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Effect of temperature on the adsorption of fluorides, nitrates and sulfates onto modified AFN membrane

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ABSTRACT

Removal of fluoride, nitrate and sulfate ions from aqueous solutions is the principal objective of many studies concerning water treatment. In this work the modified AFN anion exchange membrane was evaluated for the removal of F^-, NO_3^-, and SO_4^{2-} anions from aqueous solution. The AFN membrane was modified by adsorption of polyethyleneimine (PEI) on its surface. Surface morphology of the modified AFN membrane was compared to the unmodified one using scanning electron microscopy (SEM). The sorption isotherms for fluoride, nitrate and sulfate ions on the modified AFN membrane were investigated in the range (0.05–1 mol L^{-1}) at 283, 288, 298, 303 and 313 K. Experimental data were analyzed using the Langmuir and Dubinin–Astakhov adsorption models. The adsorption parameters of the studied models were determined by non-linear regression. The equilibrium data obtained in this study were found to follow Dubinin–Astakhov adsorption isotherm. The effect of temperature on the adsorption of fluorides, nitrates and sulfates has been attempted. It was found that the adsorption of fluoride and sulfate ions increases with rise in temperature. Thermodynamic parameters of the adsorption process have been determined. Obtained results show that adsorption of fluoride and sulfate ions onto the modified AFN membrane is an endothermic sorption process while it is an exothermic process for the nitrate adsorption. The values suggest the affinity order for the modified AFN membrane. At 283K and 288K the affinity order is: $NO_3^- > F^- > SO_4^{2-}$ and $F^- > NO_3^- > SO_4^{2-}$ at 298 K, 303 K and 313 K.

Keywords: Modified AFN membrane; Adsorption isotherm models; Nonlinear regression; Polyethyleneimine (PEI); Thermodynamic parameters

1. Introduction

Water contains various pollutants and several other substances are dissolved in it. Their concentration is useful for human body but in a specific limit. Fluoride, nitrate and sulfate are one of these pollutants in water and they have been recognized as one of the serious problems worldwide [1–4].

Several technologies have been proposed, in water treatment, for ions removal including ion exchange, reverse osmosis, nanofiltration, microbiological denitrification adsorption and chemical and biological methods etc . . . [5–12]. Among them adsorption seems to be a more attractive method for fluoride, nitrate and sulfate removal in terms of cost, simplicity of design and operation. Different adsorbents have been tested for the removals of these ions from water. Adsorption on ion exchangers are considered to be highly stable and hence considered as one of the most promising adsorbents [4,10,13].

Extensive researches [14–20] have been done to study the adsorption of ions onto ion exchange resins and membranes. It was found that removal of ions using resins and membranes has a good potential for water treatment.

In fact, Sachin et al. [13] studied removal of nitrate by adsorption onto anion exchange Indion NSSR resin. Equilibrium isotherms were fitted using Langmuir, Freundlich and Dubinin-Radushkevich models. Obtained results showed that nitrate removal had followed the Langmuir

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adsorption isotherm and that Indion NSSR resin is an effective adsorbent for nitrate removal.

Removal of nitrate anions from aqueous solution by adsorption on Amberlite IRA 400 anion exchange resin has been also studied by Chabani et al. [21], they found that the studied resin is effective for the removal of nitrate.

Haghsheno et al. [10] investigated the removal of sulfate anions from wastewater by adsorption on Lewatit K 6362 resin. Obtained results showed that isothermal data best fit Freundlich adsorption model.

Recently, Stefan et al. [22] studied the adsorption of nitrate and sulfate ions onto Purolite A-520E anion exchange resin, and experimental data were analyzed using Langmuir and Freundlich model. Results showed that equilibrium data fitted very well with the Langmuir isotherm for nitrates and with the Freudlich isotherm for sulfates. It was also found that the Purolite A-520E resin is more selective for nitrate ions than sulfates. The adsorption capacity of nitrates on Purolite A-520E is higher than that of sulfate ions.

