Optimization of Membrane Processes with Applications in Transport and Adsorption of Nitrate Ions

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In the present work, the optimization of membrane processes used for the adsorption of nitrate ion, present in different concentrations, in drinking water, was approached. The adsorption was studied by help of some composite membranes with pores dimensions of 1.0μm. The transport and adsorption were numerically modeled using COMSOL program and laboratory practice. The results presented in this paper represents a possible answer to many challenges in terms of numerical models for the transport of pollutants in drinking water, through a particular methodology for estimating the velocity and dispersion coefficients. The aqueous solution transport and adsorption were performed using the program COMSOL for surface (2D) and volume (3-D).

Keywords: membrane transport, diffusion process, adsorption, COMSOL program, dispersion coefficients

During research stage, utilization of modeling/simulation COMSOL program allows to pursuit the optimization of membrane processes for virtual testing of the different membrane materials behaviour. Characterization of materials/processes membrane gives us data or parameters required for both condition setting up and checking on the model/simulation performed [1-3].

Initially, it was analyzed the geometry that will be subject to modeling, and how finite element mesh underlies the process. The results presented discrete and smaller conclusive elements. This is a strong disadvantage, due to the volume calculation for the analysis and processing [4-6]. The time required for processing would become excessively large. Due to these considerations the process of modeling/simulation takes into account the definition of symmetric geometries (axially symmetric). Such reduction to an elementary geometry presents two main advantages, the reduction of both the computing power required (number of CPUs, memory size required) and the processing time for obtaining the results.

The mesh geometry was the next step and it aimed for the number of elements that will form the basis of modeling/simulation. This mesh could be made coarser or finer. A coarse mesh with a relatively small number of elements enables early analysis, with relatively low consumption [7-9]. A fine mesh involves a relatively large number of elements, resources and a longer time for processing.

Adsorption is used either to purify the products or to separate components [10-13]. The substances retained on a sorbent could be released by heating or by extraction, in such a way that they regain almost all initial properties and can be be retrieved.

This approach allows obtaining a series of results, which in some circumstances might be satisfactory. Meshing could be continued to an increased number of elements, leading to a better fineness, but implicitly it would use increased computing resources and longer time.

The aim of this work was the optimization of membrane processes applied to nitrate ions present in the drinking water using COMSOL program. The transport of aqueous solutions (nitrate ions) was analyzed applying two approaches: surface and volume. The experiments were conducted at two different temperatures 290K and 333K.

Experimental part

Equipment, materials and method

IR data acquisition was performed using a Spectrum100, spectrometer equipped with Spectrum for Windows v.5.01 software (UK). The absorbance measurements were performed using a Lambda 35 (UK) spectrophotometer. The pH measurements were done by the help of Jenway pH meter 370 (portable pH meter). SEM equipment was HITACHI S2600N.

Reagents and materials

All reagents used in this study ($NaNO_3$ and HCl) were purchased from Sigma Aldrich and were also used without further purification. For fused KBr disk preparation a potassium bromide IR spectral grade was used (Sigma Aldrich).

Nitrate method

Synthetic solutions were prepared using $NaNO_3$. The synthetic solutions were filtered through a 1.0 μm composite membrane [14-22] and then spectrophotometrically analyzed. The nitrate anion concentration was determined using the method with 1N HCl. The absorbance was measured at 220 nm wavelength.

Nitrate ion concentration (NO_3^-) was calculated with the formula:

$$C_{Nit} = Abs \times G_{sng} \quad (1)$$

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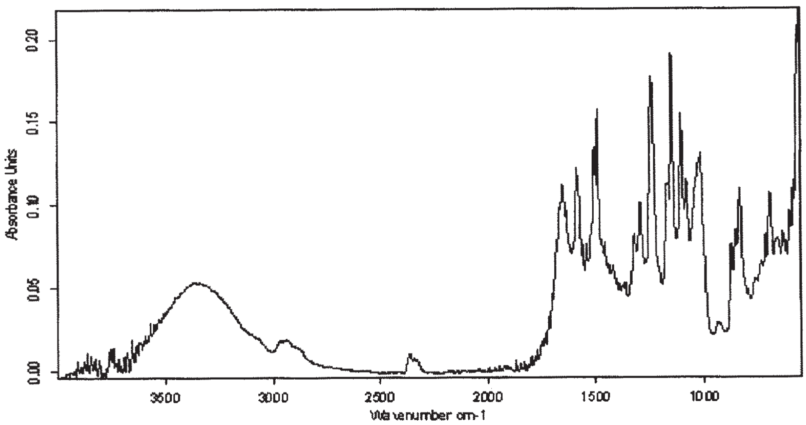


