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REMOVAL OF NICKEL FROM WASTEWATER USING ULTRAFILTRATION MEMBRANES

BY

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Abstract. In this study the asymmetric cellulose acetate membranes prepared by the phase inversion method were used for removal Ni^{2+} ions from wastewater. The membrane morphology was studied by Scanning Electron Microscopy (SEM) and the pore diameters have been determined by Bubble-point test (BPT). In the ultrafiltration experiments carried out in a flat-cell unit, the synthetic wastewater of nickel (10 mg/L) was used. The obtained results show that the flux and ion retention, increase with increasing pressure.

Keywords: membrane; cellulose acetate; ultrafiltration; nickel ions.

1. Introduction

Environmental pollution with heavy metals from various industrial effluents is a critical issue nowadays, which is receiving a lot of attention in many industrialized countries (Musilova *et al.*, 2016). The discharge into the nature of wastewater containing such metals can lead to toxic effects on human and animal health (Jaishankar *et al.*, 2014). A number of metals, especially heavy metals, even in low concentrations in natural waters can form toxic compounds (Briffa *et al.*, 2020). Currently, there are many technological

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processes involving toxic metal ions, among which can be mentioned: metal finishing, metal plating, catalysis, electronics, mining and paint industries (Masindi and Muedi, 2018). Types of heavy metals that are commonly used are lead (Pb), nickel (Ni), chromium (Cr), cadmium (Cd), arsenic (As), mercury (Hg), zinc (Zn) and copper (Cu).

Nickel is a heavy metal with wide industrial applications. The discharge of nickel-containing wastewater into nature induces many negative effects. For the human population, nickel can cause health problems, such as: skin irritations, asthma, conjunctivitis and even cancer (Cempel and Nikel, 2006). Therefore, it is very important to remove nickel ions from wastewater by various separation methods (Zare-Dorabei *et al.*, 2016; Habiba *et al*., 2017).

Currently, there is a global strategy of environmental protection, one of the objectives being the removal and recovery of hazardous metal ions from polluted municipal and industrial waters. Different separating methods of these pollutants are known, including: precipitation, ion exchange, electrochemical treatments, adsorption, and membrane filtration (Fu and Wang, 2011; Gehrke *et al*., 2015). Between these processes, the membrane filtrations are distinguished by their efficiency and feasibility (Al-Rashdi *et al*., 2011; Ciobanu *et al*., 2009; Khulbe and Matsuura, 2018).

The use of polymeric membranes for filtration and separation processes is a field which has attracted continuous attention from the scientific community due, among other reasons, to the important applications which have already been developed for the day-to-day human life. Membrane processes (nanofiltration, reverse osmosis, microfiltration, ultrafiltration etc.) are becoming increasingly attractive as an alternative to wastewater treatment. Membrane filtration is a more traditional separation method that has found some use for the removal of metal ions from solution (Chougui *et al*., 2014; Ciobanu and Carja, 2010).

Filter membranes are categorized as symmetric, asymmetric, porous or non-porous, depending on their filtration behaviour, materials used and manufacturing processes. Normally, they are manufactured from polymers, composite materials between two polymers, or between polymer and ceramic.

In the membrane separation processes a very important factor is the structure of the membrane. An important moment in membrane science is the production of asymmetric membranes by Loeb and Sourirajan in the 1960’s (Loeb and Sourirajan, 1963). These membranes with an asymmetric structure can be obtained by a dry / wet phase inversion method. From a structural point of view, asymmetric membranes are formed by overlapping layers with specific characteristics: a very thin dense and selective skin layer (less than 0.1 μm), supported by a much thicker (100 - 200 μm) highly permeable non-selective layer (which provides structural support), and a bottom layer. The skin layer of these asymmetric membranes becomes defect-free by introduction an evaporation step (Ciobanu and Ciobanu, 2015).

Today most membranes are fabricated by phase inversion process. Cellulose acetate membranes are used extensively in reverse osmosis for the removal of salt from water. Over the past 30 years, many other polymers have been fabricated into asymmetric membranes for a variety of specific separation and purification applications. The ongoing challenge for researchers in membrane science is to keep pace with the growing demand for membranes with superior selectivity and flow capacity (flux) (Nasef and Yahaya, 2009).

The objective of this research was to study the Ni^{2+} ions removal from wastewater using cellulose acetate membranes. These membranes were prepared by the phase inversion method from a ternary system consisting of cellulose acetate, acetone and formamide or water. The filtration experiments were carried out in flat-cell unit, and membrane performance was investigated at constant pressure.

