Comparison of adsorption models for the removal of fluorides, nitrates and sulfates by adsorption onto AFN membrane

Fatma Guesmi, Islem Louati, Chiraz Hannachi and Béchir Hamrouni

ABSTRACT

The main purpose of this work was to determine adsorption characteristics of fluoride, nitrate and sulfate ions on the AFN membrane. The sorption isotherms for F^-, NO_3^- and SO_4^{2-} ions on the AFN membrane were investigated in the range of 0.05–1 mol.L^{-1} at 298 K. The suitability of the Langmuir, Dubinin–Astakhov (D-A) and Redlich–Peterson adsorption models to the equilibrium data was investigated. The sorption parameters of the studied models were determined by non-linear regression and discussed. Equilibrium data obtained in this study were found to best fit the Langmuir isotherm. The ΔG° values deduced from the Langmuir isotherm suggest that the affinity order of the AFN membrane for the studied anions is: $NO_3^- > SO_4^{2-} > F^-$. In order to improve their selectivity towards monovalent ions, the AFN membrane was modified by adsorption of polyethyleneimine on its surface. Adsorption parameters values of the studied models were determined for the modified AFN membrane. The D-A model provides the best fit to the experimental points. 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. Desorption of fluoride from the modified AFN membrane by nitrate and sulfate ions was investigated.

Key words | adsorption isotherm models, AFN membrane, nonlinear regression, polyethyleneimine (PEI)

Fatma Guesmi (corresponding author)
Islem Louati
Chiraz Hannachi
Béchir Hamrouni
Faculty of Sciences of Tunis,
University of Tunis El Manar, UR11ES17 Desalination and Water Treatment,
2092 Tunis,
Tunisia
E-mail: *guesmi_fatma@yahoo.fr*

SYMBOLS

q_e	sorption capacity of the membrane at equilibrium (mmol g^{-1})
C_0	initial anions concentrations (mmol L^{-1})
C_e	concentrations at equilibrium (mmol L^{-1})
V	volume of the solution (L)
m	mass adsorbent (g)
q_0	maximum adsorption capacity (mmol g^{-1})
K_L	Langmuir constant (L mol^{-1})
E	adsorption energy (kJ mol^{-1})
n_D	homogeneity parameter
ϵ	Polanyi potential
β_{RP}	degree of heterogeneity
A and B	Redlich–Peterson parameters
T	absolute temperature (K)
R	universal gas constant (J mol^{-1} K^{-1})
R^2	correlation coefficient
χ^2	chi-square test
ΔG°	Gibbs free energy (kJ mol^{-1})

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INTRODUCTION

Various anthropogenic and natural substances can be found dissolved in water. Some are harmful but others are beneficial. When it comes to humans, the latter category must be at a specific dose. In terms of harmful substances or contaminants, fluoride, nitrate and sulfate in water have been recognized as serious problems

worldwide (Chabani *et al.* 2009; Dron & Dodi 2011; Ranjana 2012; Samadi *et al.* 2014). Several processes were used to remove these contaminants such as ion exchange, electrodialysis, reverse osmosis, nanofiltration, microbiological denitrification, chemical treatment, biological treatment, adsorption, etc. (Tehobanoglous 1979; Du Preez *et al.* 1992; Schoeman & Steyn 2001; Bae *et al.* 2002; Sehn 2008; Haghsheno *et al.* 2009; Solangi *et al.* 2009; Dolar *et al.* 2011). Among them the adsorption process is simpler and more effective for fluoride, nitrate and sulfate removal. Adsorption on ion exchangers is considered to be highly stable and hence is considered as one of the most promising adsorbents (Haghsheno *et al.* 2009; Sachin *et al.* 2011; Samadi *et al.* 2014).

Extensive investigations (Chia-Hung *et al.* 2007; Meenakshi & Viswanathan 2007; Jeng-Shiou *et al.* 2008; Xu *et al.* 2012; Abdelwahab *et al.* 2013; Hannachi *et al.* 2014) were carried out to study the adsorption of contaminant ions onto ion exchange resins and membranes. Investigators found that removal of ions using resins and membranes has a good potential for water treatment. In fact, Chabani *et al.* (2006) studied the adsorption of nitrate on Amberlite IRA 400 resin. They found that this resin is an effective adsorbent for the removal of nitrate from aqueous solution.