Fig. 1. FT-IR spectrum of the composite membrane with a pore size of 10 μm

Table 1
THE MAIN ABSORPTION BANDS IDENTIFIED FOR MEMBRANE COMPOSITE

Wavenumber, cm^{-1}	Assignment
1165	C-O
1104	C-C
1336	C-H
1500-1600	C=N
1000-1300	C=O
3000-3600	Hydrogen extended bonds (=N-H… N-, =N-H…O=)

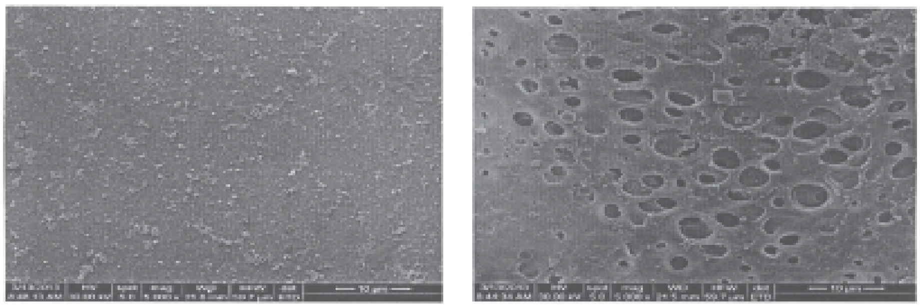


Fig.2 SEM image of 1.0 μm composite membrane a) top surface; b) bottom surface

where:

C_{Nit} is the nitrate anion concentration, in mg L^{-1};

Abs - the measured absorbance for nitrate anion;

G_{sng} - the gradient for the calibration standard of nitrate anion.

The concentration of nitrate ions was measured both at the beginning and at the end of the experiment.

Characterization of sorbent material (composite membrane)

Composite membrane was prepared in the laboratory of Analytical Chemistry and Environmental Engineering Department from the Politehnica University Bucharest by phase inversion process with chemical reaction [14-17]. For this study were chosen composite membranes obtained from polymeric solutions with 12% polysulfone – 1% polyaniline (PSf-PANI). The membranes structure (fig. 1) was characterized by infrared spectroscopy (FTIR). The morphology of used membrane samples prepared by immersion precipitation method [18-22], phase inversion with chemical reaction techniques relieved asymmetrical structure and 100-120 μm thickness, and 1.0 μm medium diameter of pores (fig. 2).

The range used for FT-IR technique was between 4000 - 400 cm^{-1}. The FT-IR technique identified the main absorption bands chemical bonds of the composite membrane as are presented in table 1.

From the SEM characterization performed it could be concluded that the composite membrane shows asymmetrical, cvasi-cylindrical pore of 1.0 μm medium size as can be seen in figures 2.

Transport and surface adsorption of aqueous solutions (2D)

The geometry considered in the model is shown in figure 3. In this case, the model involves a small cylindrical tube, and the surface is provided with an active area, that being the composite membrane on the adsorption of ions occurs. This is a simple example through which it could be

