Removal of Humic Substances from Drinking Water by Microfiltration, Ultrafiltration, and Nanofiltration membranes

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ABSTRACT

In this research, three types of flat sheet membranes were fabricated from polysulfone and N, N diamthelyformamide (DMF) by using wet phase inversion method. Microfiltration (MF), ultrafiltration (UF), and nanofiltration (NF) membranes. The mean pore size diameter of these membranes were calculated which are (0.2 µm, 10 nm and 0.1nm) respectively. The efficiency of membranes was examined to remove humic acid (HA) from synthetic water containing different concentration (3,6,8, and 10 mg/L), and their performances were compared. UV254nm absorbance was used to determine the % of HA compounds eliminated from permeates and retentate samples. To analyze the flux decay and biofouling induced by organic matter, three samples of each membrane were tested using a cross flow filtering system with a single flat sheet membrane. Filtration test of synthetic water containing 8mg/L HA shows removal efficiency 100% for nanofiltration membrane, while ultrafiltration and microfiltration membranes shows removal efficiency 88% and 15% respectively. However, the NF membrane removed 100% of HA and their good efficiency for removing conductivity and turbidity (90, 75%) respectively, but UF membrane is seem to be more convenient from practical point of view, due to their good rejection of HA and turbidity (88% and 70%)) respectively in addition, their good recovery of flux after back washing (88%). The most draw back against NF membrane are their high cost, and high pressure required for operation. Also NF removed the hardness from the water, which are important in proper drinking water quality.

Keywords: Humic acid, drinking water, micro, ultra, Nano filtration

Introduction: -

Humic substances are resulted from the microbiological degradation of vegetation and animal decay and enter surface waters through rainwater run-off from the adjacent land. The concentration of these substances varied from seasons depending on the wet seasons and rain density. High concentration in wet seasons and lower concentration in dry seasons. Humic substances are complex, acidic organic molecules, despite their beneficial effects on soil structure, water retention projects, and nutrient status; they offer a concern for the water supply business. Natural organic matter (NOM) removal is critical in water purification, and it has become a difficult research topic in recent water treatment developments due to its impact on water odor, color, and taste, as well as its role as a precursor to disinfection by-products (DBP), which are derived from the reaction of organic material with free chlorine, which is used as a disinfectant in traditional water treatment plants. Halogenated organic compounds such as trihalomethanes (THM) and halo acetic acids are among the most toxic DBPs that have recently been identified as human carcinogens (HAAs). DBPs can be regulated by reducing organic matter in raw water, lowering disinfection doses in treatment plants, or eliminating DBPs using membrane technology.

Coagulation and flocculation (Wang W. et al. 2014; Zulfikar M. et al. 2014), photocatalytic degradation (Aziz H. et al. 2015; Singh P. et al. 2016). In addition, oxidation and ozonation (Hutagalung S. et al. 2014; Yan W. et al. 2005), adsorption (Mozia S. et al. 2005), and membrane filtering (Ariono D. et al. 2017) have all been employed to remove NOM from water. Among these approaches, the membrane process has grown in popularity in recent years in the manufacture of drinking water, as it offers various advantages over traditional treatment, including a compact module, lower energy usage, and a high-quality result.

The majority of commercial membranes are made using the immersion precipitation method, which includes converting a liquid membrane phase into a solid membrane matrix in an immersion bath with a non-solvent. The content of the membrane solution, non-solvent type, and operation conditions in the immersion bath all influence the final membrane structure in the immersion precipitation process (Rohani R. et al. 2016). The majority of UF membrane manufacturing research focuses on changing the composition of the membrane solution to achieve the desired membrane shape (Nevstrueva D. et al. 2015). It has been found that enhancing the membrane hydrophilicity can reduce humic acid fouling on the membrane structure (Chen X. et al. 2015; Jones K. L. et al. 2000).

(Katsoufidou K. et al. 2005) investigated humic acid rejection on a polyether sulfone hollow fiber membrane with a molecular weight cutoff of 150 kDa, obtaining rejection of up to 75% in the absence of calcium and up to 20% in the presence of 2 Mm Ca+2.

