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# Preparation and evaluation of heavy metal rejection properties of Polyetherimide/Porous activated bentonite clay nanocomposite membrane

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## *Abstract*

The acid activated bentonite clay ranging from 1.0 to 4.0 wt % were incorporated into the Polyetherimide membranes and extensively studied for its morphology, porosity, membrane hydraulic resistance and hydrophilic properties. The nanocomosite membrane has shown an increment in porosity, hydrophilictiy and reduction in hydraulic resistance. Elemental mapping studies confirmed the intercalation of activated bentonite clay within the polymer matrix. Studies have been conducted to analyse the permeate flux and rejection towards Cu (II), Ni (II) and Cd (II) ions by varying the pH and initial feed concentration. The results revealed that, membrane with higher clay dosage showed enhanced flux and rejection whereas lower rejection was observed in case of lower pH and higher initial feed concentrations. It has also been demonstrated that, affinity of metal ions to form the hydration sphere and adsorption capacity towards bentonite clay plays a vital role in the effective removal of metal ions. The membrane showed good rejection towards heavy metal ions without any external chelating agent. The membranes showed maximum rejection of 69.3%, 76.2% and 82.5% for 250 ppm of Cd (II), Ni (II) and Cu (II) ion solutions. The low level of the heavy metals concentration in the permeate implies that water with good quality could be reclaimed for further reuse.

Key words: Bentonite, nanoporous membrane, polyetherimide, heavy metal

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## *1. Introduction*

Possessing an evil property of being non-biodegradable and environmentally persistent, the heavy metals constitute the most hazardous environmental pollutants in nature. Even the lower concentrations of these pollutants accumulated in an organism's tissue causes severe and fatal damage to the health due to its extreme toxicity. [1-2] It is for the observation of naked eyes that, the industrial development is ultimately contributing to this harmful advancement in the decline of health. The industries such as metal plating facilities, mining operations, fertilizers and pesticide industries, tanneries, batteries and paper industries are the ones which discharge heavy metals into the environment in the name of the industrial sewage. Toxic heavy metals draw the attention of scientists for the purification attempts of waste water consisting of cadmium, nickel, zinc, copper, mercury, chromium and lead.[3] In particular, copper has very important role in animal metabolism. The intake of unnecessary copper into the body can cause severe health concerns like vomiting, cramp, convulsion and even death.[4] Presence of nickel beyond the permissible limit can cause severe harm to lungs, kidney and disorders such as skin dermatitis, pulmonary fibrosis and gastrointestinal distress. And importantly it is also a known carcinogen. Cadmium has been categorized by the U.S. Environmental Protection Agency as a potential human carcinogen. Cadmium exposes human to severe health risks. Prolonged exposure to cadmium brings about kidney dysfunction and high levels of exposure will result in death. [5-6] These examples illustrate how dangerous if the heavy metals are accumulated in the body, it is so necessary that these should be eliminated from the water, which is directly or indirectly consumable.

Polymer- clay nanocomposite membranes put forward a very promising result in the above mentioned needs. These are the mixed matrix material consisting of a polymer with uniformly dispersed clay nanoparticles. They offer better separation properties of membranes because of their acquiring properties of both organic and inorganic materials with good permeability, selectivity, mechanical strength, thermal stability and chemical resistance.[7] The strong interactions between the polymer chains and the clay mineral platelets make them significant in the field of membrane science.

Though there are several clay materials available for this purpose, smectic clays are commonly used in preparation of nanocomposite membranes such as bentonite, hectorite, montmorillonite (MMT) and synthetic mica. Structurally bentonite clay is made up of two basic building blocks, the aluminium octahedral sheets and the silica tetrahedral sheets (Fig.1). A single unit cell consists of one aluminium octahedral sheet sandwiched between two tetrahedral silica sheets. These silicate layers have a slight negative charge that is compensated by exchangeable cations in the intermediate layers.[8] The charge is so weak that the cations ($Na^+$, $Mg^{2+}$ or $Ca^{2+}$ ions) can be adsorbed with an associated hydration shell. The cations held in this pattern in the clay can be easily replaced by ion exchange. Bentonite clay with this structure along with polymer can be considered as an important technique to produce nanocomposite material. It is very interesting to observe that, the addition of even less than 10 wt % of clay material to the polymer makes a lot of difference in the properties like hydrophilicity, adsorption capacity and permeability, the usual observation being an enhancement.[9]

**Figure-1**

There are a limited number of studies that report the use of clay as an additive in the preparation of membranes. Eren et al. demonstrated the applicability of $MnO_2$ doped bentonite for removal of lead from water.[10] The study revealed that, adsorption of lead (Pb) by the bentonite clay was influenced by pH and ionic strength of the solution. Ghamei et al. reported the synthesis of polyethersulphone nanocomposite membranes with organomodified montmorillonite clay. These membranes showed a thinner skin layer as well as smaller surface pore size.[11] Alexandre et al. reported the preparation of polyamide/ montmorillonite nanocomposite membranes, which displayed superior barrier properties to water and gas as compared to neat polyamide film.[12] Ma et al. reported polysulfone/ organomodified montmorillonite nanocomposite membrane with dimethyl acetamide as the solvent, water as a non-solvent and PEG 400 as the pore forming additive. The report revealed that addition of clay was responsible for the increase in porosity and permeability (from 0.095 $Lm^{-2}\,s^{-1}$, 0 wt % clay to 0.106 $Lm^{-2}\,s^{-1}$, 6 wt % clay).[13] The effect of aluminium pillared bentonite clay for the rejection of cobalt (II) from aqueous solution was reported by Manohar et al. The results revealed that maximum rejection of 99.8 % and 87.0 % took place at pH 6.0 from an initial concentration of 10.0 and 25.0 mg $l^{-1}$ respectively.[14] Bereket et al. studied the role of bentonite clay in the removal of Cu (II), Pb (II), Cd (II) and Zn (II) from contaminated water.[15]

PEI membranes, which have superior film forming ability, low cost, outstanding acidic and alkaline resistance, strong mechanical and chemical stability and good mechanical property have been generally used as ultrafiltration and microfiltration membranes in many industrial fields. [16] In spite of having all these superior advantages, these membranes are prone to severe membrane fouling and flux decline because of their hydrophobic nature, makes a setback for their extensive use in water treatment. Bentonite has high heavy metal adsorption and ion exchange capacity and also offers a real advantage in terms of the physical isolation of heavy metals from the contaminated water. Not only this, it also increases the hydrophilic nature of the membrane. Additive such as PVP, PEG and LiCl were often needed in the preparation of membranes as the pore forming agents and PEI (Polyetherimide) membrane prepared without additive has lower permeability. [17]

In the present protocol, PEI/ activated bentonite clay nanocomposite membranes were prepared by an immersion precipitation method using PEG 1000 as pore former. The difference in morphology and hydrophilicity of the membranes with different amount of clay dosage was determined by SEM and the contact angle analyzer. The presence of bentonite clay and its uniform distribution in polymer matrix was confirmed by EDX and elemental analyses. The performance of these membranes was analyzed in terms of water flux, porosity, membrane hydraulic resistance and heavy metal ion rejection study.

## 2. Materials and methods

### 2.1. *Materials*

Polyetherimide (PEI) purchased from Sigma Aldrich, N-methyl pyrrolidone (NMP) of analytical-grade purity was obtained from Merck. Bentonite clay was obtained as a gift sample from the department of civil engineering, NITK Surathkal, India. Polyethylene glycol (Mw =1000), Analytical grade copper nitrate, nickel nitrate and cadmium nitrate were procured from Sigma Aldrich. Deionized and distilled water was used for the preparation of metal ion solutions with different initial feed concentrations.

