

THE USE OF ULTRAFILTRATION MEMBRANE SYSTEMS TO TREAT WASTE WATERS GENERATED FROM HARD COAL MINING

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Abstract

The recent studies regarding the membrane technologies indicate that the membrane process applications involve for providing the high quality drinking water and increasing the use of industrial water consumption. Within this scope, it has been considered that membrane treatment systems are necessary for removing the bacteria, viruses, suspended solids causing the high turbidity in water resources and heavy metals such as arsenic and cadmium. In this study, the possibility of using AgNP-PS composite membrane system producing for treatment of waste waters generated from underground coal mining works in Kozlu Hard Coal Basin, Turkey will be investigated. The average 11000 m³ of the waste waters are pumped from 500 meters of underground to surface, daily. The UF membrane filtration system used in the experimental studies was composed of the capillary hollow fiber UF membrane module equipped with Polyethersulphone (PES) membranes purchased from IMT membranes, Holland. In the first stage of the study, commercial membrane was employed and various water quality parameters such as turbidity, conductivity, TSS, Total coliforms, pH, temperature, Total Dissolved Matters, COD and Cadmium concentrations were detected before and after the waste water treated, and each of the membrane performance were calculated. In the second stage of the study, the polysulfone (PS) composite UF membrane will be prepared by phase inversion technique to treat the waste waters and to compare the water quality results obtained from the commercially available UF membrane.

Key words: Polysulfone (PS), silver nanoparticle (AgNP), composite membrane

INTRODUCTION

Membrane filtration is basically based on placing a selective barrier between two phases. As a result of exerting a driving force to one side of the membrane, components are transported towards the membrane surface. Therefore, some components pass through the membrane (permeate) and others are retained according to their size (retentate). In the particular industrial application, different membrane systems and configurations might be arranged, including pretreatments and other treatment stages based upon different technologies, in order to meet those target water quality standards that this industrial application may specifically demand from reclaimed municipal wastewater (Ordóñez et al., 2014).

Membrane filtration has developed since 1950s and primarily used in large scale industrial plants for clarifying, concentrating and

sterilizing dairy products, oily wastes, alcoholic beverage and brine recovery (Vigneswaran et al., 2012)

Interfacial polymerization and multilayer composite casting and coating were developed for applying high performance membranes. By means of these processes, membranes with selective layers as thin as 0.1 µm or less are now being produced by a number of companies. Methods of packaging membranes into large-membrane-area spiral-wound, hollow-fine-fiber, capillary, and flat sheet modules were developed. Microfiltration, ultrafiltration, reverse osmosis and electro dialysis were established processes with plants (Baker, 2004).

Ultrafiltration (UF) membranes involve with pore sizes in the range of 0.1 to 0.001 µm and are applied for the removal high of molecular-weight substances, and organic polymeric molecules.

Manufacturers produce membrane modules using such as a materials (e.g., polypropylene, polysulfone, polyvinylidenedifluoride, polyether-sulfone, cellulose acetate, aromatic polyamide, regenerated cellulose, titanium oxide, etc.) showing different physicochemical behaviors (e.g., mechanical strength, oxidant tolerance, pH operating range, etc.) (Ordonez et al., 2014).

Polysulfone is greatly used polymers in the production of ultrafiltration and microfiltration membranes owing to its properties. Polysulfone have high thermal resistance, good mechanical and chemical stabilities and its superior film-forming properties (Vidaurre et al., 2002; Phelane et al., 2014; Phelane et al., 2014; Goosen et al., 2004).

Polysulfone membranes are usually used as sublayers in composite membrane for reverse osmosis, gas separation and pervaporation. However, polysulfone has hydrophobic characteristic caused membrane fouling which shortens membrane life. Modification of the membrane can be done to develop its hydrophilicity. Technique of modification which can be used to improve hydrophilicity involves modifying the polymer with metal oxides (Phelane et al., 2014; Summers et al., 2001).

Recently, inorganic nanocomposite membranes formed by inorganic particles, including the size of 1–100 nm, uniformly embedded in a polymer matrix and the membranes use gas separation, pervaporation, and ultrafiltration. They show an interesting approach to develop the separation properties of polymer membranes because of possessing properties of organic and inorganic membranes such as good permeability, selectivity, mechanical strength, thermal and chemical stability (Cong et al., 2007).

The structure and performance of nanocomposite membranes are generally a function of the physical and chemical properties of the polymer matrix and nanoparticles due to the method of nanoparticle incorporation (Shi et al., 2012)

The nanoparticles have been typically produced in aqueous solutions in the by means of water-soluble polymers, where metal ions are reduced either by an added reductant or by the water-

soluble polymers themselves (Hazer et al., 2010).

AgNP can be applied by directly coating to the membrane surface or by mixing the polymer matrix of the membrane during phase inversion technique (Koseoglu-Imer et al., 2013; Gussemeet al., 2011).

