

Optimization of Membrane Processes with Polysulfone/Polyaniline Composite Membranes

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In this paper we studied the optimization of the process parameters of membranes. We studied four ions: nitrate, sulfate, chloride and phosphate. The results of the experimental study were processed using the following mathematical models: Langmuir, Freundlich and Temkin – Pyzhev. The four ions were microfiltered through a composite membrane with pores of different sizes (0.1 μm and 0.5 μm). The four ions analyzed were: nitrates, sulfates, phosphates and chlorides. To determine these, ions were used together with spectrophotometric and titrimetric methods. Experiments were conducted at three different temperatures: 288K, 308K, 328k. The sorption parameters and the fitting of the models were determined by nonlinear regression and then discussed. Wastewaters containing these ions were filtered through polysulfone/polyaniline (PSf/PANI) membrane composites. The morphological characterization of the membrane was performed using scanning electron microscopy (SEM) and the structural characterization was performed using infrared spectroscopy (FT-IR). The best results were obtained using the Langmuir model for nitrate ions and Temkin–Pyzhev for chloride ions. The following parameters for each ion in part were: initial ion concentration, solution pH, working adsorption capacity, size and thickness of the composite membrane and temperature. The best results for the adsorption capacity were obtained with 0.1 μm composite membranes for nitrate and sulfate ions.

Keywords: composite membrane, nitrate, sulfate, phosphate, chloride, mathematical models

Membrane processes are increasingly becoming a widespread approach to achieve better water quality in terms of improved removal of some ions from water. The implementation and maintenance of membrane-based drinking water treatment processes are however often constrained by the membrane [1-3].

The factors affecting microfiltration separation that can also play an important role in membrane separation of different ions are as follows:

- membrane properties such as surface roughness, pore size distribution, membrane thickness, membrane charge type and charge density;

- the chemistry of the treated solution such as the solute composition, the size, geometry and the charge of the components, the concentration of the ions, the pH and the zeta potential of the solution and its interaction with the membranes;

- the processes environment—temperature and pressure [4].

The presence of the phosphate in industrial and domestic wastewater contributes to eutrophication when it is released into the aquatic environment. Orthophosphate, polyphosphate with smaller amounts of organic phosphate are generally the major phosphorus compounds in wastewater [5].

The presence of elevated concentrations of nitrate (NO_3^-) in drinkable water has become a serious concern worldwide over the past few decades. Nitrate is a water soluble ion that does not readily bind to the soil causing it to be highly susceptible to run-off migration [6].

The increasing levels of chloride, fluoride, sulfate and nitrate ions in drinking and groundwater due to natural and anthropogenic activities has been recognized as one of the major problems worldwide. This imposes a serious threat to the human health and environmental issues. Thus, a renewed interest in the removal of ions from domestic and industrial wastewaters has been greatly increased. Moreover, technologies for the removal of ions from water are of great relevance in waste treatment processes, which aim to achieve efficient strategies to obtain acceptable levels of disposal of the aforesaid ions [7].

This study was performed to highlight the use of composite membranes for wastewater remediation with nitrate, phosphate, sulfate and chloride ions content.

Experimental part

Reagents

All the reagents were purchased from Sigma Aldrich. All reagents were analytical grade.

Material

The synthesis of polysulfone-polyaniline (PSf/PANI) composite membranes from the polysulfone/aniline/ non-solvent (oxidant) system and a polysulfone / aniline-DMF/ non-solvent (oxidant) system was performed through phase inversion with chemical reaction [9-15].

Porous PSf membranes can be successfully obtained using phase separation techniques. The pore parameters of these porous membranes can be effectively controlled by mainly altering the concentration of ethanol solutions.

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It was found that the conductivity of the composite membrane could be affected by the pore parameters, the amount of the oxidant and the ratio of the oxidant to the polysulfone monomer [16-20].

The scanning electron microscopy was performed using a FESEM Hitachi S4500.

The infrared spectroscopy analysis was performed using a Bruker Vertex 70 instrument with diamond ATR annex.

Uv-Vis analyses were performed using Jasco V530 apparatus.