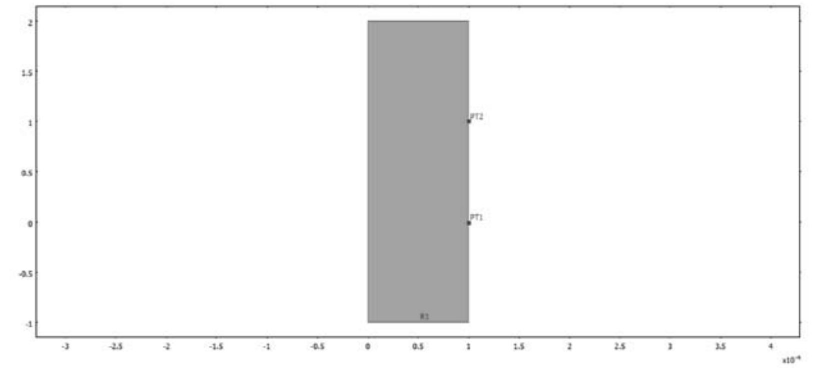


Fig.3. Elementary geometry for the transport and adsorption of nitrate ions

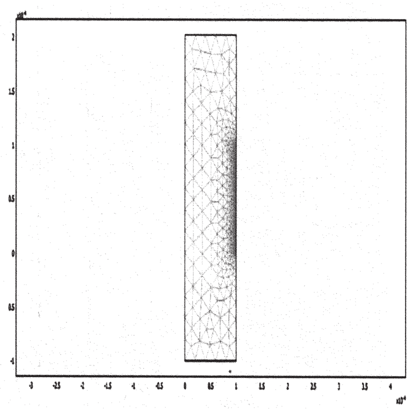


Fig. 4. Coarse discretization of the system

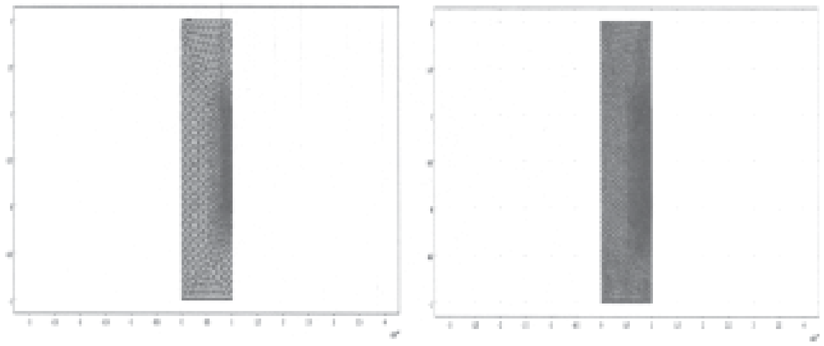


Fig.5. 2D representation of the discretized model with two degrees of fineness

Table 2
MODEL INPUT PARAMETERS

Element	Value	Description
ρ	1 [kg/m^3]	Density
c_0	200 [mol/m^3]	Initial concentration of nitrate anion
v_0	2 [cm/s]	Indoor Speed
D_s	1e^{-11} [m^2/s]	The diffusion coefficient for the membrane
D	1e^{-9} [m^2/s]	The diffusion coefficient of the anion aqueous solution
δ	4 [mm]	Channel width
L	20 [mm]	The length of the channel
M	10 [μm]	Size of composite membrane
ξ	1e^{-5} [Pa*s]	Viscosity

Table 3
BOUNDARY CONDITIONS APPLIED TO THE SYSTEM

Boundary conditions Navier Stokes		The boundary conditions for convection-diffusion	
input	$u \cdot n = v_0$, $p = p_1$	input	$c = c_0$
walls	$u=0$	normal gradient of the wall	$n \cdot (-D_S \nabla c_S) = 0$
output	$p = p_2$	Output	$n \cdot (-D\nabla c + cu) = -k_{ads} c(\theta_0 - c_S) + k_{des} c_S$

modeled the transport over surface, diffusion and adsorption of nitrate ions, as presented in figures 4 and 5.The geometry of the pattern is reduced to a suitable size, considering the in a rectangular geometry. This rectangle is the channel through which the transport and adsorption of the anions from studied aqueous solutions occur. On the surface side of the composite membrane channel is the adsorbed pollutant (nitrate ion) deposed as solid material.

In order to simulate the structures there was designed Comsol Multiphysics program (purchased from LABVIEW). In this model has been considered an aqueous solution of input data are presented in table 2, the pollutant containing nitrate ion.

