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Microfiltration/ultrafiltration polyamide-6 membranes for copper removal from aqueous solutions

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Abstract. Microfiltration/ultrafiltration (MF/UF) Adsorptive polyamide-6 (PA-6) membranes were prepared using wet phase inversion process. The prepared PA-6 membranes are characterized by scanning electron microscopy (SEM), porosity and swelling degree. In this study, the membranes performance has examined by adsorptive removal of copper ions from aqueous solutions in a batch adsorption mode. The PA-6/H_2O membranes display sponge like and highly porous structures, with porosities of 41-73%. Under the conditions examined, the adsorption experiments have showed that the PA-6/H_2O membranes had a good adsorption capacity (up to 120-280 mg/g at the initial copper ion concentration (C_0) = 680 mg/L, pH7), fast adsorption rates and short adsorption equilibrium times (less than 1.5-2 hrs) for copper ions. The fast adsorption in this study may be attributed to the high porosities and large pore sizes of the PA-6/H_2O membranes, which have facilitated the transport of copper ions to the adsorption. The results obtained from the study illustrated that the copper ions which have adsorbed on the polyamide membranes can be effectively desorbed in an Ethylene dinitrilotetra acetic acid Di sodium salt (Na_2EDTA) solution from initial concentration (up to 92% desorption efficiency) and the PA-6 membranes can be reused almost without loss of the adsorption capacity for copper ions. The results obtained from the study suggested that the PA-6/H_2O membranes can be effectively applied for the adsorptive removal of copper ions from aqueous solutions.

Keywords: adsorptive membrane; preparation PA-6; copper removal; desorption

1. Introduction

The main resources of water are significant importance to mutually natural ecosystem and human developments. In these days, pollution of water sources such as rivers and seas constructs significant problems for water treatment systems. The release of soluble chemical species produced by natural or industrial pollution sources is a global problem that becomes a growing threat to the environment. For this reason, the removal of contaminants is the main objective of waste water treatment to such degree so that the effluents can be reused for industrial or municipal purposes.

Among the number of polluting species which need a special concern are the ions of heavy metals which exist in aqueous waste streams of many industries (Fu and Wang 2011, Järup 2003), such as metal plating facilities, mining operations, tanneries. Unfortunately, the ions of heavy metals are not biodegradable and tend to accumulate in living organisms (Oliver 1997). The

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accumulation of heavy metals throughout the food chain leads to serious ecological and human health problems (Singh *et al*. 2010, Bessbousse *et al*. 2012). The ions of heavy metals such as Cu, Hg, Cd (Pedersen 2003), Zn, Cr (Aroua *et al*. 2007) and Pb are the most hazardous among the chemical-intensive industries because of their non degradability and high toxicity (Ali and Abdallah 2009, Senna *et al*. 2013).

Copper discharged with many industrial effluents, present severe threat to the environment and wastewater treatment works. On one hand, the copper ions have high solubility in the aquatic environments; also, they can be absorbed by living organisms (Chedly *et al*. 2012). On the other hand, the presence of copper contaminates in effluent water might cause vomiting, diarrhea, stomach cramps, nausea, greenish or bluish stools and saliva and might have severe effect in the brain and liver of people (Wang *et al*. 2007, Bojic *et al*. 2009). Copper ions contaminates can reach to water sources through discharges from industrial activities, metal plating facilities, mining operations, smelting, tanneries, municipal wastes and sewage sludge (Sun *et al*. 2013, Bouzid *et al*. 2008), also from natural sources such as sea salt sprays, wind blown dusts, volcanogenic particles and decaying vegetations (Chen *et al*. 2009, Zhou *et al*. 2009). Therefore, the removal of copper ions from wastewater is very important to protect the main water sources, environmental and human health. For these reasons, the applications of several frequently extra technologies are required in waste water treatment.

The removal of heavy metals ions from waste water effluent can be achieved by conventional physical and chemical treatment methods (Kurniawan *et al*. 2006) such as chemical precipitation, neutralization, ion exchange (Dabrowski *et al*. 2004), solvent extraction (Kislik 2012), coagulation, adsorption (Hamadi *et al*. 2001), biosorption, and electrochemical removal (Barakat 2011).The disadvantages of these processes are incomplete metal removal, high-energy requirements, and production of toxic sludge. According to that, the removal of heavy metals are progressively superseded by membrane processes, which are probably the most attractive and efficient methods for removing heavy metals. Separation of heavy metals using adsorptive membrane has been increased due to its convenient operation.

Although, adsorptive membranes have great potentials for the removal of heavy metal ions from aqueous solutions (Chen *et al*. 2004, Salehi *et al*. 2012), commercially available adsorptive membranes have so far been rather limited. Most commercial membranes are made from relatively inert polymers, such as polysulfone, polyvinylidenedifluoride, polypropylene, polyethylene, etc., and these polymers are lack of reactive functional groups on their backbones. As a shortcoming, membranes prepared from pure polymers cannot offer sufficient mechanical stability for application in flow processes. To overcome this problem, techniques of polymer coating and blending have been employed by researchers (Cheng *et al*. 2010, Steenkamp *et al*. 2002, Liu and Bai 2006).