Results and discussions

Morphological-structural characterization of the membranes

We characterized two composite membranes with pore sizes of 0.1 μm and 0.5 μm . The membrane with a pore size of 0.1 μm shows spherical pores, while the membrane with a pore size of 0.5 μm shows a cylindrical shape of the pores. Both composite membranes were prepared in the laboratory by phase inversion with chemical reaction [13-15].

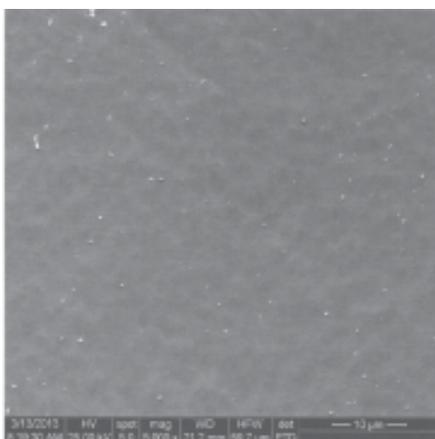


Fig.1. SEM image of 0.1 μm membrane

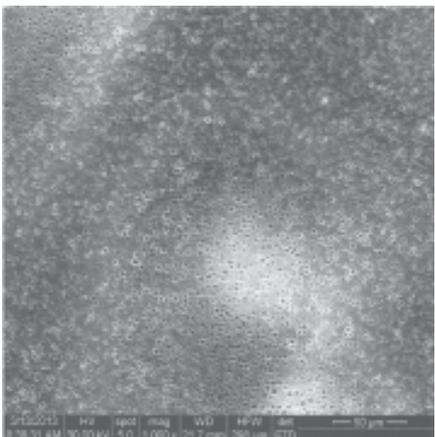


Fig.2. SEM image of 0.5 μm membrane

Band position, (cm ⁻¹)	Assignment
1165	C-O
1104	C-C
1336	CH
1500-1600	C=N
1000-1300	C=O

Work procedures and mathematical models

The basic data were obtained through classical procedures and consecrated mathematical models [21-23] shortly presented here:

The chloride procedure

The chloride level was determined titrimetrically according to AOAC [22].

This method employs the silver nitrate as a titrant and the potassium chromate as the end point indicator. The ion present in the sample is precipitated as white silver chloride:



About 5 mL of sample were pipetted into a conical flask and was titrated with 0.1 N silver nitrate (AgNO_3) using potassium chromate as indicator (K_2CrO_4). The appearance of a brown reddish precipitate marked the end point or the titre value which is noted. The chloride concentration (mg L^{-1}) was thus calculated as:

$$C_c = T_v \times 35.5 \quad (2)$$

where:

C_c is the chloride concentration and T_v is the titre value.

The nitrate procedure

The status of the nitrate was determined from the samples using the colorimetric method as adapted by AOAC [3]. Here, in the presence of the sodium salicylate, nitrate ions react to give a yellow sodium para-nitrosalicylate, which can be determined colorimetrically. Five milliliters of sodium salicylate were added to the sample and made up to 50 mL using distilled water. About 1 mL of this solution was pipetted into a test tube and 10 mL of distilled water added and allowed to stand for about 20 min then the absorbance was read at 415 nm in the spectrophotometer using distilled water as blank. The value was read off from the nitrate standard calibration graph. Then, the concentration of the nitrate ion (NO_3^-) in mg L^{-1} was calculated thus:

$$C_N = A_b \times G_{\text{mg}} \quad (3)$$

where:

C_N is the concentration of the nitrate ion,

A_b - the absorbance and

G_{mg} - the gradient of the standard nitrate calibration graph.