The domain discretization was done with tetrahedral type finite elements, of 20 mm length, resulting in total discrete elements 1042, 4168 and 16672.

All elements of the core network are tetrahedral, while the boundary is triangular. These data were extracted from the mesh Statistics program menu COMSOL.

The boundary conditions applied to dynamic solution/ solvent (conditions Navier Stokes) and the convection-diffusion are presented in table 3. The pressure difference between inlet and outlet and the concentration of ions in solution, the input: $c_i = c_{i0}$, with i = 1, n. Applying the chosen geometry, it was possible to get data on membrane material and processes respectively, from the contour representation (fig. 6a and b) of the anions concentration.

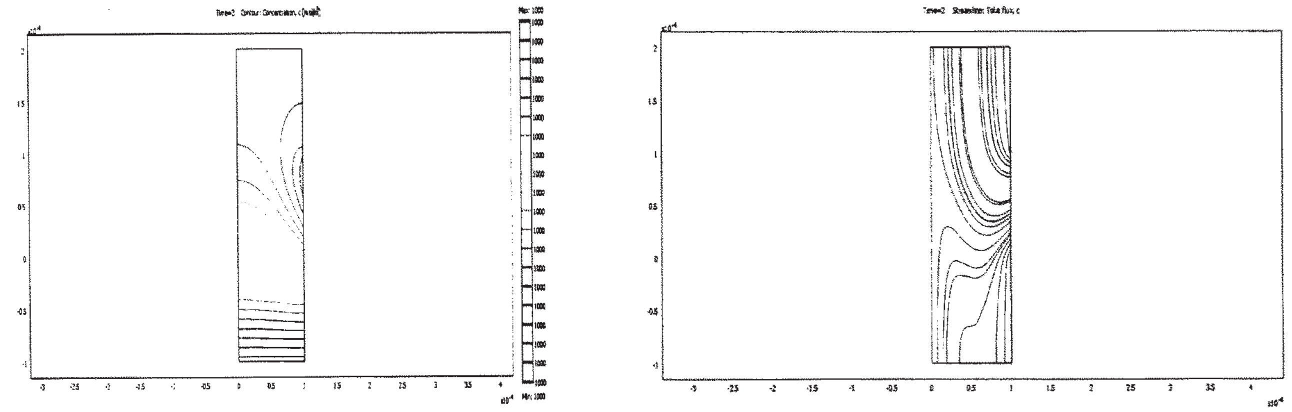
Taking into account the concentration required, the following analysis was done to assess the migration of nitrate ions in solution (the solution was introduced into the canal with nitrate anion). Figures 7a and 7b illustrate absorption and transport on the membrane in longitudinal section.

As it can be seen from the figures after the first few seconds it is established a quasi-permanent regime for migration of ions on the surface, as a result of the constant flow of the solution.

In the first period of time (2 s) the ions are attracted to the surface as already existing volume (channel), and also those which are due to the flow of the solution (fig. 7a and b.

Rapid movement of ions on the surface of the entrance membrane is due to the speed of transport of ions on the face side of the channel.

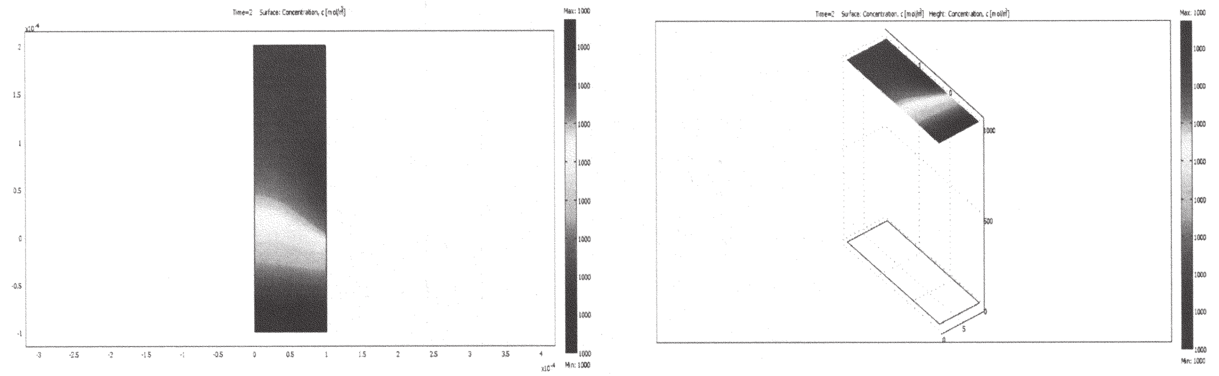
It can be seen that the response is very fast and reach a state of equilibrium of the solution within a very short time of about 2 min and the concentration of the adsorbed species c_S have a spatial distribution and have greater value for the membrane than at the beginning of the process, this is particularly due to the phenomenon of diffusion.



