Separation of Heavy Metals Salts from Aqueos Solutions by Reverse Osmosis Membranes (317K-2)

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ABSTRACT

The aim of this work was the separation of heavy metal salts dissolved in water with coal modified-cellulose acetate (317K-2) heterogeneous RO membranes. Reverse osmosis membranes have been used to study their selectivity properties implying different feed solutions such as aqueous solutions of $HgCl_2$, $KMnO_4$, $CrCl_3$ and $CuSO_4$. The composition of cellulose acetate and powdered coal in ratio (1:1.75 by weight) in casting solvent (acetone) and casting conditions are tested. The powdered coal was modified with 4-nitrobenzene diazonium salt in acetonitrile. Like the cellulose acetate membrane, the cellulose acetate-coal modified membranes separate the trivalent and bivalent ions more than the univalent ions. Regarding the separation of salts solutes with the cations of the same valence, separation increases with the decrease of the cation radius.

Keywords: heavy metal salts, membrane, modified coal, reverse osmosis.

INTRODUCTION

The heterogeneous asymmetric reverse osmosis (RO) membranes have gained an important place in chemical technology and are use in a broad range of applications. In the last decades the use of membrane technology has grown significantly also in wastewater treatment. Reverse osmosis can be considered very effective method for the removal of organic and inorganic compounds from wastewater. Certainly, this study is focused on reverse osmosis.

The ionic transport and selectivity of reverse osmosis membranes mainly depend upon three effects: charge repulsion, steric/hydrodynamic and dielectric effects. The first effect is caused by the charged nature of the membrane and electrolytes, while the second effect is caused by the relative size of ions to the membrane pores; third effect is caused by the differences in dielectric constant between bulk and membrane pore. Additional phenomena can affect the membrane performance, i.e. ion-membrane affinity, specific adsorption and hydration.

Size exclusion is another important mechanism of RO. Ion transport is significantly impacted by hydrated radii and hydration strength because size variations can determine which ions are able to pass through the membrane pores via convection or diffusion[1-3].

Ions with relatively smaller crystal radii have higher charge, higher hydration numbers, larger hydrated radii, and hold hydration shells more strongly[1]. Conversely, ions with larger crystal radii have weaker hydration shells and smaller hydrated radii, and hence may be able to detach from their hydration layer when passing through the membrane. Hydration strength is impacted by ionic structure and solution composition as well as

environmental factors such as pH, ionic strength, and temperature[1]. It is of interest to understand whether trade off relations between water permeability and water/salt selectivity.

The objective of this work was the study of the criterion for the separation of toxic ions in aqueous solution with the cellulose acetate-coal membranes.

MATERIALS AND METHODS

Materials

Solution of heavy metals was prepared by dissolving required quantity of their salts ($HgCl_2$, $CrCl_3 x6H_2O$, $KMnO_4$ and $CuSO_4 x5H_2O$) in the distilled water.

Cellulose acetate (Eastman Kodak 398-3) with a degree of acetylation of 39.85 % and Kosovo coal namely lignite was used for preparation of heterogeneous asymmetric RO membranes.

The powdered coal was treated with water at 353 K under stirring conditions to remove all dissolved materials, i.e. inorganic part, colored substances, etc. The residual coal after filtering was dried at 378K to constant weight, ground and sieved.

The powdered coal fraction of sieve size 0.09 mm was used for modification with 4-nitrobenzen diazonium salt in acetonitrile.

Membranes prepared from cellulose acetate and modified coal we have marked as (317K-2) membranes.

Film Casting Details

The film casting details for the membranes investigated are casting solution composition cellulose acetate (E 393-3) 10 wt. %, modified coal 17.5 wt. %, acetone 58.8 wt. % water 12.25 wt. % magnesium perchlorate 1.45 wt. %.