Studies made AgNP-polymeric membrane preparation can be said that AgNPs produced the more hydrophilic membrane and improved the selectivity of membrane (Koseoglu-Imer et al., 2013; Yong et al., 2010; Zodrow et al., 2009).

Some nanoparticles such as silver (Ag), copper (Cu), zinc oxide (ZnO), and titanium oxide (TiO₂) show high toxicity to against microorganisms including bacteria, fungi, viruses, So they have been studied as antibacterial agents in different areas (Bao et al., 2011).

According to other nanoparticles, AgNP is widely used in different fields because AgNP has excellent antibacterial performance and low cytotoxicity to human cells (Beer et al., 2012).

The recent studies regarding the membrane technologies indicate that the membrane process applications involve for providing the high quality drinking water and increasing the use of industrial water consumption. Within this scope, it has been considered that membrane treatment systems are necessary for removing the bacteria, viruses, suspended solids causing the high turbidity in water resources and heavy metals such as arsenic and cadmium.

In the first stage of this study, commercially available Polyethersulphone (PES) UF membrane was employed and various water quality parameters were detected before and after the waste water treated, and each of the membrane performance were calculated. Turbidity, conductivity, TSS, Total coliforms, pH, temperature, Total Dissolved Matters, COD and Cadmium concentrations were examined in the raw and treated waste water. In the second stage of the study, the polysulfone (PS) composite UF membrane will be prepared by phase inversion technique to treat the waste waters and to compare the water quality results obtained from the commercially available UF membrane.

MATERIALS AND METHODS

Experimental Studies

In first stage of this study, the possibility of using ultra filtration (UF) membrane systems for treatment of waste waters generated from underground coal mining works in Kozlu Hard Coal Basin, Turkey was investigated. The average 11000 m³ of the waste waters are pumped from 500 meters of underground to surface, daily. After the waste waters of 35 m³/hare treated using the UF membrane filtration system, they are used by the mining workers for the bathing. The UF membrane filtration system was composed of the capillary hollow fiber UF membrane module equipped with Polyethersulphone (PES) membranes purchased from IMT membranes, Holland. The membrane has a filter area of 50 m², average pore diameter of 0.02 μm, inner and outer diameters of 0.9 and 4.3 mm, respectively. During the membrane filtration process, UF membrane system was run at maximum operation pressure of 7.5 bar and trans-membrane pressure (TMP) of 4.5 bar. Chemical cleaning of membrane was automatically carried out using 200 ppm NaOCl and 500 ppm H₂O₂ using chemical dosage pumps in order to avoid the membrane fouling from the microbial contamination.

In the second stage of this study, composite membranes will be prepared by adding AgNP to the Polysulfone (PS) dope solution. Scanning electron microscopy (SEM), contact angle, and atomic force microscopy (AFM) techniques will have used to characterize the membranes. And then various water quality parameters, which are conductivity, TSS, Total coliforms, pH, temperature, Total Dissolved Matters, COD and Cadmium concentrations, will be detected before and after the waste water treated, and each of the membrane performance will be calculated. Laboratory scale membrane flow diagram was given in Figure 1.

Polysulfone UF Membrane Preparation

Polysulfone (PS, Mw_22,000Da), N-methyl-2-pyrrolidinone(NMP) and AgNP were purchased from Sigma-Aldrich. Polyethylene glycol (PEG) having different molecular weight

of 4000, 10, 000, 20, 000, 35,000Da were purchased from Aldrich.

PS based UF membrane preparation are added slowly to NMP solvent and is stirred at room temperature for 24 h in order to form a homogeneous solution. PS beads are added into this solution and stirred. For PS membrane with AgNP (AgNP-PS composite membrane) is dispersed in NMP using an ultrasonication probe (ultrasonic bath) at 20 min until completely dissolved. Then PS beads are added to this solution as previously described (Koseoglu-Imer, 2013). Then the casting solutions of bare PS and AgNP-PS composite are spread casted on a glass plate. The casting films are left for evaporation and then the glass plates are immediately immersed in a deionized water bath to obtain polymer precipitation. After then, the membranes are removed from the water bath and washed thoroughly with deionized.

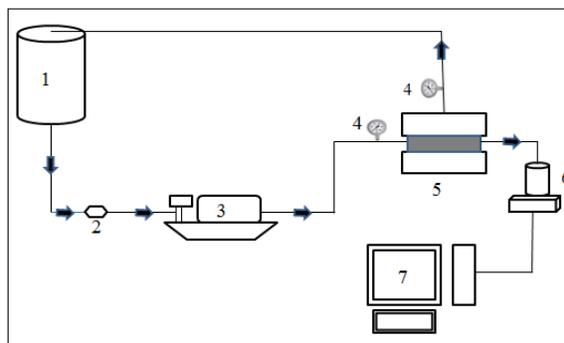


Figure 1. Laboratory scale membrane flow diagram (1. Waste water tank 2. Flow meter 3. High pressure booster pump 4. Manometer 6. Precision scales 7. Computer)

Feeding raw water to the system from a tank having a volume of 15 L are provided. High pressure pump speed can be adjusted by frequency converter. The desired water pressure in the membrane cell by means of high-pressure pump may be transmitted. Membrane input and membrane output and concentrated on the line pressures to be measured manually manometer and transmembrane pressure (TMP) is calculated. Clean water permeating the membrane is stored in the tank on precision scales and measuring dates are transferred to computer. Also membrane concentrate by means of recycle line is sent to the feed tank.

