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Synthesis and characterization of polysulphone/clay membrane: effect of natural clay differences

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ABSTRACT

Polysulphone/clay ion-exchange membranes were prepared by the phase inversion method using N-methyl-2 pyrrolidone as solvent. The aims of this work were to synthesize and investigate the effect of different natural clays from different locations on the morphology, hydrophilicity, structure, swellability, metal extraction from water and ion-exchange capacity (IEC) of the membranes prepared. The characterization techniques used were scanning electron microscopy, X-ray diffractometry, Fourier transform infra-red spectroscopy and contact angle. The clays from locations 1 (N4) and 2 (N6) had a good dispersion in the polysulphone matrix and exhibited high IEC, swellability and hydrophilicity. The 2θ of the polysulphone/clay membranes compared to polysulphone membrane was lower, indicating an increase in the d-spacing between layers of the clays and also intercalation of clay layer silicates in the polymer matrix. Extraction/adsorption of Pb^{2+} by all the tested membranes was faster (10 min) compared to Cu^{2+}, and it was approximately 100%.

Keywords: Adsorption; Clay; Ion-exchange membrane; Polysulphone; Synthesis

1. Introduction

The effort for access to clean drinking water in Africa has been an issue that touches all aspects of development including agricultural productivity, stability and peace, health, education and opportunities of women and children as well as economic productivity. High concentration of heavy metals such as Hg, Cd, Pb, Cu, Ni and Zn in the environment, which leads to the contamination of water systems, is part of the limiting factors resulting in water scarcity. Excessive ingestion of these metals by humans can cause accumulative poisoning, cancer, nervous system damage and ultimately death [1,2].

In recent years, different treatment techniques for wastewater filled with heavy metals were developed in order to decrease the amount of wastewater produced and improve the quality of treated effluent. Manufacturing industries generate about 0.24 million tons/year of Hg, Cd, Pb, Cu, Ni and Zn, while metal industries, waste disposal, agricultural activities and fuel/power industries generate 0.39, 0.72, 1.4 and

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2.4 million tons/year, respectively [3–5]. The main techniques used to reduce heavy metals in effluents include chemical precipitation, ion-exchange resins, adsorption processes, membrane processes and electrolytic methods [6]. For dilute metal concentrations, ion-exchange, reverse osmosis and adsorption can be applied. However, the common use of ion-exchange and reverse osmosis is restricted by the high operating cost. Several other adsorption processes had been designed and tested using different adsorbent as an alternative to chemical precipitation and other separation processes used in water treatment [7]. However, the manufacturing, disposal and regeneration of these sorbents are always associated with high cost. It is, thus, necessary to search for cost-effective sorbents and modelling of the sorption processes.

Ion-exchange membranes find applications in metal extractions and recovery of valuable ions from effluents. The charges on the surface of the membranes often influence applications and the membrane selectivity. The controlled ion-exchange capacity (IEC) of polysulphone (PSf) membrane makes it possible to change its IEC. This can be achieved by incorporating inorganic/nano-composite materials such as clay with better ion-exchange to PSf matrix. It was envisaged that the IEC of a PSf membrane modified with clay would be of great importance in extracting metals from water.

Most of the work done on PSf/clay nano-composite membranes had focused on the mechanical and thermal stabilities, anti-corrosion, anti-microbial and barrier properties as well as application in fuel cells [8–10]. These membranes were also prepared using solution dispersion methods. PSf/clay nano-composite membranes were synthesized by Unnikrishnan et al. [11] and the membranes were used as proton exchange membranes in fuel cells. These nano-composite membranes were prepared by solvent evaporation and they showed optimum mechanical performance. As a result, the membranes exhibited lower water uptake characteristics in the polar–polar interaction between the clay used and the PSf at the interface. Intercalation of PSf into clay galleries was studied using X-ray diffraction (XRD), while SEM was used to evaluate the dispersion of clay in the membranes. An increase in basal spacing from 18.5 Å in nanoclay to 24.3 Å in the nano-composite membranes confirmed the intercalation of PSf chains into clay galleries of nanoclay. SEM micrographs showed effective dispersion of nanoclays and improved pore distribution in PSf/clay nanocomposite membrane. Other tests that were carried out include thermal stability, conductivity and single-cell performance tests.