To our knowledge, preparation of homogenous polyamide-6(PA-6) adsorptive membrane has not been reported elsewhere. In the present study, we have focused on the development of PA-6 membrane for removal of copper; using this approach dependent on the PA-6-NH_2 functional groups which act as adsorption sites throughout the membrane. On the other hand, the current methods for preparing adsorptive PA-6/H_2O membranes have been mainly through surface modification of membrane using water as additive even though the pore sizes of the membranes may be suitable for the dimensions of the metal ions. SEM and porosity measurements were carried out to characterize the membranes. Batch adsorption experiments were conducted to study the adsorption. In addition, reusability of the prepared PA-6/H_2O membranes was examined using Na2EDTA as eluting agent.

Table 1 Composition of the prepared membranes

*Membrane	Casting polymer solution		
	PA-6%	FA%	Water%
M1	20	80	0
M2	20	80	5
M3	20	80	10

*Starting dope solution, before water addition was prepared by 20 wt.% PA6; 80 wt.% FA as M1, Pre-concentration time (1 min), immersion in water bath 1 hour at 28 ± 2℃. Where; P: polymer, W: Water, FA: formic acid

2. Experimental

2.1 Raw materials

Polyamide-6 (PA-6) polymer was used to prepare adsorptive flat sheets membranes with bulk density of 0.25 gm/ml, particle size 50–160 μm and it was purchased from Leuna Werke AG (Germany). Formic acid (FA) was used as a solvent with a molar mass 46.02538 g/mol, density1.198 gm/cm^3 at 20℃, and boiling point 100.7℃. Formic acid and methanol both of analytical grade were purchased from Sigma-Aldrich chemical company and used without further purification. Copper sulphate ($CuSO_4 \cdot 5H_2O$), an analytical grade from Sigma Aldrich was used to prepare the copper ion solutions in the adsorption experiments. All the copper (II) ion solutions were prepared using deionized water. Ethylene dinitrilotetra acetic acid Di sodium salt (Na_2EDTA, Acros) was used as received for desorption. NaOH and HCl were used for pH adjustment.

2.2 Membranes preparation

PA-6 adsorptive membrane was prepared using wet phase inversion method. The polymer dope solution (20 wt.% in formic acid) was casted onto a glass plate using a film applicator at 20 ± 2℃ and the evaporation time was 1 minute. The glass plate was subsequently immersed in a gelation bath (containing pure water at 28 ± 2℃). It was rinsed in pure water to remove residual solvent. Then, the membranes sheets were dried at 100℃ for one hour. The effect of water addition to polymer dope solution was studied (as; M2, M3).The composition of the prepared membranes by casting technique was depicted in Table 1.

2.3 Membrane characterizations

2.3.1 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) was used to observe the morphology of the polyamide-6 (PA-6) membranes; however samples of membranes were coated with gold to provide electrical conductivity. The cross sections, top and bottom snapshots of membranes were taken on a JEOL 5410 scanning electron microscope (SEM) which was operating at 10 kV. Where, significant views of surfaces were recorded.

2.3.2 Membrane porosity measurement

Porosity of asymmetric PA-6 membranes was measured. However, membrane porosity plays an important role in describing its performance. In order to evaluate the porosity of the membranes, they were initially impregnated with water then weighed after wiping superficial water with filter papers. After that, the wet membranes were placed in an air-circulating oven at 80°C for 24h to be completely dried and finally, the dry membranes were weighed. The porosity of membranes was calculated using the following equation (Zheng *et al*. 2006).

$$P(\%) = \frac{W_0 - W_1}{V} * 100 \tag{1}$$

Where P is the membrane porosity; W_0 and W_1 are the weights of wet and dry membranes (g), respectively; $V = A*t$ where A is the membrane surface area (cm^2) and t is the membrane thickness (cm). In order to minimize the experimental errors, the membrane porosity of each sample was measured several times (at least 3 times) and the results were reported in average (the error of porosity ± 2%).

2.3.3 Swelling degree

A swelling study of PA-6 Membrane films was carried out by soaking the membranes pieces in pure water at ambient temperature (26 ± 2℃) for 48 hours then weighed after wiping superficial water with filter papers. After that, the wet membranes were placed in an air-circulating oven at 100°C for 1hour to be completely dried. The swelling degree (SD) was determined by accurately weighing each piece both in the dried and swelled states after applying the following equation

$$\text{SD\%} = (m_s - m_d / m_d) \times 100 \tag{2}$$

Where, m_s and m_d are the weights of the wet and oven-dried membranes, respectively. All tests were repeated three times and the mean values were applied.

2.3.4 Fourier transform infrared (*FTIR*) spectrophotometer

FTIR analysis at 16 scans per minute at a resolution of 4 cm-1 was performed on raw polyamide membrane without water addition and polyamide membrane after water addition, also, the FTIR analysis was carried out on membrane after copper adsorption experiments to indicate the efficiency of adsorptive membrane.

