MEMBRANE OPTIMIZATION SEPARATION PROCESS

STUDY OF ADSORPTION KINETICS OF SULFATE AND NITRATE IONS

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Abstract - In this paper we studied the kinetics adsorption of sulfate and nitrate ions on a cellulosic membrane. Adsorption studies were performed according to two parameters: pH and temperature solutions. Since the pseudo first order kinetics satisfactorily described the adsorption process Arrhenius equation was used to calculate apparent activation energy. Langmuir equation characterized very well the experimental data for both nitrate ion and sulfate ion. Maximum adsorption capacity for nitrate ion was higher compared to that of sulfate ion which means that cellulose membrane has a much higher adsorption capacity for nitrate ion than sulfate ion. The result of this study demonstrated that the potential use of cellulosic membranes for nitrate and sulfate ions removal from wastewater.

Keywords: nitrate anion, sulfate anion, cellulose membrane, adsorption studies

1. Introduction

Water is an essential resource for the living organisms, playing a proeminent part in the development processes. It is a fundamental source for humankind and other organisms' survival and for the economy's operation. The need of fresh water for mankind grows every year, at the same time with the growth of the polluted water quantity. Besides natural factors (floods, storms, landslides, air and soil natural pollution), techno-industrial development along with demographic explosion, raises much more dramatic the problem of deterioration of quality water through pollution. Physical and chemical pollution affect both surface and ground water. Physical pollution could be caused by: the overflow of insoluble materials (minerals, fiber, wood, etc.), radioactive contamination, and the overflow of waste hot water [1-3]. Sources of chemical pollution are spills of chemicals and industrial of waste water (heavy metals-

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processing plants, complex animals decrease, canneries, etc.), synthetic organic chemicals (pesticides, detergents, oils, phenols, dyes, oil, fertilizers, municipal waste, etc.) and many others.

Many countries, have passed innovative legislation regarding drinking water quality in order to reduce water pollution. Thus, in our country the law 458/2002 on drinking water quality parameters and indicators defines microbiological and chemical water's quality to the maximum permitted levels for each parameter and indicator in side.

In moderated amounts, the nitrate anion (NO_3^-) is a harmless constituent for food and water. It could become a polluted source for water, only if it has a high concentration that could be found in drinking water. One of the nitrate's source is considered to be the use of nitrogen fertilizers.

If the water contains high nitrate level, it may cause methemoglobinemia, known also as blue baby syndrome. In plants nitrates are used to satisfy nutrient requirements and may be accumulated in leaves and stems. In fact, harmful is the nitrite resulting from nitrate under certain condition. The body and abiotic reservoirs and galvanized pipes, where nitrates are reduced to nitrites, generate a secondary toxicity [7-8].

Another pollution source could be the sulfate anion (SO_4^{2-}). Sources of human activities cause also environmental problems by throwing huge ammounts of sulfates. The major and most important pollutans of sulfates and sulphites are the steel industry, metallurgy, mining pulp and paper, acid gas processing industries, burning of fossil fuels etc [9-10].

The objective of this study consisted of using a cellulose membrane to remove pre-established concentrations of sulfate and nitrate anions

2. Experimental part

2.1. Materials and methods

All reagents used in this study (Na_2SO_4, $NaNO_3$ and HCl, etc.) were purchased from Sigma Aldrich and were also used without further purification. Cellulose membrane was purchased from Merck having a pore size of 0.2µm. Synthetic solutions was prepared using the sulfate salts Na_2SO_4 and $NaNO_3$ for nitrates. Synthetic solutions (sulfates and nitrates) were filtered through a cellulose membrane of 0.2µm and then analyzed spectrophotometrically. The concentration of nitrate anions was determined by UV–VIS spectroscopy using the method with 1N HCl, and measuring the absorbance at a wavelength of 220 nm. The determination of anions sulfate content was also made by means of a spectrophotometrical method at a wavelength of 380 nm. Absorbance measurements were performed using a

JASCO V530 UV-Vis spectrophotometer. The pH value was measured on a Jenway pH meter 370 (portable pH meter).

3. Discussion and results

The kinetic study was conducted at three different temperatures 290, 313 and 333 K and pH 5.58±0.02 for a period of 0-48 h. Experimental results are shown in Fig. 2 for nitrate and Fig. 3 for sulfate.

The kinetic experiments were used to investigate the influence of the pH solution and the temperature in the adsorption rate for nitrate and sulfate anion on a cellulose membrane.

The anion concentration in solid phase (membrane) was calculated as difference between the mass of the initial anions obtained in the solution and the mass anions from the solution at a certain time reported, when the membrane was merged in the system.

The presented relation is:

$$a = \frac{V \cdot (C_i - C_c)}{m} \qquad (1)$$

Were:

a - sorption capacity at time t, the amount of anions retained per unit mass of membrane [meq/g];

V- volume of solution containing anions [L]

C_i and Cc –the initial concentration of the anion and curent concentration in the system [meq/g];

m – membrane mass [g].