2. Experimental

Materials: Cellulose acetate (CA) with 39.8% acetyl content (from Fluka) was used as a membrane material. Acetone (from Merck) was used as a solvent, formamide (F) (from Merck) and water (W) were used as non-solvents, whereas water was used as coagulation medium. Analytical reagent grade, nickel (II) sulphate hexahydrate (98%, from Aldrich) was used. Salt solution was prepared with demineralised water with a conductivity of about 10 μS/cm.

Membrane preparation: The cellulose acetate membranes were prepared by the phase inversion method starting from a ternary system of cellulose acetate, acetone and formamide or water. Different solutions with various cellulose acetate compositions were used for membrane preparation.

Membrane characterisation: The morphology of samples was studied by Scanning Electron Microscopy (SEM) on TESLA-BS-300 instrument. The pore diameters have been determined by Bubble-point test (BPT) with a laboratory instrument. The some physical characteristics of the prepared cellulose acetate membranes in our laboratory are summarised in Table 1.

Table 1
Some Physical Characteristics of the Prepared Cellulose Acetate Membranes

Characteristic	MAC – 1F*	MAC – 2W*
Thickness (μm)	240	375
Pore diameter in top surface (μm)	0.2 - 2.5	0.5 - 8.5
Void diameter in substructure (μm)	5 - 7	6 - 15

*The non-solvent is formamide (F) or water (W).

Filtration: In the ultrafiltration experiments, the synthetic wastewater of nickel (10 mg/L) is used. The parameters of synthetic wastewater samples, such as pH and conductivity were determined using a multi-parameter analyser

CONSORT C831. The concentration of Ni^{2+} ions was determined by complexometric titration.

The filtration experiments were carried out in flat-cell units. In a cylindrical membrane test cell, a circular membrane disc with an effective permeation area of 12.5 cm^2 was mounted. The filtration process was carried out a constant pressure of 0.5, 1 and 2 bar and the flux was recorded at 1, 10, 30, 60, 90 and 120 minutes. The total filtration time in each experiment was 120 minutes then the membrane was washed four times.

For filtration process, the membrane productivity is expressed as the permeate flux through the membrane. The flux rate, J ($L/m^2\cdot h$), is a function of the difference between volume permeation rate, V/t (L/h), and the membrane area, A (m^2):

$$J = \frac{V}{t \cdot A} \quad (1)$$

The selectivity of a membrane for a given solute (*i.e.* heavy metal ion) is usually expressed by the percentage of retention (rejection), R(%), which is defined by the concentration of solute in the permeate phase, C_p, relative to the concentration of the solute in the feed solution, C_f:

$$R(\%) = \left[1 - \frac{C_p}{C_f}\right] \cdot 100 \quad (2)$$

3. Results and Discussions

Microporous membranes prepared in our laboratory (*e.g.*, MAC-1F and MAC-2W samples) consist of three-dimensional polymeric structure, with pore sizes of molecular dimensions, which offers specific permeability to a component in a process feed to the membrane. These membranes have a quite complex, open, colloidal-type structure, with a small fraction of the membrane volume occupied by the polymer substrate.

All cellulose acetate membranes obtained have an asymmetric structure consisting of an ultrathin skin layer (active layer) and the underlying region which is a tightly packed nodular transition layer, both supported by an open-cell, sponge-like substructure, as presented in literature (Ciobanu *et al.*, 2008; Ciobanu and Ciobanu, 2016).The pore size differs from one layer to another, so in the active layer the pores are much smaller than the pores in the supported layer. Accordingly, the molecular sieve property of cellulose acetate membranes appears to be determined by the pore size in the top layer of the cellulose acetate membranes.

The filtration of solutions which contained Ni^{2+} ions were carried out to evaluate the efficiency of ultrafiltration membranes prepared for rejection of toxic metal. In order to evaluate the behaviour of the membrane for removal of the Ni^{2+} heavy metal ions in wastewater, the filtration was performed and the effect of pressure was investigated. Figs. 1 and 2 show the effect of time on permeate flux and retention of Ni^{2+} ions through the MAC-2W membrane at various pressures.