Amilia et al. [12] synthesized PSf/clay membrane using N,N-dimethyl acetamide (DMAc) as solvent and added pore-forming/filler reagent (polyethyleneglycol (PEG)). The clays used were obtained from South Lampung, Indonesia, and they were identified by XRD to consist of montmorillonite, chabazite and cliptonilolite. The clays used were calcined and the synthesized PSf/clay membranes were used in dextran removal from water. The authors also studied the permeability of the membranes. The membranes produced were found to be in microfiltration range with 30–48% dextran rejection, permeation of 45.76–642.18 $\mathrm{L\,m^{-2}\,h^{-1}\,atm^{-1}}$ for pure water flux (PWF) and 12.80–501.71 $\mathrm{L\,m^{-2}\,h^{-1}\,atm^{-1}}$ for dextran, respectively.

Similarly, Ma et al. [13] studied the performance of PSf/clay membranes prepared using non-solvent-induced phase inversion technique, and N,N-dimethyl acetamide, deionized water and LiCl were used as a solvent, a coagulant and a pore-forming agent, respectively. The properties of the membranes such as PWF, protein rejection, porosity, contact angle, tensile strength and elongation at break were evaluated. The results from the evaluation showed that clay had a good dispersion in the PSf matrix; addition of clay additive improved the hydrophilicity of the membranes and increased the ratio of large pore in the skin layer. Also, the PWF and porosity of membranes increased with the increase in clay content. Thus, far, few works had been reported on the application of PSf/clay ion-exchange membranes in metal extraction from water [14]. As a result, this study presents the synthesis and application of PSf/clay ion-exchange membranes in the extraction of metals from water. The effect of contact time on the extraction/adsorption capacity of the membranes was studied to know at what point the optimum extraction could be obtained in order to reduce cost and energy.

2. Materials and methods

2.1. Materials

The polysulphone used was obtained from Solvay Advanced Polymer (South Africa) and was used as received without any treatment or cross-linking. The two different natural clay samples (N4 and N6) used were collected from the Democratic Republic of Congo (DRC) around Kinshasa and were used without any treatment. Water sample was collected from a mining site in the Limpopo Province of the Republic of South Africa. N-methyl-2 pyrrolidone (NMP) (Merck) was used as a solvent for membrane preparation, while deionized water was used as a precipitating “non-solvent”.

2.2. Polysulphone/clay composite membrane preparation

Polysulphone membrane and polysulphone/clay ion-exchange membranes were prepared using the phase inversion technique. Accordingly, 0.1 g of each clay type (see Table 1) was mixed with measured amount of NMP under stirring for 0.5 h at room temperature. Polysulphone (15 wt.%) was dissolved in the premixed solution at 80˚C and was allowed to mix for at least 4 h to guarantee complete dissolution of the polymer. The prepared solution was kept for 24 h without stirring at room temperature to remove air bubbles. The solution was cast uniformly onto a glass plate by means of a hand-casting knife with a knife gap set at 250 μm and the glass coated with the wet polymer solution was immediately immersed into a water bath at room temperature for 1 h. The membrane produced was allowed to dry at room temperature and sandwiched between plain sheets of paper for storage. The obtained membranes were named according to the clay types (Table 1).

2.3. Natural clay characterization

2.3.1. Zeta potential, conductivity cation exchange capacity

The zeta potential and the conductivity of the clays were acquired using a zeta nanosizer, while the cation exchange capacity (CEC) of the clays was obtained first by determining the concentration of potassium (K), magnesium (Mg) and calcium (Ca) present in the clays and then using the equation below to calculate the CEC [15].

$$\mathrm{CEC} = \mathrm{K} + \mathrm{Mg} + \mathrm{Ca} + 1.2 \tag{1}$$

where K is the milliequivalent of K, Mg is the milliequivalent of Mg, Ca is the milliequivalent of Ca and 1.2 is the milliequivalent of neutralizable acidity.

2.3.2. XRD and chemical composition of clay

The crystallinity of the natural clays was examined using a Rigaku UltimaIV X-ray Diffractometer. XRD analysis was performed at 40 mA, 40 keV, Cu Kα radiation ($\lambda = 0.1540562$ nm), divergence slit of 1/8˚, anti-scatter slits of 1/4˚, 5 mm, over a range of 4˚–80˚ on the 2θ scale. The chemical composition of the clays was carried out using X-ray fluorescence spectrometer.

2.4. Polysulphone/clay composite membrane characterization

2.4.1. Fourier transform infra-red analysis

The functional groups present in all the membranes and clays were established using a Perkin Elmer 100-Spectrometer FTIR/ATR system and the result was recorded with characteristic peaks in wavenumbers from 650 to 3,500 cm^{-1}.