Recently, Sachin *et al.* (2011) investigated the removal of nitrate by adsorption onto anion exchange Indion NSSR resin. Freundlich, Langmuir and Dubinin–Radushkevich models were used to fit the equilibrium isotherms. The results showed that nitrate removal had followed the Langmuir adsorption isotherm and that Indion NSSR resin is effective for nitrate removal.

Removal of sulfate anions from Sarcheshmeh copper complex wastewater by adsorption on Lewatit K 6362 anion exchange resin has been studied by Haghsheno *et al.* (2009) in order to determine the adsorption equilibrium data and adsorption isotherms. Their results showed that isothermal data best fit a Freundlich adsorption isotherm and the adsorption of sulfate ions on the Lewatit K 6362 ion exchange resin followed reversible first-order kinetics. Samadi *et al.* (2014) 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.

Recently, Hannachi *et al.* (2013, 2014) investigated adsorption of fluoride, nitrate and sulfate ions on AFN and AMX anion exchange membranes at various temperatures. They showed that the adsorption linear pattern on the AMX membrane followed Langmuir isotherms. It was also found that at 298 K the AMX membrane has more affinity for sulfate than nitrate than fluoride, while for the AFN membrane the affinity order is $NO_3^- > SO_4^- > F^-$.

On the other hand, studies on separation using ion exchange membranes have resulted in difficult separations. One of the unsolved problems of ion exchange membrane is the separation of ions with the same charge and different valences. Several studies have shown that the efficiency of separation of ions from water using ion exchange membranes is dependent of the selectivity of these membranes for monovalent ions against multivalent ones. In this context, modification of ion exchange membranes was carried out showing the improvement of the selectivity (Sata & Mizutani 1979). Several studies (Cortina *et al.* 1997; Biesuz *et al.* 2001; Serarols *et al.* 2001; Amara & Kerdjoudj 2003, 2007; Gohil *et al.* 2006) have been realized to modify the properties of ion exchange resins and membranes in order to improve their selectivity towards ions which are different in size and valence.

Therefore, in the present investigation, attempts were made to determine adsorption characteristics of fluoride, nitrate and sulfate ions on the unmodified and the modified AFN membranes. The latter was modified by adsorption of polyethyleneimine (PEI) on its surface. The adsorbed amount of PEI on membrane surface was determined as a function of the following parameters: initial PEI concentration, pH and molecular weight of the PEI. To investigate the influence of these parameters an experimental design methodology by means of a full factorial design (2^3) was adopted and the different data were analyzed with MINITAB software.

The adsorption of the ions was investigated through the most commonly used single-component adsorption isotherms: Langmuir, Dubinin–Astakhov (D-A) and Redlich–Peterson (R-P). The adsorption parameters of the experimental models were determined from the non-linear regression.

EXPERIMENTAL PROCEDURE

Membrane characteristics

The commercial anion exchange membrane evaluated in this investigation is the AFN membrane provided by Tokuyama Soda. The base polymer of this membrane is styrene and divinylbenzene, and the ionic fixed sites are quaternary ammonium groups, rendering the membrane a strong anion exchanger. The main characteristic of the AFN are presented in Table 1.

Adsorption experiments

To obtain adsorption isotherms of F^-, NO_3^- and SO_4^{2-}, different samples of the AFN membrane (25 cm^2) in Cl^- form were immersed in 200 mL of fluoride, nitrate or sulfate ions solutions at different initial concentrations (from 0.05 to 1 $mol.L^{-1}$). All experiments were carried out at 298 K. The solution and membrane were then shaken at 150 rpm in a thermostatic bath until equilibrium was achieved.

The nitrate, fluoride, and sulfate ions concentration in the solution were determined, at equilibrium, by ion chromatography using a Metrohm 761 compact IC with conductivity detector and chemical suppression, 4.6 × 250 mm Metrosep A Supp 1 (6.1005.300), an eluent of 3 $mmol.L^{-1}$ sodium carbonate at 1 $mL.min^{-1}$, an injection volume of 20 μL, and a pressure of 8–9 MPa.