2.4. Adsorption performance for copper ions

2.4.1 Effect of membrane type on the adsorption uptakes

Effect of polyamide flat sheet membranes types on the adsorptive performance were conducted with copper ion solutions in a series of batch experiments. The dry flat sheets membranes (M1, M2 and M3) with an about 0.045 g weight were suspended in 50 mL solution with initial copper ions concentration of 680 mg/l, pH = 7 and room temperature of 27℃ under continuous magnetic stirring for 48 hrs, after that the amount of copper ions have been determined by weighting the samples after experiments. Adsorption performance was tested in terms of adsorption kinetics, adsorption isotherms, and effect of solution pH.

2.4.2 Adsorption kinetic study

The adsorption kinetic of copper ion solution on prepared membrane was studied using initial solution pH was set at 7 and the initial copper ion concentration of 200 mg/l. An about 0.045 g of dry sheets of the prepared membranes were added into 500 ml of the copper ion solution in a 1-L flask separately. The content of the flasks were shaken in a shaker at 3.33 Hz (200 rpm) and under room temperature (27°C) for a period of up to 10 hrs. Samples were taken at various time intervals and analyzed for copper ion concentrations.

2.4.3 Effect of different copper concentrations

The effect of various copper concentrations in the range of 3-1000 mg/l were conducted at room temperature and pH = 7. An about 0.045 g amount of dry membranes sheets were added in100 ml flasks, each containing 50 ml of the copper ion solution with various concentrations. The contents of the flasks were shaken in an orbit shaker at 3.33 Hz (200 rpm) for a 10 hrs and the concentrations of copper ions in the solutions were analyzed.

2.4.4 Effect of pH

To examine the effect of solution pH, adsorption experiments of Polyamide membranes were conducted with copper ion concentration of 200 mg/l and different pH value in the range of 3–7. Approximately 0.045 g amount of dry membranes sheets pieces were added into 500 ml of a copper ion solution in a 1-L flask. The contents of the flasks were shaken in an orbit shaker at 3.33 Hz (200 rpm) and room temperature for a period of up to 2hrs. The final copper ion concentrations in the solutions were analyzed. All the samples of copper ion concentration in this study were analyzed with an Analyst 400 atomic absorption system Perkin Elmer Germany.

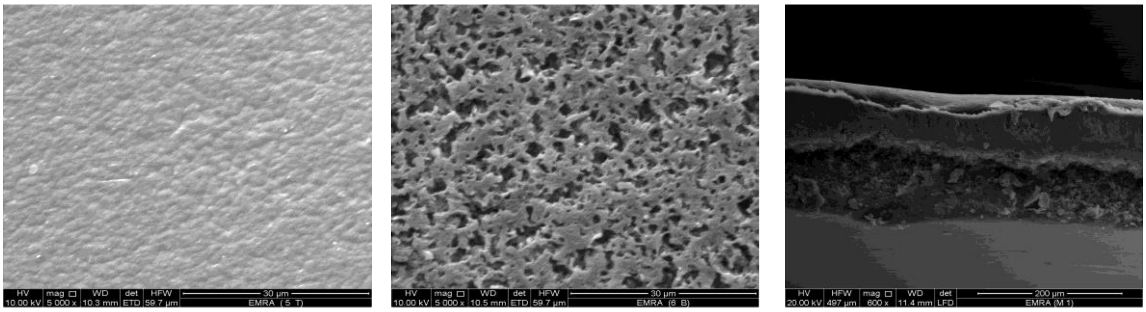
Copper ion adsorptions on the membranes were calculated by measuring differences in Cu(II) concentration in the solution before and after equilibrium using the following expression

$$Q_e = \frac{V(C_0 - C_e)}{m} \tag{3}$$

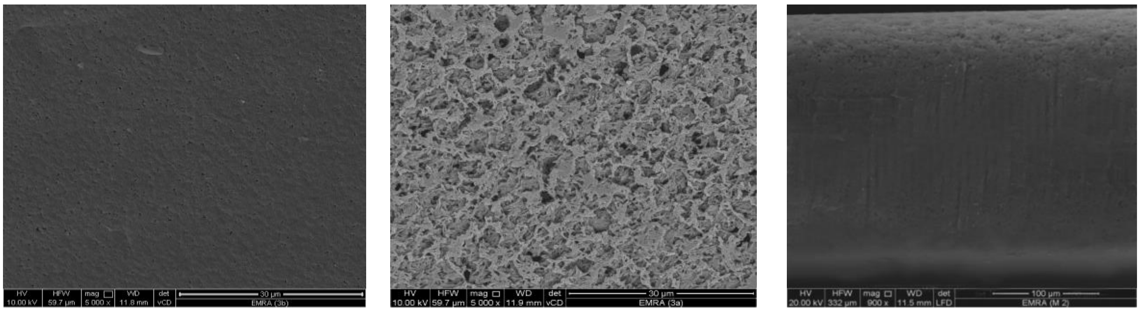
Where, Q_e is the equilibrium adsorbed amount of copper ions on the membrane (mg/g), V is the volume of the solution (l), C_0 and C_e are the initial and final concentrations of copper ions (mg/l) in the solution, respectively, and m is the mass of the adsorptive membrane (g).