The authors investigated the effect of a PEG addition on the shape and performance of polysulfone ultrafiltration membranes. They discovered that the inclusion of PEG significantly increased the hydrophilicity and porosity of the membrane. PEG decreases the thermodynamic stability of the membrane solution, resulting in the creation of finger-like pores in the membrane structure (Ma Y. et al. 2011). The removal of heavy metals such as cadmium and copper was explored using humic substances assisted ultrafiltration. The elimination of cadmium and copper increased as the mumic concentration increased (Kitae Back et al. 2005). The efficiency of ultrafiltration membranes with molecular weights of 3kDa, 5kDa, and 10kDa is investigated in this work. All three membranes were shown to extract humic acid with an efficacy close to 90% (J. LOWE et al. 2008).

The purpose of this study is to determine the efficiency, flux decay, and biofouling induced by organic matter of three different types of polymeric membranes: MF, UF, and NF with average mean pore diameters of (0.2 m, 10 nm, and 0.1 nm, respectively. The phase inversion approach was used to produce these membranes, which used polysulfone and N, N Dimethyl form amide as solvents.

2. Materials and methods

2.1 membrane fabrications

Membranes were manufactured in the Chemical Engineering laboratory at Baghdad University of Technology. Sigma-Aldrich, polysulfon ((C27H22O4S)n Appearance Pellets with a density of 1.24 g/mL at 25 degrees Celsius, an average Mw of 35,000, and N, N Dimethyl formemide ((C3H7NO) appeared as a whitish liquid with a fishy, ammoniac odor and a molar mass of 73.09 g mol 1. were employed to produce the membranes by the wet phase inversion procedure. Polyvinylpyrrolidone ((C6 H9 NO)n Sigma-Aldrich, molecular weight: 25000g mol-1, crystalline form, White is utilized as an additive in the casting of the polysulfone support layer. The phase inversion casting process was used to generate polysulfone support layers with and without MWCNTs (Abdulkhaleq K. Mahmood. 2015). (15 gm, 18 gm and 22 gm) Polysulfone pellets (Sigma–Aldrich, St. Louis, MO, USA) were degassed in an oven at 150 0C for 5 hours and then dissolved in

(84 gm, 81 gm, and 77 gm) N, N-dimethylformamide (DMF) (Sigma–Aldrich, St. Louis, MO, USA). To the polysulfone solution, 1.0 weight percent polyvinyl pyrrolidone (PVP) (Sigma–Aldrich, St. Louis, MO, USA) was added as an addition. The solution mixing glass flask and all the laboratory tools required to make a polymer solution are shown in Figure (1.2).

For 24 hours, the mixture was continuously swirled at (500r/min.) at 50 C0. The stirrer's purpose is to ensure that the polymer (polysulfone) and solvent (N-N DMF) are thoroughly combined to produce a homogenous solution. Throughout the mixing procedure, the thermometer recorded the temperature. The heater should maintain a temperature range that is adequate and optimal for processing. To minimize the amount of bubbles in the casting solution, it was maintained in the dark. To reinforce the membrane, nonwoven polyester fabric was used. The casting solution was applied to the nonwoven fabric; the coated fabric was then secured to a glass plate and the solvent was evaporated for 1 minute to obtain a consistent support layer surface. Membrane casting was performed with a stainless steel knife. The thickness was estimated to be around 200 m. To eliminate residual solvents, the glass plate was placed in a water bath at room temperature (23 C^0) for 1 hour. The casted membrane was rinsed with hydrochloric acid (18.2 M. cm) and kept at 4 C^0 in dilute hydrochloric acid. The different types of membranes are described in detail in Table 1.2. Three samples of each type (micro, ultra, and nano filtration) with dimensions 6*10 cm where selected to performs filtration tests.

Table (1-2) Composition of the three types of membranes.

Type of membrane	Polymer type	Solvent	Additives	Mean pore diameter
MF	15% PS	84% DMF	1%PVP	0.2 micron
UF	18% PS	81% DMF	1%PVP	10 nm
NF	22% PS	77% DMF	1%PVP	0.1 nm

2.2 Experimental apparatus

Experiments on a cross flow tangential pilot plant equipped with a single flat sheet polysulon membrane were done. The pilot plant is schematically depicted in Fig. 2.2. Each type of flat sheet me membrane was tested three times. Fig. 3.2. shows the pilot plant used in the filtration test, It includes the following subsystems:

1. The treatment system is comprised of (feed tank No.1, mixer, heater, pump, and thermometer).
2. Membrane cell: (cell body, and membrane sheet).
3. The washing system is comprised of (tank No.2, mixer, heater, pump, and thermometer).
4. Tank No.3 gathers the synthetic water that has been treated.