2.4.2. Polysulphone/clay composite membrane crystallinity

The crystallinity of the polysulphone/clay membranes was examined using a Rigaku UltimaIV X-ray diffractometer. XRD analysis was performed at 40 mA, 40 keV, Cu Kα radiation ($\lambda = 0.1540562$ nm), divergence slit of 1/8˚, anti-scatter slits of 1/4˚, 5 mm, over a range of 4˚–35˚ on the 2θ scale.

2.4.3. IEC determination

The IEC of the membranes was determined using back titration method. The membranes were immersed for 24 h in a 100 ml of 1 M HCl aqueous solution to give the membranes the H-form. The membranes were then washed with deionized water in order to remove excess HCl and were further equilibrated with deionized water for 4 h, with frequent changes of the water to remove the last traces of acid. The membranes were then equilibrated with exactly 50 ml of 0.01 M NaOH aqueous solution for 24 h and the IEC was determined from the reduction in alkalinity determined by back titration. The IEC of the membranes was calculated from Eq. (2) [16].

$$\mathrm{IEC} = \frac{M_{\mathrm{o,NaOH}} - M_{\mathrm{E,NaOH}}}{W} \tag{2}$$

Table 1
Natural clay properties

Clay types	Colour	Zeta potential (mV)	CEC (meq/100 g)	Conductivity (mS/cm)
N4	Cream	−23.6 ± 6.6	238	0.0207
N6	Forn	−27.9 ± 7.3	320	0.0178

where $M_{\mathrm{o,NaOH}}$ is the moles of NaOH in the flask at the start, $M_{\mathrm{E,NaOH}}$ is the moles of NaOH after equilibration, and W is the weight of the dry membrane (g).

2.4.4. Contact angle (sessile drop method)

The contact angle measurement of membranes was carried out with a Data Physics optical contact angle measuring instrument, with the droplet size controlled by a Gilmont syringe. Deionized water was used for analysis. Water droplets were placed onto a flat membrane surface at nine different locations and data were taken four times at each point to obtain a series of contact angle pairs.

2.4.5. Conventional swellability tests

The membranes were initially weighed and then soaked in deionized water for about 24 h. The wet membranes were removed from deionized water and were gently wiped by pressing between soft filter papers. The weighing of the samples was further carried out using an analytical balance. The percentage swellability at time t [Q_t (mol%)] of the immersed membranes was obtained using Eq. (3) [17].

$$Q_t\,(\%) = \frac{m_{\mathrm{w}}/M_{\mathrm{w}}}{m_{\mathrm{c}}} \times 100 \tag{3}$$

where m_{w} is the mass of water sorbed in g, m_{c} is the mass of the composite measured in g and M_{w} is the molar mass of water.

2.4.6. Scanning electron microscopy analysis

The surface morphology of the membranes was obtained by mounting samples on a high resolution scanning electron microscope (TESCAN HRSEM) and irradiated with a beam of electrons at 20 kV. This was followed by proper magnification and precise focusing for better viewing of the membranes' surfaces.

2.5. Extraction/adsorption tests

The quantitative analysis of Cu^{2+} and Pb^{2+} was done using an atomic absorption spectroscopy to determine the concentration of metals in the water sample before and after the adsorption tests. The real water sample was dominantly Cu^{2+} (23.6 ppm) and Pb^{2+} (7.4 ppm). Other metals present in the real water sample were Co (0.14 ppm) and Al (4.81 ppm). The membranes were cut into a square and were weighed before using them in the extraction/adsorption processes. The membranes were immersed in vial containing 10 ml real water sample and were agitated using a shaker bath at 50 rpm for 60 min and water samples were taken every 10 min for quantitative analysis.

3. Results and discussion

3.1. Natural clay characteristics

Table 1 shows some characteristics of the clays used in the membrane preparation and the colours of the clays are shown in Fig. 1. It shows that the location of structural charge within a clay layer and the existence of hydrophobic patches on its surface provide important variations in the CEC [18]. The effect of clay mineral structure and hydrophobicity on the configurations of adsorbed water molecules increases with increase in the sizes of the interlayer cation. The zeta potential of the clay increased in an order of N4 > N6. The clay that exhibits the lowest zeta potential will possibly produce ion-exchange membrane with high contact angle. The results showed that the