The sorption capacity q_e ($mmol.g^{-1}$) of the membrane at equilibrium was given by the following equation:

$$q_e = (C_0 - C_e).\frac{V}{m}$$

Table 1 | Main characteristics of the AFN membrane

Ion exchanger	AFN
Ion exchange capacity ($meq.g^{-1}$)	2–3.5
Humidity percentage in Cl^- form (%)	45.35
Thickness (mm)	0.15–0.2
Resistance ($\Omega.cm^2$)	0.4–1.5
Membrane density ($g.cm^3$)	1.09
Transport number of Cl^-	0.92

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

Surface modification

The AFN membrane surface was modified by adsorption of PEI which was obtained from Sigma-Aldrich. The PEI used in this investigation is a branched chain polymer that contains primary, secondary and tertiary amine groups in a ratio of approximately 1/4, 1/2 and 1/4, respectively.

The methodology used to modify the AFN membrane has been described extensively in our previous studies (Guesmi *et al.* 2012, 2013). The AFN membrane (25 cm^2) was immersed in 250 mL of a stirred PEI aqueous solution of a given concentration at 25 °C for 6 days. At the equilibrium, the membrane was rinsed with ultrapure water to eliminate the excess of PEI. Several parameters affecting the modification of ion exchange membrane and the initial concentration of PEI, the molecular weight of PEI and the pH of the solutions were evaluated in this investigation.

The polyethyleneimine concentration was determined using the UV absorption spectrum of copper-PEI complex. The solution containing PEI was mixed with a cupric sulfate solution and then analyzed by UV absorption spectrum. The maximum absorption of the copper-PEI complex was located at 326 μm.

RESULTS AND DISCUSSION

Adsorption isotherms onto unmodified AFN membrane

Adsorption isotherms establish the relationship between the amount of anion adsorbed per gram of membrane, q_e ($mmol.g^{-1}$), and the amount of anions left in equilibrium solution, C_e ($mmol.L^{-1}$). They can give information about the distribution of the adsorbate anions between the solution and the membrane phases when the adsorption process reaches the equilibrium state (Vasiliu *et al.* 2011). Several isotherm models were used to describe adsorption characteristics. The adsorption of fluoride, nitrate and sulfate ions onto

Table 2 | Isotherm constants for parameter models by non-linear regression

Models	Non-linear form	Calculated parameters
Langmuir	$q_e = \frac{q_0.K_L.C_e}{1+K_L.C_e}$	q_0 and K_L
D-A	$q_e = q_0.exp\left[-\left(\frac{\varepsilon}{\sqrt{2}.E}\right)^{n_D}\right]$	E and n_D
R-P	$q_e = \frac{A.C_e}{1+B.C_e^{\beta_{RP}}}$	A, B and β_{RP}

the AFN membrane were analyzed using the Langmuir (1918), D-A (Dron & Dodi 2011) and Redlich & Peterson (1959) models.

The Langmuir model is the most frequently used isotherm to describe the adsorption equilibrium. Indeed, it assumes a monolayer adsorption phenomenon onto a completely homogenous surface. On the other hand, the D-A model is based in the Polanyi adsorption potential theory which defines an adsorption potential and is related to the adsorption energy. It is also used in order to distinguish between physical and chemical adsorption processes. The R-P is an empirical isotherm used to represent adsorption equilibrium over a wide concentration range. It has features of both the Langmuir ($\beta = 1$) and Freundlich (at higher concentrations) isotherms, and consequently, it can be used either in heterogeneous or homogenous systems.

The non-linear forms of the studied models are given in Table 2.

The characteristic parameters, for the adsorption of F^-, NO_3^- and SO_4^{2-} on the unmodified AFN membrane were determined from the non-linear regression using the