Samadi et al. [4] investigated equilibrium and kinetic parameters for the removal of fluoride ions from water by adsorption on anion exchange resin. They found that the removal of fluoride was high at natural pH and was improved for increasing contact time and adsorbent dosage.

On the other hand, removal of ions from water by adsorption on ion exchange membranes has been developed by different authors [14,16,19,20,23,24]. In fact, adsorption onto cation exchange membranes P81 and anion exchange membranes DE81 have been used by Lin and Suen [24] for the separation of proteins. Obtained results indicate that the adsorption of proteins onto ion exchange membranes is a heterogeneous process.

Furthermore, removal of natural organic matter by adsorption on ion exchange membrane has been realized by Do Hee et al. [23] because it has been found to be a problematic solute for the electrodialysis. In another report Chia-Hung et al. [14] analyzed the removal of anionic reactive dye Cibacron blue 3GA and Cibacron red 3BA by adsorption on anion exchange membranes. Removal of cationic dye from water by adsorption on cation exchange membrane has been also studied [16].

In previous study, Hannachi et al. [19,20] investigated the adsorption of fluoride, nitrate and sulfate ions onto AFN and AMX anion exchange membranes at various temperatures. It was found that the AFN membrane has more affinity for nitrate than fluoride than sulfate at 283 K. At 298 K and 313 K the affinity order for the AFN membrane is $NO_3^- > SO_4^{2-} > F^-$.

In our previous investigation [25] attempts were made to study the adsorption of fluoride, nitrate and sulfate ions on the AFN membrane. The sorption isotherms for the studied anions on the AFN membrane were studied in the range of 0.05–1 mol L^{-1} at 298 K. Experimental data were analyzed using Langmuir, Dubinin–Astakhov and Redlich–Peterson adsorption models and obtained results were found to best fit Langmuir adsorption isotherm. It was found that, at 298 K, the AFN membrane has more affinity for nitrates than sulfates than fluorides. To improve their selectivity towards anions, the modification of AFN membrane surface by adsorption of polyethyleneimine (PEI) has been attempted. Adsorption parameters values of the studied models were determined for the modified AFN membrane at 298 K. Results showed that the modified AFN membrane had higher adsorption capacities for fluoride and nitrate than the unmodified membrane. In fact, removal of fluoride and nitrate ions by adsorption on the modified AFN membrane was more effective than the adsorption on the unmodified one.

Therefore the main objective of this investigate is to study the effect of temperature (from 298 to 313K) on the adsorption of fluoride, nitrate and sulfate ions on the modified AFN membrane. The adsorption of the studied ions was investigated through the most commonly used adsorption isotherms which have been modeled by: Langmuir and Dubinin–Astakhov isotherms. The adsorption parameters of the experimental models were determined from the non-linear regression. The thermodynamic parameters for the adsorption process will be studied and discussed.

2. Theory of equilibrium isotherm models

Adsorption isotherm models are applied for fitting the data to examine the relationship between the adsorbed amount of anion, q_e (mmol g^{-1}), and the amount of anions left in equilibrium solution, C_e (mmol L^{-1}). They give information about the distribution of the adsorbate anions between the solution and the membrane phases when the adsorption process reaches the equilibrium state [26]. In this investigation, the experimental data obtained during equilibrium study have been fitted to different adsorption isotherm equations such as Langmuir [27] and Dubinin–Astakhov [2] models to discuss the equilibrium characteristics of the adsorption process.

The Langmuir model is one of the most common isotherm models used to describe the adsorption equilibrium. It assumes that adsorption occurs onto a homogeneous surface by monolayer sorption without interaction between adsorbed species. The nonlinear form of the Langmuir isotherm is commonly expressed as:

$$q_e = \frac{q_0 \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \tag{1}$$

where q_o is the maximum adsorption capacity (mmol g^{-1}), and K_L is the Langmuir constant adsorption related to the free energy of adsorption (L mol^{-1}).