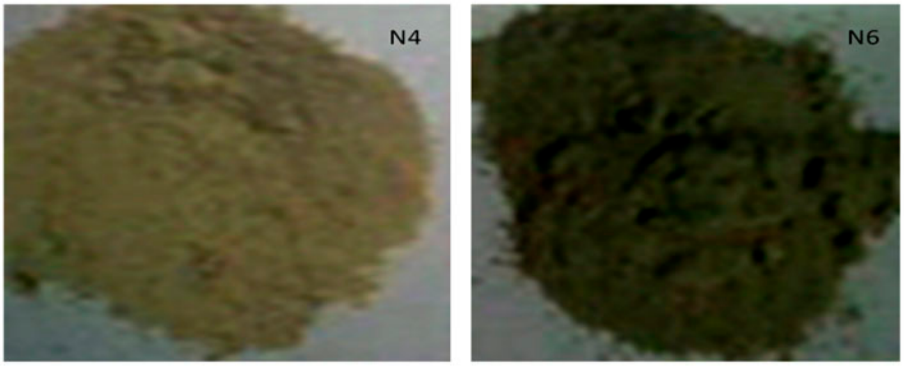

Fig. 1. Various natural clay colours: cream and forn are N4 and N6 natural clays, respectively.

Table 2
Elemental compositions of clays

Samples/elements	N4 (%)	N6 (%)
Na	0.0341	0.0284
Mg	0.4316	0.8584
Si	47.697	46.741
Al	19.075	15.496
P	0.0500	0.1051
S	0.0601	0.0846
Cl	0.0279	0.0162
K	0.6665	1.1089
Ca	0.0792	0.0341
Ti	0.4953	0.7468
Fe	0.4967	4.6316
Rb	0.0027	0.0038
Sr	0.0020	–
Zr	0.0266	0.0222
Nb	0.0013	0.0019
Cr	–	0.0149
Mn	–	0.0090
Ni	–	0.0049
Cu	–	0.0041
Zn	–	0.0054
As	–	0.0039

higher the zeta potential of the clay, the higher the clayey conductivity, but the CEC is lower. The obtained CEC results are not conclusive since the actual cation exchangers that were responsible for the exchange in these analyses were not known (there could be random isomorphic cation substitutions in the clay structures) [19]. An investigation of the effect of layer charge on the adsorption of water and hydrocarbon molecules by smectites clay has shown that surface hydrophobicity increases as the layer charge decreases [20–22].

Table 2 displays the elemental composition of the natural clays. Sample N4 contains higher silicon (Si) (silicate in its oxide form) and aluminium (Al) (aluminates in its oxide form) compared to N6. Calcium (Ca) and sodium (Na) are higher in N4, but magnesium (Mg) is more in N6 than in N4. Also, it was observed that the potassium (K) content of sample N4 is lower compared to sample N6. The higher Mg and K in N6 were responsible for the higher CEC of N6 compared to N4. The sample N6 contains chromium (Cr), manganese (Mn), nickel (Ni), copper (Cu), zinc (Z) and arsenic (As), which are absent in sample N4. However, N4 contains strontium (Sr), which is not in N6.

3.2. Fourier transform infra-red of clays and membranes

It was shown from the study of the functional groups of the studied natural clays that the vibrations at 675, 784 and around 1,000 cm^{-1} can be ascribed to vibration of valence bands of Si–O–Si and Si–O–Al, and vibration of deformation bands of Si–O–Al (Fig. 2(a)). In addition, a vibration of deformation band of Al–OH was found at 909 cm^{-1}. The vibration of valence bands of Al–OH was found at 3,678 cm^{-1}, while OH vibrations of water in the clay hydration were found around 3,386 cm^{-1} [23].

Fig. 2 shows the FTIR spectra of polysulphone membrane and the membranes made from polysulphone and clay from different locations. The bands observed at 1,679 and 1,577 cm^{-1} are assigned to –C–C– benzene deformation bands. Therefore, SO_2 and C–O–C stretches were found in the range of 1,000–350 cm^{-1}. The IR absorption band of polysulphone shows the presence of the sulphonic group (O=S=O) in the polymer back bond at 1,147 and 1,236 cm^{-1}. The membrane made from N4, N6 and polysulphone membrane spectra show a band associated with aromatic –CH vibration at approximately 3,067 cm^{-1}. The band present at 2,921 cm^{-1} corresponds to –CH stretching absorption while the peak at 2,856 cm^{-1} is ascribed to aliphatic $-CH_2$ asymmetric stretching. The –CH vibration and stretching are attributed to the polymer phase of the membranes [24].

The vibrations around 1,000 cm^{-1} and those between 699 and 797 cm^{-1} are vibrations of valence bands of Si–O–Si and Si–O–Al, and deformation vibration bands of Si–O–Al (18). Broad bands between 2,500 and 3,700 cm^{-1} cover all the vibrations observed in clays [23]. The spectra for polysulphone/clay membranes show the vibration bands of the polysulphone overlapping those for clays; and Benchabane and Bekkour [25] and Dau and Lagaly [26], who worked with clay–polymer composites, also made similar observations.

