

# Study of Adsorption Kinetics of Sulphate and Chloride Ions on Two Types of Membrane

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*This study describes the adsorption kinetics studies for sulphate and chloride ions on the two types of membrane. We used two types of membranes: cellulosic and composite membranes. Composite membranes (polysulphones) were prepared in the laboratory, while cellulosic membranes are commercial membranes. All experiments were performed at ambient temperature. Adsorption studies followed three parameters: the equilibrium concentration, time and pH of the working solutions. We used three adsorption isotherms to get the results: SIPS, Langmuir and Redlich-Petterson. Maximum adsorption capacity on the membrane sulphate ion was higher than that of chloride ion. The results of this study have highlighted the potential use of composite membrane for the removal of sulphate ions from drinking water.*

*Keywords: sulphate, chloride, cellulosic membrane, composite membrane, adsorption kinetics*

Membranes are filter elements with submicron pore, allowing separation of complex mixtures. Depending on pore size, their surface membranes can retain particles in suspension so (microfiltration) and dissolved compounds (by ultrafiltration, nanofiltration, reverse osmosis).

Due to the advantages it shows the filter media from the classical (effective separation at ambient temperature, high productivity by selecting an optimal flow regime, ease of operation, etc.), membranes and membrane techniques currently known in the world, being also in a continuous development [1,2].

With conventional membranes, whose applicability is due to the effect of separating components of a mixture based on the difference between their molecular size there were obtained membranes with superior properties in the recognition and separation of chemical species in complex liquid media [2,3].

The ability of microfiltration membranes for processing salty solutions is partially based on the presence of chemical functional groups carrying positive or negative charges. This is an interesting technique in many aspects. The fouling mechanism of the charged nanofiltration membrane is represented by sieving and using the electrostatic properties of the membrane. In some cases, the membrane surface charge attracts the solution counter ions and the electrostatic interactions lead to considerable adsorption of particles on the membrane [4-9].

Sulphate and chloride are common constituents of many natural waters and wastewaters, which are present as dissolved compounds in seas and oceans or as insoluble salts. Industrial wastewaters are responsible for most anthropogenic emissions of sulphate and chloride into the environment. Domestic sewage typically contains between 20 and 500 mg/L sulphate and 30-600 mg/L chloride while certain industrial effluents may contain several thousands of milligrams per liter. The main source of sulphate and chloride in the laboratory wastewaters are the use of sulphuric acid and hydrochloric acid in many routine chemical analyses [10,11].

Sulphur compounds are also present in wastewaters used in the research activities, such as those from the pulp and paper industry, the food processing industry, and the photographic sector, among others.

The source of wastewater containing chloride ion is extensive, discharging from such as landfill, tanning, pickling, seafood canning. The high salt content in the wastewaters could cause the corrosion of waste pipe, or the agricultural wreck of crops by damage from salt [12,13].

The main processes for treating sulphate ion and chloride ion-bearing water are as follows: biological degradation, membrane filtration, adsorption and/or ion exchange and chemical precipitation [12,13].

The aim was to remove sulfate ions and chloride ions in drinking water. We used a synthetic solution of sulphate ions and chloride ions with a concentration of 200 ppm (200 µg/mL).

## Experimental part

### Reagent and apparatus

All reagents were of analytical grade.

Two types of membranes were used: a commercial membrane (light blue 0.20 µm pores) purchased from Merck - Germany and a composites (polysulphones) membrane obtained in the laboratory (Politehnic Institute of Bucharest laboratory) (light white 0.20 µm pores) [14-17].

He used a type UltiMate 3000 HPLC (Dionex, USA), with a detector UVD 3000, C18 column, 4mm, 3400 LPG-A gas pump, maximum pressure: 50 MPa, the column thermostat mode, complete chromatography software CHROMELON 6.0.

Mobile phase: 8mm 1mM Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub>, temperature 300C, flow rate 1.2 mL/min, injection volume 25 mL.

Before placing the sample in the autosampler vial, each sample was filtered through cellulose membrane and through composite membrane.

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### Methods of Analysis

There were prepared several solutions of various concentrations, were filtered through two types of membrane, by a specific microfiltration plant. We analyzed each solution obtained after microfiltration. For the working standard there were used solutions: NaCl for chloride ions and Na<sub>2</sub>SO<sub>4</sub> for sulfate ions.

There was prepared separately for each ion a solution with a concentration 200 ppm. The working solution pH varied in the range: 3.5 to 5.5. Flow velocity solutions membrane was 2 mL/min. We worked at room temperature T = 25°C. We worked at constant pressure (P = 720 mmHg). Maximum capacity (Q<sub>max</sub>) adsorption membrane was 250 ppm.