Dubinin–Astakhov (D-A) model is based in the Polanyi adsorption potential theory (ε), given by Eq. (4), which defines an adsorption potential and is related to the adsorption energy (E). It is also used in order to distinguish between physical and chemical adsorption processes. The nonlinear D-A equation is given by:

$$q_e = q_0 \cdot exp\left[-\left(\frac{\varepsilon}{\sqrt{2}.E}\right)^{n_D}\right] \tag{2}$$

where n_D is the homogeneity parameter

$$\varepsilon = \mathrm{R}TLn\left(1 + \frac{1}{C_e}\right) \tag{3}$$

3. Experimental procedure

3.1. AFN membrane characteristics and surface modification

The AFN membrane experimented in this investigation is a commercial product provided by Tokuyama Soda. The base polymer of this membrane is styrene and divinyl benzene, and the ionic fixed sites are quaternary ammonium groups. The main characteristic of the AFN membranes are as follows: ion exchange capacity of 2–3.5 meq g^{-1}, humidity percentage in Cl^- form of 45.35% and thickness of 0.15– 0.2 mm.

Before experiments the membrane was acid conditioned with 0.1 mol L^{-1} HNO_3 and HCl several times to remove impurity from the membrane.

The AFN membrane surface was modified by adsorption of polyethyleneimine (PEI). The methodology used to modify the AFN membrane has been described in our previous study [25].

3.2. Batch adsorption experiments

Adsorption isotherms of F^-, NO_3^-, and SO_4^{2-} were obtained at 283, 288, 298, 303 and 313 K. Different samples of the modified AFN membrane (25 cm^2) in Cl^- form were immersed in fluoride, nitrate or sulfate ions solutions at different initial concentrations (from 0.05 to 1 mol L^{-1}). The solution and the modified membrane were maintained at a fixed temperature under vigorous stirring, until equilibrium was achieved.

At equilibrium, ion chromatography using a Metrohm 761 compact IC with conductivity detector and chemical suppression was used to determine the anions concentration in the solution. The adsorption capacity q_e (mmol g^{-1}) of the membrane was determined using the following equation:

$$q_e = \left(C_0 - C_e\right) \cdot \frac{V}{m} \tag{4}$$

where C_0 (mmol L^{-1}) and C_e (mmol L^{-1}) are the initial anion concentration and the concentration at equilibrium respectively, V the volume of solution and m the mass adsorbent.

4. Results and discussion

4.1. Characterization of the modified membrane

As shown in Fig. 1, which presents the commercial and the modified AFN membrane, after the membrane modification by adsorption of polyethyleneimine (PEI) the membrane color changed and became dark brown.

To further verify the differences between these two membranes, the membrane surface morphology was observed by SEM. A scanning electron microscope (JOEL JSM 5400 Scanning Microscope) with an accelerating voltage of 15 kV was used. It was found from obtained SEM images shown in Fig. 2 that after AFN membrane surface modification the morphology of the membrane was significantly affected and forms a flat membrane. Modified membrane looks like a sticky-like surface. This form confirms the presence of polyethyleneimine on the membrane surface [28].

4.2. Effect of temperature on the adsorption of F^-, NO_3^-, and SO_4^{2-} ions

Adsorption isotherms for fluoride, nitrate and sulfate at 283, 288, 298, 303 and 313 K are shown in Fig. 3. Obtained results show that for the modified AFN membrane, the adsorption capacities, q_e, of F^-, NO_3^-, and SO_4^{2-} increased as the equilibrium concentrations of these anions in solution increased, progressively saturating the membrane surface. It can be also seen that the rise in temperature was accompanied by an increase in adsorption capacity of the modified AFN membrane for fluorides and sulfates adsorption while it decreases for the nitrate adsorption. These results confirmed the preference of high temperature for the adsorption of fluorides and sulfates.

The characteristic parameters, for the adsorption of F^-, NO_3^-, and SO_4^{2-} on the modified AFN membrane were determined from the non-linear regression using the OriginPro software. The different parameters of the Langmuir and D-A models along with regression coefficients (R^2) obtained from the non-linear regression are presented, respectively, in Tables 1 and 2.