3.3. Natural clays and polysulphone/clay composite membrane crystallinity

XRD results showing the crystallinity of the natural clays and polysulphone/clay membranes are shown in Fig. 3. The N6 clay exhibits higher intensity which corresponds to higher crystallinity than the N4 clay. The N4 clay contains crystalline peaks of Sodalite, $Na_8Al_6Si_6O_{24}$, 84%, Quartz, SiO_2, 9.4%, Birnessite, $KO_{48}Mn_{1.94}O_{5.18}$, 2.38% and Carnegieite, $NaAlSiO_4$, 3.8%, while N6 clay contains Clinohypersthene, $Mg_{0.31}Fe_{0.87}$, 80%; Alumino-phosphate, $Al(PO_4)$, 8.9% and Quartz, SiO_2, 11.1% [23].

Crystalline peak is observed between 27° and 30° on all the polysulphone/clay membrane (N6). However, polysulphone and N4 membranes do not exhibit this characteristic. The intensity of PSf membrane is lower compared to those of N4 and N6 membranes.

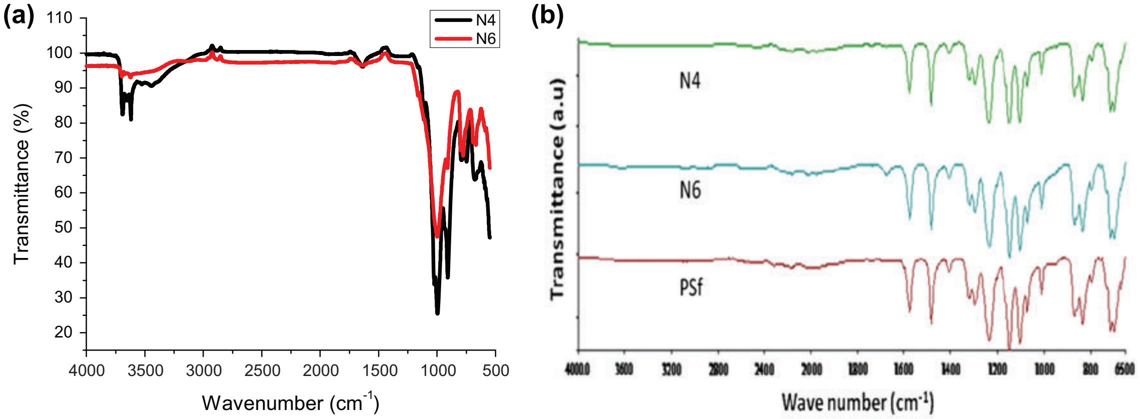

Fig. 2. FTIR spectra of the (a) clays (b) membranes: associated wavenumbers of different functional groups present in the composite membranes.