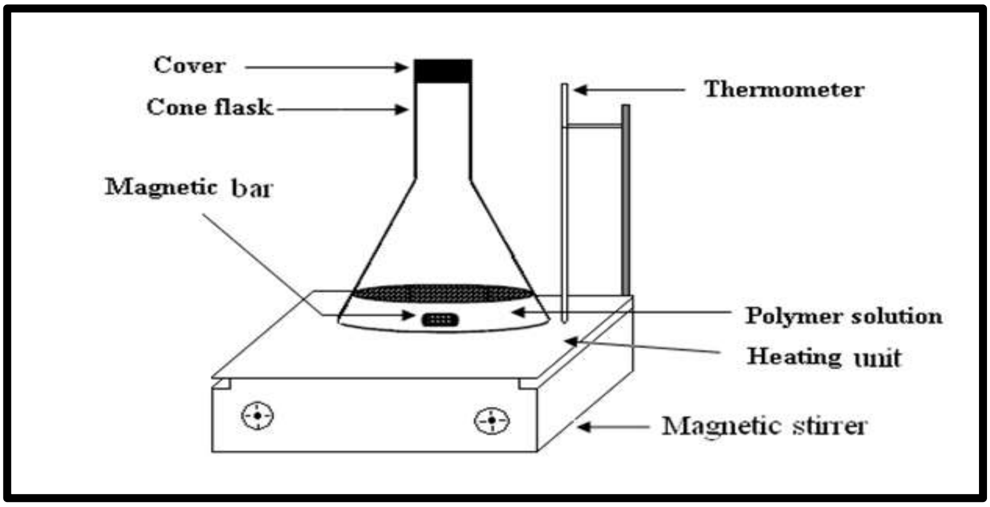

Figure (1.2) Equipment used for polymer solution preparation

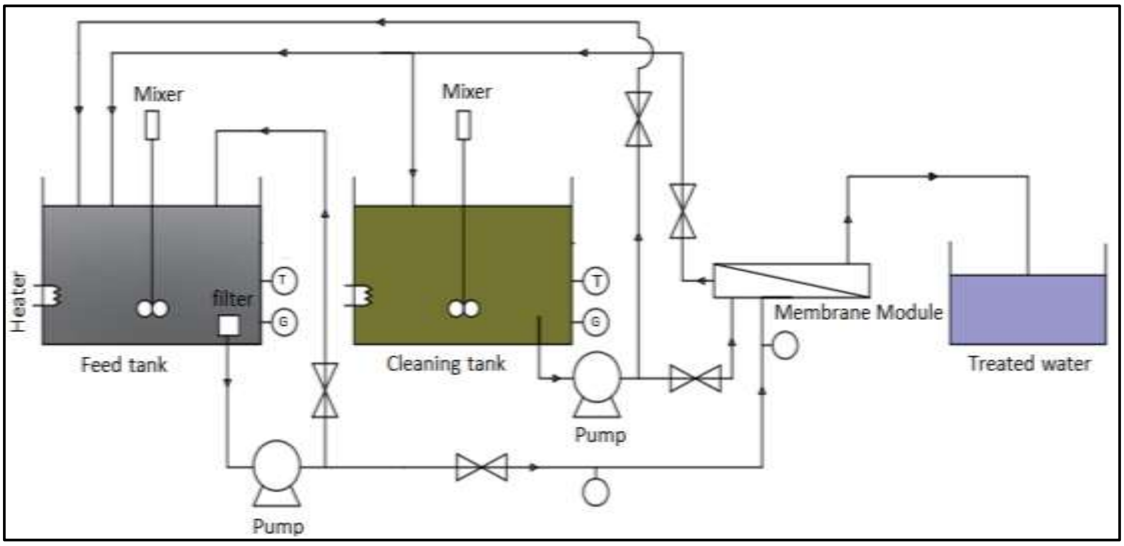

Figure (2.2) Schematic flow diagram of the pilot plant

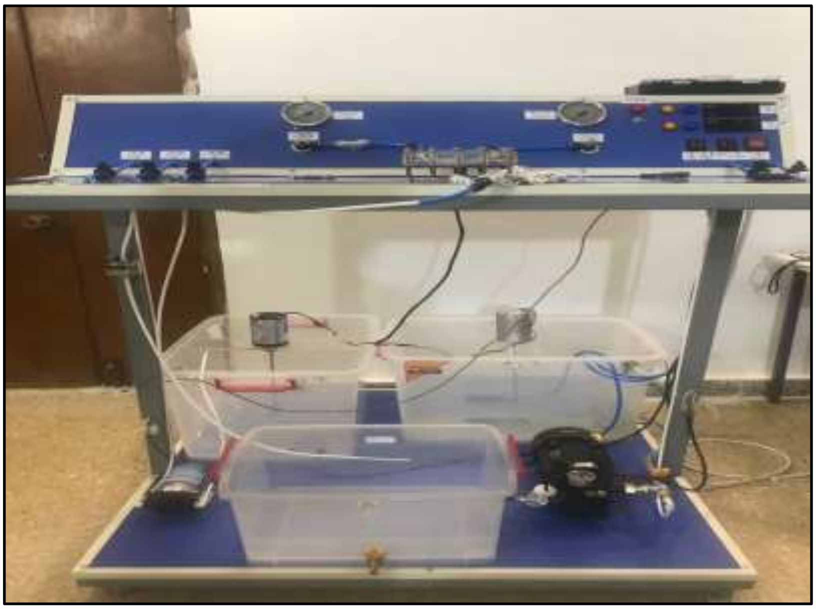

Fig. (3.2) Photographic view of cross flow pilot plant

2.3 Feed water characteristics

Humic acid was purchased commercially. 100 mg humic acid was dissolved in 1L distilled water to make humic acid. The solution's PH was corrected to 10 by adding NaOH, as humic acid did not dissolve at low PH. The solution was then supplemented with $NaOHCO_3$ and $CaCl_2$ and the required humic acid content was adjusted using humic acid stock solution. After adding all components, the solution was stirred for an hour with a magnetic stirrer. The characteristics of synthetic water are listed in Table 2.2.

Table 1.2 characteristics of synthetic water

material	concentration
Humic acid	3, 6, 8, 10 mg/L
kaolinite	2.5 mg/L
Alumina	2.5 mg/L
$NaHCO_3$	0.5 mM
$CaCl_2$	0.5mM

2.4 The procedure of testing

Each type of membrane was evaluated for its ability to remove varying quantities of humic acid from solution. Additionally, the performance of several membrane types is investigated. Each membrane type was subjected to permeability, flux decay, and concentration tests. Temperatures were monitored and maintained at 23 C^0. Permeate flow was manually recorded for 4 hours, and samples from permeate and retentate were collected and examined for characteristics such as humic acid concentration, turbidity, and pH. UV 254nm absorbance was utilized to determine humic acid concertation. EC/Inole 720, Germany used for conductivity measurement, Lovebond pH meter for pH measurement.

3.0 Results and discussion

In this research three types of membranes were tested (micro, ultra, and nonfilter membrane) to evaluate the effects of membrane mean pore size on the water flux, and removal percentage of HA, turbidity, and conductivity). All membrane configurations were flat sheet with dimensions (6 * 10 cm).

3.1 Permeability and flux test

All membranes were tested for permeability using cross flow system shown in fig.2.2. the permeability tests were carried out to show the effects of mass transfer represented by different concentrations of HA. All tests were carried out by measuring the flux (ml/L) towards different transmembrane pressure with constant (velocity, pH, and temperature). Fig 1-3, 2-3, and 3-3 shows the flux against pressure for the three types of membranes at different concentration of HA (3mg/L, 6mg/L, 8mg/L, and 10mg/L).

The analysis of figures shows that, the permeate flux increases with increasing transmembrane pressure and decreases with increasing HA concentrations. At pressure 25 psi the flux of micro, ultra, and nanofilter membranes were (105, 35and 25 ml/min) respectively when the HA concentration 3mg/L. increasing the HA concentration to 10mg/L shows decreasing of fluxes to (25, 12 and 16 ml/min) respectively with the same conditions of temperature and pH.