2.5. Reuse desorption

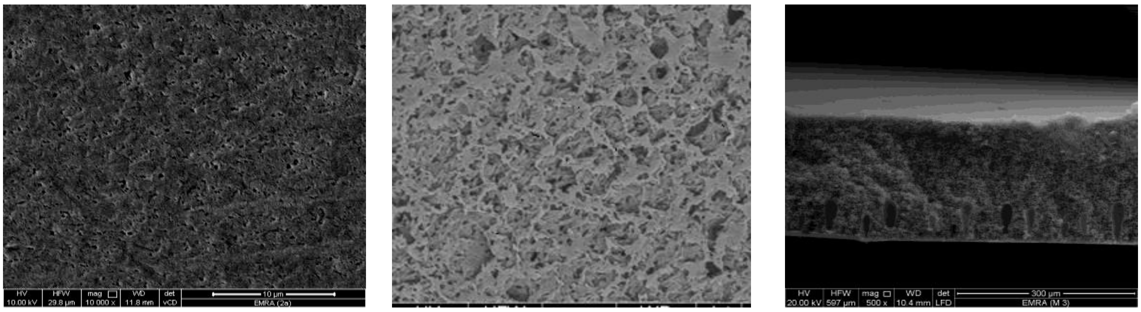
The prepared PA-6 membranes were tested for the regeneration experiments. Distinct amount of the membranes (0.045 g) were incubated in 50 ml of copper ion solutions with the initial concentration of 200 ppm at 27°C and pH 5.5 for 10 h. After calculating the amount of copper ion adsorbed, the membranes were washed with distilled water and then immersed in 50 ml of 10 mM (0.2 g/l) Na2EDTA solution under stirring at 200 rpm for 10 h. After washing with 50 mM of NaOH and then distilled water, the regenerated membranes were used for the next adsorption stage according to the same procedure as described. The adsorption/regeneration cycles were conducted to evaluate the reusability of the membranes. The adsorption–desorption experiments were conducted for five cycles. An Analyst 400 atomic absorption system Perkin Elmer Germany was used to determine the copper (II) ions concentrations of all samples.



(a) MI – Top surface (b) MI – Bottom surface (c) MI – Cross section



(d) MI2 – Top surface (e) MI2 – Bottom surface (f) MI3 – Cross section



(g) M3 – Top surface (h) M3 – Bottom surface (i) M3 – Cross section

Fig. 1 SEM Photograph of asymmetric PA-6 membranes (M1, M2, M3)

3. Results and discussion

3.1 Membrane morphology (*SEM*)

In this study,the polyamide-6 membranes were successfully fabricated through the wet phase inversion method with formic acid as solvent and water as additive. Fig. 1 indicates the SEM snapshots of the top and bottom surfaces of M1, M2 and M3, where the bottom surface is highly porous for the all membranes. It can be found that, the M2 and M3 exhibit a porous top surface while the M1 shows a relatively dense surface. The formation of a more porous surface of M2 and M3 membranes is due to the fact that the addition of water affects the phase inversion step of the polymer solution during coagulation. This result also indicates that a more addition of water (5-10 wt.%,) can affect the top surfaces to be as porous as the bottom surfaces or in order to make the top surface more porous.

Cross sections surfaces of membranes shows that the PA-6 membrane with water as additive becomes much more porous. This is clearly shown in Fig. 1 where the cross section of M2 and M3 is observed to be much more porous than that of M1.

3.2 Swelling ratio and porosity

In this work, three types of PA-6 membranes were prepared. The (M2, M3) membranes are macro-porous membranes microfiltration/ultrafiltration (MF/UF) while the asymmetric membrane (M1) is in the region of a micro-porous nanofiltration/reverse osmosis (NF/RO) membranes, according to that the porosity was measured using equation1 for the two first macro-porous membranes and in order to do the right comparison between three membranes, the porosity of third micro-porous membrane was measured also by using equation 1. The membrane porosity of each sample was measured several times (at least 3 times) and the results were reported in an average (the error of porosity ± 2%).

As depicted in Table 2, the trend of porosity changes is in agreement with the result of the SEM images. The porosity of the PA-6 membrane increases by increasing the addition of water from 5 to10 wt.%. The water content of the polymeric membranes is directly connected to their swelling properties. As shown in Table 2, the results demonstrated that the PA-6 membranes have been swelled in a higher degree, due to hydrophilic nature of the $-NH_2$ which can offer considerable hydrogen bonding with hydrophilic groups (NH_2 functional groups act as adsorption sites throughout the membrane).