The temperature of casting solution and casting atmosphere was 297 K, and the casting was done in ambient with air relative humidity, 60%. The films were cast on a clean glass plate using a metal cylinder with uplifted edges to obtain the required film thickness (0.12 mm). The glass plate was kept at the same temperature as the casting solution. The casting was done practically without any evaporation period, i.e. the cast solution was immediately dipped into a gelatin bath consisting ice cold water. The duration of the film setting in ice cold water was 1h. Before the reverse osmosis experiments the membranes were preshrunk under water at different temperatures (350, 353, 358 and 361 K). And initially each film was subjected to pure water pressure treatment for 1h at 20% higher pressure than that to be used in reverse osmosis run. All experiments were of the short run type and performed at laboratory temperature.

Reverse Osmosis Procedure

Reverse osmosis experiments were carried out at an operating pressure of 17.6 x 10^5 Pa using a standard reverse osmosis apparatus. The RO apparatus is illustrated schematically in Figure 1.
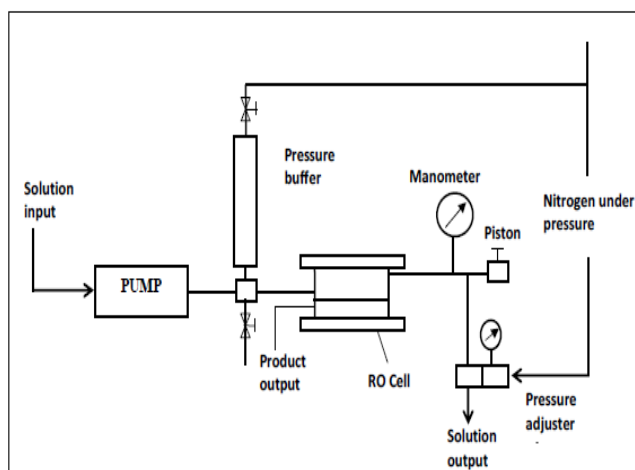
Figure 1: Schematic Representation of the RO Set-up

The main part of the apparatus of the reverse osmosis is the RO cell of very small thickness in which can be placed the filter paper with a blue stripe and membrane. The cell is built from non-corrosive steel (WNr.4301) and contains two separated parts. The upper part has a hole wherein passes the solution at certain pressure while the bottom part of the cell consists of the porous plates. Over the porous plate, first is putted the filter paper and then is placed the membrane. Active area of the membrane is 11.92 cm^2.

The membrane performance data were obtained for conditions of feed concentration of NaCl 6.8 x 10^{-3} mol/dm^3 (as a reference system) and solutions of heavy metals salts ($HgCl_2$, $CuSO_4$, $KMnO_4$ and $CrCl_3$) of the same concentration as the reference system. Feed flow rate of

450 cm^3/min was used, giving a mass transfer coefficient k = 45 x 10^{-4} cm/s on the high pressure side of the membrane. All performance data (i.e. data on solute separation and product rate) were compared at the above value of k which was constant in all experiments. The initial and final concentration of salts in the tested solutions was determined by the conductometer, Radiometer CDM_3.

The solute separation f was calculated from the relation:

$$f = \frac{c_f - c_p}{c_p} * 100 \qquad (1)$$

C_f- solute concentration in feed (mol/dm^3), Cp-solute concentration in product (mol/dm^3).

The product rate PR (g/h) and pure water permeation PWR (g/h) were determined at pressure 1.74 MPa.

The values of the solute transport parameter $D_{AM}/K\delta$ (cm/s) and the pure water permeability constant A (mol/cm^2*s*Pa) were calculated from the experimental data using the following expressions:

$$\frac{D_{AM}}{k\delta} = \left(\frac{PR}{3600*S*d}\right) * \left(\frac{1-f}{f}\right) * \left(e^{\frac{PR}{3600*S*k}}\right)^{-1} \qquad (2)$$

$$A = \frac{PWR}{M_W*S*3600*P} \qquad (3)$$

where S = effective membrane area (cm^2), k = mass transfer coefficient on high-pressure side of the membrane (cm/s), d = density of solution (g/cm^3), PR = product rate (g/h), PRW = pure water permeation rate (g/h), P = pressure (MPa), and M_W = molar mass (g/mol) of water. The reverse osmosis separation of four inorganic salts in aqueous solutions have been tested at the same conditions as in permeability test using heterogeneous cellulose acetate-coal reverse osmosis membranes.