The value of the Langmuir constant, K_L, reflects the affinity of the membrane towards studied anions. Results

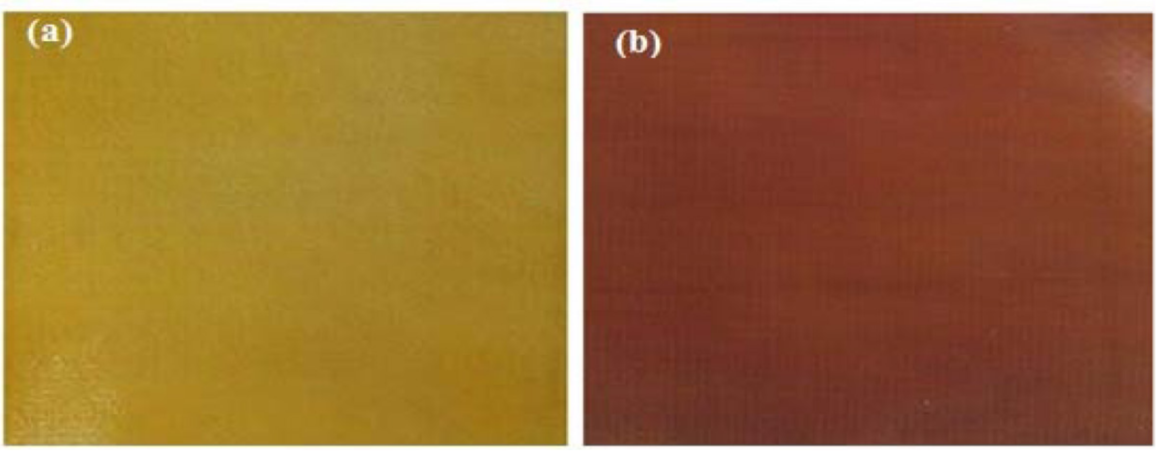

Fig. 1. Images of (a) the unmodified and (b) the modified AFN membrane.

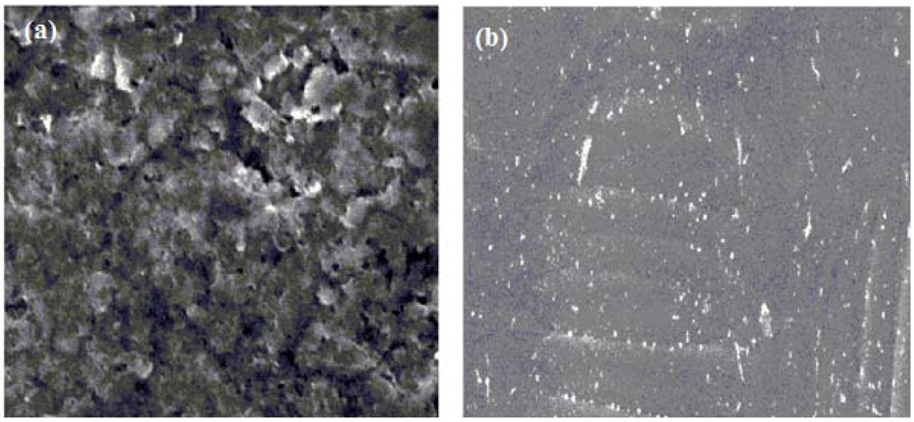

Fig. 2. SEM images of (a) the unmodified (b) the modified AFN membranes.