3.3 Fourier transform infrared (FTIR) spectroscopy

The Fig. 2 Indicates the FTIR spectrum of flat sheets membranes for unmodified polyamide-6 membrane (blue curve), and polyamide-6/water membrane (**red curve**) and complexation of copper with polyamide-6/water (**green curve**).

The spectrum shows the characteristic bands of polyamide-6 at 3312 cm−1 (H-bonded N–H stretch vibration), 1665 cm−1 (amide I, C–O stretch), and 1562 cm−1 (amide II, C–N stretch and CO–N–H bend).

The peak of 1668 cm−1 (amide I) is observed for the polyamide-6/water (spectrum (**red**) which is attributed to the amino groups of polyamide 6/water flat sheet membrane.

In spectrum (**red**), a broadband at 3,316 cm−1 and 3066 due to amine N–H and O–H of polyamide- 6/water is obvious. In addition to the peak at 1,560 cm−1, assigned to amide II, there were also peaks at 1,668 which have been recognized as amide I bands. A peak around 1,055 cm−1

Table 2 Effect of membrane morphology on porosity

Membrane	Thickness	Porosity%	SD%
M1	200µm	32%	94
M2	200µm	41%	161
M3	220µm	73%	192

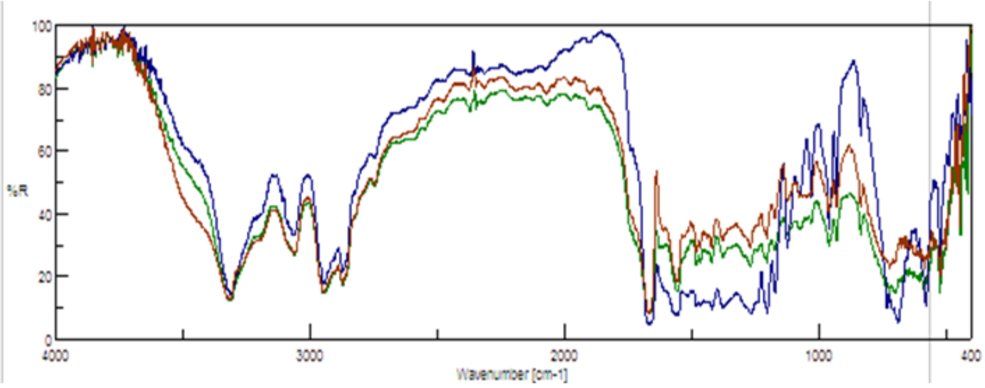


Fig. 2 FTIR spectra of unmodified membrane (blue) and the (red) one is PA6/water while the (green) spectra belonged to PA6/water loaded with copper

is corresponding to C–O bending, typical of polyamide structure.

Generally, the difference in frequencies, intensity, and shape of these bands in the region 3600–3100 cm^{-1}, implies that in complexes where there is the displacement of H_2O molecules by O–H groups in the first coordination sphere of the copper(II) ion. Water protons take part in the formation of relatively weak hydrogen bonds. The peak at 520 and 446 cm^{-1} may be due to Cu-O bending.

From the Fig. 2 it can be seen that all five FTIR spectra present distinct peaks in the following ranges: 3905–3065 cm^{-1}, 2941–2871 cm^{-1}, 1665–1668 cm^{-1}, 1423–1428 cm^{-1}, 1078–1055–1075 cm^{-1}, and 520 cm^{-1}. From the curve (**red**) the broad and strong band situated in the range 3200–3418 cm^{-1} can be attributed to overlapping of –OH and –NH stretching also the peaks at 3905 cm^{-1} and at 3844 are missing in this curve (**green**) and the O-H stretching would not have been there since this would have been due to complexation of Cu with polyamide (**green curve**). These results revealed that chemical interactions between the copper ions and the hydroxyl groups occurred on the modified membrane surface. The band from the range 2940–2941 cm^{-1} and from 2868 to 2871 to 2870 cm^{-1} is attributed to the C-H stretching vibrations. The strong peak at 1665-1668–1667 cm^{-1} can be due to a C = O stretching in amide groups. The peak at 1423–1428 cm^{-1} is attributed to N-H bending in amine group. The band observed at 1078–1055–1075 cm^{-1} was assigned to the CO stretching of alcohols and carboxylic acids. Thus polyamide 6-water flat sheet membrane contains hydroxyl, carboxyl and amine groups on surface.

From the curve (**green**) it can be seen that the peak observed for unmodified membrane at 1665 cm^{-1} is shifted to 1668 cm^{-1} or 1667 cm^{-1}. This increase in the wave number of the peak characteristic for C = O group which revealed that interacts with carbonyl functional group are present between modified polyamide 6 membrane and copper ions. No frequency changes were observed in the C-H and -NH_2 groups of biomass after copper adsorption. In addition, all FTIR spectrum of PA6/ water membrane loaded with copper ions contain band at 588, 520, cm^{-1} which can be attributed to Cu-O stretching modes.