RESULTS AND DISCUSSION

Membrane were tested with reference system NaCl solution of feed concentration 6.8*10^{-3} mol/dm^3 and feed flow rate corresponding to a mass transfer coefficient of 45 x10^{-4} cm/s. In Table 1 are presented the results for water permeability constant (A), solute transport parameter ($D_{AM}/K\delta$), solute separation (f), product rate (PR), and pure water permeation rate (PWR) for NaCl reference system with heterogeneous RO membranes (317K-2).

Table 2 presents the results for product rate of solute (PR), pure water permeation rate (PWR) and solute separation of heavy metal salts for heterogeneous RO membranes (317K-2), under the same conditions as the reference system.

Table 1: Comparative Characteristics of Membrane-type (317K-2) for NaCl system.

| Membrane	Temp. of Processing (K)	$A \times 10^{-11}$ mol H_2O/(cm^{2}sPa)	$D_{AM}/k\delta$ 10^{-4} (cm/s)	F (%)	PR (g/h)	PWR (g/h)
1	358	1.60	0.753	87.37	25.75	24.79
2	358	3.79	2.55	79.73	57.02	58.60
3	358	4.406	4.77	69.76	65.19	68.054
4	353	4.49	5.09	68.77	66.93	69.42
5	353	6.168	8.02	63.45	94.69	95.27
6	353	7.105	1.65	46.84	99.26	109.75

Table 2: Comparative Characteristics of Membrane-type (317K-2) for Different Systems.

|	Membrane	Temp. of Processing (K)	Pure Water Permeation Rate (g/h)	Product Rate (g/h)	Separation (%)
NaCl	1	358	65.24	25.75	87.37
	2	358	86.42	57.02	79.73
	3	358	55.16	65.19	69.76
	4	353	131.74	66.93	68.77
	5	358	89.41	94.69	63.45
	6	350	112.40	99.26	46.84
CuSO$_4$	1	358	65.24	65.07	93.00
	2	358	86.42	85.65	84.21
	3	358	55.16	54.75	94.21
	4	353	131.74	129.90	76.31
	5	358	89.41	89.06	81.05
	6	350	112.40	122.08	77.89
KMnO$_4$	1	358	68.643	59.523	95.92
	2	358	52.824	47.135	95.60
	3	353	61.914	54.816	93.28
	4	358	50.76	45.547	93.12
	5	353	70.638	62.216	90.56
	6	350	76.08	66.814	90.08
CrCl$_3$	1	361	99.70	93.69	70.53
	2	–	58.72	56.49	84.41
	3	–	24.94	25.56	91.47
	4	–	72.98	66.75	66.00
	5	–	69.78	63.93	71.10
	6	–	108.52	98.53	49.29
HgCl$_2$	1	361	99.58	93.55	69.78
	2	–	58.69	55.49	84.41
	3	–	23.00	30.01	89.41
	4	–	73.00	66.75	65.10
	5	–	69.68	64.2	73.30
	6	–	107.9	98.57	50.10

Like the cellulose acetate membranes, the heterogeneous RO membrane (317K-2) separates the solute of salts with trivalent and bivalent cations more than the salt with the univalent cation (the solution of NaCl is a reference system)[1,4].

In Figure 2 are presented comparative characteristics of membranes (317K-2) for solute with univalent, bivalent and trivalent cations associated with chloride ions.