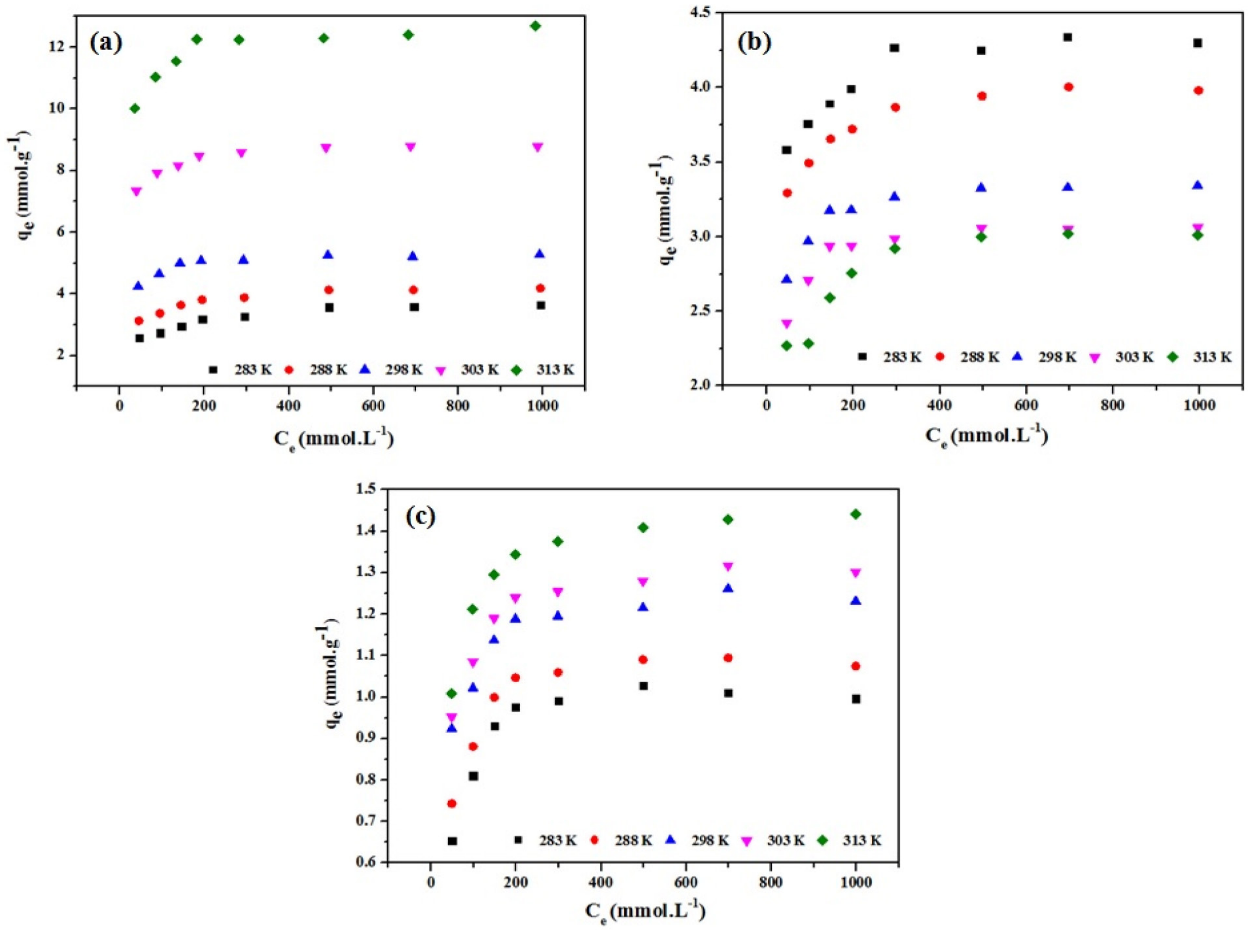

Fig. 3. Effect of temperature on the adsorption of fluoride (a), nitrate (b) and sulfate (c) ions onto the modified AFN membrane.

given in Table 1 show that the K_L value increases with increasing temperature for F^- and SO_4^{2-} ions, which indicates that the selectivity of the modified AFN towards fluorides and sulfates increases with temperature. At 283 K the modified AFN membrane presented high selectivity for nitrate (K_L = 89.83 L mol^{-1}) than fluoride (K_L = 40.14 Lmol^{-1}) and sulfate (K_L = 35.03 L mol^{-1}). The same behavior was observed at 288 K. At 298, 303 and 313 K the membrane becomes more selective for fluorides. This result suggests that fluoride can be separated from sulfate and nitrate at higher temperature.