a)The concentration contour representation (2D)

b) Representation of the total flow of solution by contour lines (2D)

Fig.6. Constant value line distribution (outline) of concentration [mol/m^3] in the channel at t = 2min



a)Adsorption and transport on the membrane surface (2D): concentration distribution on the channel and in the membrane region [mol/m^3]

b) Adsorption and transport on the membrane surface (3D): concentration distribution on the channel and in the membrane region [mol/m^3]

Fig.7. Adsorption and transport on the membrane surface: concentration distribution on the channel and in the membrane region

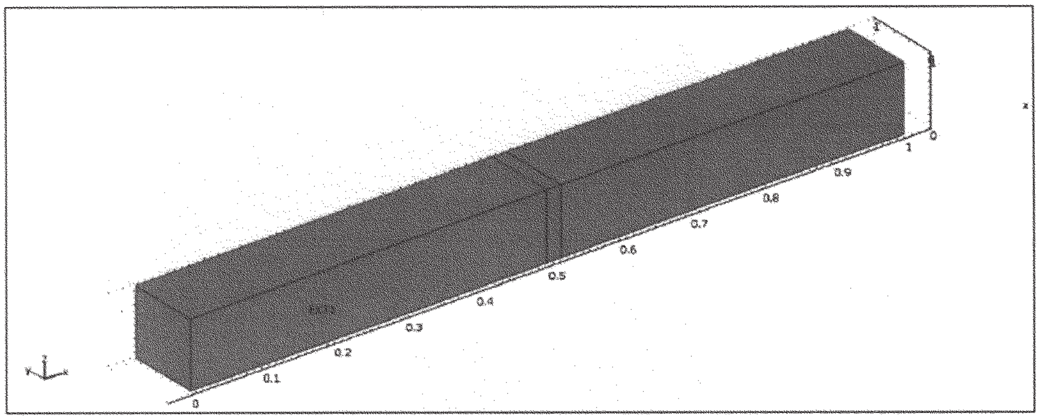


Fig. 8. The system geometry (3D)

The results show that a difference of pressure between input and output is sufficient for the adsorption of 99% of each ions species in the membrane.

Transport and surface adsorption of aqueous solutions (3D)

This model is used for convection-diffusion equations and Navier-Stockes dynamic conditions to describe the process. Geometric model for analysis is shown in (fig. 8).

Figures 9a and b show the transport of studied anions in an established concentration and *p*H. The filtering system is made up of a cylindrical tube and in the middle of this system was placed the composite membrane.

Figures 10a and b shows the distribution of anions concentration adsorbed on the membrane. In graphical representation, the intense left colour does not necessarily indicate that in this microchannel the concentration is zero but the fact that in these regions, the value of the concentration is much lower than the maximum concentration, which is represented by the intense right colour). It is observed that ions are adsorbed on the composite membrane and the process is more intense in the central region of the membrane.

This study demonstrated the possibility of using the composite membrane with 10μm size, for the removal of nitrate ions from drinking water. At 290K temperature, the membrane permeability is lower, as it can be seen from the figure 11.

Substances retained on a sorbent could be released by heating or by extraction, then regains almost all initial properties and can be reused.

The amount of nitrate ions retained per unit weight of the membrane increases with increasing initial concentration of the aqueous solution within the concentration range studied.

