APPLICATION OF ADSORPTION MODELS FOR FLUORIDE, NITRATE, AND SULFATE ION REMOVAL BY AMX MEMBRANE

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ABSTRACT

An anion exchange membrane, (AMX) that carries a quaternary ammonium functional group has been investigated for its adsorption of fluoride, nitrate and sulfate from aqueous solutions. Fitting of the Freundlich, Langmuir, and Dubinin–Radushkevich adsorption models to the equilibrium data was performed at different temperatures in the range of 283–313K. The sorption parameters of the studied models were determined by linear regression and discussed. Adsorption analysis results obtained at various temperatures showed that the adsorption pattern on the membrane followed Langmuir isotherms. Thermodynamic studies revealed that the adsorption of the AMX membrane to the studied ions was spontaneous. The ΔG_T^0 values suggested the affinity order of the membrane for the studied anions. At 283K and 298K, the affinity order was: $SO_4^{2-} > NO_3^- > F^-$. This order was: $F^- > SO_4^{2-} > NO_3^-$ at 313K. The standard enthalpy change and the standard entropy change were found to be −11.63 kJ/mol and −9.93 J/mol.K for the adsorption of nitrate, 7.42 kJ/mol and 58,73 J/mol.K for the adsorption of sulfate, and 74.21 kJ/mol and 274.9 J/mol.K for the adsorption of fluoride, respectively. The negative values of standard free energy ΔG_T^0 indicate the spontaneous natures of adsorption of studied anions onto the AMX membrane.

Keywords: Adsorption models; AMX membrane; Fluoride; Nitrate; Sulfate

1. INTRODUCTION

Fluoride, nitrate, and sulfate anions represent very important water and wastewater pollutants in southern Tunisia. Several processes that serve to reduce these anions in water have been developed, including membrane separation (Lebrun et al., 2007), ion exchange (Schoeman & Steyn, 2001), and adsorption (Zhou et al., 2009; Lin et al., 2008). Among them, adsorption is one of the most feasible because it is simple, easily implemented and highly efficient for ions removal. Additionally its has the advantages of low cost, easy operation, and no secondary pollution (Gonzalez-Munoz et al., 2006; Yu et al., 2011; Maturana et al., 2011). The study of adsorption equilibrium allows the evaluation of the material capacity to adsorb various ions. The most used adsorption models to describe adsorption equilibrium are the Langmuir, Freundlich, and Dubinin–Radushkevich models. Adsorbent membranes and resins were considered to be most promising owing to their chemical stability and ability to control surface chemistry.

In recent years, many studies regarding the adsorption of ions on ion exchange resins such as Amberlite IRA400 (Chabani et al., 2009), Amberlite IRN 9766 (Dron & Dodi, 2011), Lewatit (Haghshenoa et al., 2009), Amberlite IRC 748 (Zainol et al., 2009) and Indion NSSR (Milmile et al., 2011) have been reported. Chabani et al. (2006) investigated equilibrium sorption for the removal of nitrate onto the ion exchange resin, Amberlite IRA 400. Among the used adsorption models (Langmuir, Freundlich, Redlich–Peterson, and Sips), the Sips model gives the best fit to the adsorption isotherm data. Dron and Dodi, (2011) studied the removal of chloride, nitrate, and sulfate ions from aqueous solutions by the strong anion exchange resin Amberlite IRN 9766. They investigated by means of Langmuir, Freundlich, Dubinin-Radushkevitch (D-R) and Dubinin-Astakhov (D-A) adsorption isotherms. To remove perchlorate anions from groundwater, Yoon et al. (2009) studied the adsorption and desorption of perchlorate on the anion exchange resin SR-7. They found that perchlorate was adsorbed on the resin through electrostatic attraction between the anion and positively charged surface sites.