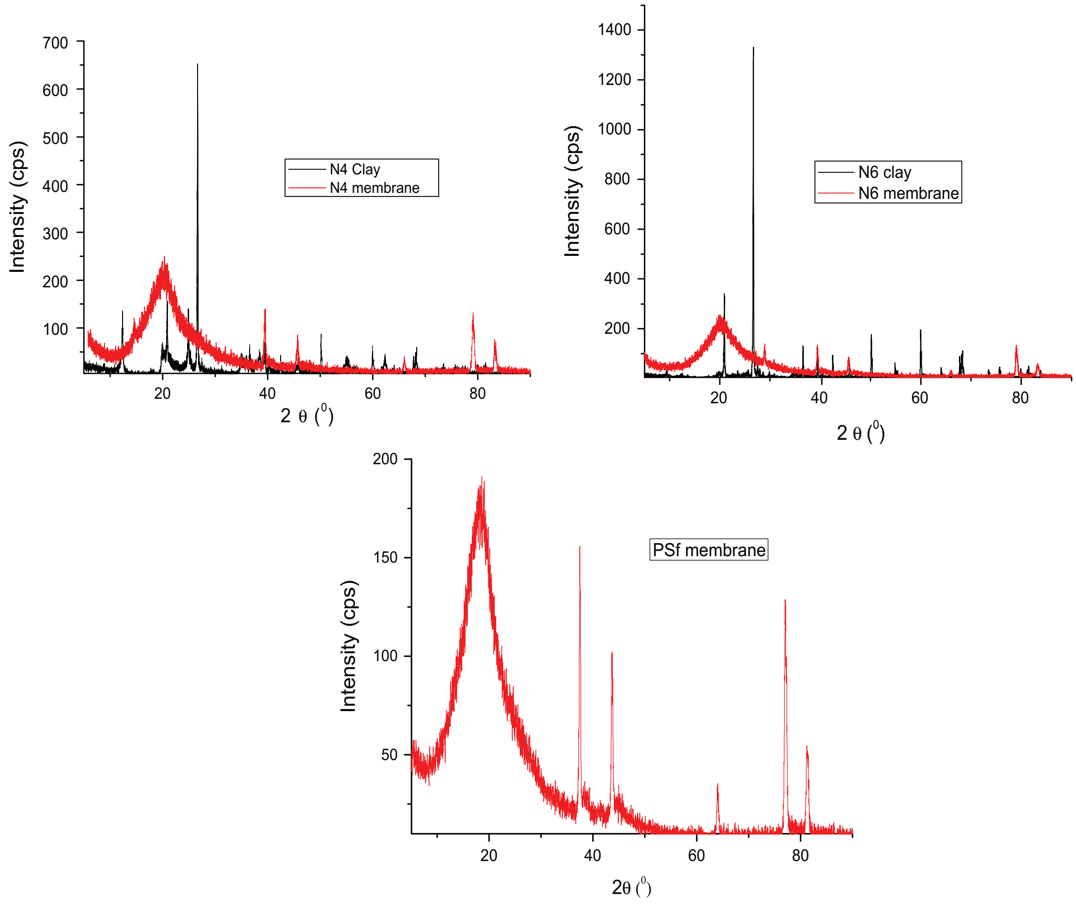

Fig. 3. XRD pattern of the clays and membranes.

So, N4 membrane is seen to be more crystalline than the N6 membrane and more crystalline peaks are found between 80° and 85° on the N4 membrane's spectra.

In order to confirm polysulphone intercalation into the silicate layer of the clays, the differences in *d*-spacing was measured by XRD technique. The XRD pattern of polysulphone membrane shows a peak at $2\theta = 18.34^\circ$, which corresponds to a *d*-spacing of 0.488 nm. However, when clays were added to polysulphone to produce polysulphone/clay ion-exchange membranes, 2θ shifted to a higher value of 18.49˚ for membrane obtained from N4, but a lower value of 18.18˚ for membrane made from N6. A decrease in 2θ angle of the composite membranes was also observed by Sanglimsuwan et al. [27], this decrease resulted from an increase in clay content incorporated into polyvinyl acetate (PVA) matrix.

The observed *d*-spacing of the polysulphone/clay membranes were 0.472 and 0.475 nm for N4 and N6, respectively. The lower 2θ angle observed for N6 membrane and the decrease in *d*-spacing of all the polysulphone/clay membranes compared to polysulphone membrane indicated an increase in the *d*-spacing between layers of the clay. This behaviour also showed that clay silicate layers intercalated within the polysulphone matrix. Membrane made from N6 exhibited the highest intercalation compared to the membrane made using N4. This explains why N4 membrane shows more crystallinity compared to N6 membranes.

3.4. IEC measurement

The IEC values for the prepared membranes are listed in Table 3. It can be observed from Table 3 that the N4 polysulphone/clay ion-exchange membrane exhibited the highest IEC value (0.6438 mmol g^{-1}), but no significant decrease is seen in the IEC values of N6 ion-exchange membrane compared to N4 membrane. The miscibility differences and the surrounding of the hydrophilic structure of clay by a compact structure of polysulphone can also be responsible for the lower IEC value of N6 ion-exchange membrane. According to Khodabakhshi et al. [28], high miscibility between two structures can lead to the most impaction and less accessibility of the functional groups, which can result in a decrease in IEC. It was observed that the CEC of the clays did not show any significant effect on the IEC of the membranes as one would have expected (Table 3).

On the other hand, Hosseini et al. [29] suggested that increase in IEC values may be a result of the formation of voids and cavities in the membrane matrix, which could facilitate the ion transportation between the solution and membrane phase.

3.5. Contact angle and swellability of the membranes

Table 3 also shows the contact angles and the swellability of the membranes. It was observed that all the polysulphone/clay membranes exhibited lower contact angles compared to the polysulphone membrane (64.8 ± 7.3). The membrane that was prepared from natural clay N6 showed the lowest contact angle (39.7 ± 4.2), compared to the polysulphone membrane and N4 ion-exchange membrane. The lower contact angle exhibited by the polysulphone/clay membranes can be attributed to the presence of vibration of valence bands of Si–O–Si and Si–O–Al, which are nonexistent on the polysulphone membrane (Fig. 2).