For the Dubinin-Astakhov model the adsorption energy, *E*, was used to estimate the adsorption process type. As shown in Table 1, the *E* values at studied tem-

Table 1
Langmuir parameters for F^-, NO_3^- and SO_4^{2-} adsorption onto the modified AFN membrane at different temperatures

Langmuir					
Systems	Temperature (K)	q_0 (mmol g^{-1})	K_L (L mol^{-1})	R^2	Reference
Cl^-/F^-	283	3.64	40.14	0.890	This study
	288	4.20	54.55	0.935	This study
	298	5.33	86.62	0.977	This study
	298	5.34	86.62	0.978	[25]
	303	8.96	90.12	0.916	This study
	313	12.64	100.08	0.955	This study
Cl^-/NO_3^-	283	4.33	89.83	0.877	This study
	288	4.00	86.23	0.944	This study
	298	3.39	84.69	0.985	This study
	298	3.38	86.20	0.982	[25]
	303	3.13	75.09	0.976	This study
	313	2.99	64	0.818	This study
Cl^-/SO_4^{2-}	283	1.07	35.03	0.945	This study
	288	1.14	39.79	0.961	This study
	298	1.27	51.48	0.959	This study
	298	1.27	51.48	0.959	[25]
	303	1.33	53.45	0.979	This study
	313	1.45	57.04	0.971	This study

Table 2
D-A parameters for F^-, NO_3^- and SO_4^{2-} adsorption onto the modified AFN membrane at different temperatures

Dubinin–Astakhov						
System	Temperature (K)	q_0 (mmol g^{-1})	n_D	E (kJ mol^{-1})	R^2	Reference
Cl^-/F^-	283	3.85	1.43	9.23	0.972	This study
	288	4.27	1.89	9.37	0.977	This study
	298	5.28	2.79	9.49	0.980	This study
	298	5.28	2.80	9.49	0.980	[25]
	303	8.87	2.81	9.77	0.928	This study
	313	12.64	2.38	11.34	0.966	This study
Cl^-/NO_3^-	283	4.47	1.46	14.21	0.949	This study
	288	4.06	1.90	11.54	0.987	This study
	298	3.36	2.79	9.45	0.987	This study
	298	3.35	2.82	9.45	0.985	[25]
	303	3.09	2.78	9.32	0.978	This study
	313	3.17	1.66	9.24	0.919	This study
Cl^-/SO_4^{2-}	283	1.04	2.76	6.83	0.960	This study
	288	1.11	2.89	7.13	0.974	This study
	298	1.26	2.37	8.33	0.962	This study
	298	1.25	2.61	8.33	0.964	[25]
	303	1.32	2.53	8.49	0.984	This study
	313	1.47	2.01	8.84	0.973	This study

peratures lies between 8 and 16 kJ mol^{-1}, for the adsorption of fluoride and nitrate ions. Thus it is concluded that the adsorption of F^- and NO_3^- on the modified AFN membrane is an ion exchange process in the range of temperature from 283 K to 313 K. The adsorption energy of sulfate on the modified AFN membrane is below 8 kJ mol^{-1} at 283 K and 288 K which corresponds to a physical adsorption process.

On the other hand, the affinity order of the modified AFN membrane for the studied anions can be deduced from the adsorption energies E. Obtained results show that at 283 K and 288 K, the affinity order is: $NO_3^- > F^- > SO_4^{2-}$, while it was $F^- > NO_3^- > SO_4^{2-}$ at 298 K, 303 K and 313K.

The heterogeneity parameter, n_D, determined from the D-A model dependent on the adsorbent surface properties. Hence, higher values of n_D ($n_D > _3$) indicate a greater homogeneity of the materials [2]. In this investigation n_D the values were found to be below 3, at studied temperature, indicating the heterogeneity of the modified AFN membrane. This finding is due to the layer of the PEI adsorbed in the surface of the membrane.