On the other hand, a number of ion exchange membranes such as SB6407 and DE81 (Chia-Hung et al., 2007) have been used to remove ions from water. However, adsorption on the ion exchange membrane has been studied to remove natural organic matter from water because it has been found to be a problematic solute for electrodialysis (Do Hee et al., 2002). To remove anionic reactive dyes from water (Chia-Hung et al., 2007), have studied the adsorption characteristics of Cibacron Blue 3GA and Cibacron Red 3BA as anionic reactive dyes using two types of commercial anion exchange membranes, strong basic (SB6407) and weak basic (DE81).

In the present work, therefore, the adsorption of fluoride, nitrate, and sulfate ions on the AMX membrane at various temperatures (298–313K) was studied. Experimental data were analyzed using the Langmuir, Freundlich, and (D-R) isotherm models. A discussion regarding thermodynamic parameters for the adsorption process follows.

2. EXPERIMENTAL
2.1. Adsorption Experiments
Adsorption equilibrium experiments were performed with the aqueous/synthetics pollutants NaF, $NaNO_3$, and Na_2SO_4 salt solutions. All chemicals of analytical grade were purchased from Sigma_Aldrich. Synthetic AMX membrane in chloride form was obtained from Eurodia. Some properties and some main characteristics of this membrane, such as humidity percentage and ion exchange capacity, were determined in previous works (Guesmi et al., 2010). The pH of the aqueous solutions did not vary significantly with dilution (i.e., from 6 to 7). Equilibrium experiments were carried out by establishing contact, of the membrane with fluoride, nitrate or sulfate solutions at various temperatures (i.e., 283–313K). The solutions were placed in flasks at a constant agitation speed of 150 rpm for 24 h. the concentrations of residual nitrate, sulfate and fluoride ions were determined by ionic chromatography (CI). The adsorption capacity at equilibrium q_e (mg/g) was obtained as follows:

$$q_e = (C_0 - C_e)\frac{V}{m} \quad \text{(mg/g)} \tag{1}$$

where C_0 (mg/L) and C_e (mg/L) are the initial anion concentrations and concentrations at equilibrium (mg/L), respectively; $V(L)$ is the volume of solution and m(g) the mass adsorbent. The same experimental protocol was followed for the adsorption of nitrate, and sulfate on the AMX membrane.

2.2. Adsorption Models

Adsorption isotherms describe the relationship between the amount of adsorbate on the adsorbent and the concentration of dissolved adsorbate in the liquid phase at equilibrium (Sohn & Kim, 2005). Equations often used to describe the experimental isotherm data are those developed by Freundlich (1906) Langmuir (1918), and Dubinin–Radushkevich (Hsieh &Teng, 2000). Freundlich, Langmuir, and D-R isotherms are the most commonly used to describe the adsorption characteristics of adsorbents used in water and wastewater.

The Langmuir model represents one of the first theoretical treatments of non-linear sorption, and it has been successfully applied to a wide range of systems that exhibit limiting or maximum sorption capacities. The Langmuir isotherm is given by:

$$q_e = \frac{q_0 k_L C_e}{1 + k_L C_e} \quad (mg/g) \tag{2}$$

where, q_0 and k_L are the Langmuir constants, related to the adsorption capacity and energy of adsorption, respectively.

The linear form of the Langmuir isotherm is given by the following equation:

$$\frac{C_e}{q_e} = \frac{C_e}{q_0} + \frac{1}{k_L q_0} \quad (g/L) \tag{3}$$

For the Langmuir model adsorption process, the separation factor R_L can be used to predict the favorability of adsorption, which is defined as follows(Ningmei & Zhengkui, 2013):

$$R_L = \frac{1}{1 + k_L C_0} \tag{4}$$

The Freundlich model can be applied to non-ideal adsorption on the heterogeneous surfaces as well as multilayer sorption; it is expressed as follows:

$$q_e = k_f C_e^{1/n} \quad (mg/g) \tag{5}$$

where k_f is the Freundlich constant that relates to sorption capacity, and n is the Freundlich exponent that relates to sorption intensity. In most cases values of n are between 1 and 10, indicating favorable adsorption (Bilgili, 2006). The linear plot of Lnq_e versus LnC_e is given by the following equation:

$$Lnq_e = Lnk_f + \frac{1}{n} LnC_e \tag{6}$$

The D-R adsorption model describes the characteristic adsorption curve related to the porous structure of the adsorbent. The adsorption data was applied to the D-R model to distinguish between physical and chemical adsorption (Donat et al., 2005). The following equation represents the D-R model:

$$Lnq_e = Lnq_0 - \beta \varepsilon^2 \tag{7}$$

where β is the activity coefficient related to mean sorption energy (Chabani et al., 2006, 2007, 2009) and ε is the Polanyi potential that is given by,

$$\varepsilon = RTLn(1 + \frac{1}{C_e}) \quad (J/mol) \tag{8}$$

where R is the gas constant (kJ/mol K) and, T is the absolute temperature (K).

The slope of the plot of *Lnq_e* versus ε^2 gives β (mol^2/kJ^2) and the intercept yields the adsorption capacity, *q_0* (mg/g). The mean adsorption energy (E) is defined when one mole of ion is transferred from infinity in solution to the surface of the membrane. It is calculated from the β value using the following equation:

$$E = \frac{1}{\sqrt{2\beta}} \quad (Kj/mol) \tag{9}$$

3. RESULTS AND DISCUSSION

3.1. Adsorption Isotherms

Adsorption of fluoride, nitrate, and sulfateions on the AMX membrane was determined at various temperatures (i.e., 283, 298, and 313K). Obtained isotherms are given in Figure 1. A relationship was observed between the amount of adsorbed ions on the adsorbent surface and the remaining ion concentration in the aqueous phase at equilibrium. It is evident that the adsorption capacity increased with the equilibrium concentration of ions in solution. It was also shown that the adsorption amount of SO_4^{2-}, NO_3^- and F^- decreased with increasing temperature.
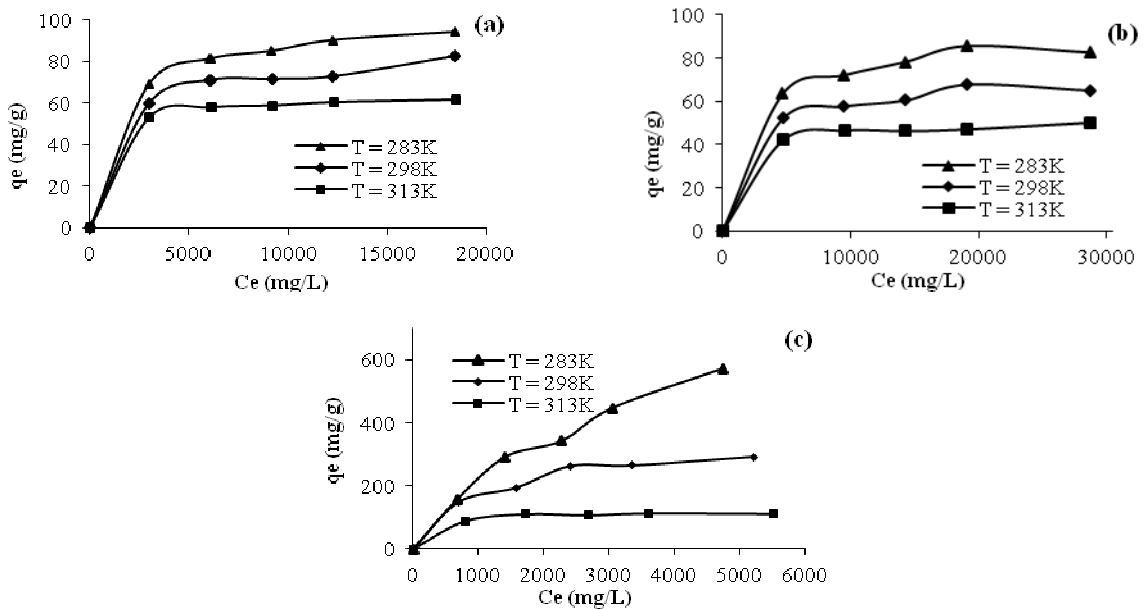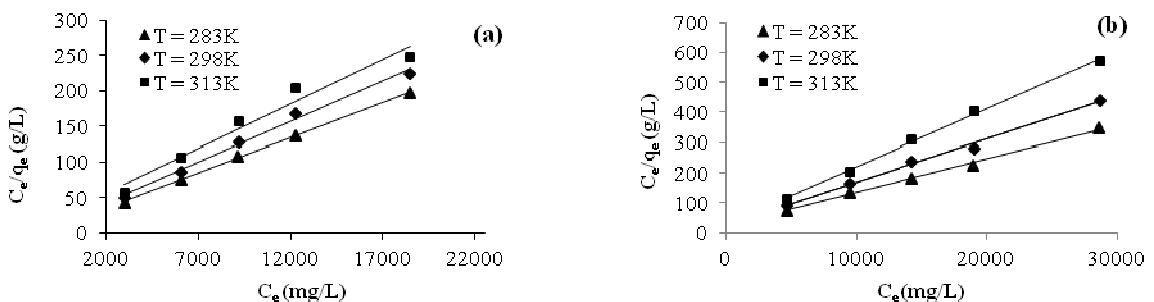