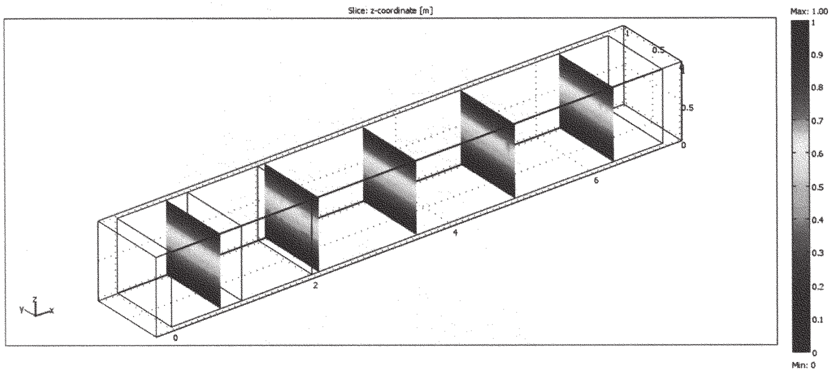


Fig. 9a. Concentration distribution representation of ion species at t=10s (iso-surfaces) (3D) : concentration distribution [mol/m^3]

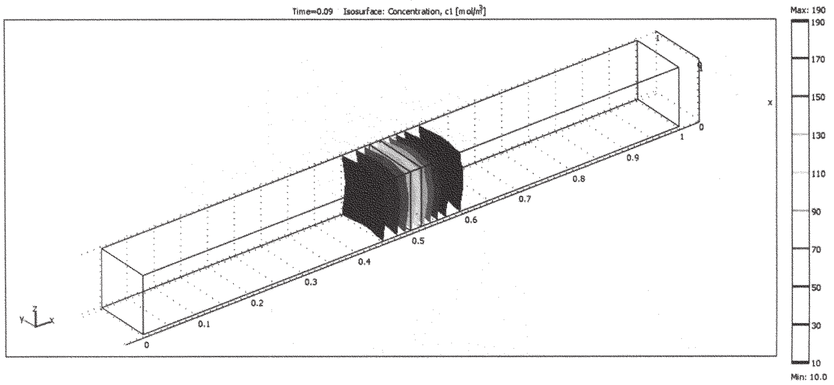


Fig. 9b. Concentration distribution representation of ion species at t=40s (iso-surfaces) (3D) : concentration distribution [mol/m^3]

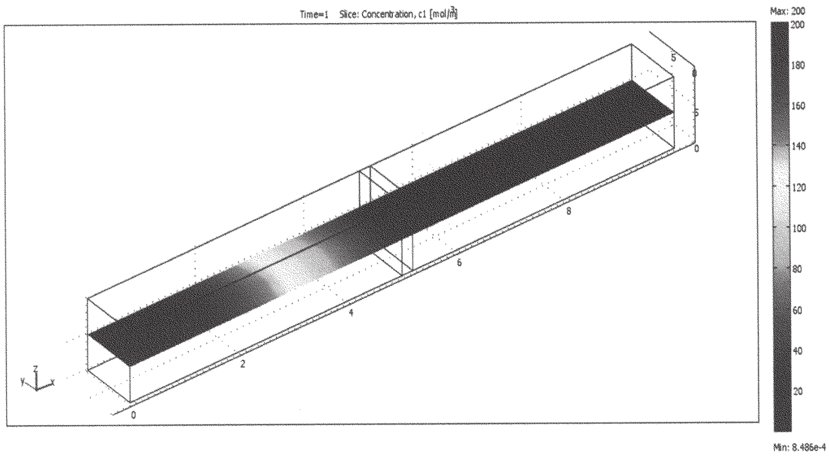


Fig. 10a. Transport of ions nitrate, sulfate, phosphate and chloride in volume (3D): concentration distribution [mol/m^3]