According to the regression coefficients (R^2) all studied models matched experimental data. So comparison of adsorption isotherm models cannot be based only on the comparison of the regression coefficients as the sole criterion. The statistic chi-square test, χ^2, was used to evaluate the best fit of isotherm equations for the studied adsorption models to the experimental data. The statistic chi-square test, χ^2, is given by the following equation :

$$\chi^2 = \sum_{i=1}^{n} \frac{\left(q_{e,exp} - q_{e,cal}\right)^2}{q_{e,exp}} \tag{5}$$

where $q_{e,exp}$ and $q_{e,cal}$ are the experimental and calculated equilibrium capacities (mmol g^{-1}).

The best isotherm was judged as the isotherm with the highest values of the regression coefficients, R^2, and the lowest value of the chi-square test χ^2. Obtained values are given in Table 3.

Based on the values of the chi-square test χ^2 (Table 2), the Dubinin–Astakhov model presents the best fit to the experimental data for the adsorption of fluorides, nitrates and sulfates on the modified AFN membrane at studied temperature.

4.3. Thermodynamic study

In engineering practice, thermodynamic parameters should be considered to determine what processes will occur spontaneously. Standard thermodynamic parameters for the adsorption of F^-, NO_3^-, and SO_4^{2-} on the modified AFN membrane, such as standard enthalpy change $\Delta H°$, standard entropy change ($\Delta S°$) and the Gibbs free energy ($\Delta G°$), can be evaluated from the Langmuir constant, K_L and the temperature. The Gibbs free energy ΔG° is related to the Langmuir constant by the following equation:

$$\Delta G° = -RTLnK_L \tag{6}$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T (K) is the absolute temperature.

The standard enthalpy change ($\Delta H°$) and the standard entropy change ($\Delta S°$) were determined, respectively, from the slopes and the intercepts of the plots of $ln K_L$ against 1/T according to the Van't Hoff equation:

$$\ln K_L = \left(\frac{\Delta S°}{R}\right) - \left(\frac{\Delta H°}{R}\right).\frac{1}{T} \tag{7}$$

The calculated thermodynamic parameters for the adsorption of F^-, NO_3^-, and SO_4^{2-} on the modified AFN membrane at different reaction temperatures (283, 288, 298, 303 and 313 K) are given in Table 4.

The results in Table 4 show that standard enthalpy change ($\Delta H°$) is positive for the adsorption of fluoride and sulfate ions onto the modified AFN membrane indicating an endothermic sorption process. For nitrates the negative values of $\Delta H°$ showed the exothermic adsorption process of this anion. The positive entropy change ($\Delta S°$) values reflect the increase in the randomness on the membrane-solution interface during the adsorption process. The Gibbs free energy

Table 3
Comparison of regression coefficients, R^2, and the statistic chi-square test χ^2

Systems		Langmuir		Dubinin–Astakhov	
	T (K)	R^2	χ^2	R^2	χ^2
Cl^-/F^-	283	0.890	2.10 10^{-2}	0.972	6.37 10^{-3}
	288	0.935	1.11 10^{-2}	0.978	3.71 10^{-3}
	298	0.977	3.33 10^{-3}	0.980	3.55 10^{-3}
	303	0.916	2.20 10^{-2}	0.928	1.88 10^{-2}
	313	0.955	4.19 10^{-2}	0.966	3.79 10^{-2}
Cl^-/NO_3^-	283	0.877	1.16 10^{-2}	0.949	5.7 10^{-3}
	288	0.944	1.35 10^{-3}	0.987	1.01 10^{-3}
	298	0.985	8.19 10^{-4}	0.987	8.04 10^{-4}
	303	0.976	1.34 10^{-3}	0.978	1.24 10^{-3}
	313	0.818	2.13 10^{-2}	0.919	1.13 10^{-2}
Cl^-/SO_4^{2-}	283	0.945	1.05 10^{-3}	0.960	9.26 10^{-4}
	288	0.961	6.97 10^{-4}	0.974	4.6810^{-4}
	298	0.959	6.34 10^{-4}	0.962	7.17 10^{-4}
	303	0.979	3.26 10^{-4}	0.984	2.83 10^{-4}
	313	0.971	6.96 10^{-4}	0.973	7.7 10^{-4}