Figure 1 Adsorption isotherm of (a) nitrate; (b) sulfate; and (c) fluoride ions on AMX membrane

The analytical equation (3) of the Langmuir model for the adsorption of studied anions is presented in Figure 2.
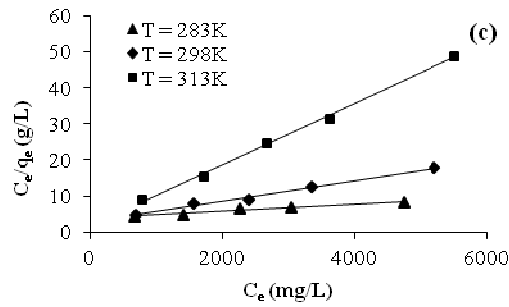
Figure 2 Langmuir isotherm plot for the adsorption of (a) nitrate; (b) sulfate; and (c) fluoride ions by the AMX membrane

The Freundlich adsorption isotherms for fluoride, nitrate, and sulfate adsorption are obtained by plotting the graph of Lnq_e versus LnC_e, as in Figure 3, from which the constants of Freundlich adsorption model have been determined.
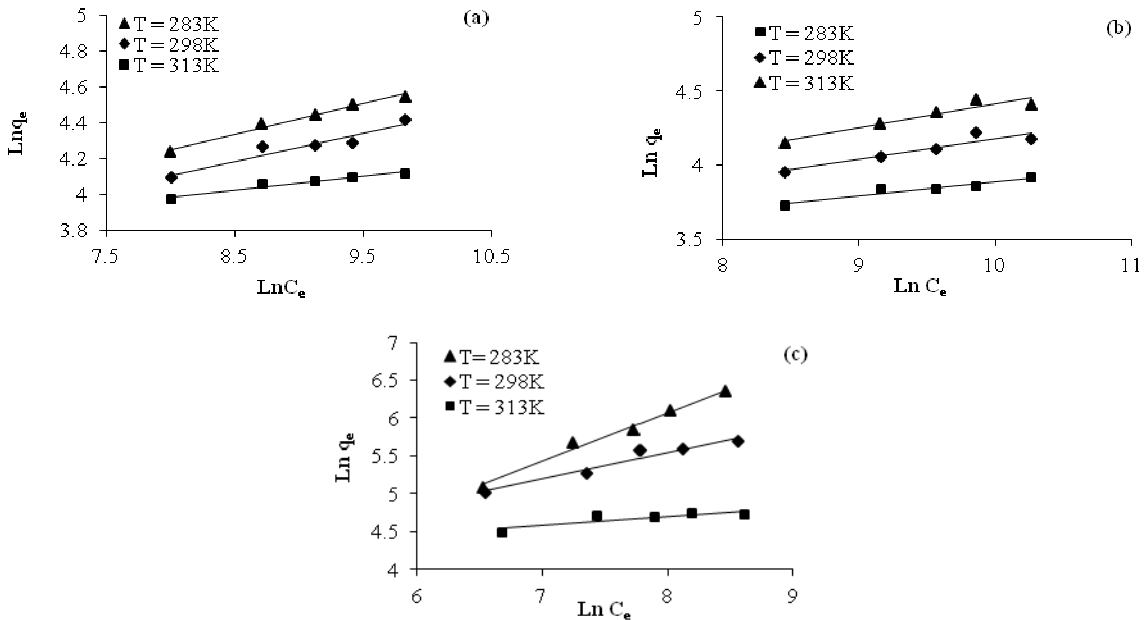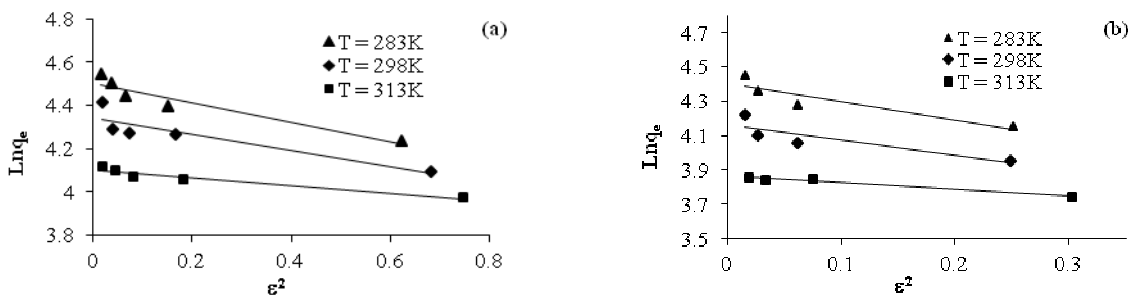