RESULTS AND DISCUSSIONS

As shown Table I, the removal efficiency of total suspended solids (TSS) and turbidity is 99% and 90%, respectively. In other words, the removal performances of TSS and turbidity for UF system were relatively high. In the meantime, total coliform as a bacteriological parameter has been found at the permeate water in the commercially available UF membrane system. Therefore, we will try to completely remove total coliform bacteria using AgNP-UF composite membrane having antibacterial properties. As a result, if we remove completely total coliform bacteria and provide drinking water standards, waste waters generated from hard coal mining will be used not only bath water but drinking water as well.

Table I. Treatment performance of the commercially available UF membrane system

Water quality parameters	Waste water from underground mining	Permeate of UF membrane system	Removal efficiency (%)
pH	7.2	7.4	
Temperature	21	21	
Turbidity	25	1	99
TSS	48	5	90
COD	48	19	60
Sulphate	202	36	82
Cd	0.044	0.008	82
T.coliform (#/100 ml)	48400	3100	94

CONCLUSIONS

In first stage of this study, the possibility of using ultra filtration (UF) membrane systems were employed to treat waste waters generated from underground coal mining works. It was found that the water quality was good except some bacteriological agents. In the second stage of this study antibacterial composite membrane will be prepared to apply the waste water for comparison of the water quality of both the UF membrane systems.

In addition, it may be need to remove bacteria without disinfectant chemicals via the UF composite membrane prepared with AgNP having antibacterial ability.

REFERENCES

- Ordóñez R., Hermosilla D., Merayo N., Gascó N., Blanco C. & A., 2014. Application of Multi-Barrier Membrane Filtration Technologies to Reclaim Municipal Wastewater for Industrial Use. *Separation & Purification Reviews*, 43:263–310,
- Koseoglu-Imer D. Y., Kose B., Altinbas M., Koyuncu I., 2013. The production of polysulfone (PS) membrane with silver nanoparticles (AgNP): Physical properties, filtration performances, and biofouling resistances of membranes, *Journal of Membrane Science* 428 620–628
- Vigneswaran S., Sathanathan S., Shon H.K., Kandasamy J., and Visvanathan C., 2012. Delineation of membrane processes, copyright 2012 american society of civil engineers (ASCE) retrived from www.knovel.com
- Beer C., Foldbjerg R., Hayashi Y., Sutherland D.S., Autrup H., 2012. Toxicity of silver nanoparticles—nanoparticle or silver ion? *Toxicol.Lett.* 208 286–292.
- Bao Q., Zhang D., Qi P., 2011. Synthesis and characterization of silver nanoparticle and graphene oxide nanosheet composites as a bactericidal agent for water disinfection, *J. Colloid Interface Sci.* 360 463–470.
- Kalaycı O., Comert F., Hazer B., Atalay T., Cavicchi K.A., Cakmak M., 2010. Synthesis, characterization, and antibacterial activity of metal nanoparticles embedded into amphiphilic comb-type graft copolymers, *Polym. Bull.* 65:215–226
- Yong L., Mohammad A. W., Leo C. P., Hilal N., 2010. Polymeric Membranes Incorporated with Metal/Metal Oxide Nanoparticles: A Comprehensive Review, *Desalination*.
- Zodrow K., Brunet L., Mahendra S., Li D., Zhang A., Li Q., Alvarez P.J.J., 2009. Polysulfone ultrafiltration membranes impregnated with silver nanoparticles show improved biofouling resistance and virus removal, *Water Res.* 43 715–723.
- Cong H., Radosz M., Towler B.F., Shen Y., 2007. Polymer–inorganic nanocomposite membranes for gas separation, *Sep. Purif. Technol.* 55 281–291.
- Baker R.W., 2004. Membrane technology and applications, Copyright 2004 John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester, West Sussex PO19 8SQ, England
- Goosen M.F.A, Sablani S.S., Ai-Hinai H., Ai-Obeidani S., Al-Belushi R., Jackson D., 2004. Fouling of reverse osmosis and ultrafiltration membranes: a critical review *Sep. Sci. Technol.* 39 2261–2297.
- Castro Vidaurre E.F., Achete C.A., Gallo F., Garcia D., Simao R., Habert A.C., 2002. Surface Modification of Polymeric Materials by Plasma Treatment, *Materials Research, Materials Research* 5 37–41.