### 2.2. *Activation of bentonite clay*

The activated bentonite clay was prepared using the procedure reported in the literature. [18] In brief, bentonite clay (5g) was mixed with a 7N sulfuric acid solution (100 ml). The obtained suspension was heated to 90$^{o}$ C for 18 h under constant stirring. The reaction was carried out in a glass flask furnished with a reflux condenser in order to avoid evaporation of solvent during the experiment. After acid activation, the slurry was filtered and the filtrate was thoroughly washed with de-mineralized water until it is free from sulfate ions (tested by $BaCl_2$ solution). The acid activated sample was dried initially at room temperature and then at $70^o$ C for 3 h.

### *2.3. Preparation of composite membrane*

PEI/activated bentonite clay nanocomposite membranes were prepared by non-solvent induced phase separation method. Calculated amount of activated bentonite clay (1 wt % to 4 wt % of PEI dosage) was mixed with the desired volume of NMP and magnetically stirred for 1.0 h at room temperature. PEI was added to premixed solution along with 5 % PEG 1000 as an invariable additive (pore forming agent) and heated to 65 ° C. The solution was stirred continuously for 16 h in order to ensure the complete dissolution of the polymer. So obtained homogeneous solution was kept for 5 h without stirring at the same temperature to get rid of trapped air bubbles in the solution. The homogeneous casting solution was cast over the clean glass plate using doctor's blade and gently immersed in non-solvent bath containing water as non-solvent. Thus obtained membrane was kept immersed in distilled water for 24 h to ensure complete phase inversion and then it was washed with distilled water for several times. Overviews of the experimental conditions were described in Table 1.

**Table-1**

### 2.4 *Porosity and contact angle*

Porosity of membrane was analyzed by dry-wet weight method. [19] The membrane soaked in distilled water was weighed after wiping the surface water with blotting paper. Then the wet membrane was placed in an air-circulating oven at 70° C for 24 h prior to measure the dry mass. From the two weights (the dry sample weight and the wet sample weight), the porosity of the membrane was calculated using equation (1).

$$P(\%) = \frac{W_w - W_d}{\rho_w \times A \times \delta} \times 100 \qquad (1)$$

Where $'P'$ is the porosity of the membrane, $W_w$ is the weight of wet sample (g), $W_d$ is the weight of dry sample (g), $\rho_w$ is the density of pure water (0.998 g/$cm^3$), $'A'$ is the area of membrane in wet state (cm$^2$) and $'\delta'$ is the thickness of membrane in wet state (cm). In order to minimize the experimental error, each membrane was measured for three times and the average value was reported.

The hydrophilic property of the membrane surface was analysed by the water contact angle (WCA) measurement. It was measured with a FTA-200 Dynamic contact angle analyzer according to the sessile droplet method. The reported values were the average of the contact angles of five droplets.

### *2.5 Morphology of the membranes*

The surface and cross-section images of the composite membranes were studied using SEM. For this purpose, the dry membrane samples were fractured cryogenically using liquid nitrogen and sputtered with a thin layer of gold using a sputtering apparatus. After gold sputtering, the cross-sectional morphologies of the asymmetric membranes were observed with Joel JSM-6380LA scanning electron microscope. In addition to this, the presence of silicon, aluminium, sodium and other element in bentonite clay was analyzed by energy dispersive X-ray Microanalysis (EDX).

### *2.6 Water flux study*

The pure water flux (PWF) of the membranes was determined using lab fabricated dead end filtration unit having an effective membrane area of 5cm$^2$. The setup was aided with nitrogen cylinder as the pressure source. Each membrane was compacted at 4 bar pressure for 30 min before commencing the experiment. After compacting, deionized water passed through the membrane for 80 min at 3 bar pressure to obtain PWF $J_w$ (L/m$^2$h). The flux was calculated using the formula (2).

$$J_w = \frac{Q}{\Delta t\ A} \qquad (2)$$

Where, $J_w$ is PWF and '$Q$' is the amount of water collected for $\Delta t$ (h) time duration using a membrane of area $'A'$ (m$^2$).

### *2.7 Membrane hydraulic resistance ($R_h$)*

The pure water flux of the membranes was measured at different transmembrane pressure (TMP).[20] The hydraulic resistances of the membranes ($R_h$) were evaluated from the slope of the plot of pure water flux versus pressure difference ($\Delta P$) using the equation (3)

$$R_h = \frac{\Delta P}{J_w} \qquad (3)$$

Where $J_w$ is the pure water flux ($L/m^2h$), $\Delta P$ (kPa) is the pressure difference and $R_h$ is the membrane resistance ($kPa/Lm^{-2}h^{-1}$).

*2.8 Heavy metal ion rejection study*

The heavy metal ion rejection performance of all membranes was carried out by using self-constructed dead end filtration cell. The feed solutions of cadmium nitrate, nickel nitrate and copper nitrate with concentration of 250 ppm, 500 ppm and 1000 ppm were used for the metal ion rejection study. The feed solution was filled into a filtration tank and pressurized as required using a nitrogen cylinder. Then permeate was collected for a regular interval of time and the concentration of the heavy metal ion was measured using an atomic absorption spectrometer. The percentage of rejection of the membranes was determined by using the equation (4).

$$\%R = \left(1 - \frac{C_p}{C_f}\right) x100 \qquad (4)$$

Where, $C_p$ and $C_f$ are the concentration of permeate and feed solution respectively.

## 3. Results and discussion

*3.1Chemical composition*

Table 2 shows the changes in the chemical composition of the bentonite clay after acid treatment. The acid activated bentonite clay exhibit significantly different physicochemical characteristics compared to their non-activated counterparts. One of these physicochemical properties is surface area. The surface area and the porous structure of bentonite can be changed to the desired extent by acid activation. During acid treatment, the structure of the raw clay is opened and becomes porous. [21] At the same time $H^+$ ion replaces the metallic ions in the structure such as $Fe^{+3}$, $Na^+$, $Mg^{+2}$, resulted in clay with highly active structure.

Bentonite was subjected to EDX analysis to determine the elemental composition. From the Fig. 2, the untreated clay consists of Na, Mg, Si, Al and other elements. After acid treatment, peak corresponding to Na and Mg were disappeared in the clay. This confirms the exchange of sodium and magnesium ions with protons.

**Table-2**

**Figure-2**

### *3.2 Porosity and contact angle*

In general, the skin layer of an asymmetric membrane decides its performance and the supporting layer has only minor influence. The rejection and intrinsic permeation properties are determined by the porosity and average pore size distribution of the membranes. Our experiments revealed that, the addition of different amounts of inorganic material to the polymer solution affects the performance of the resulting membrane. [22] In order to substantiate this, there was a remarkable change in the porosity and morphology of membranes, which was due to different bentonite clay dosage. The porosity of the PEI/ activated bentonite clay nanocomposite membranes has been shown in table 3. It can be observed that with the increase in clay content, the porosity increased from 39.2 % for PBM-0 membrane to 61.4 % for PBM-4 membrane. This change was due to the effect of the addition of a certain amount of clay to the membrane dope. With lower clay content, the surface and macrovoid showed a less dense structure with less number of pores (Fig.4). McKelvey and Koros[23] proposed that the high diffusivity of the polymer poor polymer phase solvent promotes the composition of the solvent just outside the poor phase similar to the interface bath solution. Therefore, the membrane surface and the macrovoid have less porous structure. When the clay dosage was increased, the surface became more dense, and the macrovoid became more porous, which indicated that the coagulation conditions and the interface film are different due to the slow diffusion within the film. Consequently, an instant collapse of the surface occurred upon addition of the non-solvent. On the other hand, as the non-solvent molecule moves to the interior of the film, concentration gradients were observed due to the presence of particles and the diffusion decreased resulting in the formation of pores in the macrovoid walls.