Figure 3 Freundlich isotherm plot for the adsorption of (a) nitrate; (b) sulfate; and (c) fluoride ions by the AMX membrane

The D-R isotherms are presented in Figure 4 from a plot of Lnq_e versus ε^2, which shows the linear graphs for the sorption of fluoride, nitrate and sulfate.
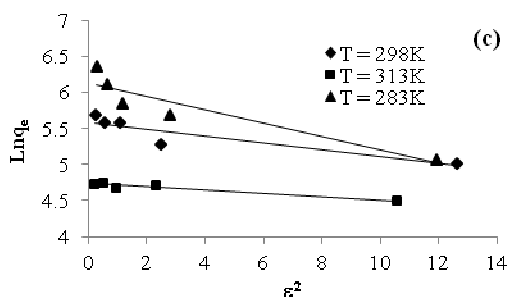
Figure 4 Dubinin–Radushkevich (D-R) isotherm plot for the adsorption of (a) nitrate; (b) sulfate; and (c) fluoride ions by the AMX membrane

The adsorption isotherm coefficients (q_0, k_L, n, k_f, R_L and β) can be determined from the slopes and the intercepts of the linear plots. These parameters as well as the correlation coefficient are given, respectively, in Tables 1 and 2.

Table 1 Isotherm constants for the adsorption of SO_4^{2-}, NO_3^- and F^- by the AMX membrane at various temperatures

		Langmuir			Freundlich		Dubinin–Radushkevich	
	T [K]	q_0 [meq/g]	k_L [L/mol]	R_L	n	k_f	q_0 [meq/g]	β
Cl^-/NO_3^-	283	1.73	40.60	0.07-0.33	5.8	18.01	1.46	0.452
	298	1.41	36.63	0.08-0.35	6.3	17.35	1.24	0.370
	313	1.28	25.16	0.11-0.44	12.5	28.28	0.97	0.180
Cl^-/SO_4^{2-}	283	0.93	50.64	0.06-0.28	6.1	16.2	0.85	1.076
	298	0.73	56.34	0.05-0.26	7.1	16.1	0.67	0.904
	313	0.54	68.65	0.05-0.22	10.5	18.8	0.50	0.521
Cl^-/F^-	283	52.63	5.12	0.39-0.79	1.5	2.4	23.98	0.0921
	298	18.79	18.39	0.15-0.52	2.8	15.2	14.12	0.0485
	313	6.19	106.43	0.03-0.16	8.5	42.7	6.01	0.023