It had been reported that water molecules can be intercalated between clay layers to create an interlayer ionic solution that causes swelling phenomenon related to electrical double layer properties [30,31]. The membrane swelling mainly depends on the intercalation of the clays in the polymer matrix. It had also been observed by other researchers that the ion-exchange membranes prepared using polysulphone as a base polymer will possibly undergo a dimensional change during flocculation. This dimensional change eventually results in defects and change in IEC due to high water affinity [32]. Thus, the affinity of the membrane to water increases with increase in *d*-spacing of the membranes.

3.6. Scanning electron microscopy

The SEM micrographs of the top surface (air side) of polysulphone and polysulphone/clay membranes were recorded at 5 KX magnifications. The surfaces of the ion-exchange membranes show a smooth structure with N6 membrane showing an even distribution of clay on the membrane surface. The surfaces of N4 and N6 membranes show the clay distribution within the polysulphone matrix. A smooth surface of the polysulphone membrane without any natural clay is seen in Fig. 4(a). The presence of spherical and dark voids of

Table 3
Contact angle, swellability and IEC of membranes

Membrane types	Contact angle (˚)	Swellability (mol%)	IEC (mmol/g)
Polysulphone	64.8 ± 7.3	0.20	0.5818
N4	44.2 ± 2.6	0.33	0.6438
N6	39.7 ± 4.2	0.23	0.6289

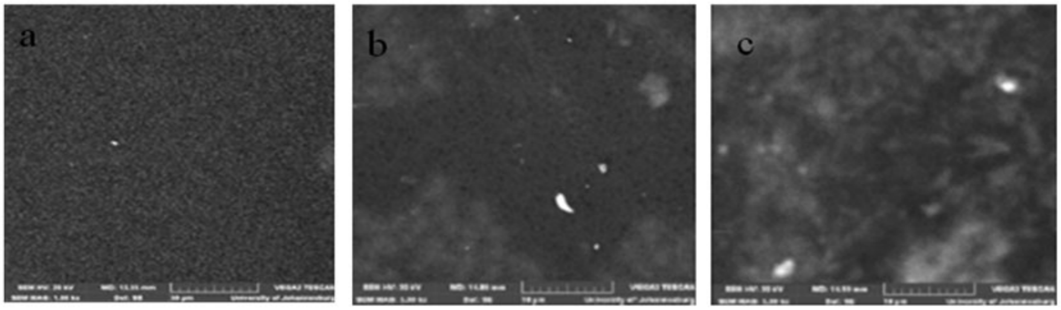

Fig. 4. Surface micrographs of (a) PSf, (b) N4 and (c) N6 membranes; N6 membrane showing an even distribution of clay on the membrane surface.

uniform dimensions is also seen on the surfaces of all the membranes.

3.7. Cu^{2+} extraction from water

Fig. 5 shows the results obtained from the adsorption of Cu^{2+} from real water onto PSf/clay ion-exchange membranes as a function of time (10–60 min). The percentage adsorption for Cu^{2+} from the real water increases with time for polysulphone and N6 membranes. However, N4 PSf/clay ion-exchange membrane showed a different trend with the percentage adsorption of Cu^{2+} decreasing after a 50 min period. At the beginning of the experiment, the PSf/clay ion-exchange membranes showed highest metal extraction compared to the PSf membrane; however, at 40 min of the experiment, PSf membrane exhibited the highest metal extraction. The behaviours of the PSf/clay membranes showed that less active site of the PSf/clay ion-exchange membranes is involved with increasing metal concentrations in the aqueous solution. PSf membrane extracted 66% of Cu^{2+} at 60 min, which was the amount of Cu^{2+} extracted by the N4 PSf/clay ion-exchange membrane at 50 min.

The N6 PSf/clay ion-exchange membrane showed the highest Cu^{2+} extraction from the real water sample on the average followed by the N4 PSf/clay ion-exchange membrane and PSf membrane the least. Metal ions usually move through the pores of the membranes and channels of the lattice during the ion-exchange process to replace exchangeable cations in the clay (mainly sodium and calcium) [33]. The higher performance of the N6 PSf/clay ion-exchange membrane in the real water sample resulted from its higher CEC compared to N4 PSf/clay ion-exchange membrane. On the other hand, lower extraction of metal capacity exhibited by N4 and N6 ion-exchange could be due to possible formation of other metal salts from the cations present in the clay.