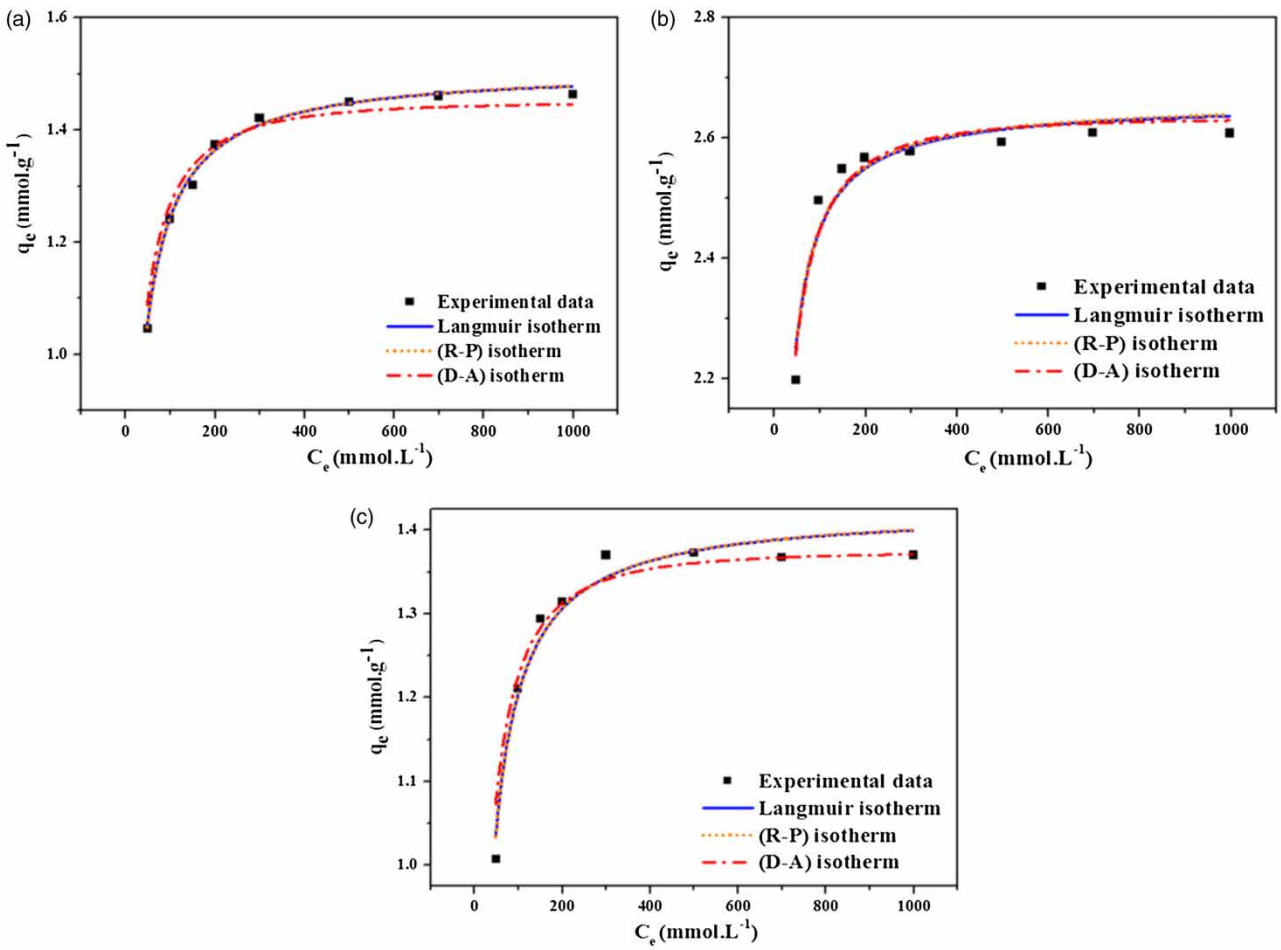

Figure 1 | Experimental data and adsorption isotherms determined by non-linear regression of fluoride (a), nitrate (b) and sulfate (c) ions onto unmodified AFN membrane at 298 K.

Table 3 | Langmuir, D-A and R-P parameters determined from non-linear regression for the adsorption of F^-, NO_3^- and SO_4^{2-} on the unmodified AFN membrane

	Langmuir			D-A				R-P			
Systems	q_0 (mmol.g^{-1})	K_L (L.mol^{-1})	R^2	q_0 (mmol.g^{-1})	n_D	E (kJ.mol^{-1})	R^2	A	B	β_{RP}	R^2
Cl^-/F^-	1.51	47.09	0.994	1.43	3.05	8.12	0.967	0.07	0.05	1	0.994
Cl^-/NO_3^-	2.66	116.46	0.934	2.63	3.06	9.88	0.943	0.31	0.12	1	0.934
Cl^-/SO_4^{2-}	1.42	54.7	0.967	1.37	3.11	8.44	0.950	0.08	0.05	1	0.967