The flux of microfiltration membrane is greater than ultra, and nanofiltration membrane due to high mean pore size 0.2 m also no flux decline occurred over the running time, which are 4 hr. due to minimal polarization concentration.

3.2 Reject tests

Table 1-3 shows the percentage rejection of the three parameters (HA, Turbidity, and conductivity). These parameters represented the organic matter, dissolved solids and dissolved salts in surface water respectively. Both ultra and nonfilter membrane shows good rejection of HA (88-100%) respectively, there for both membranes are suitable for human substances removal in drinking water treatment. Although the rejection of the nanofiltration membrane was 100% but they have also removed all other compounds (e.g. total hardness), which are important for the drinking water quality. So the ultrafiltration membrane with 10nm mean pore size are more suitable for drinking water treatment due to their low cost and low pressure required relative to nano filter, so the membrane is seeming optimal to produce proper water quality.

For turbidity and conductivity rejection, ultrafiltration membrane still effective to remove (75, 50%) respectively, while microfiltration is very effective to remove turbidity about 90%, but its rejection is low for conductivity (10). Nanofiltration membrane is very effective to remove dissolved salts there for their reduction of conductivity about 90%.

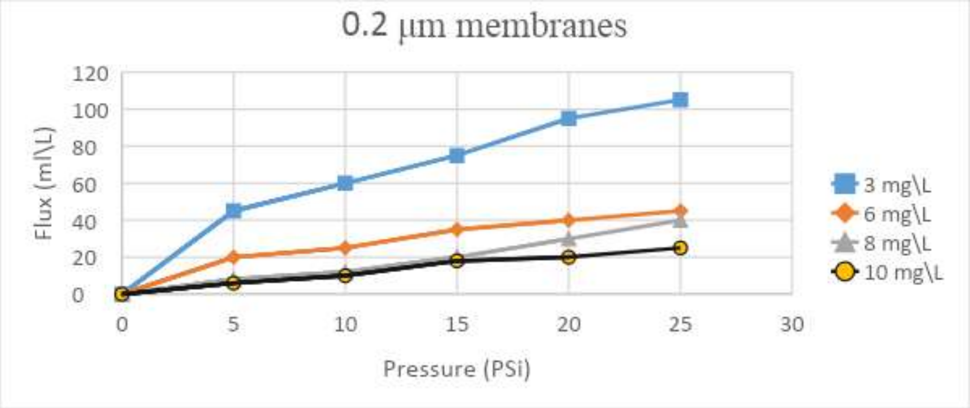

Fig. 1-3 Influence of flux with pressure for different concertation of HA in synthetic water solution for microfiltration membrane. pH 7, temp. 23C.

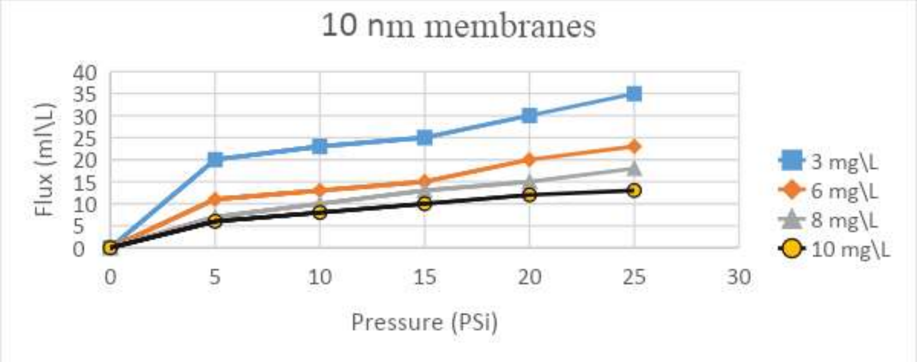

Fig 2-3Influence of flux with pressure for different concertation of HA in synthetic water solution for ultrafiltration membrane. pH 7, temp. 23C.