The hydrophilic properties and wetting characteristic of the membrane surface were analyzed by water contact angle measurements. In general, smaller the contact angle, higher is the hydrophilicity of the membrane.[24] The membranes showed little decrease in the contact angle with increase in the activated bentonite clay (Table 3). This may be due to bentonite being negatively charged clay and it has the capacity to hold the water molecule. Since, it enhances the hydrophiicity with the increase in the clay content of the membrane.

**Table-3**

*3.4 Morphology of the membranes*

It is well known that the performance of membranes strongly influenced by surface porosity, compactness, the sub-layer morphology and top layer thickness. [25-26] The effect of concentration of activated clay as the additive on the membrane morphology was investigated by SEM. The presence of activated bentonite clay and uniform distribution across the membrane was confirmed by conducting elemental mapping of silicon and aluminium (Fig.3). Fig.4 represents the cross sectional image of the PEI/ activated bentonite clay composite membranes with different amount of clay dosage. All membrane has shown the typical asymmetric structure comprising of dense top skin layer and porous sublayer. The skin layer functioned as a separation layer and the porous sublayer or support layer provided the mechanical strength. The surface morphology might be due to the instantaneous demixing of membrane casting solution and rapid precipitation of polymer matrix.[27]

**Figure-3**

**Figure-4**

From the literature, it can be noticed that, the presence of activated bentonite clay in the membrane dope might have been responsible for major influence on the morphological features of the membranes. The layered silicate arrangement of the clay and polymer (PEI) are likely to form intercalated and exfoliated structures. This results in reduced interaction among polymer chains and enhances the nano-scale interaction between polymer and activated bentonite clay. Due to this, delayed demixing was taking place in the coagulation bath. On the other hand, due to the hydrophilicity of bentonite clay and possibility of formation of hydrogen bond between N-Methyl-2-pyrrolidone (NMP) and bentonite clay. Since the rate of non-solvent (water) inflow increases and solvent (NMP) outflow decreases.[11] Both phenomena resulted in the delay of the coagulation of polymer in the presence of bentonite clay. Consequently, the growth of the skin layer is diminished and the formation of finger-like pores in the support is improved.

### *3.5 Pure water flux*

Porosity and hydrophilicity are considered to be key factors which decide the flux of the membrane. [28] PWF has a direct relationship with the porosity and the average pore size of the membrane surface. The time dependent pure water flux of the membranes has been measured and Fig.5 represents the time dependent flux behavior of membranes with different amount of clay dosage measured at 0.3 MPa TMP. Initially gradual decrease in PWF was observed for all the membranes during compaction due to mechanical deformation of the polymeric membrane matrix. The clay content has more effect on PWF of the membranes. It can be seen from Table 3, membrane with 1.0 % of clay content showed flux of 177.9 L $m^{-2}h^{-1}$ and it was increased to 210.6 L $m^{-2}h^{-1}$ for 4.0 % of clay dosage. The increase of PWF may be attributed to the increase of membrane porosity and hydrophilicity of the membranes. In addition to this, bentonite clay has the capacity to hold the water and membrane certainly becomes wet. Due to this water molecules easily pass through the membrane.

**Figure-5**

### *3.6 Hydraulic resistance of membranes*

The pure water flux of the membranes was measured at different transmembrane pressures (Fig.6) and the hydraulic resistance of the membranes were calculated as the inverse of the slope of the plots of PWF against the respective transmembrane pressure. The hydraulic resistance offered by the membranes with different amount of activated clay shown in Table 4. The membrane with 1 wt % of activated clay showed hydraulic resistance of 1.1242 kPa/$Lm^{-2}h^{-1}$ and it was observed to decline to 0.9483 kPa/$Lm^{-2}h^{-1}$ when membrane with 4 wt % of clay content. It was observed that, the decline in the hydraulic resistance was observed with increased content of clay. This can be explained by the fact that, bentonite clay being negatively charged imparts hydrophilicity to the membranes. When surface exhibits hydrophilicity, the water molecules form weak interaction with the molecules of the surface. Due to this phenomenon membrane easily became wet and shows less resistance to the water to pass through it.[29] In addition to this, the presence of clay content leads to formation of pores on the membrane surface. Since, increase in flux, thereby decreases in membrane hydraulic resistance.

**Figure-6**

**Table-4**

### *3.7 Heavy metal ion rejection study*

### *3.7.1 Effect of initial metal ion concentration*

The prepared membranes were studied for cadmium, nickel and copper rejection performance and the rejection performance were measured at various initial feed concentrations. Fig.7, Fig.8 and Fig.9 shows the variation of Cd (II), Ni (II) and Cu (II) rejection of all prepared membranes with different initial feed concentrations. From the results, two observations were made, one being that, the rejection of metal ion has decreased as the initial feed concentration increased and other being that the rejection of metal ion has increased with the increase in Bentonite clay content in the membrane. For the Cd (II), Ni (II) and Cu (II) ions, the rejection at feed concentration of 250 ppm was 69.3 %, 76.2 % and 82.5 % and this has dropped down to 56.8 % ,64.8 % and 71.3 % respectively at 1000 ppm feed concentration. Similar results for heavy metals and other salts were reported for NF 270 membranes by Al-Rashdi et.al [30] and Al-Zoubi et al. [31] This trend can be explained as follows, PEI is hydrophobic in nature, having insignificant interaction with metal ions, whereas bentonite is hydrophilic clay which plays a major role in rejection of heavy metal ion. [32] The amount of rejection increases gradually with higher bentonite clay loading. At a low metal ion concentration, the ratio of metal ions to the number of available active adsorption sites is less, but as the metal ion concentration increases, the competition for adsorption sites becomes intense. As a result, the extent of adsorption comes down considerably, however the amount of metal ion adsorbed per unit mass of the adsorbent increases.[33] Further, above results can be substantiated by comparing the element mapping analysis of both virgin and PBM-4 membrane after the rejection experiments (Fig.10). In the virgin membrane, the amount of metal ions present on the membrane surface is very less, however very high concentration of rejected heavy metal ion was present on the surface of PBM-4 membrane. Hence it can be concluded that, the presence of activated bentonite clay in the membrane matrix exhibited very high adsorption capacity of heavy metal ions.

**Figure-7**

**Figure-8**

**Figure-9**

**Figure-10**

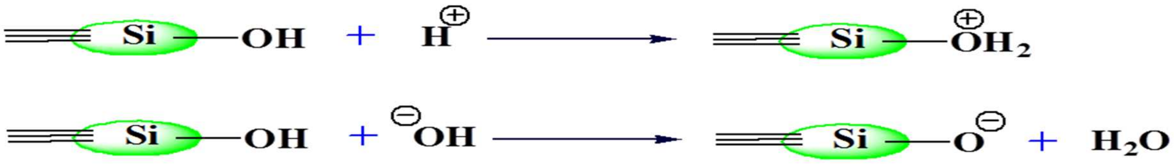
The rejection increases in the order of Cd (II) < Ni (II) < Cu (II). This can be explained in terms of cation hydration capacity.[34] Tansel et al.[35] described that, metal ion with smaller ionic radius tend to hold their hydration sphere (i.e. Are strongly attached to water molecules) thus would be more rejected by the membrane. Since copper is comparatively smallest ion with highest positive charge density, therefore the extent of hydration is maximum in copper as compared to nickel and cadmium. Due to this, diffusion of metal ion occurs slowly and couldn't pass through the smaller diameter pores of the membranes (Fig.11). However, only size exclusion is not the main mechanism to explain heavy metal ion rejection. Metal deposition and charge exclusion play very significant roles which cannot be ignored.