The sulfate procedure

The status of the sulfate was determined turbidimetrically according to AOAC [22]. This method is based on the fact that barium chloride (BaCl_2) precipitates sulfate (SO_4^{2-}) in its solution to form barium sulfate (BaSO_4) which is insoluble in water and the turbidity measured spectrometrically. Five milliliters of sample were made up

Table 1
CORRELATION BETWEEN
FUNCTIONS AND THE IR BAND
POSITION

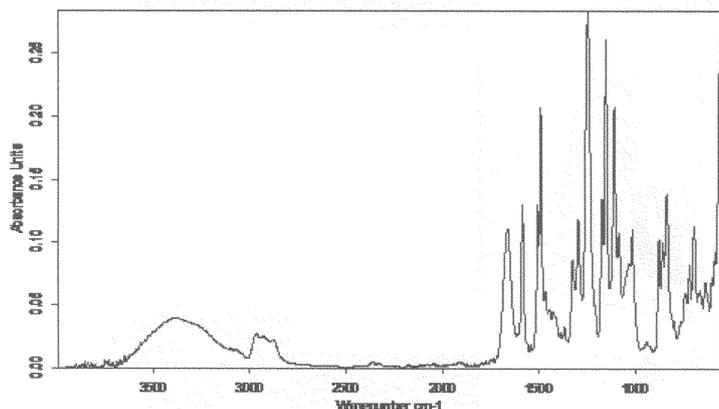


Fig.3. FT-IR spectrum for the composite membrane

to 50 mL using distilled water. Again, about 5mL of the filtrate were then pipetted into a test tube and a pinch of BaCl_2 crystal added which was allowed to stand for one and a half hours. The absorbance was then read off spectrometrically at a wavelength of 425 nm. The value was read off from the sulfate standard calibration graph. The concentration of the sulfate ion (SO_4^{2-}) in mg L^{-1} was thus calculated:

$$C_s = A_s \times G_{\text{sg}} \quad (4)$$

where:

C_s is the concentration of the sulfate ion,
 A_s is the absorbance and
 G_{sg} is the gradient from the standard sulfate calibration graph.

The phosphate procedure

The phosphate status was determined colorimetrically (AOAC) [22]. 0.5 g of the sample was weighed into a well washed and dried crucible. Five milliliters of sample were made up to 50 mL with distilled water. Approximately 5 mL of the diluted sample were pipetted into a test tube and 2 mL ammonium molybdate and 10N sulfuric acid solution were added. The mixture was stirred for 10 min. The absorbance was read at 420 nm using distilled water as blank. The standard solutions were treated as test samples. The calibration graph for the phosphate standard was used to read off the concentration of the phosphate:

$$C_p = A_p \times G_{\text{pg}} \quad (5)$$

where:

C_p is the concentration of the phosphate,
 A_p - the absorbance and
 G_{pg} - the gradient from the standard plot of the phosphate concentration.

The adsorption procedure

We prepared synthetic waters with 300 mg/L concentrations in nitrate, sulfate, chloride and phosphate. We used sodium nitrate, sodium sulfate, sodium chloride, monobasic sodium phosphate salts for nitrate, sulfate, chloride and phosphate ions. Then, the solutions were filtered by a composite membrane with 0.50 and 0.10 μm pore dimension and were analyzed after the filtration. All the experiments were made at room temperature.

Adsorption isotherms and analysis of equilibrium concentrations

The adsorption isotherms of nitrate, sulfate, chloride and phosphate were determined by means of batch experiments. Experimental data were fitted with several common adsorption isotherms: Langmuir, Freundlich and Temkin – Pyzhev.

During the adsorption study, the pH of the ions solutions was also measured. As sodium nitrate ions as well as sodium sulfate ions are strong acids and weak bases, the pH values of their solutions were weakly acid, from 5.5 to 4.5. The adsorption experiments started at these pH values. It is obvious that the pH in these solutions increased after the adsorption, which is caused by the ion exchange of the interlayer cations with the hydrogen ions.

Isotherm description

The Langmuir, Freundlich and Temkin – Pyzhev adsorption models were used for the mathematical description of the adsorption of four ions.

Langmuir equation:

$$\frac{1}{q_e} = \frac{1}{qm} + \frac{1}{qmK_L C_e} \quad (6)$$

where:

qm is the maximum capacity of adsorbent,
 K_L - the Langmuir adsorption equilibrium constant in dm^3/mg .
 C_e - the equilibrium capacity of the adsorbent

Freundlich equation:

$$\log q_e = \log K_F + \frac{1}{n} \times \log C_e \quad (7)$$

where:

K_F is the Freundlich constant in mg/g and
 n - the heterogeneity factor

Temkin – Pyzhev equation

$$\theta = \left(\frac{RT}{b}\right) \times \ln(KTC) \quad (8)$$

where:

Θ is the proportion of occupied sorption sites and is similar to the Freundlich equation in that it can only hold for small enough C .