Table 2 Correlation coefficients parameters for SO_4^{2-}, NO_3^- and F^- adsorptions

	Correlation coefficients R^2								
Systems	Cl^-/NO_3^-			Cl^-/SO_4^{2-}			Cl^-/F^-		
T[K]	283	298	313	283	298	313	283	298	313
Langmuir	0.999	0.991	0.964	0.996	0.995	0.998	0.947	0.990	0.998
Freundlich	0.977	0.914	0.958	0.902	0.876	0.909	0.985	0.943	0.719
Dubinin–Radushkevich	0.910	0.813	0.935	0.856	0.787	0.860	0.857	0.831	0.945

From Table 1, it is seen that adsorption capacities (q_0) decrease with increasing temperature. For the Langmuir and D-R models, the highest values of q_0 were obtained at 283K for each

anion. The values decreased with increases in temperature, thus confirming the suitability of low temperatures for adsorption. The decrease in adsorption capacity of the membrane at higher temperatures may be attributed to inactivation of the membrane surface (Dizge et al., 2009). In the range 283-313K, the experimental data fit better to the Langmuir model ($0.947 < R^2 < 0.999$) than to the Freundlich ($0.719 < R^2 < 0.985$) or D-R ($0.787 < R^2 < 0.945$) models (Table 2). Furthermore, the calculated R_L values were all in the range of $0 < R_L < 1$, revealing that SO_4^{2-}, NO_3^- and F^- adsorption on the AMX membrane are favorable.

The adsorption energy E, calculated using Equation (9), according to the D–R isotherm model was used for estimating the type of adsorption mechanism. For a magnitude of E between 8 and 16 kJ/mol, the adsorption process followed the chemical ion exchange, and values of E below 8 kJ/mol were characteristic of a physical adsorption process (Chabani et al., 2009). Obtained results (Table 3) show that the E values at studied temperatures were below 8 kJ/mol, thus corresponding to physical adsorption.

Table 3 Adsorption energy E values

	T [K]	Cl^-/NO_3^-	Cl^-/SO_4^{2-}	Cl^-/F^-
	283	1.05	0.68	2.33
E [kJ/mol]	298	0.86	0.74	3.19
	313	1.66	0.98	4.66

3.2. Thermodynamic Studies

Thermodynamic parameters should be considered for determining which processes will occur spontaneously. For the studied systems (Cl^-/NO_3^-), (Cl^-/SO_4^{2-}) and (Cl^-/F^-), standard enthalpy change (ΔH_T°), standard free energy (ΔG_T°) and standard entropy change (ΔS_T°), can be evaluated from the energy of adsorption, k_L, and temperature. The standard free enthalpy (ΔG_T°) of the adsorption process is given by the following formula:

$$\Delta G_T^0 = -RTLn\,k_L \tag{10}$$

where R is the universal gas constant (8.314 J/mol·K), and T(K) is absolute temperature. ΔG_T° (kJ/mol) can be also defined as:

$$\Delta G_T^\circ = \Delta H_T^\circ - T\,\Delta S_T^\circ \tag{11}$$

Substituting Equation (10) into Equation (11) gives the following equation which can be used to determine the thermodynamic parameters ΔH_T° and ΔS_T°:

$$Ln\,k_L = \left(\frac{\Delta S_T^\circ}{R}\right) - \left(\frac{\Delta H_T^\circ}{R}\right)\cdot\frac{1}{T} \tag{12}$$

