Abstract

Membrane technology has emerged as an alternative technology for the treatment of acid mine drainage (AMD) over conventional methods because they either produce large volume of toxic sludge and pose a secondary pollution or they achieve partial treatment. Polymeric materials have gained enormous attention for membrane synthesis application due to their non-toxic and biodegradable properties. Polyethersulphone (PES) and polysulphone (PSf) based membranes have gained significant progress in AMD treatment because of their high chemical and thermal resistance, mechanical stability in hot and wet conditions and high permeability. Although PES exhibits higher degree of hydrophilicity compared to PSf, its inherent hydrophobic character generated by the sulfonyl group linking the two phenyl rings results in serious membrane fouling which leads to deterioration in permeation flux, shortening of the membrane lifespan and producing unpredictable separation efficiencies. To this effect, several interventions have been made to increase PES membrane's hydrophilicity to avoid quick membrane deterioration, enhance low fouling character and the ability to restore water flux after cleaning during wastewater treatment.

This study proposed infusing chitosan within PES membrane by blending chitosan with PES suspension and coating the surface with polyamide layer via the co-solvent assisted interfacial polymerization technique to enhance its antifouling character and permselectivity. This modification aims to localize the hydrophilic materials on the membrane surface and within the pores to positively influence membrane flux and selectivity. The study investigated the effect of chitosan content inside the PES membrane matrix on its performance during synthetic AMD treatment. It further explored the effect of coating polyamide layer on the PES membranes infused with chitosan. The fouling and operational stability of the optimized PES/chitosan and PES/chitosan/PA membranes were evaluated.

Chitosan used in the study was derived from chitin through deacetylation process, which is treating chitin with a strong alkaline solution. Chitin is the second most abundant polymer after cellulose and is naturally occurring in the exoskeletons of arthropods. Chitosan contains one primary amino and two free hydroxyl functional groups which can act as contaminate binding sites. Effect of temperature and strength sodium hydroxide solution on chitosan's degree of deacetylation was investigated. The experimental results showed that higher NaOH concentration (40% NaOH) promotes degradation of acetyl group and exposure of amine groups, thus increasing chitosan's degree of deacetylation. They further showed that temperature of 100 ^oC was enough to induce enough energy to cause degradation of acetyl groups. As such, higher degree of deacetylation of 96% was achieved with NaOH concentration of 40% and temperature of 100 ^oC.

The research also investigated the influence of chitosan content on the performance of the synthesised membranes during synthetic AMD treatment. Permeate flux of pristine PES membrane was increased from 97 to 102 and 133L/m^2.hr when chitosan content was 0.5 and 0.75 wt%, respectively. This was attributed to the increased hydrophilic character of chitosan used to modify the membrane. When chitosan was increased further to 1wt%, it induced a flux decline to 116 L/m^2.hr. Chitosan loading of 0.75 wt% was selected for further investigations. Coating polyamide layer on the PES/chitosan membrane revealed that permeability increased with increasing chitosan content. This behaviour was attributed to the fact that, the interaction of chitosan's amine group and PA active layer's unreacted acylchloride group created a thin layer on the membrane surface. Moreover, amine groups which could not interact with unreacted acylchloride groups favoured sorption of water molecules by the membrane. This behaviour showed that higher chitosan's degree of deacetylation enhanced membrane permeability and selectivity.

Influence of operational parameters was also investigated. Literature has shown that pH values corresponding to a peak in flux reporting the lowest rejection of ions by a membrane indicates the isoelectric point (IEP) or zero potential charge of the membrane. Similar behaviour for both PES/chitosan and PES/chitosan/PA membranes was observed at a pH of around 5.5. Therefore, it was concluded that the IEP of the membranes was at a pH of 5.5. Moreover, it was concluded that the surface charge of both PES/chitosan and PES/chitosan/PA membranes becomes positive at pH lower than 5.5 and at pH above 5.5 have negative charges. It was observed that cation rejection was high when pH was lower than IEP and anion removal was high at pH values higher than IEP. Coating polyamide layer onto the PES/chitosan membrane to produce PES/chitosan/PA membrane introduced amide, amines, carboxylic and alcoholic functional groups. It was observed that, rejection of ions by PES/chitosan/PA membranes was slightly higher than that of PES/chitosan membranes and this was due to increased number of available functional groups provided by polyamide. Investigation of initial feed concentration and pressure is very essential to assess the applicability range and determine optimum conditions for an efficient membrane separation operation. The experimental results showed that membrane flux was increasing with increasing pressure and this was due to increased forces which forces water molecules through the membrane. Moreover, solutions with low concentration reported high permeated flux due to low number of ions being trapped on the membrane surface and subsequently blocking the pores and forming a layer obstructing flow. Rejection experimental tests showed that rejection increased with increasing pressure and significantly reduced with increasing initial ions concentrations.

Lastly, after optimizing chitosan loading and its degree of deacetylation to synthesise PES/chitosan and PES/chitosan/PA membranes, operational stability and fouling potential of the membranes were investigated using real industrial AMD. When pure water was filtered through the membranes after AMD permeation, the new pure water flux reported 14 and 27%

loss of the initial flux for PES/chitosan and PES/chitosan/PA membrane, respectively. After backwashing, it was evidently clear that the initial flux of the membranes was almost restored with only 1.7 and 2% loss of flux compared to the original fluxes of PES/chitosan and PES/chitosan/PA membranes, respectively. The fouling experimental data confirmed superior characteristics of PES/chitosan and PES/chitosan/PA membranes against fouling. Hermia's filtration models fitted with the experimental deduced that the dominating fouling mechanisms taking place during filtration of AMD through PES/chitosan and PES/chitosan/PA membranes are complete and cake or gel layer formation blocking models.

The results obtained from this research demonstrated outstanding antifouling and permselectivity properties of PES membranes infused with chitosan and coated with polyamide layer. These findings further provide a basis for scale-up operation to test the membranes against the traditional technologies for AMD treatment.