It predicts that the total occupation ($\Theta = 1$) will occur at a finite equilibrium concentration C_{max} .

The Temkin equation is linearized to:

$$\Theta = A + B1 \ln(C) \quad (9)$$

where:

$$B1 = RT/b \text{ and } A = B1 \ln KT \quad (10)$$

However, in the present context in which the measured dependent variable is x/m , fitting the equation:

$$x/m = A' + B1' \ln(C) \quad (11)$$

implies the inclusion of a constant βT that represents the number of sorption sites per gramme of sorbent:

$$B1' = \beta TRT/b, A' = B1' \ln KT, \text{ and } b' = RT/B1' = b/\beta T. \quad (12)$$

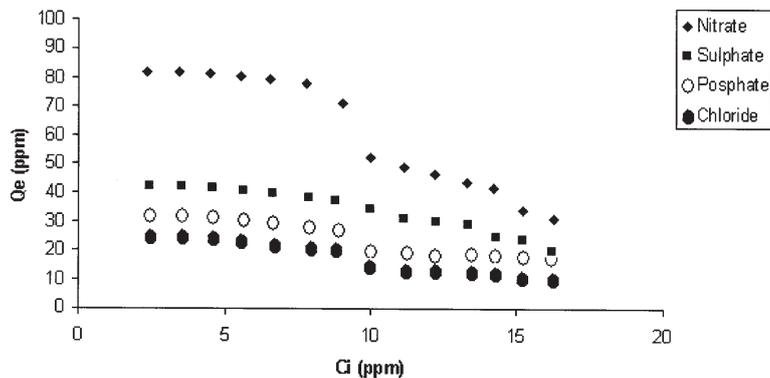


Fig.4. Influence of initial concentration of ions on the adsorption capacity at equilibrium

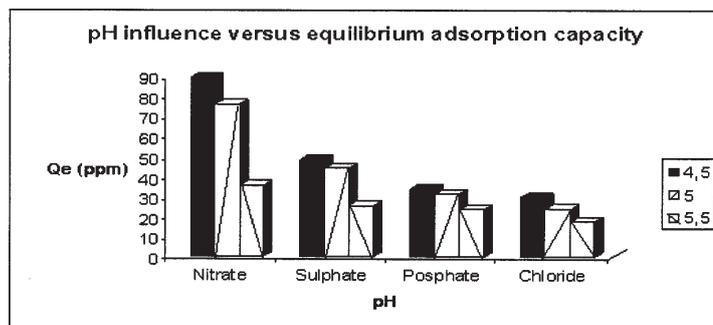


Fig. 5. Influence of initial solution pH on the equilibrium adsorption capacity of nitrate, sulfate, phosphate and chloride ions

Yet the number of sorption sites per gramme of sorbent is what is measured by the Langmuir parameter βL . βT may therefore be identified with βL which makes it possible to calculate the width of the range of the sorption energies: $b = \beta L b'$.

SIPS isotherm model

The SIPS isothermal model considers the adsorption capacity limited by the high concentration of ions in the solution. This model is similar to the Langmuir isotherm model, with the exception of a parameter representing heterogeneous system. The SIPS equation is:

$$Q_e = Q_{\max} \times \frac{(K_s \times C_e)^\gamma}{1 + (K_s \times C_e)^\gamma} \quad (13)$$

where:

- C_e – equilibrium concentration (ppm)
- Q_e – total capacity adsorbed at equilibrium (ppm)
- Q_{\max} – maximum adsorption capacity of the membrane
- K_s – adsorption constant (dissociation parameter)
- n - number of variable parameters (3)

The SIPS model reduces to the Langmuir's model when $\gamma = 1$.