3.8. Pb^{2+} extraction from water

Fig. 6 represents the relationship of percentage Pb^{2+} extraction by the membranes with contact time. Approximately, 100% Pb^{2+} was sorbed by all the

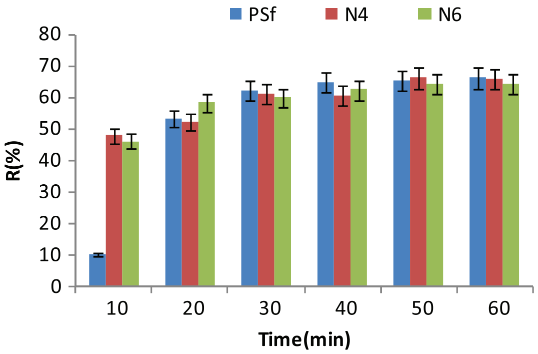

Fig. 5. Percentage Cu^{2+} ion extraction from real water with time; maximum adsorption was achieved at different contact times for all the membranes.

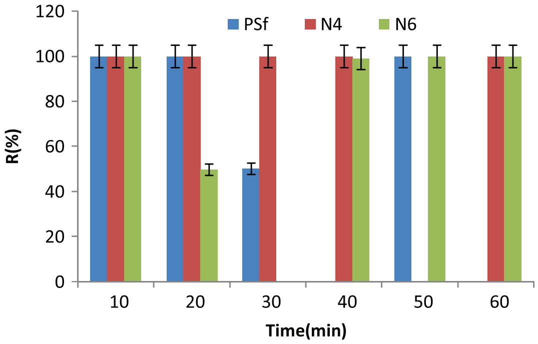

Fig. 6. Percentage Pb^{2+} ion extraction from real water with time; about 100% adsorption/extraction was achieved at a contact time of 10 min for all the membranes.

membranes during the first 10 min of the adsorption tests. At the 30th min of the tests, the Pb^{2+} initially adsorbed by the N6 membrane desorbed into the solution resulting in an increase in the concentration of the water sample. This could be that Cu^{2+} displaced Pb^{2+} in order to occupy the active site on the membrane's surface. The N4 and PSf membranes showed desorption at contact time of 40 min (PSf), 50 min (N4) and 60 min (PSf). Generally, the ion-exchange membrane prepared from N4 natural clay showed more stability in the extraction of the metals of interest. The rapid adsorption that was observed at the initial stage of the tests could be due to the initial concentration gradient between Pb^{2+} in solution and the number of active sites available on the membranes' surfaces at the beginning of the tests.

It had been reported that electronegativity of a metal ion enables it to form a bond with another atom or ion, especially when it exhibits a high electronegativity [34]. It was further stated that a sulphate group in an adsorbent can facilitate a fast adsorption of Pb^{2+} more than Cu^{2+} (32). This is relative to the observation made with the fast adsorption of Pb^{2+} more than Cu^{2+} by PSf membrane, in this study. Similar to the observation made by other researchers, there is a possibility that the initial concentration of Cu^{2+} did not favour its competition with Pb^{2+} for the same available adsorption site on the membranes surfaces [35]. This could be the reason for the lower extraction of Cu^{2+} from the water sample.

4. Conclusions

Ion-exchange membranes composed of clay particles homogeneously dispersed in polysulphone were developed. The SEM micrographs and XRD analysis had shown that clays from locations 1 and 2 were well dispersed and intercalated within the polymer matrix. The incorporation of various natural clays into the membrane structure affects the hydrophilicity and swellability of the membranes, which, as a result, improved the IEC of the membranes. The polysulphone/clay membranes exhibited lower contact angles compared to the polysulphone membrane. The natural clay types, N4 and N6, show irreversible property in ion-exchange phenomenon, thus, a long term ion-exchange phenomenon might be possible in clay composite membranes. Also, the natural clays can be activated in order to further improve the IEC of polysulphone membranes. Different adsorption times were observed for each metal by various membranes. The removal of Pb^{2+} was greater than Cu^{2+} for all the membranes, suggesting that the functional groups and exchangeable ions on the surface of these membranes had a relatively stronger affinity for Pb^{2+} than for Cu^{2+}. The results from this work indicated that there was a complex interaction between each metal species in the adsorption process. An antagonistic competitive effect between these metallic species present in the real water was observed. Extraction/adsorption of Pb^{2+} by all the tested membranes including PSf membrane was faster (10 min) compared to Cu^{2+}, and it was ~100%. Based on the adsorption results, PSf/clay ion-exchange membrane prepared using N4 natural clay showed higher affinity towards Pb^{2+} and Cu^{2+} at a contact time of 40 min. It can, therefore, be concluded that the N4 membrane could be used in the adsorption of combined metals (Pb^{2+} and Cu^{2+}) from an effluent.

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