### Adsorption studies

There were retained sulphate and chloride ions on the membrane surface. Solutions were prepared with different concentrations of these ions and then were filtered through the cellulose and through the composite membranes. Microfiltration plant functioned discontinued and the samples were collected from 20 to 20 min and were analyzed to determine the final concentration of ions analyzed.

With the final concentration there was calculated the maximum amount of ions adsorbed on the membrane. On the membrane surface appeared Wan der Walls forces (weak forces of attraction) and ion-dipole type interactions.

The maximum amount of ions adsorbed Q<sub>e</sub> was calculated with the following formula:

$$Q_e = \frac{(C_0 - C_e) \times V}{m} \quad (1)$$

where :

- C<sup>o</sup> - initial ions concentration
- C<sup>e</sup> - equilibrium ions concentration
- V<sup>e</sup> - volume solution (100 mL)
- m - membrane weight (0.1g)

### SIPS isotherm model

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

where:

- C<sup>e</sup> - equilibrium concentration (ppm)
- Q<sub>e</sub> - the total capacity adsorbed at equilibrium (ppm)
- Q<sub>max</sub> - maximum adsorption capacity of the membrane (250ppm)
- K<sub>s</sub> - adsorption constant (dissociation parameter)
- n - number of variable parameters (3)

The SIPS model reduces to Langmuir's model when γ = 1.

$$Q_e = Q_{\max} \times \frac{(K_s \times C_e)^\gamma}{1 + (K_s \times C_e)^\gamma} \quad (2)$$

### Redlich -Peterson isotherm model

$$Q_e = \frac{Q_{\max} \times K_{RP} \times C_e}{1 + K_{RP} \times C_e \times \beta} \quad (3)$$

where:

- Q<sub>e</sub> = maximum adsorbed at equilibrium (ppm)
- Q<sub>max</sub> and K<sub>RP</sub> = isotherm constants

### Langmuir isotherm model

$$Q_e = \frac{q_0 \times b \times C_e}{(1 + b \times C_e)} \quad (4)$$

where:

Q<sub>e</sub> (ppm) maximum capacity adsorbed at equilibrium (ppm)

C<sub>e</sub> equilibrium concentration

q<sub>0</sub> (ppm) is the maximum amount per amount of membrane ion to form a single layer on the membrane surface

C<sub>e</sub> and b are constants for bonds formed between layers

### Results and discussions

The main results obtained are the following for sulphate and chloride ions filtered through the cellulose and composite membranes. The maximum amount adsorbed was analyzed by high performance liquid chromatography (HPLC).

With the adsorption isotherms (SIPS, Langmuir and Redlich-Peterson) there have been obtained mathematical modeling results.

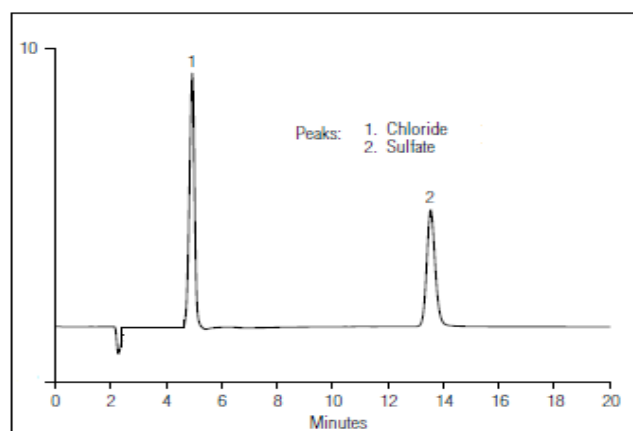


Fig.1. The chloride and sulphate ion chromatogram for 200ppm solution, obtained through the cellulose membranes

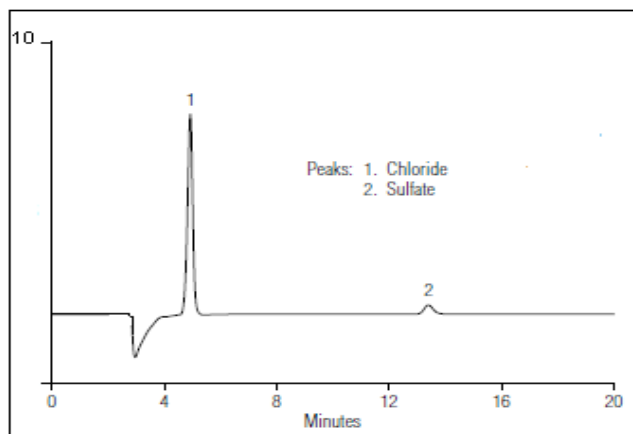


Fig.2. The chloride and sulphate ion chromatogram for 200ppm solution, obtained through the composite membrane

As it can be seen from the chromatograms 1 and 2, the sulphate ions through composite membranes are better retained in comparison with chloride ions.