The received linear plots of $1/q_e$ versus C_e and $\log q_e$ versus $\log C_e$ (fig. 6 and 7) prove the opportunity of application of the Langmuir and Freundlich equations for the description of the adsorption process of nitrate, phosphate, sulfate and chloride ions on composite membranes.

The influence of the ions initial concentration on the adsorption capacity at equilibrium was determined with the initial concentration of each ion studied equivalent to 300 ppm. If the initial concentration increases, the adsorption capacity remains constant, as can be seen from figure 4.

Based on the results there are significant differences between the four analyzed ions.

There was an increase in the high equilibrium adsorption capacity in the case of the nitrate ion.

The influence of the initial solution pH on the equilibrium adsorption capacity of the nitrate, sulfate, phosphate and

chloride ions reveals different membrane behaviors. (fig. 5).

As the pH of the initial solution decreases the equilibrium adsorption capacity increases. The best results were obtained for nitrate ions at pH = 4.5.

Adsorption isotherms

Langmuir, Freundlich and Temkin-Pyzhev were made at three different working temperatures: 288K, 308K and 328K.

Applying the regression line, it can be said from figure 6 that the nitrate ion shows the best results. This was achieved through composite membrane microfilter on 0.1 μm . The nitrate ion and phosphate ion are followed by sulfate ions and chloride ions. These claims were based on the values of the regression factor obtained from processing results using the Langmuir isotherm. The regression factors obtained for ions through the membrane of 0.1 μm presented values between 0.9987 for sulfate ion at a temperature of 328K and 0.9996 for a nitrate ion of 288K temperature.

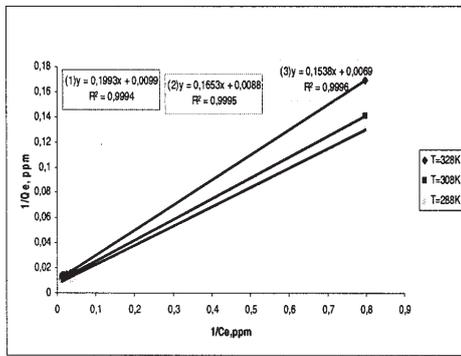
The size of 0.50 μm composite membrane was obtained with poor results for the nitrate, phosphate, chloride and sulfate ions which were held in smaller amounts. Regression factors showed values between 0.8815 to 0.9024 for the sulfate ion and nitrate ion.

From figure 7, it is to be noticed that the phosphate ion showed better results compared with other ions, obtained by microfiltration composite membrane with a pore size of 0.1 μm . In terms of regression factors obtained for Freundlich isotherms it can be said that the phosphate ion is followed by the nitrate, chloride and sulfate ions. The regression factors showed the following values:

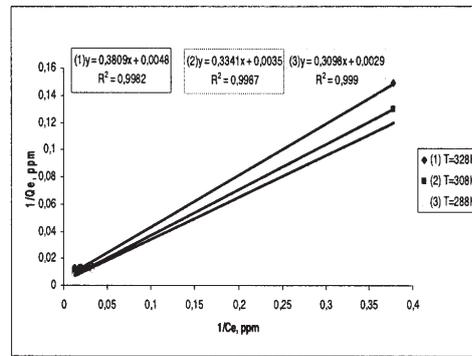
$$0.9978 \text{ (phosphate)} > 0.9931 \text{ (nitrate)} > 0.9912 \text{ (chlorides)} > 0.9897 \text{ (sulfate)}$$

For the composite membrane with a pore size of 0.5 μm poor results were obtained and these results were not taken into consideration.