Maximum adsorption capacity for nitrate ion is about 2.1 meq/g and for the sulfate ion is about 0.9 meq/g. Cellulose membrane has a much higher adsorption capacity for nitrate ion in comparison with the sulfate ions. Because Langmuir and Freundlich models are currently used to fit isotherms' adsorption, we have also used these models for our experimental data.

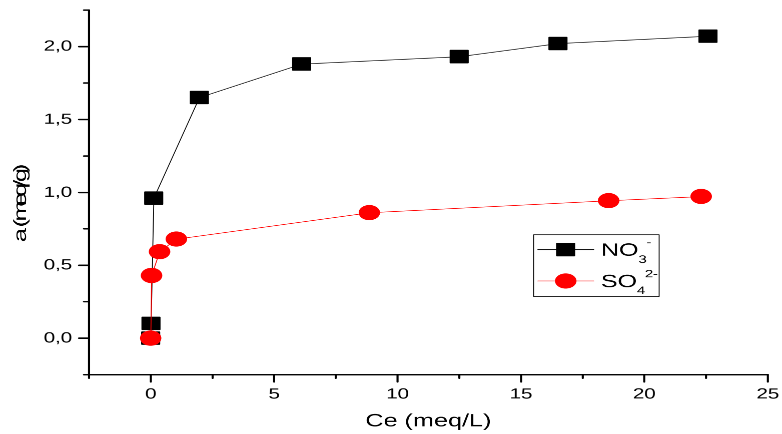

Fig.1. Adsorption isotherms for sulphate and nitrate anions

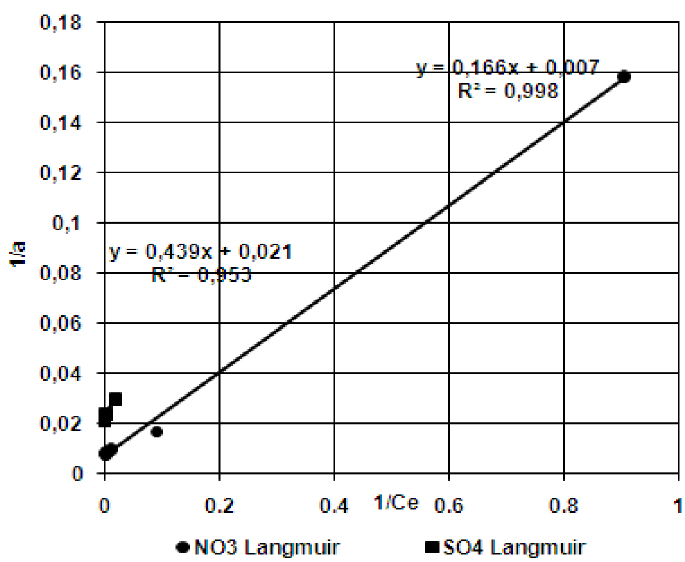

Fig.2. Liniarized Langmuir equations 1/a =f (1/C_e)

Langmuir equation defined very well the experimental data for both nitrate and sulfate anion, R^2 having values above 0.95, a thing which could be considered well enough for the adsorption of both anions (fig.2). For Freundlich model the regression coefficient has values of about 0.99 for sulfate and of 0.81 for nitrate. It means that this equation characterizes very well the sorption for the sulfate ion, instead for the nitrate ion, not being a characteristic adsorption (fig.3).

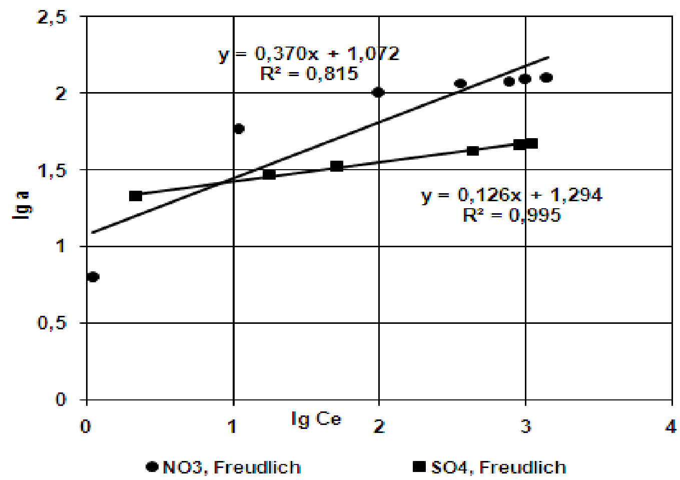

Fig. 3. Liniarized Freundlich equations log a = f(log C_e)

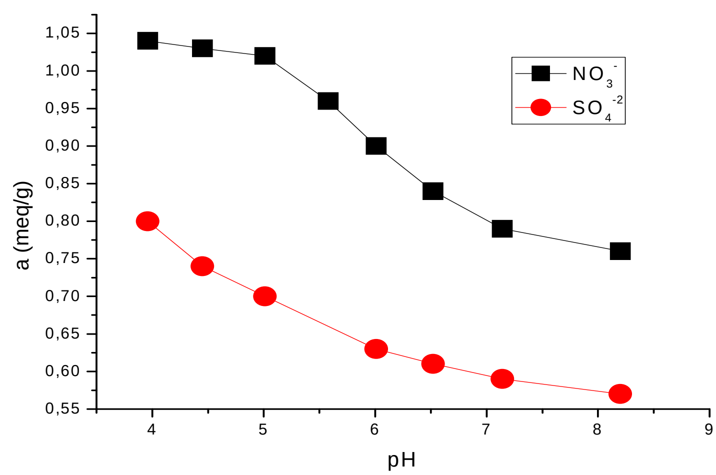

Fig.4. Variation of pH sorption capacity for the nitrate and sulphate anions

As it was obvious, the pH influences also the adsorption process: as it increases the adsorption capacity decreases (fig.4).