Table 4
Thermodynamic parameters for the adsorption of F^-, NO_3^- and SO_4^{2-} on the modified AFN membrane

Systems	T (K)	$\Delta G°$ (kJ mol^{-1})	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J mol^{-1} K^{-1})
Cl^-/F^-	283	–8.69	22.77	112.07
	288	–9.57		
	298	–11.05		
	303	–11.34		
	313	–11.99		
Cl^-/NO_3^-	283	–10.58	–7.90	9.71
	288	–10.67		
	298	–10.99		
	303	–10.87		
	313	–10.82		
Cl^-/SO_4^{2-}	283	–8.37	12.44	73.90
	288	–8.82		
	298	–9.76		
	303	–10.02		
	313	–10.52		

$\Delta G°$ during the sorption process at all studied temperatures were negative, suggesting that the adsorption of F^-, NO_3^-, and SO_4^{2-} onto the modified AFN membrane is favorable.

The $\Delta G°$ values obtained from Langmuir model are consistent with the adsorption energies, E, determined from the Dubinin–Astakhov and suggest the same affinity order: $NO_3^- > F^- > SO_4^{2-}$ at 283 K and 288 K, and $F^- > NO_3^- > SO_4^{2-}$ at 298 K, 303 K and 313 K. It can be concluded that the modified AFN membrane exhibited high selectivity for fluoride at higher temperature, which suggests that this anion can be easily separated from nitrate and sulfate.

5. Conclusion

The adsorption behavior of fluoride, nitrate and sulfate ions on the modified AFN membrane was studied at various temperatures. The suitability of the Langmuir and Dubinin-Astakhov adsorption models to the equilibrium data was investigated. Adsorption parameters were determined from non-linear regression and results showed that the Dubinin-Astakhov model satisfactorily described the adsorption data at all studied temperatures. Thermodynamic studies revealed that adsorption process onto the modified AFN membrane is an endothermic process for fluoride and sulfate ions and exothermic for the nitrate adsorption. The $\Delta G°$ were negative at all studied temperature, indicating that the adsorption process was spontaneous. The $\Delta G°$ values suggest the affinity order for the modified AFN membrane. At 283 K and 288 K the affinity order is: $\mathbf{NO_3^- > F^- > SO_4^{2-}}$. This order is: $F^- > NO_3^- > SO_4^{2-}$ at 298 K, 303 K and 313 K. Obtained results showed that the modified AFN membrane had higher adsorption capacities for fluoride than nitrate and sulfate at higher temperature. Thus the modified AFN membrane is an effective adsorbent for the removal of fluorides from aqueous solutions at higher temperature.

Symbols

q_e – Sorption capacity of the membrane at equilibrium (mmol g^{-1})
C_O – Initial anions concentrations (mmol L^{-1})
C_e – Concentrations at equilibrium (mmol L^{-1})
q_o – Maximum adsorption capacity (mmol g^{-1})
K_L – Langmuir constant (L mol^{-1})
$\Delta G°$ – Gibbs free energy (kJ mol^{-1})
$\Delta H°$ – Standard enthalpy change (kJ mol^{-1})
$\Delta S°$ – Standard entropy change (J mol^{-1} K^{-1})
n_D – Homogeneity parameter
E – Adsorption energy (kJ mol^{-1})
m – Mass adsorbent (g)
R – Universal gas constant (J mol^{-1} K^{-1})
R^2 – Correlation coefficient
T – Absolute temperature (K)
V – Volume of the solution (L)
E – Polanyi potential
χ^2 – Chi-square test

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