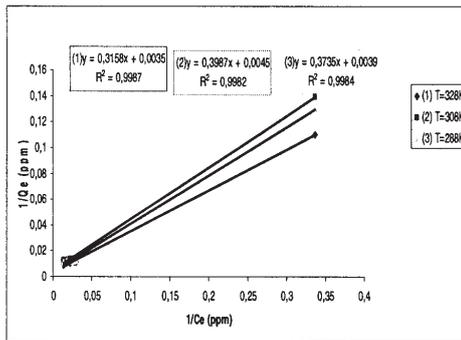
Using Temkin isotherm - Pyzhev better results were obtained for the chloride ion as compared to the other ions. Regression factors showed the following values:



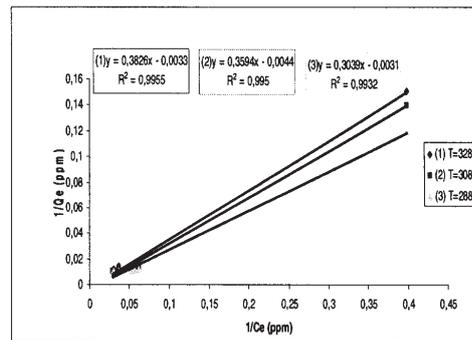
(I-a) nitrate



(I-b) phosphate

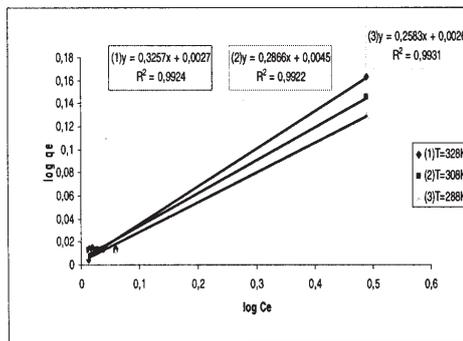


(I-c) sulfate

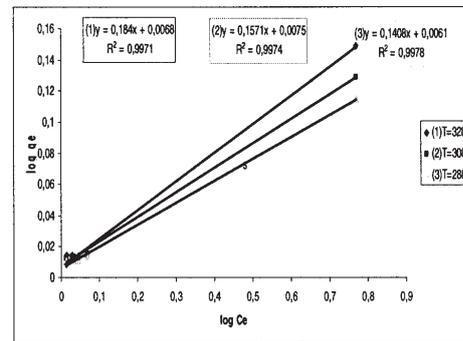


(I-d) chloride

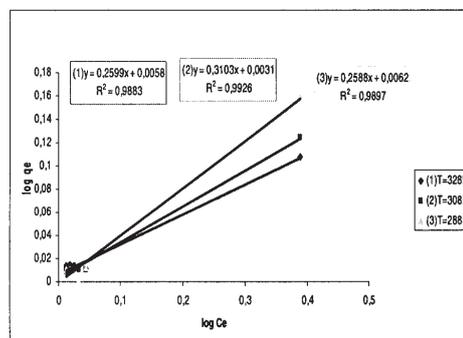
Fig. 6. Lagmuir linear representation model (I) for adsorption of ions nitrate (I-a), phosphate (I-b), sulfate (I-c) and chloride (I-d)



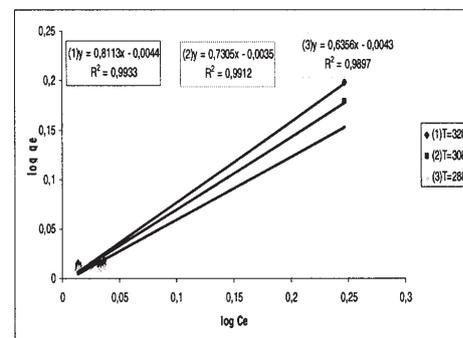
(II-a) nitrate



(II-b) phosphate



(II-c) sulfate



(II-d) chloride

Fig. 7. Freudlich linear representation model (II) for adsorption of ions nitrate (II-a), phosphate (II-b), sulfate (II-c) and chloride (II-d)

0.9974(chlorides) > 0.9960(phosphates) >
0.9913(sulfate) > 0.9824(nitrates)

The Temkin - Pyzhev isotherm is suitable to be used only for modeling the chloride ion and the phosphate ion. Chloride ions showed a regression factor of 0.9974 at an operating temperature of 308K and at a 4.5 working pH.