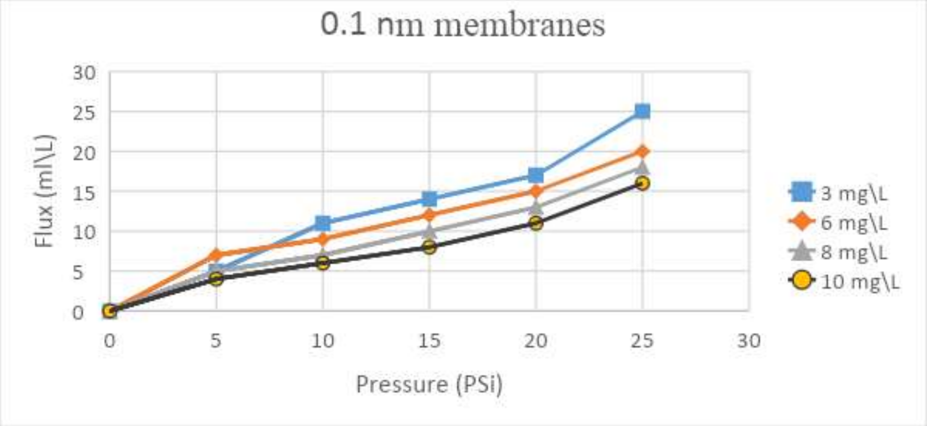

Fig 3-3 Influence of flux with pressure for different concertation of HA in synthetic water solution for nanofiltration membrane. pH 7, temp. 23C.

Table 1-3 percent rejection of HA, Turbidity, and conductivity for different type of membrane, temp. 23C, pressure 25 psi, HA concentration 8 mg/L, and pH 7.

Type of membrane	Percent HA rejection	Percent conductivity decreased	Percent turbidity removed
Micro filter membrane 0.2 µm	15	10	85

Ultrafilter membrane 10 nm	88	50	75
Nanofilter membrane 0.1 nm	100	90	75

3.3 flux decay and recovery

Flux decay were calculated for the membranes for two concentration of HA, 3mg/L and 8mg/L. The minim and optimal concentration. Test conditions were, pH 7, temperature 23 $C^{0,}$ pressure 25 psi. fig 4.3 shows influences of time towards the flux when the HA concentration 3.5 mg/l. the reduction of fluxes were after 3 hr. operation 13.3%, 21.2% and 44% of MF, UF and NF respectively. The minim reduction of flux in Mf, due to their large mean pore size (0.2µm) in which most of HA will pass through the membrane. While fig 5.3 shows that the flux decay of membranes under the same condition but at optimal HA concentration 8mg/L were increased to 20%, 28% and 47% respectively due to organic biofouling on membrane surface. Since the MF rejected only 15% of HA, there for the flux decay were not affected like UF and NF, which they rejected 88% and 100% of HA in solution.

3.4 Back washing and flux recovery

The effect of back washing and flux recovery for membranes were conducted after washing the membranes with distilled water for ten minutes by back washing pump in pilot plant. Fig 6.3 showed, that the membranes recovered 90%, 88% and 61.5% of their original flux. The high flux recovered of MF is due to their low rejection of HA, while the UM shows good recovery also their good rejection of HA about 88%. The flux recovery of NF is 61.5%, which may be not perfect since it required higher pressure to remove the organic fouling on its surface. In general, UF membrane seem to be more proper for water surface treatment due to their good HA removal and their efficiency for removal turbidity and conductivity in addition their good flux recovery after back washing.

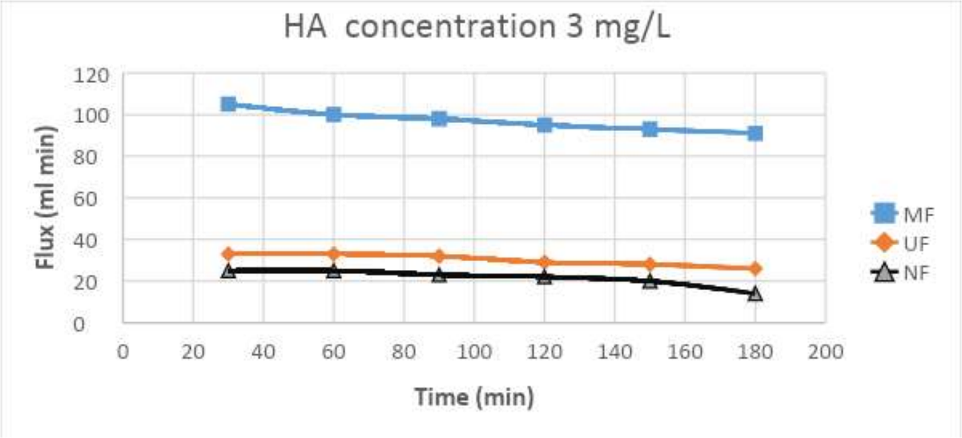

Fig. 4.3 Influences of flux decay with time for MF, UF and NF at pressure 25 psi, PH 7 and HA concentration 3 mg/L.