**Figure-11**

### *3.7.2 Effect of pH on rejection of heavy metal ion*

Fig.12 describes the effect of pH on rejection of the heavy metal ion solution showed by the PBM-4 membrane. The rejection of copper, nickel and cadmium was found to increase with increased pH of feed solution. The results indicate that pH exerts great influence on heavy metal ion rejection. At the lower pH there is a competition between the metal ions and $H_3O^+$ ions for active adsorption sites on bentonite clay. Since the number of $H_3O^+$ ions exceeds several times that of the metal ions and the surface is most likely shielded with $H_3O^+$. Hence the deposition of metal ion on the membrane is found to be less. When the pH increases, more and more $H_3O^+$ ions leave the clay surface, making the sites available to the metal ions. As pH changes, there will be change in concentration of $H^+$ and $OH^-$ ions in the solution, [36-37] which triggers the modification of surface functional groups as shown in Scheme.1.

**Figure-12**



**Scheme-1**

According to Scheme.1, as the pH of the feed solution increases, it enhances the negative charge on the membrane surface by reacting with hydroxyl group present on the clay. Therefore, bentonite acquires higher negative charge density resulting from the spread of isomorphous substitution in octahedral and tetrahedral sheets of bentonite. That is, higher negative charged surface allows the metal ions to have more electrostatic interaction with bentonite clay.[38] In addition to this, when the pH of the solution is acidic, the hydration sphere of the heavy metal ions was affected by the proton, which might cause the decrease in the size of the hydration sphere of cation.[34] Since there is a decrease, in the rejection was observed to decrease in pH of the feed solution.

## *Conclusions*

The ability of polyetherimide / activated bentonite clay nanocomposite membrane has been studied from the perspective of separation of Cu(II), Ni(II) and Cd(II) ions from aqueous solution. The uniform distribution of clay in the membrane has been confirmed by elemental mapping studies. The activated bentonite clay immobilized membranes showed enhanced porosity, permeate flux and lower membrane hydraulic resistance. The membrane showed the good rejection towards the heavy metal ions without any external chelating agent. The rejection follows the order, Cu(II) > Ni(II) > Cd (II) attributed to the adsorption capacity and extent of hydration sphere of the corresponding metal ion. The membrane with higher clay dosage showed maximum rejection of 69.3 %, 76.2 % and 82.5 % for 250 ppm of Cd (II), Ni (II) and Cu (II) ion solutions. The removal of heavy metal ion from aqueous solution involves both adsorption and sieving mechanism. Overall, the improved performance of activated bentonite composite membrane attributed to its hydrophilicity, average pore size and ability of activated bentonite clay to adsorb the heavy metal ions.

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List of abbreviations

| | |
|---|---|
| PEG | Polyethylene glycol |
| PEI | polyetherimide |
| PVP | Polyvinylpyrrolidone |
| SEM | Scanning electron microscope |
| EDX | Energy dispersive X-ray microanalysis |
| NMP | N-methyl-2- pyrrolidone |

| | |
|---|---|
| WCA | Water contact angle |
| PWF | Pure water flux |
| TMP | Transmembrane pressure |

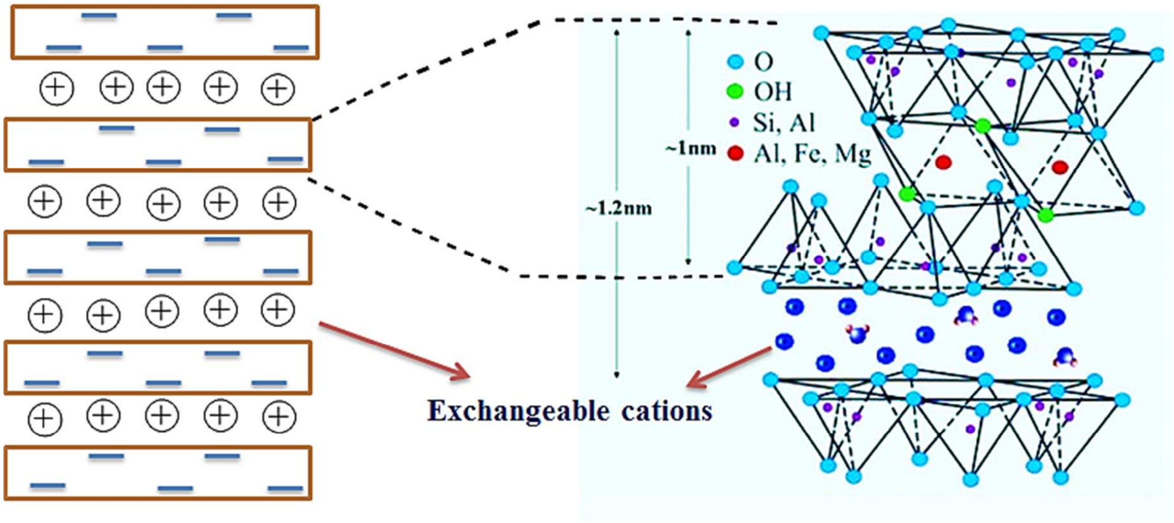


**Fig.1.** A diagrammatic sketch of the structure of bentonite clay [Alexandre et. al]

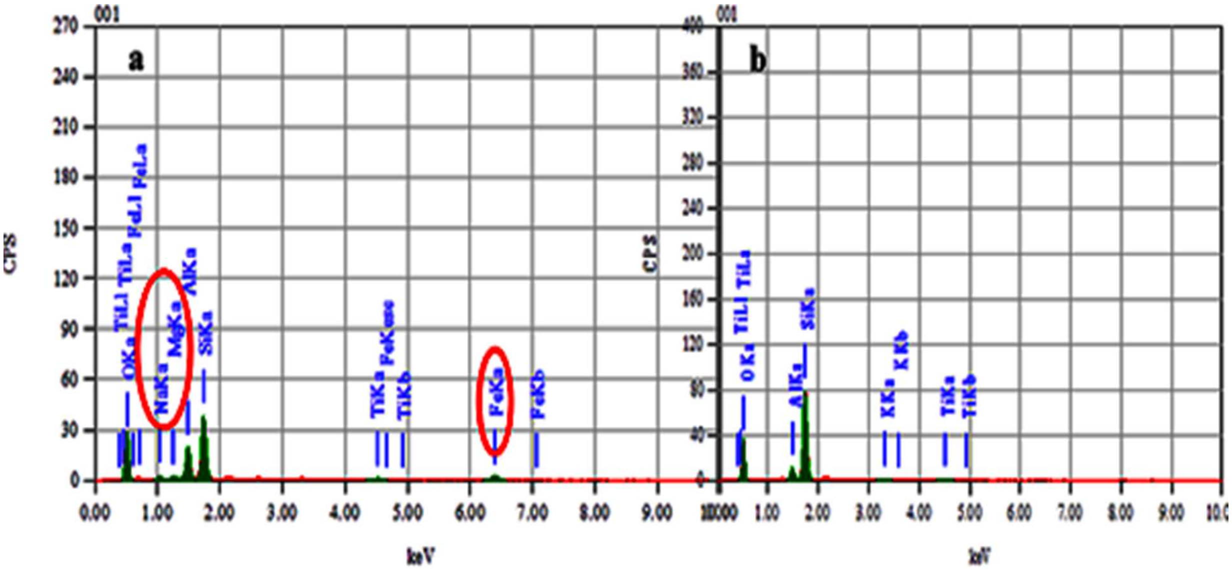


Fig.2 EDX analysis of bentonite clay a) before acid activation b) after acid activation