The maximum capacity adsorbed (ppm) depending on time was graphically represented for each ion separately. The sulphate ion concentration achieved an equilibrium in 1450 min (fig. 3). The maximum adsorbed capacity was represented by isothermal SIPS and was of 15 mg/mL (150ppm).

In the case of chloride ion the period to achieve maximum concentration equilibrium was 24 min. The

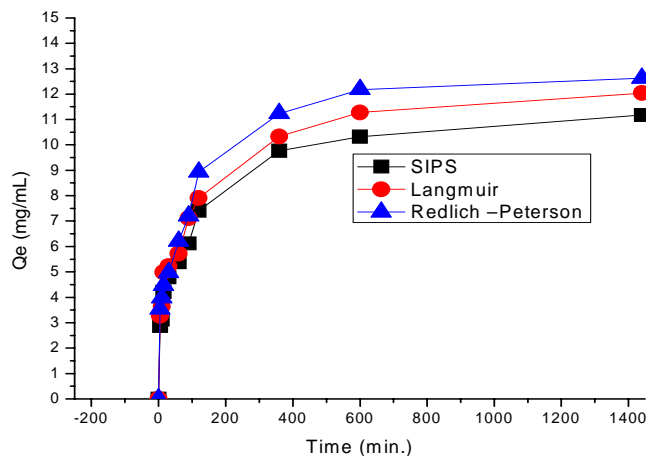


Fig.3. Graphic representation of the three isotherms for sulfate ion: adsorption capacity depending on time

Langmuir isotherm represented the adsorption process for chloride ion and was 9 mg/mL (90ppm).

The SIPS isotherm characterized very well the sulphate adsorption process, while Langmuir isotherm characterized well the adsorption process for chloride ion. The regression factor for isothermal SIPS was 0.9999 and for the Langmuir isotherm was 0.9995.

### Conclusions

The maximum adsorption capacity on sulphate ion through composite membrane was higher than that of chloride ion. The sulphate ions adsorption was favorable, while the chloride ions adsorption was difficult. With HPLC techniques there was demonstrated the quantity of sulphate ion retained on composite membrane. The sulphate ions were retained better on composite membrane instead of chloride ions, because the sulphate ions are not found in high concentrations in the final solution obtained after microfiltration.

The adsorption capacity was assessed using SIPS, Langmuir and Redlich-Peterson isotherms. It was noticed that the experimental data were very well fitted with the SIPS, Langmuir and Redlich Peterson equations. Isothermal SIPS was used successfully for the adsorption of sulphate ions, while the Langmuir isotherm was used for the adsorption of chloride ions. The results of this study have highlighted the potential use of composite membrane for removal of sulphate ions in low concentrations present in drinking water.

*Acknowledgements: Authors recognize the financial support from the European Social Fund through project POSDRU/89/1.5/S/63700, 2010-2013, 'Human Resource Development by Postdoctoral Research on Micro and Nanotechnologies' and also through project POSDRU/107/1.5/S/76813.*

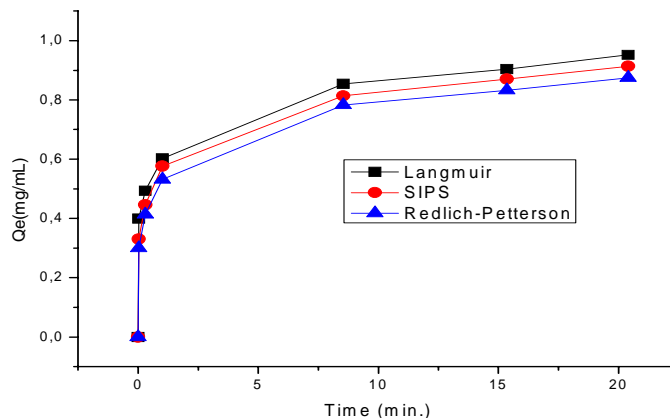


Fig.4. Graphic representation of the three isotherms for chloride ion: adsorption capacity depending on time

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Manuscript received: 16.01.2013