3.3 Adsorption performance

3.3.1 Effect of membrane pores size on the adsorption uptakes

Some of researchers (Ali and Abdallah 2012, Reddy and Patel 2008, Ghaee *et al*. 2010) had a

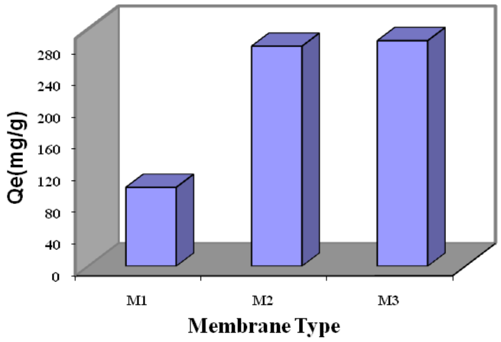


Fig. 3 Effect of membrane pores size on copper ion adsorption on PA-6 (adsorption equilibrium (*Q*e, mg/g) is in terms of per gram of dry PA-6 membranes pieces, C_0 = 680 mg/L, pH 7, 48 hour)

good effort for developing a new generation of membranes with their characteristics for removal of different contaminants in water. Various types of membrane processes such as ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO), have been contributed to environmental protection by removal of heavy metals from effluent waste water streams (Kurniawan *et al*. 2006, Ghaee *et al*. 2010, Muthukrishnan and Guha 2006).

The objective of the current study is to enhance adsorption capacity as well as reusability of the PA-6 adsorptive membranes for the purpose of copper ion removal from aqueous solutions. Adsorption data for copper ion removal with the PA-6 membranes were used to evaluate their adsorptive performance. Where, the maximum adsorption uptake can be achieved at the pH value closer to the neutral level as this can reduce the need for pH adjustment in many application cases where water or wastewater may often have pH at or near the neutral level.

Fig. 3 shows the typical results of copper ion adsorption on PA-6 membranes at the neutral level of pH 7. The three membranes have different adsorption uptakes of copper ions. The trend of changes in the adsorption uptakes of copper ions on the PA-6 membranes indicates that the membrane morphology has an effect on the adsorption uptakes. The results suggest that the highly porous structures of the membranes sheets have made their adsorption sites freely accessible to the copper ions to be adsorbed. Hence, heavy metal ions can be removed from aqueous solutions when the metal ions in the solutions are in contact with the surfaces of the membranes, even though the pore sizes of the adsorptive membranes may be much larger than the dimensions of the metal ions. In comparison with the M2, M3 (MF, UF) and M1 (NF/RO) membranes, the adsorptive M2 and M3 membranes provide the advantages of high retaining efficiency for copper ions, with the benefits of low energy consumption.

On one hand, heavy metal ions such as copper ions can be removed from aqueous solutions when adsorptive membranes have reactive functional groups on the surfaces, such as –COOH, –SO_3H, and –NH_2 groups, which can bond the targeted substances through specific interactions such as, surface complexation or ion exchange. On the other hand, heavy metal ions can be removed from aqueous solutions when the metal ions in the solutions are in contact with the surfaces of the membranes, even though the pore sizes of the membranes may be much larger than the dimensions of the metal ions.

3.3.2 Effect of time on the adsorption uptakes

The effect of operating time of copper ion adsorption on PA-6 membranes (M2, M3) at an

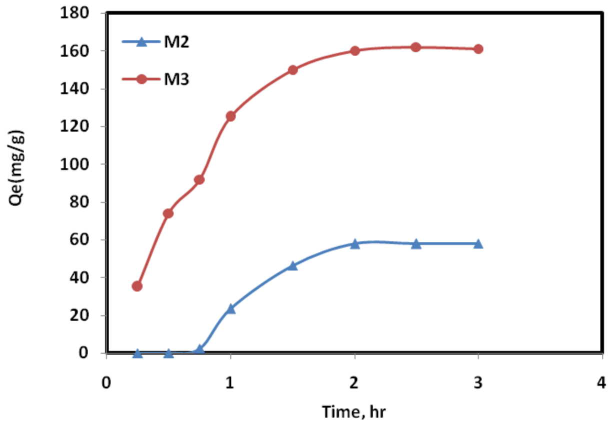


Fig. 4 Effect of retention time on the adsorbed amount of copper at equilibrium on PA-6(M2, M3) membranes (adsorption equilibrium (*Q*e, mg/g) zis in terms of per gram of dry PA-6 membranes pieces, C_0 = 200 mg/L, pH 7)

initial concentration of 200 mg/l and pH of 7 is presented in Fig. 4. Fig. 4 illustrates that the adsorption of copper ions are generally fast and reached equilibrium within 2-3 h. The results suggest that the adsorption sites of the M3 membrane are higher than M2 membrane, thus the copper ions adsorbed with M3 membrane is higher than M2. Generally, faster adsorption rates are always preferred in all adsorption separation systems. The fast adsorption in this case may be attributed to the high porosities and large pore sizes of the PA-6 membranes, which facilitated the transport of copper ions to the adsorption.