Regarding the separation of salts solutes with the cations of the same valence, separation increases with the decrease of the cation radius, (ionic radius of Cu^{2+} = 73 pm, ionic radius of Hg^{2+} =102 pm). The results of solute separation and product rate for NaCl system and other four heavy metal salts are presented in Figure 3.
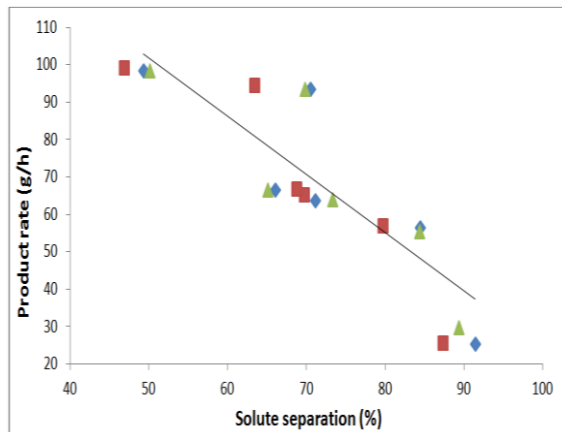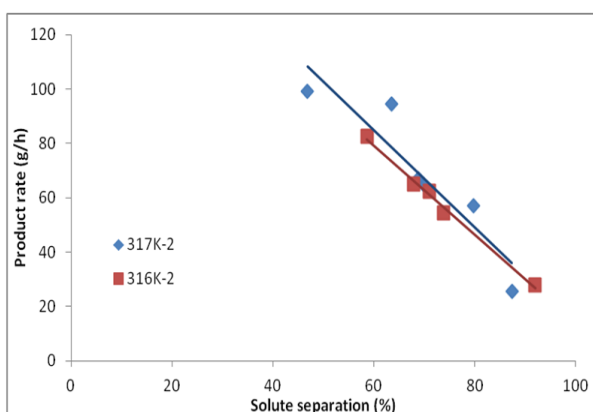

Figure 2: Comparative Characteristics of Membrane-type (317K-2) for: ■ NaCl, ▲ $HgCl_2$ and ♦ $CrCl_3$ system.
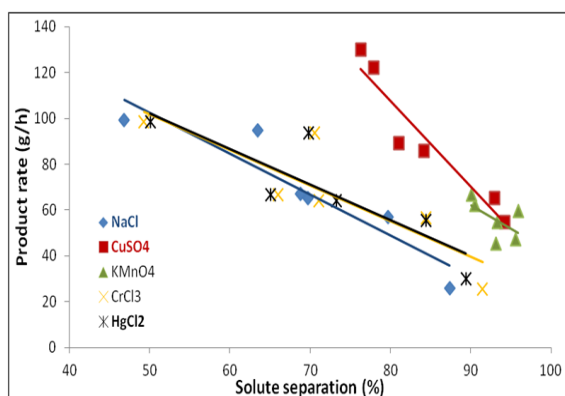
Figure 3: Comparative Characteristics of Membrane-type (317K-2) for: NaCl, $KMnO_4$, $HgCl_2$, $CrCl_3$, $CuSO_4$ system.

In Figure 4 are featured the results obtained for membranes 316K-2 and 317K-2 for the reference system. The RO membranes 316K-2 previously investigated were made from a blend of cellulose acetate and unmodified powdered coal at the same proportions by wt. (1:1.75)[5].

Figure 4: Comparative Characteristics of Membrane-type (317K-2) and (316K-2), for NaCl system.

In Figure 4 it can be seen that the membranes batches 317K-2 have showed better properties in comparison with batches 316K-2.

This is interpreted on the basis of homogenization of surface layer after the spontaneous grafting of hydrophilic nitro phenyl groups into the coal which are determinant for the improvement of the performance of reverse osmosis membranes 317K-2.

This improvement of performance of heterogenous reverse osmosis membranes is attributed to changing reology and morphology of active porous layer[6].

According to the separation values of inorganic salts solutions shown in Fig. 3 we could say that we have this sequence of separation $CuSO_4$ >$KMnO_4$>$CrCl_3$>$HgCl_2$>NaCl.