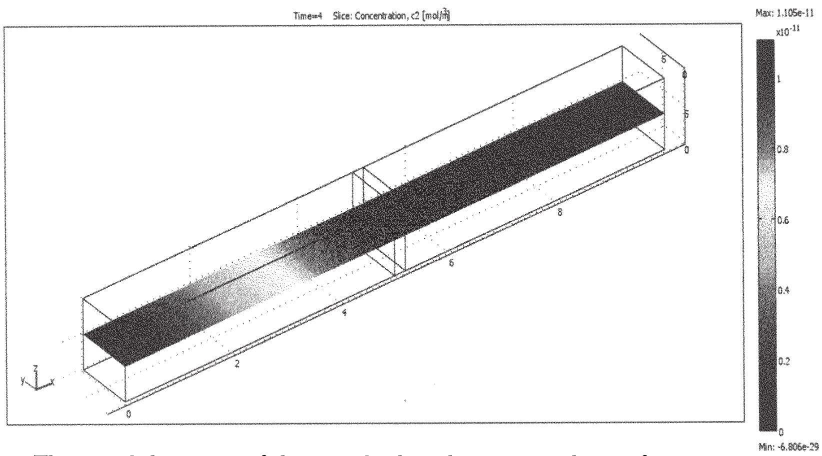


Fig. 10b. Transport of ions nitrate, sulfate, phosphate and chloride in volume (3D): concentration distribution [mol/m^3]

The models are useful to study the phenomenology of pollutant transport, the interdependence of parameters and could be a support for the development of new tools to predict and count the effects of the pollutants discharged into drinking waters. In this respect, numerical models could be used to build active systems to neutralize pollutants in drinking water in real time.

Package software design and simulation - COMSOL, is particularly useful in the development of membrane materials, as it could be used for virtual testing. Throught the information provided it is possible to predict the behaviour of the material in different working conditions imposed by changing of the input parameters, namely the boundary conditions.

COMSOL program which could be used for the virtual testing can be an useful tool in research, including reducing the number of experiments required in the development of membrane materials. At same time it allows the development of specific models for a number of applications, namely for the specific working conditions.

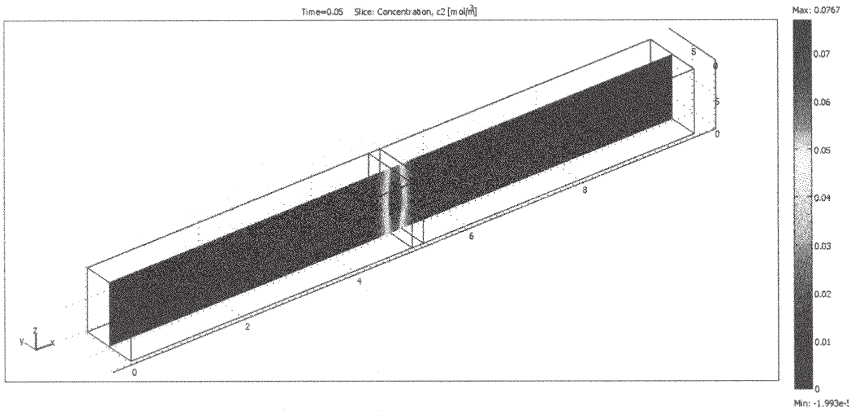


Fig.11. Concentration distribution for the anions adsorbed on the membrane [mol/m³] (3D)

Developing complex models present challenges for future research.

Conclusions

In this paper we demonstrated the possibility of using COMSOL program for optimization of membrane processes and the transport and diffusion of pollutants in drinking water.

The results of simulation show that a quasi-permanent regime is established for the migration of ions in volume due to the applied potential. The interactions of these ions studied are probable most likely electrostatic type interactions, described by FT-IR spectra for composite membrane.

Parameters characterizing the transport of pollutants into drinking water are variable over space coordinates. Trying to include all variables in 3D space could lead to very complex models to develop and to assess the difficulties relating to the availability of experimental data.

The alternative is the use of 1D and 2D models that are also able to represent the model system in a satisfactory manner. In general, 1D model is easier to use and all the data needed to build and evaluate this type of models are available at lower experimental costs compared with 2D or 3D data. A 2D model represents several important features of the system, but it requires more data.

Models that describe a particular case were designed for the pollutants and for the transport of the pollutants into drinking water.

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