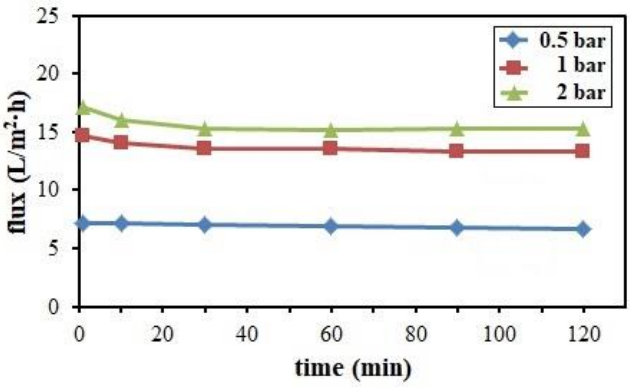

Fig. 1 – Effect of time on permeate flux through MAC-2W membrane at various pressures.

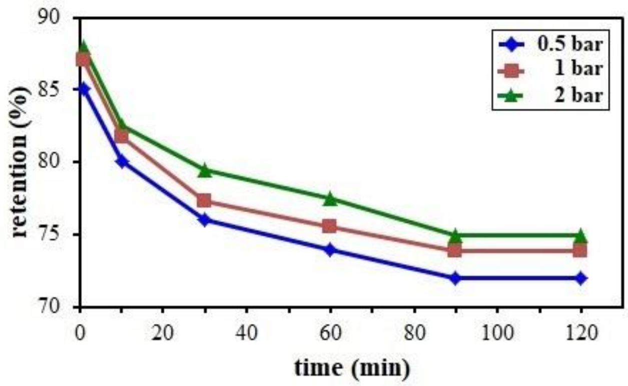

Fig. 2 – Effect of time on retention through MAC-2W membrane at various pressures.

As follows from the data presented in Figs. 1 and 2, an optimum value of the operating pressure is 2 bar. The maximum retention of Ni^{2+} ions by MAC-2W membrane was reached at that pressure.

The obtained results show that the flux and retention increase with increasing pressure. This is the classical behavior for ultrafiltration membranes.

For the two cellulose acetate membranes prepared in our laboratory, the flux rate (*J*) and percentage of Ni^{2+} ions retention (*R*%) are presented in Table 2. According to the experimental data, the flux and percentage of retention were increased at cellulose acetate membranes prepared with water as non-solvent (MAC-2W sample).

Table 2

The Ni^{2+} Ion Metal Removal by Cellulose Acetate Membranes

Pressure (bar)	Membrane			
	MAC – 1F		MAC – 2W	
	J (L/m²·h)	*R* (%)	*J* (L/m²·h)	*R* (%)
0.5	6.8	80.5	7.2	85.1
1	13.5	83.1	14.7	87.0
2	16.3	86.3	17.1	87.9

The results showed that the membrane performance is affected by the membrane structure, determined by the conditions of membrane preparation, *i.e.* composition of the casting solution.

4. Conclusions

The asymmetric porous cellulose acetate membranes can be fabricated by wet phase inversion method from a cellulose acetate, acetone, formamide and / or H_2O casting system quenched in water. The cellulose acetate membranes consist of an ultrathin skin layer, a tightly packed nodular transition layer and a sponge-like substructure.

The cellulose acetate membrane presents interesting retention properties with regard to the heavy metal ions (*i.e.* Ni^{2+}), their retention depends strongly on the applied pressure. An optimum value of the operating pressure has been determined and it is 2 bar. The results showed that the membrane performance is affected by the membrane structure, determined by the conditions of membrane preparation, i.e. composition of the casting solution.

The results of this work suggest that the cellulose acetate membranes prepared from a cellulose acetate, acetone and H_2O casting system can be effectively used for removal of Ni^{2+} ions from aqueous solutions.

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ÎNDEPĂRTAREA NICHELULUI DIN APE REZIDUALE UTILIZÂND MEMBRANE DE ULTRAFILTRARE

(Rezumat)

În acest studiu au fost preparate membrane asimetrice din acetat de celuloză prin metoda inversiei de fază, membrane care apoi au fost utilizate pentru îndepărtarea ionilor Ni^{2+} din ape reziduale. Morfologia membranelor a fost studiată prin microscopie electronică cu baleiaj (SEM), iar diametrele porilor au fost determinate prin metoda Bubble-point (BPT). În experimentele de ultrafiltrare efectuate într-o unitate de filtrare plană, s-a utilizat apă reziduală sintetică cu un conţinut de nichel de 10 mg/L. Rezultatele obținute indică faptul că fluxul și retenția de ioni cresc odată cu creșterea presiunii.