Since the pseudo first order kinetics satisfactorily described the adsorption process, Arrhenius equation was used to calculate apparent activation energy.

From Figs. 5 and 6 we can notice that as the temperature increases the adsorption rate increases so that, the time to achieve the concentration's equilibrium at a temperature of 290 K gets to 1400 minutes. At a higher temperature of 313K the necessary time to reach the equilibrium is of about 1000 minutes and, at the highest temperature of 333K are necessary about 600 minutes to reach the equilibrium.

These results could be explained by the fact that, as diffusion is an endothermic process, the temperature's increase leads to an increase of the diffusion rate of the adsorbate molecules across the external boundary layer and within the pores.

Since the pseudo first order kinetics describes correspondingly the sorption process, the Arrhenius equation can be used to calculate apparent activation energy for nitrate and sulfate anions adsorption on cellulose membrane with a pore size of 0.2 µm (equation no. 2).

$$K_1 = K_0 \cdot e^{-Ea/RT1} \tag{2}$$

Influence of temperature on adsorption kinetics is shown in Figs. 5 and 6 for the studied anions.

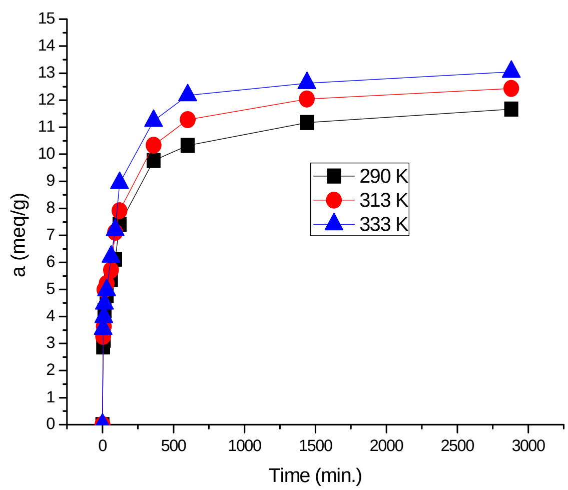

Fig. 5. Variation of concentration of anions nitrate adsorbed on cellulose membrane comparing with time at different temperatures

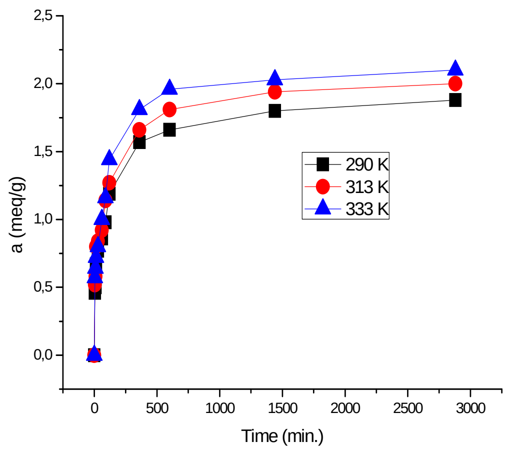

Fig. 6. Variation of concentration of anions sulfate adsorbed on cellulose membrane comparing with time at different temperatures

Table 1

The calculated values of activation energy for nitrate and sulfate anion

Sample	ΔT, K	Activation energy calculated, kcal/mol
NO_3^-	290 – 313 313 - 333	E_a = 1.0051 E_a = 1.1605
SO_4^{2-}	290 – 313 313 - 333	E_a = 1.0090 E_a = 0.4177

Examining the table 1, it can be said that the activation energy for anion nitrate for the two temperatures' values is greater than the activation energy for the anion sulfate.

6. Conclusions

A study of kinetics adsorption for sulfate and nitrate ions on cellulose membrane was made. Maximum adsorption capacity for nitrate ion is about 13.05 meq/g and for the sulfate ion is about 2.1 meq/g, which means that the cellulose membrane has a much higher adsorption capacity for nitrate ion than for the sulfate ion. Langmuir equation characterized very well experimental data both for the nitrate and the sulfate ions.

The Freundlich equation characterizes very well the adsorption of sulfate anion and not so well the adsorption of nitrate anion. These conclusions were made on the basis regression coefficient' results (0.81 for nitrate anion and 0.99 for sulfate anion).

The pH influences the adsorption process: as it increases the adsorption capacity decreases.

Temperature influences the time required to achieve equilibrium adsorption process, as it increases, the time required to achieve equilibrium decreases for both anions. Cellulose membrane with a pore size of 0.2μm is suitable to be used for retaining nitrate and sulfate ions from drinking water.

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R E F E R E N C E S

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