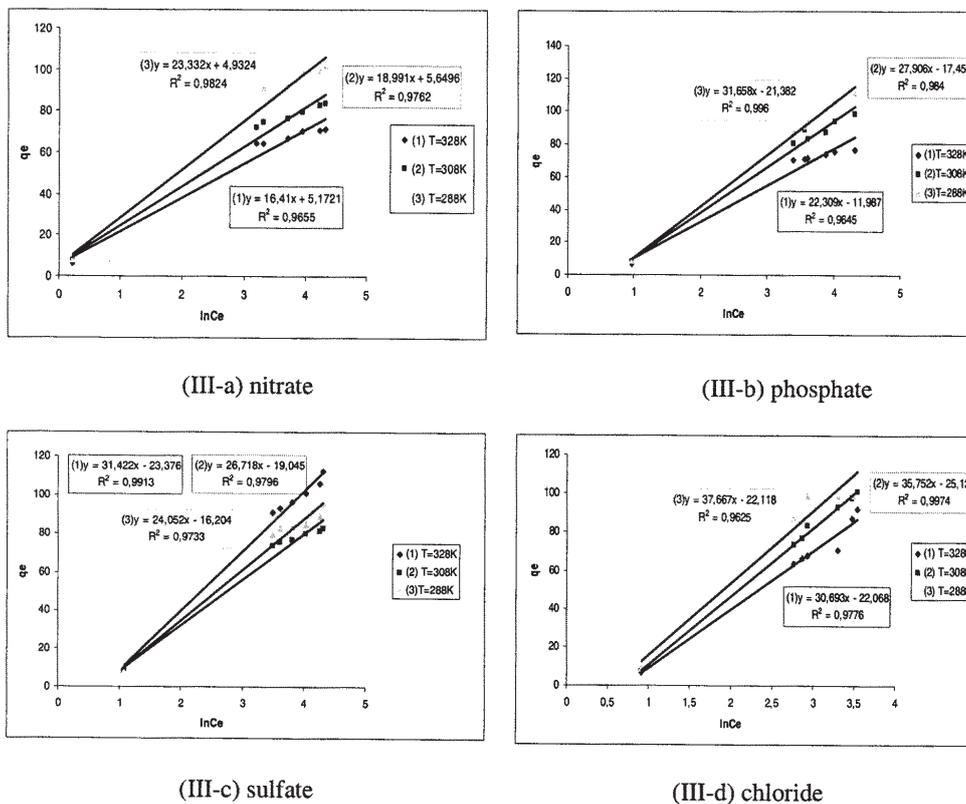


Fig. 8. Temkin - Pyzhev linear representation model (III) for adsorption of ions nitrate (III-a), phosphate (III-b), sulfate (III-c) and chloride (III-d)

Conclusions

In this study, the removal of nitrate, sulfate, chloride and phosphate ions, respectively, was achieved by adsorption using an adsorbent such as composite membranes with a pore diameter of 50 to 0.1 μm in dynamic conditions. The amount of ions retained on the unit mass of the adsorbent increases with the increasing pH of the initial solution. The highest values of the parameters of adsorption were obtained at pH 5.0. The ion adsorption behaviour of the nitrogen, phosphate, sulfate and chloride was influenced by temperature, which increases from 288K to 328K. The most representative results were obtained at a temperature of 288K for nitrate ions.

The use of a buffered medium (to maintain a constant pH value of the original solution) does not improve the efficiency of the adsorption process. The retention efficiency of the nitrate, sulfate, chloride or phosphate ions in the aqueous solution and the composite membrane depends on the membrane pore size. The amount of the nitrate, sulfate, phosphate or chloride ions retained per unit weight of the membrane increases with their initial concentration in the aqueous solution, given the concentration range studied.

FT-IR spectra recorded on membranes show that the adsorption process predominantly involved functional groups on the surface of the membrane, while the study of the interaction between these and the ions indicates most likely electrostatic-type interactions.

The retention of the nitrate, sulfate, chloride and phosphate ions in the aqueous solution or membrane is best described by the Langmuir isotherm. Chloride and phosphate ions results were represented well by the Temkin-Pyzhev isotherm.

This study demonstrated the potential use of the 0.1 μm size composite membrane for the removal of nitrate, phosphate, sulfate and chloride ions from wastewater. The highest adsorption capacity of the nitrate ion was recorded with a value of 87ppm. The results of other ions studied are influenced by temperature and the working pH . The

phosphate ions show the same behaviour for the adsorption capacity as the nitrate ions.