Fig.3 The aluminium and silicon mapping of PBM-4 membrane

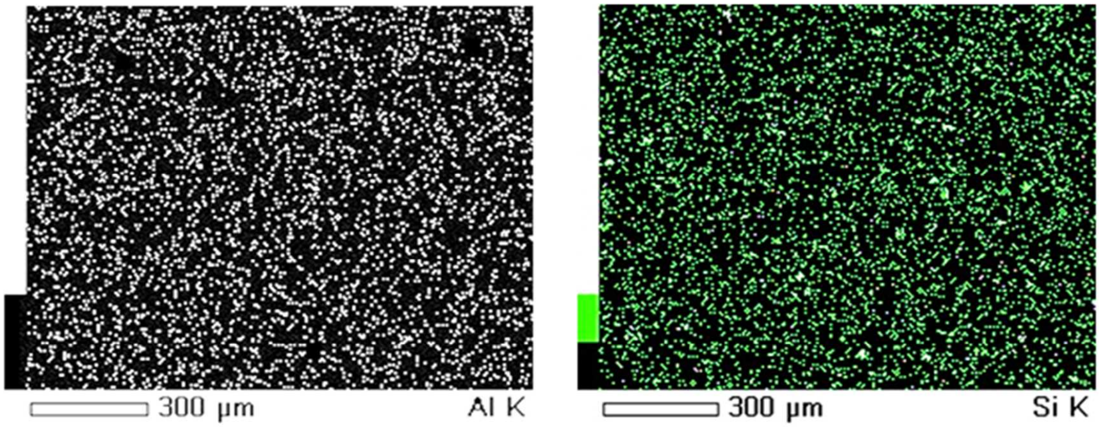
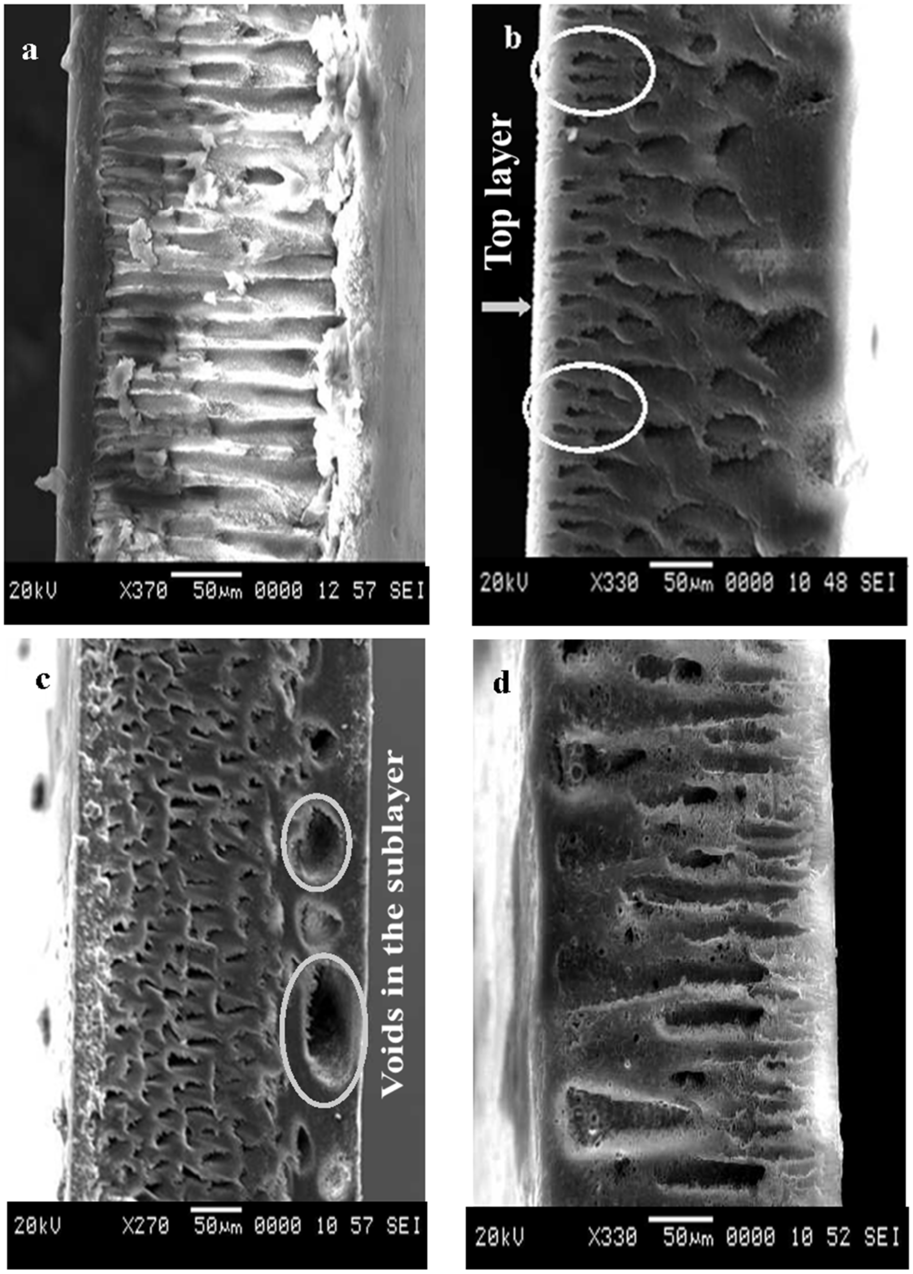


Fig.4 Cross sectional SEM images of a) PBM-0, b) PBM-1, c) PBM-2, d) PBM-3, e) PBM-4, f) Magnified cross sectional image of PBM-4 membrane