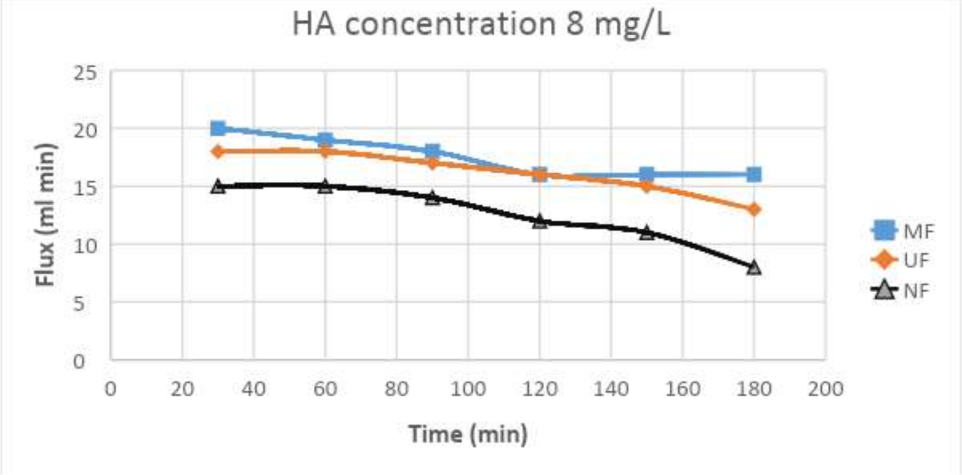

Fig. 5.3 Influences of flux decay with time for MF, UF and NF at pressure 25 psi, PH 7 and HA concentration 8 mg/L.

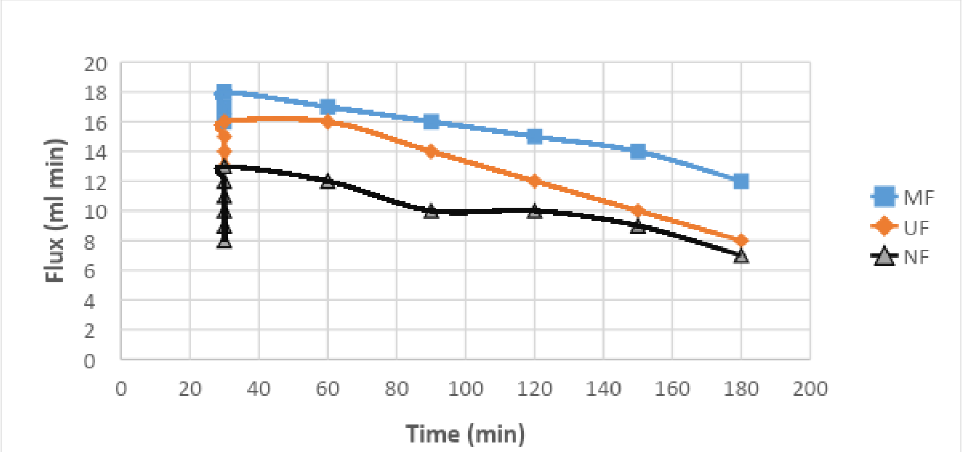

Fig. 6.3 Influences of flux recovery after back washing with time for MF, UF and NF at pressure 25 psi, PH 7 and HA concentration 8 mg/L

4.0 Conclusions

Results shows that MF membrane is not effective in removing HA from synthetic water solution in which their removal efficiency was less than 15%. while UF membrane seems to be more suitable for producing proper water quality of water for their efficiency in removing both turbidity and HA (75, 88%) respectively, in addition their good flux recovery after back washing from synthetic water containing 8 mg/L HA. However, the NF membrane removed 100% of HA and their good efficiency for removing conductivity and turbidity (90, 75%) respectively, but UF membrane is more convenient from practical point of view due to high cost and high pressure required for operation NF membrane and removing hardness from water which are important in proper water quality.