3.3.3 Effect of pH values on the adsorption uptakes

The typical results of copper ion adsorption on PA-6 membranes (M2, M3) at different solution pH values are illustrated in Fig. 5. In general, the adsorption uptakes increased with the increase of the solution pH values. At pH below 3 no significant adsorption occurred. In the pH range of 4–6 the adsorption uptakes have been increased significantly with solution pH and reached the highest

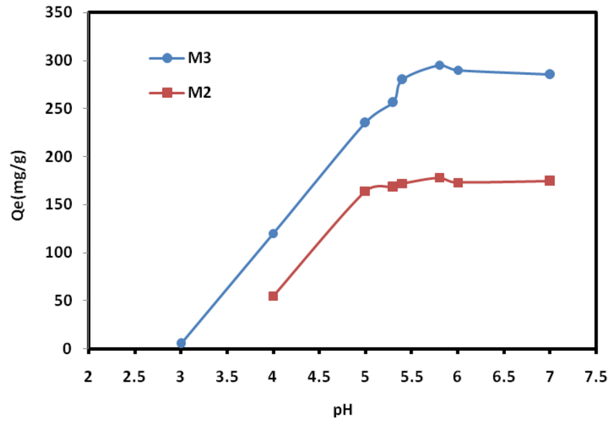


Fig. 5 Effect of pH values on copper ion adsorption on M2 and M3 membrane (Q_e is in terms of per gram of dry PA-6 membranes pieces, C_0 = 680 mg/L, 10 hours)

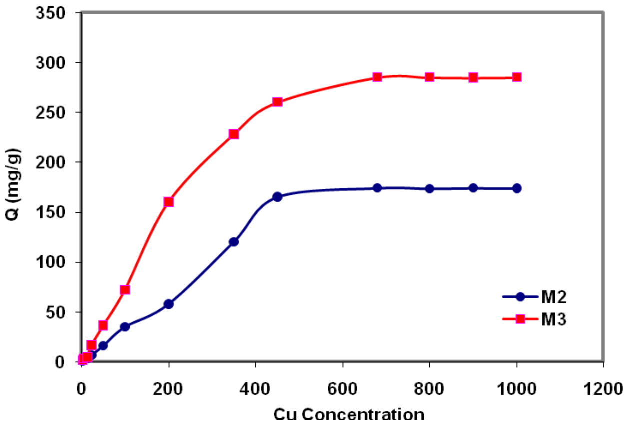


Fig. 6 Effect of copper concentration on copper ion adsorption on M2 and M3 membranes (Q_e is in terms of per gram of dry PA-6 membranes pieces, pH = 7, 10 hours)

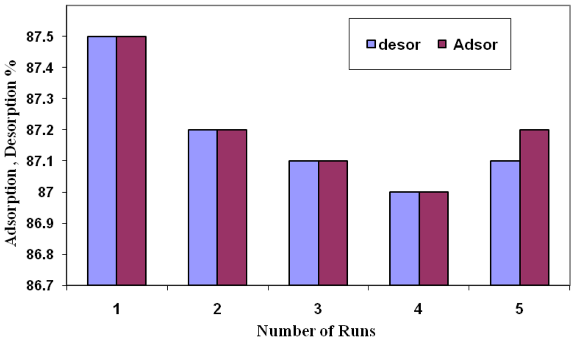
uptakes at pH 5.8. The trend of changes in the adsorption uptakes of copper ions on the PA-6 membranes with the solution pH values is attributed to the protonation of the amine groups of PA-6 at lower solution pH values, which create greater electrostatic repulsion to the copper ions to be adsorbed and, therefore, reduced the amount of adsorption at a lower solution pH values.

3.3.4 Effect of copper concentration on the adsorption uptakes

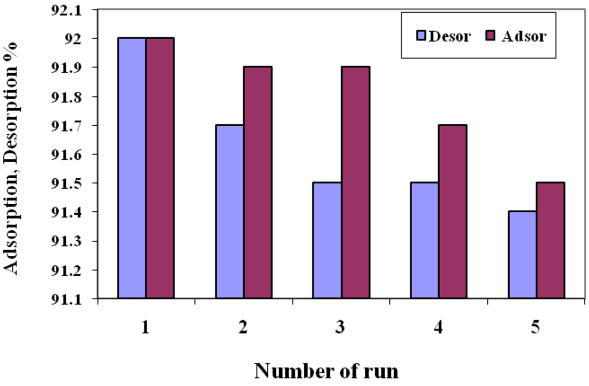
The experimental isotherm adsorption results were conducted at room temperature and at different copper ion concentration. Fig. 6 shows the amounts of copper ions adsorbed at adsorption equilibrium (Q_e, mg/g) on the PA-6 membranes (M2,M3) in an initial copper ion concentration ranged ($C0$, mg/l) from 3 to 1000 mg/l. It is clear from Fig. 6 that the adsorption uptake amounts increases with the initial or, more precisely, the equilibrium copper ion concentrations in the solution approached the maximum at high equilibrium concentrations. In general, the equilibrium adsorption amounts (Q_e) increases with the increase of the initial copper ion concentrations and the copper ions adsorbed with M3 membrane is higher than M2.