CONCLUSION

The 317K-2 membranes that have been prepared from cellulose acetate and coal modified with 4-nitrobenzen diazonium salt in acetonitrile, show improved performance in comparison with those of cellulose acetate and unmodified coal, previously investigated (316K-2).

The heterogenous cellulose acetate-coal membranes batches 317K-2 membranes showed better performance in separation values of inorganic salts solutions than 316K-2 membranes.

The secuence of separation is $CuSO_4$>$KMnO_4$>$CrCl_3$>$HgCl_2$>NaCl.

Based on experimental data for solute separation the membranes 317K-2 are suitable for separation of inorganic salts solutions which can be found in a real system and waste water.

REFERENCES

1. Tansel B, Sager J, Rector T, J Garland, Strayer R, Langfang L, Roberts M, Hummerick M, Bauer J. Significance of hydrated radius and hydration shells on ionic permeability during nanofiltration in dead end and cross flow modes, *Sep. Purif. Technol.,* 51, 2006, 40-47.

2. Van Der Bruggen B, Koninckx A, Vandecaseele C. Separation of monovalent and divalent ions from aqueous solution by electrodialysis and nanofiltration, *Water Res.,* 38(5), 2004, 1347-1353.

3. Paugam L, Diawara KC, Schlumpf PJ, Jaouen F, Quemeneur F. Transfer of monovalent anions and nitrates especially through nanofiltration membranes in brackish water conditions *Sep. Purif. Technol.*, 40(3), 2004, 237-242.

4. Gashi S, Daci N, Selimi T, Berisha S. Preparation and properties of cellulose acetate – coal heterogenous reverse osmosis membranes, *Environ. Protect. Eng.*, 26(4), 2000, 29-37.

5. Selimi T. Studimi i strukturës dhe vetive të membranave heterogjene të osmozës së kundërt, *Doctoral dissertation*, University of Prishtina, 2006.

International Journal of Pharmaceutical Sciences Review and Research
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286

6. Gashi S, Daci N, Podvorica F, Selimi T, Thaçi BS. *Desalination,* Effect of modification time of coal with aryldiazonium salts on performance of cellulose acetate-coal heterogeneous reverse osmosis membranes, 240, 2009, 1-8.

7. Kunst B, and Sourirajan S. Development and performance of some porous cellulose acetate membranes for reverse osmosis desalination, *J. Appl. Polym. Sci.*, 14, 1970, 2559–2568.

8. Kastelan-Kunst L, Dananic V, Kunst B, Kosutic K. Preparation and porosity of cellulose tri acetate reverese osmosis membranes, *J. Membrane Sci.*, 109, 1996, 223-230.

9. Gashi S, Selimi T, Thaçi BS, Dylhasi A. Study of the optimization factors for preparation of heterogenous reverse osmosis membranes, *Water Sci. Technol.,* 11(6), 2011, 647-653.

10. Chaudry MA. Water and ions transport mechanism in hyperfiltration with symmetric cellulose acetate membranes, *J.Memb. Sci.*, 206(1-2), 2003, 319-332.

11. Gashi S, Daci N, Podvorica F, Selimi T, Thaçi B. Development and performance of cellulose acetate-coal heterogeneous reverse osmosis membrane, *Desalination,* 200, 2006, 414–415.

12. Hussain AA, Nataraj SK, Abashar MEE, Al-Mutaz IS, Amiabhavi TM. Prediction of physical properties of nanofiltration membranes using experiment and theoretical models, *J.Memb. Sci.,* 310, 2008, 321-336.

13. Mousavi Rad SA, Mirbagheri SA, Mohammadi T. Using Reverse Osmosis Membrane for Chromium Removal from Aqueous Solution, *World Academy of Science, Engineering and Technology,* 3, 2009, 505-509.

14. Greenlee LF, Lawler DF, Freeman BD, Marrot B, Moulin PH. Reverse osmosis desalination: Water sources, technology, and today's challenges, *Water res.*, 43(9), 2009, 2317-2348.

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