D.D. Hu, Y. Zhang. 2004. *Chin. Sc. Bull.* 49, 2026 – 2032.
[17] S. T. Sun, P. Y. Wu. 2011. *J. Mater. Chem.* 21: 4095–4097.
[18] F. Zhang, C. C. Wang. 2009. *Langmuir*. 25(14): 8255–8262.
[19] K. Yamashita, T. Nishimura, M. Nango. 2003. *Polym. Adv. Technol.* 14: 189–194.
[20] Y. W. Zhang, M. Jiang, J. X. Zhao, X. W. Ren, D. Y. Chen, G. Z. Zhang. 2005. *Adv. Funct. Mater*. 15: 695–699.
[21] Y. Y. Zhang, A. L. Yarin. 2009. *J. Mater. Chem.* 19: 4732–4739.
[22] T. Hoare, R. Pelton. 2009. *Langmuir*. 20: 2123–2133.
[23] Y. Chen, X. Xiong, G. Yang, L. Zhang, S. Lei, H. Liang. 2002. *Chin. J. Polym. Sci.* 20(4): 369–375.
[24] H. B. Öztürk, H.V. Manh, T. Bechtold. 2009. *Lenzinger. Ber.* 87: 142–150.
[25] C. M. Gary-Bobo, R. Dipolo, A. K. Solomon. 1969. *The J. Gen. Physiol*. 54: 369–382.
[26] A. E. Childress, M. Elimelech. 1996. *J. Membr. Sci*. 119: 253–268.
[27] X. Zhu, M. Elimelech. 1997. *Environ. Sci. Technol.* 31: 3654–3662.