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References

1. Wang W., Fan Q., Wang Y., Qiao Z. and Wang X. (2014). Effects of UV radiation on humic acid coagulation characteristics in drinking water treatment processes. Chemical Engineering Journal, 256, 137-143.

2. Zulfikar M., Setiyanto H., Wahyuningrum D. and Mukti R. (2014). Peat water treatment using chitosan-silica composite as an adsorbent. International Journal of Environmental Research, 8, 3, 687-710.
3. Aziz H., Alif A., Ariani R., Trisna L., Wahyuni A. and Munaf E. (2015). Biomaterials supported with titania as photocatalyst in peat water purification. Journal of Chemical and Pharmaceutical Research, 7, 6, 192-197.
4. Singh P., Vishnu M., Sharma K., Singh R., Madhav S. and Tiwary D. (2016). Comparative study of dye degradation using TiO2-activated carbon nanocomposites as catalysts in photocatalytic, sonocatalytic, and photosonocatalytic reactor. Desalination and Water Treatment, 57, 43, 20552-20564.
5. Hutagalung S., Muchlis I., Herlambang B. and Turnip A. (2014). Removal of chemical and biological contaminants on peat water by ozone-based advanced oxidation processes with reverse osmosis. Technology, Informatics, Management, Engineering, and Environment (TIME-E), second International Conference on IEEE.
6. Yan W. and Bai R. (2005). Adsorption of lead and humic acid on chitosan hydrogel beads. Water Research, 39, 4, 688-698.
7. Mozia S., Tomaszewska M. and Morawski A. W. (2005). Studies on the effect of humic acids and phenol on adsorption–ultrafiltration process performance. Water Research, 39, 2, 501-509.
8. Ariono D., Aryanti P. T. P., Hakim A. N., Subagjo S. and Wenten I. G. (2017). Determination of thermodynamic properties of polysulfone/PEG membrane solutions based on Flory-Huggins model. AIP Conference Proceedings.
9. Rohani R., Hyland M. and Patterson D. A. (2016). Effects of process parameters on polyaniline nanofiltration membranes synthesis via phase inversion-immersion precipitation method. Journal of Engineering Science and Technology, 11, Special Issue onsomche, 2015, 16-35.
10. Nevstrueva D., Pihlajamäki A. and Mänttäri M. (2015). Effect of a TiO_2 additive on the morphology and permeability of cellulose ultrafiltration membranes prepared via immersion precipitation with ionic liquid as a solvent. Cellulose, 22, 6, 3865-3876.
11. Chen X., Luo J., Qi B., Cao W. and Wan Y. (2015). NOM fouling behavior during ultrafiltration: Effect of membrane hydrophilicity. Journal of Water Process Engineering, 7, 1-10.
12. Jones K. L. and O'Melia C. R. (2000). Protein and humic acid adsorption onto hydrophilic membrane surfaces: effects of pH and ionic strength. Journal of Membrane Science, 165, 1, 31-46.
13. Katsoufidou K., Yiantsios S.G., Karabelas A.J. (2005). A study of ultrafiltration membrane fouling by humic acids and flux recovery by backwashing: Experiments and modeling. Journal of Membrane Science, 266, 40-50.
14. Ma Y., Shi F., Ma J., Wu M., Zhang J. and Gao C. (2011). Effect of PEG additive on the morphology and performance of polysulfone ultrafiltration membranes. Desalination, 272, 1, 51-58.
15. Kitae Back and Ji Won Yang (2005). Humic substances enhanced ultrafiltration for removal of heavy metals. Separation science and Technology, Volume 40, -issue1-3 published online: 09 Nov2011.
16. J.LOWE, Md.M.Hossain (2008). Application of ultrafiltration membranes for removal of humic acid from drinking water. Desalination, volume 218, Issue 1-3, pages 343-354.
17. Abdulkhaleq K. Mahmood (2015). Fabrication of nanocomposite membrane containing nanomaterial for water purification. PhD Thesis University of Technology, Building and Construction Engineering Department, Baghdad, Iraq.