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References

- GU, B., KU, Y.K., JARDINE, P.M., Environ. Sci. Technol., 38(11), 2004, p. 3184.
- DRON, J., DODI, A., 190(1-3): 2011, p. 300.
- *** A.O.A.C., Standard Official Methods of Analysis. 13th Edn., Association of Official Analytical Chemists, Washington, DC., 1980, p: 41.
- BALLET, G. T., HAFIANE, A., DHAHBI, M., Journal of Membrane Science, 290, 2007, p. 164.
- AL-AMOUDI, A., LOVITT, R. W., Journal of Membrane Science, 303, 2007, p. 4.
- BHATNAGAR, A., KUMAR, E., SILLANPÄÄ, M., Chemical Engineering Journal, 163, 2010, p. 317.
- CLECIUS, A., DE LIMA, A., NASCIMENTO, R. F., DE SOUSA, F. F., FILHO, J.M., OLIVEIRA, A. C., Chemical Engineering Journal, 185-186, 2012, p.274.
- WOJNAROVITS, L., M.FOLDVARY, C.S., TAKACS, E., Radiation Physics and Chemistry 79, 2010, p. 848.
- POPESCU, G., NECHIFOR, G., ALBU, B. G., LUCA, N., Rev. Roum. Chim., 34(2), 1989, p. 577.
- NECHIFOR, G., ALBU, B., RATA, D., POPESCU, G., Rev. Chim. (Bucharest), 47, no. 3, 1996, p. 260.
- IVAN, A., GHINDEANU, D.L., DANCULESCU, V., RADUCU, A., NECHIFOR, A.C., Optoelectronics and Advanced Materials, Rapid Communications, 6(11-12), 2012, p. 1134.
- COROBEA, C., DONESCU, D., RADITOIU, S., VOICU, S. I., NECHIFOR, G., Rev. Chim. (Bucharest), 57, no. 9, 2006, p. 981.
- VOICU, S. I., ALDEA, F., NECHIFOR, A. C., Rev. Chim. (Bucharest), 61, no. 9, 2010, p. 817.
- NECHIFOR A.C., PASCU, D. E., NEAGU(PASCU), M., TRAISTARU, G.A., Rev. Chim. (Bucharest), 64, no. 4, 2013, p. 343.
- NECHIFOR, A.C., PANAIT, V., NAFTANAILA, L., BATALU, D., VOICU, S.I., Digest Journal of Nanomaterials and Biostructures, 8(2) , 2013, p. 875.

16. VOICU, S.I., STANCIU, N.D., NECHIFOR, A.C., VAIREANU, D.I., NECHIFOR, G., Romanian Journal of Information Science and Technology, 12(3), 2009, p. 410.
17. CUCIUREANU, A., BATRINESCU, G., BADEA, N.N., RADU, D. A., NECHIFOR, G., Mat. Plast., **47**, no. 4, 2010, pp.416.
18. NECHIFOR, G., VOICU, S.I., NECHIFOR, A.C., GAREA, S., Desalination, 241, 2009, p. 342.
19. BATRINESCU, G., CONSTANTIN, M.A., CUCIUREANU, A., NECHIFOR, G. , Polymer Engineering and Science, DOI: 10.1002/pen.23707, in press.
20. NECHIFOR, A.C., PASCU, D.-E., NEAGU, M., TRAISTARU, G.A., Rev. Chim. (Bucharest), **64**, no. 4, 2013, p. 343.
21. KOTER, S., SZCZEPA SKI, P., MATEESCU, M., NECHIFOR, G., BADALAU, L., KOTER, I., Separation and Purification Technology, 107, 2013, p. 135.
22. *** A.O.A.C., Standard Official Methods of Analysis. 13th Edn., Association of Official Analytical Chemists, Washington, DC., 1984.
23. LUCA, C., DUCA, AL., CRISAN, I., "Chimie analitica si analiza instrumentala", Ed. Didactica si Pedagogica, Bucuresti, 1983

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