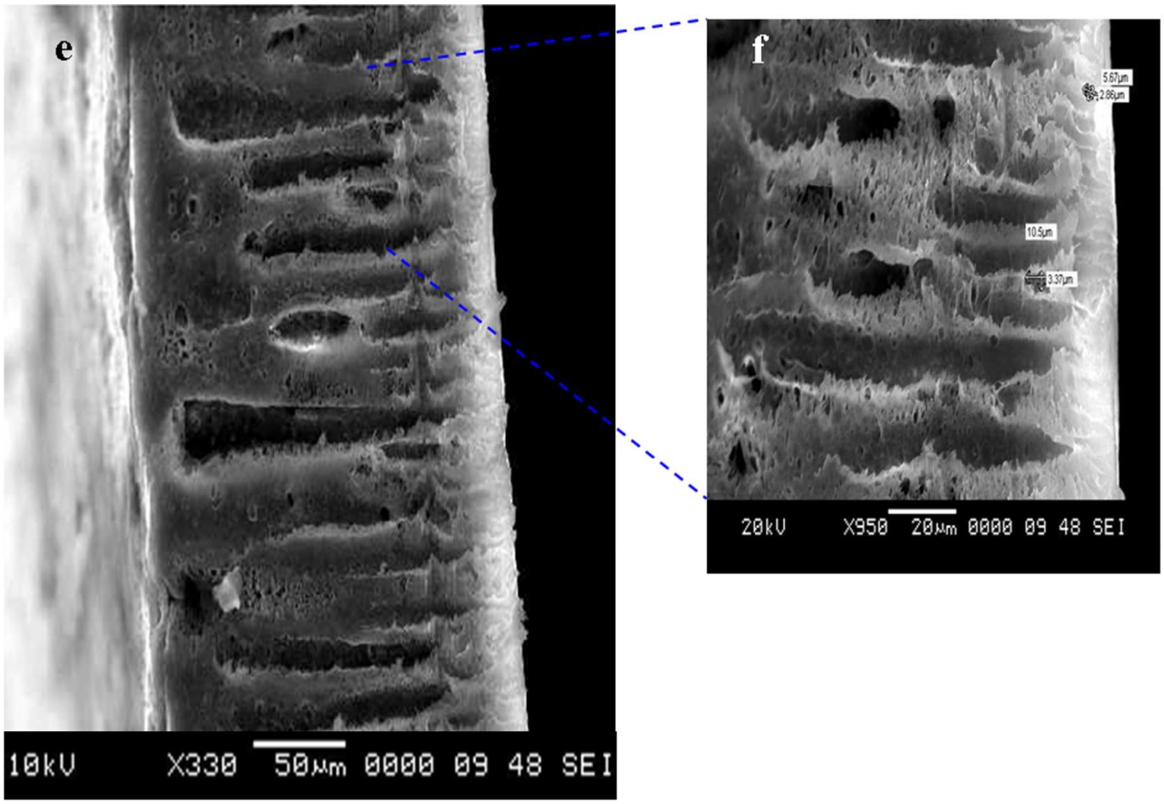

e
10kV X330 50µm 0000 09 48 SEI
f
5.67µm
2.86µm
10.5µm
3.37µm
20kV X950 20µm 0000 09 48 SEI

Fig.5. Time dependent pure water fluxes of membranes at 0.3 MPa TMP

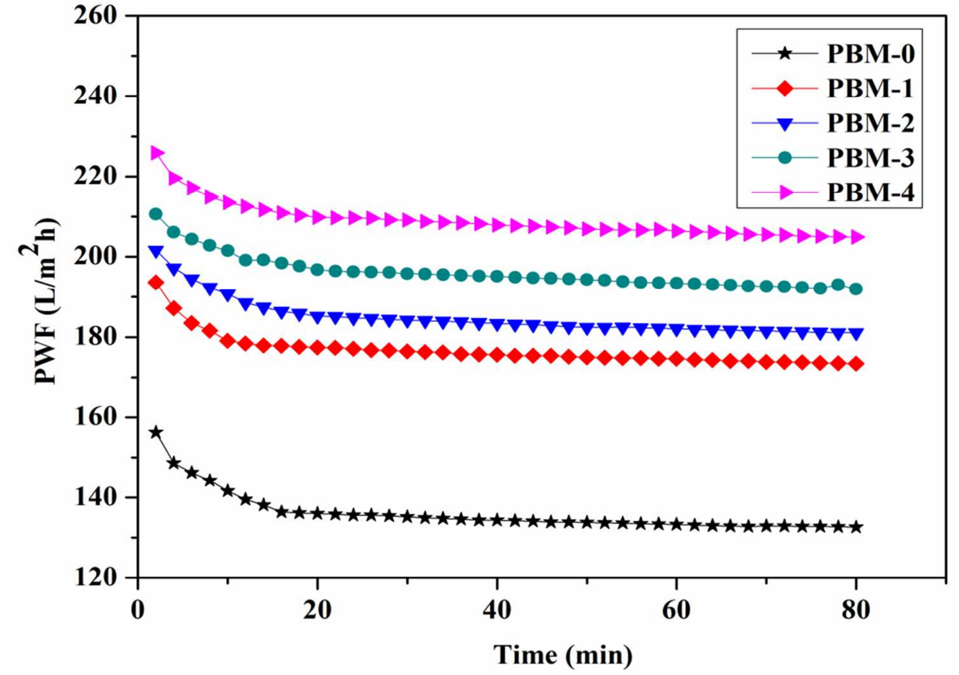


Fig.6 Pressure dependent pure water fluxes of membranes

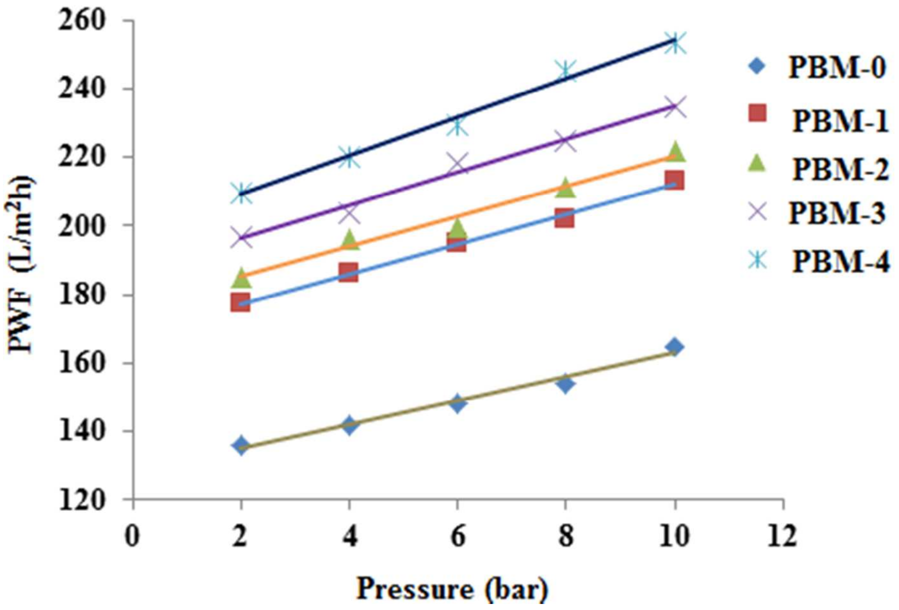


Fig.7 Variation of nickel rejection with different initial feed concentration (pH= 4±0.5)

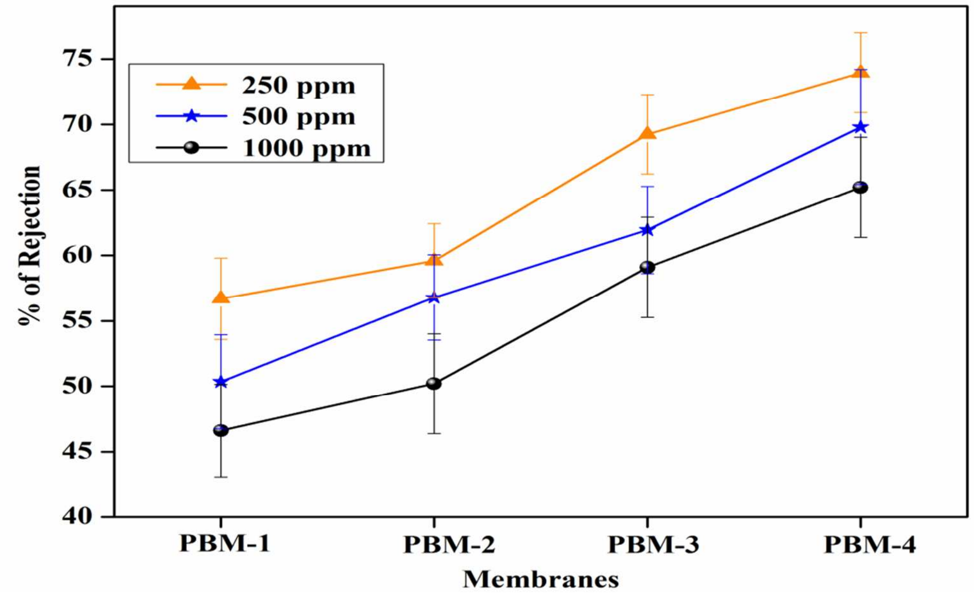


Fig. 8 Variation of cadmium rejection with different initial feed concentration (pH= 4±0.5)