According to Equation (12), the $Ln\,k_L$ versus $\dfrac{1}{T}$ plot should be a straight line, as shown in Figure 5, from which the standard enthalpy change (ΔH_T°) and the standard entropy change (ΔS_T°) (J/mol·K) of adsorption process can be obtained.
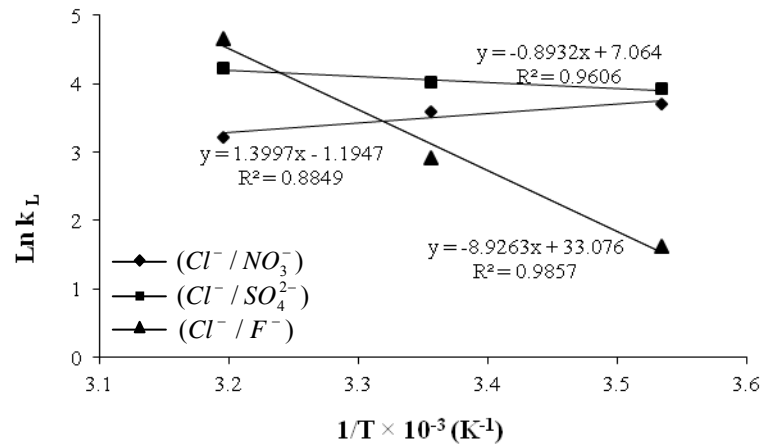
Figure 5 $Ln\,k_L$ versus $\dfrac{1}{T}$ plots

The values of ΔH_T^0 and ΔS_T^0 were determined from the slopes and intercepts, respectively. Obtained results are given in Table 4.

Table 4 Thermodynamic parameters of nitrate and sulfate adsorption by the AMX membrane

Systems	T (K)	ΔG_T^0 [kJ/mol]	ΔH_T^0 [kJ/mol]	ΔS_T^0 [J/mol·K]
Cl^-/NO_3^-	283	−8.71	−11.63	−9.93
	298	−8.92		
	313	−8.39		
Cl^-/SO_4^{2-}	283	−9.23	7.42	58.73
	298	−9.98		
	313	−11.01		
Cl^-/F^-	283	−3.84	74.21	274.9
	298	−7.21		
	313	−12.15		

Obtained results show that standard free energy levels during the sorption process at all studied temperatures were negative, corresponding to a spontaneous process of fluoride, nitrate and sulfate ions sorption onto the AMX membrane.

The negative value of the standard enthalpy change ΔH_T^0 showed that the adsorption of nitrate was exothermic. The standard entropy change ΔS_T^0 was negative, meaning that a decreased randomness appeared on the membrane-solution interface during the adsorption of nitrate.

In the range 283–313K, standard free energy ΔG_T^0 decreased with an increase in temperature, for the adsorption of fluoride and sulfate ions, indicating that the reaction was spontaneous enhanced by higher temperatures. The positive values of standard enthalpy indicate that adsorption was endothermic. The positive values of adsorption entropy corresponds to an increase in randomness at the membrane-liquid interface and may cause significant changes

occur in the internal structure of the adsorbent through the adsorption of sulfate and fluoride ions onto the AMX membrane (Dizge et al., 2009).

The ΔG_T^0 values suggest the following order of affinity of the AMX membrane for the studied anions. Obtained results show that at 283K and 298K, the affinity order is: $SO_4^{2-} > NO_3^- > F^-$. This order is: $F^- > SO_4^{2-} > NO_3^-$ at 313K. The AMX membrane exhibited high selectivity for fluoride at 313K, which suggests that this anion can be easily separated from nitrate and sulfate.

4. CONCLUSION

The adsorption behavior of fluoride, nitrate and sulfate on the AMX membrane was investigated. Adsorption analysis results obtained at various temperatures showed that the adsorption pattern on the AMX membrane followed Langmuir isotherms rather than those from Freundlich, and D–R models. Furthermore, thermodynamic studies revealed that the adsorption process was spontaneous. The ΔG_T^0 values suggest the order of the membrane for the studied anions. At 283K and 298K, the affinity order was $SO_4^{2-} > NO_3^- > F^-$. At 313K, this order was: $F^- > SO_4^{2-} > NO_3^-$.

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