3.4.5 Reuse

Reusability of the PA-6 membranes (M2, M3) were tested using, Na2EDTA which exhibited superior performance for the regeneration of the membranes. EDTA is a strong hexadentate chelating agent and capable of forming complexes Cu(II) ions. Therefore, 10 mM Na2EDTA solution was selected for our purpose based on what reported by Daraei *et al*. (2012). After five regeneration cycles, adsorption capacity loss is about 0.5% for the M3 membrane; however, this value is less 0.5 % for the M2 membrane. The results of the adsorption/regeneration cycles are shown in Figs. 7(a) and (b). Obviously, more effective regeneration has carried out using M3 membrane. This trend is in agreement with the result of the SEM image analyses, swelling properties and porosity change. The comparison between the reusability of M2 and M3 is manifested at Fig. 8. It was found that the copper ions adsorbed on the polyamide membranes can be effectively desorbed in an EDTA solution from initial concentration (up to 92% desorption efficiency) and the PA-6 membranes can be reused almost without loss of the adsorption capacity for copper ions.



(a) M2



(b) M3

Fig. 7 Efficiency of M2, M3 membrane for desorption and adsorption process

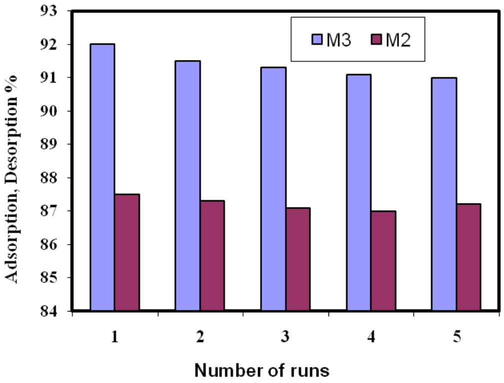


Fig. 8 Comparison between reusability of M2 and M3 at initial concentration 200 ppm, time 10 hrs and pH = 5.5)

The results of other previous works from the literature for heavy metal removal are summarized in Table 3 where it can be seen that the performance of PA-6 membranes was comparable to that obtained from the other reported membranes.

Table 3 Comparison between literature results for heavy metal removal compared to the present work

Membrane type	Materials	PH	Cu concentration	Cu removal or Max. Removal capacity	Ref.
RO	Thin film composite polyamide	-	200	98.5	Barakat 2010
Nf			200	< 90	
MF-complexation filtration technique using synthetic polymer membranes	Polyamide 6 - With PEG as complexion agent	pH > 8	500 ppm	90	
	- With PAA as complexing agent	pH > 8		91.5	
MF-UF polyamide membrane 6	PA-6 with water as an addtive	pH = 5.8	1000 mg/l for Cu(II) at, 27°C	Max. adsorption capacity = 295 mg/g Addition water molecule to PA-6 membrane enhancement the membrane performance	Our study
Emulsion Liquid Membrane (ELM)	Mobile carrier: 4% of (Alamine336). 1-5% (v/v) (SPAN 80) as a surfactant Diluent (commercial kerosene) With a special reactor deign for emulsification, absorption and stripping	pH = 8	500- 3000 ppm	At 6/1 ratio (feed/emulsion) 95% of copper in the external phase (feed) is removed	
Nano-fibrous membrane	Grafted poly (ethylene terephthalate) with acrylamide (AM)			183.25 [mg/g]	Dong *et al.* 2013
Modified PES ultrafiltration membrane	PES with Co-Fe_2O_3 nanoparticles with PEG		10-50 ppm	Max. Adsorption capacity increased by increasing metallic nanoparticles in Uf membranes to > 90%	Chan *et al.* 2015

4. Conclusions

Adsorptive PA-6 membranes were prepared and developed in this study by phase inversion method for copper ion removal. The following conclusions can be drawn from the present study:

- The morphology of the membranes samples indicates that the addition of water can increase the porosity on the membrane surface which leads to formation a spongy like structure and increases in membrane pores size. Therefore, the difference in the pores size in the upper surface of the membrane and on the lower surface shows that these membranes have asymmetric structure.

- Kinetic of copper ion adsorption on the PA-6/H_2O membranes versus time confirms that the time required for the equilibrium is less than three hours.
- The results suggested that the adsorption sites of the M3 membrane were higher than M2 membrane, thus the adsorbed copper ions with M3 membrane is better than M2.
- It was found that the adsorbed copper ions on the polyamide membranes can be effectively desorbed in an EDTA solution from initial concentration (up to 92% desorption efficiency) and the PA-6 membranes can be reused almost without loss of the adsorption capacity for copper ions.
- The developed PA-6 membranes were suitable for copper ion removal.

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