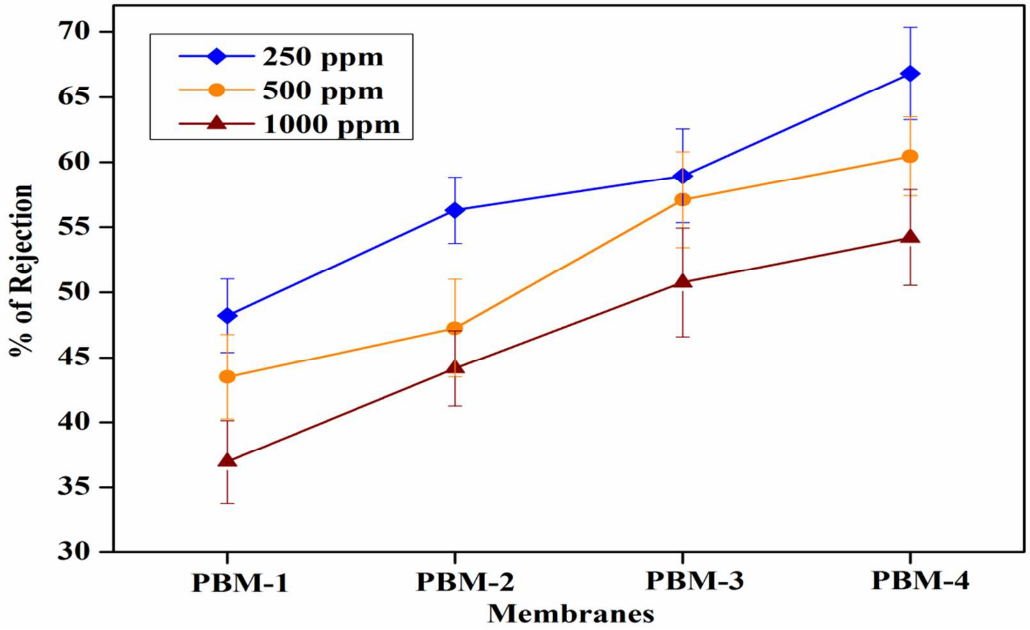


Fig.9 Variation of copper rejection with different initial feed concentration (pH= 4±0.5)

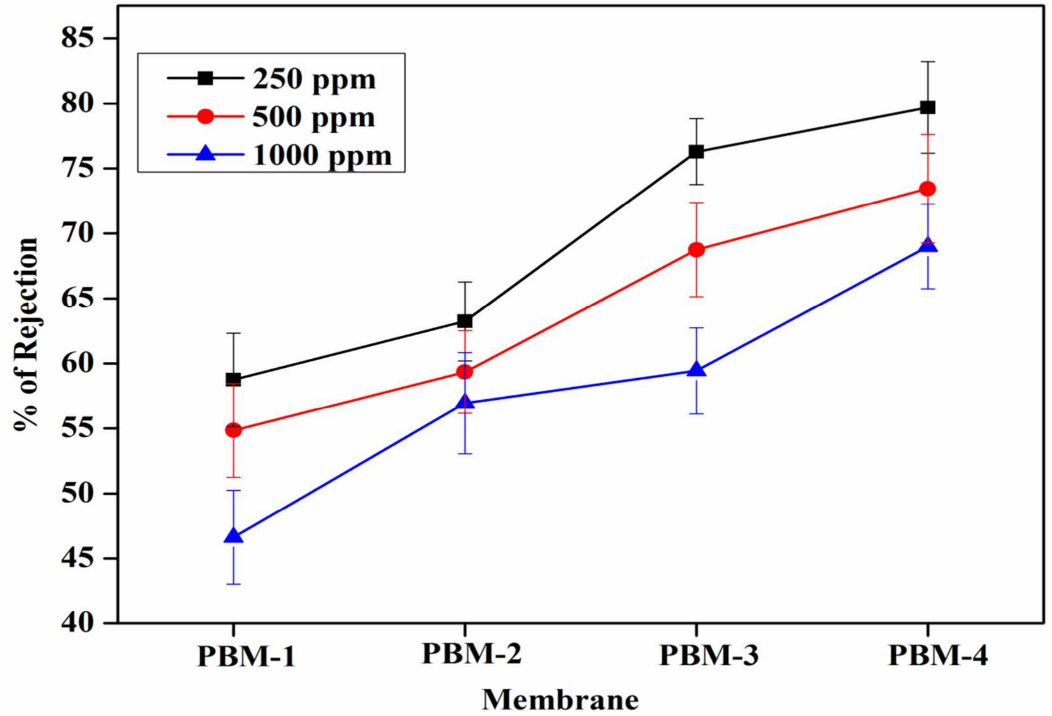


Fig.10 Elemental mapping of a) cadmium b) nickel c) copper after rejection study of PBM-4 and virgin membrane

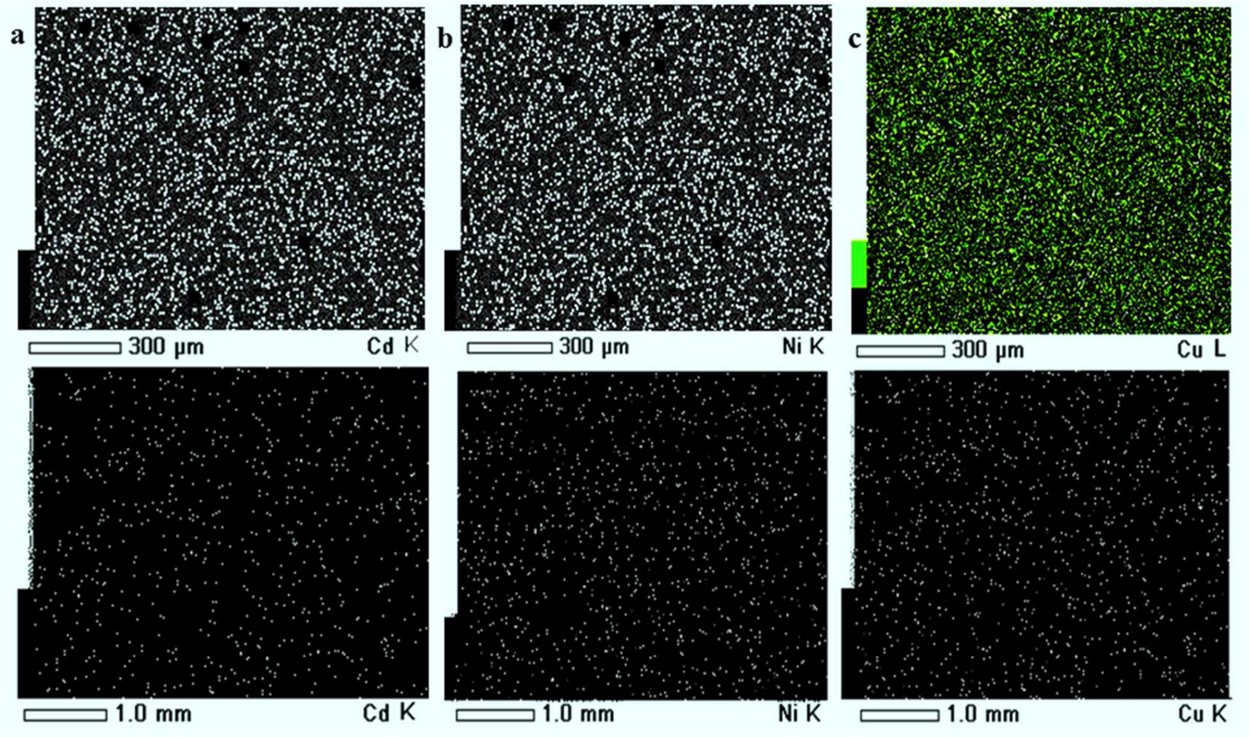


Fig.11 Transport of hydrated metal ion through the porous membrane

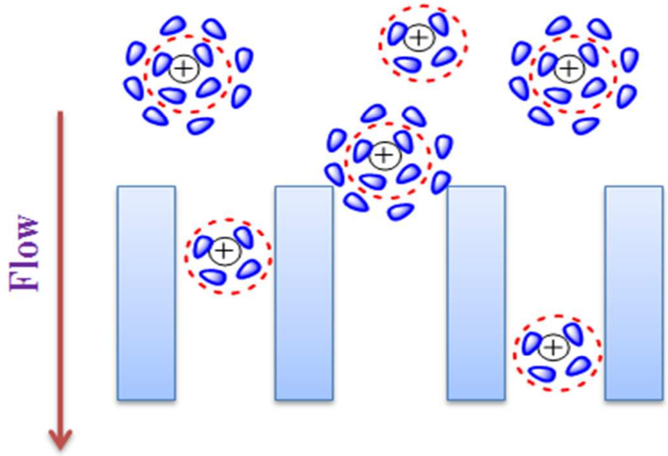


Fig.12 Rejection of heavy metal ions at different pH values for PBM-4 membrane

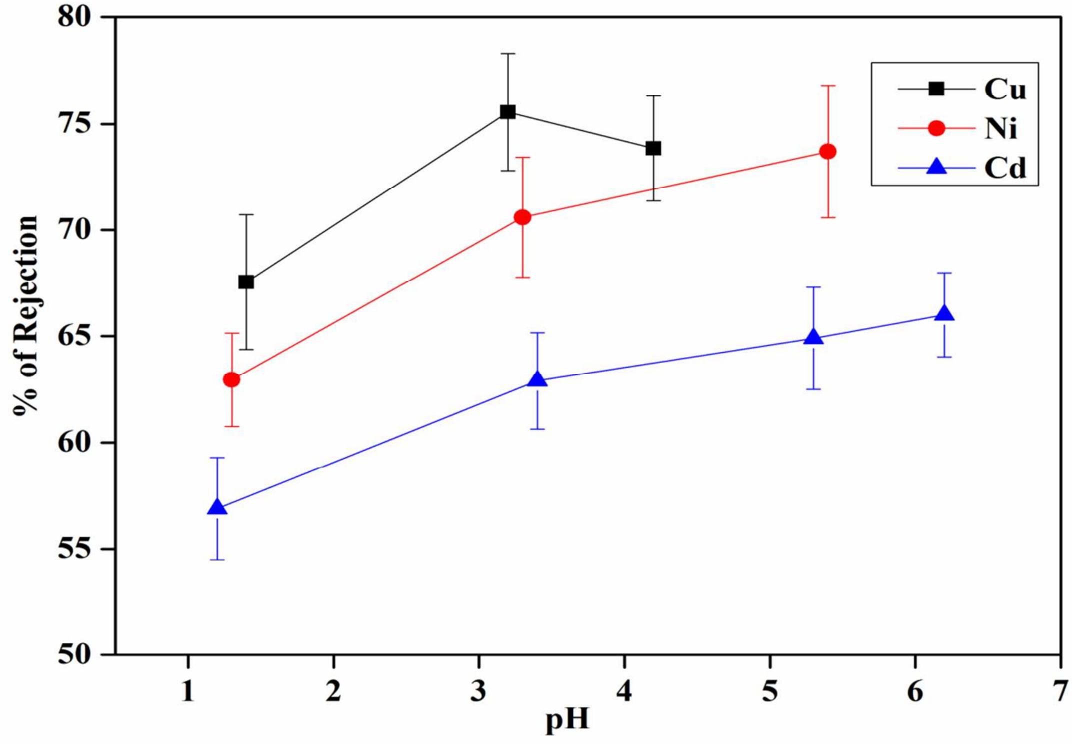


Table 1 : Compositions of casting solutions

| Membrane | PEI(g) | NMP(g) | Clay(g) | PEG 1000(g) | $W_{clay}$*(wt%) |
|---|---|---|---|---|---|
| PBM-0 | 16.5 | 78.5 | 0 | 5 | 0 |
| PBM-1 | 16.5 | 78.3 | 0.16 | 5 | 1 |
| PBM-2 | 16.5 | 78.1 | 0.33 | 5 | 2 |
| PBM-3 | 16.5 | 78.0 | 0.49 | 5 | 3 |
| PBM-4 | 16.5 | 77.8 | 0.66 | 5 | 4 |

* $W_{clay}$ : Mass ratio of clay to PEI

Table 2 : EDX analysis for acid treated and untreated bentonite clay

| Sample | % of elements | | | | | |
|---|---|---|---|---|---|---|
| | O | Si | Al | Mg | Fe | Na |
| Untreated clay | 63.56 | 20.13 | 9.88 | 1.07 | 2.72 | 2.10 |
| Acid treated clay | 68.05 | 27.57 | 3.54 | - | - | - |

Table 3: Physical properties of membranes

| Membrane code | Clay (wt%) | Membrane thickness (µm) | Skin layer thickness (µm) | Porosity (%) | Contact angle (°) | PWF (L/m$^2$h) |
|---|---|---|---|---|---|---|
| PBM-0 | 0 | 156 | 9.6 | 39.2 | 79.4 | 138.1 |
| PBM-1 | 1 | 162 | 7.5 | 45.1 | 76.1 | 177.9 |
| PBM-2 | 2 | 164 | 7.1 | 49.8 | 74.3 | 186.4 |
| PBM-3 | 3 | 158 | 6.2 | 56.5 | 72.6 | 197.7 |
| PBM-4 | 4 | 161 | 5.8 | 61.4 | 69.4 | 210.9 |

**Table.4** : Hydraulic resistance of different membranes

| **Membrane Code** | **Hydraulic membrane resistance (*$R_h$*) (kPa/Lm$^{-2}$h$^{-1}$)** |
|---|---|
| **PBM-0** | 1.4482 |
| **PBM-1** | 1.1242 |
| **PBM-2** | 1.0729 |
| **PBM-3** | 1.0116 |
| **PBM-4** | 0.9483 |

The acid activated bentonite clay ranging from 1.0 to 4.0 wt % were incorporated into the Polyetherimide membranes and extensively studied for its morphology, porosity, membrane hydraulic resistance and hydrophilic properties. The nanocomosite membrane has showed an increment in porosity, hydrophilictiy and reduction in hydraulic resistance. The membranes showed maximum rejection of 69.3%, 76.2% and 82.5% for 250 ppm of Cd (II), Ni (II) and Cu (II) ion solutions.