Table 4 | Regression coefficients, R^2, and chi-square statistic χ^2

	Langmuir		D-A		R-P	
Systems	R^2	χ^2	R^2	χ^2	R^2	χ^2
Cl^-/F^-	0.994	$0.14\ 10^{-3}$	0.967	$0.94\ 10^{-3}$	0.994	$0.17\ 10^{-3}$
Cl^-/NO_3^-	0.934	$1.44\ 10^{-3}$	0.943	$1.50\ 10^{-3}$	0.934	$1.73\ 10^{-3}$
Cl^-/SO_4^{2-}	0.967	$0.60\ 10^{-3}$	0.950	$1.12\ 10^{-3}$	0.967	$0.72\ 10^{-3}$

OriginPro software. Isotherms for the studied anions are shown in Figure 1.

Table 3 displays the different parameters of the Langmuir, D-A and R-P models along with regression coefficients (R^2) obtained from the non-linear regression.

Results show that for the Langmuir isotherm, the value of K_L reflects quantitatively the affinity of the membrane towards fluorides, nitrates and sulfates. The unmodified AFN membrane exhibited high selectivity for nitrate ($K_L = 116.46$ L.mol^{-1}) than sulfate ($K_L = 54.7$ L.mol^{-1}) and fluoride ($K_L = 47.09$ L.mol^{-1}).

The adsorption energy of a solute on the sorbent is determined from the Langmuir isotherms as the corresponding change in Gibbs free energy ΔG°, deduced from $\boldsymbol{K_L}$ as follows:

$$\Delta \boldsymbol{G}^\circ = -\boldsymbol{RTLnK_L}$$

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

For the adsorption of fluoride, sulfate and nitrate on the unmodified AFN membrane, the ΔG° values were found to be –9.54 kJ.mol^{-1}, –9.91 kJ.mol^{-1} and –11.79 kJ.mol^{-1}, respectively. Results show that the standard free energy during the sorption process at 298 K were negative for the studied ions, and indicate that the adsorption process onto the unmodified AFN membrane is a favorable and spontaneous process in the standard conditions. The ΔG° values suggest the affinity order of the AFN membrane for the studied anions. Results show that the affinity order is: $\boldsymbol{NO_3^- > SO_4^{2-} > F^-}$.

For the R-P model the β_{RP} magnitudes for the adsorption of F^-, NO_3^- and SO_4^{2-} ions were found to be equal to 1. Hence, in this study, the R-P isotherm is approaching the Langmuir but not the Freundlich isotherm because the values of β_{RP} are close to unity. It can be concluded that the surface of the unmodified AFN membrane is homogenous for fluoride, nitrate and sulfate ions adsorption.

For the D-A model, the maximum adsorption capacities values are almost in agreement with the q_0 values determined from the Langmuir isotherm. The magnitude of the adsorption energy, E, deduced from D-A model is useful

Table 5 | Experimental range and levels investigated for the modification of the AFN membrane

			Experimental field	
Coded variables (X_i)	**Factors (U_i)**	**Unit**	**Low value**	**High value**
X_1	(PEI)	g.L^{-1}	0.5	1.5
X_2	M (PEI)	g.mol^{-1}	1,300	10^6
X_3	pH	–	8.8	10.8

for estimating the adsorption process type. Results (Table 3) show that the E values lies between 8 and 16 kJ.mol^{-1}, thus it is concluded that the adsorption of fluoride, nitrate and sulfate on the unmodified AFN membrane is an ion exchange process. Adsorption energies, E, determined from the D-A are consistent with the ΔG° values obtained from the Langmuir, and suggest the same affinity order: $NO_3^- > SO_4^{2-} > F^-$.

For the D-A model the heterogeneity parameter n_D was also estimated. This parameter is dependent on the adsorbent surface properties (Dron & Dodi 2011). It was mentioned that higher values of n_D ($n_D > 3$) indicate a greater homogeneity of the materials. In this study the n_D values were determined to be in the range $3.05 < n_D < 3.11$ indicating the high homogeneity of the unmodified AFN membrane.

In order to evaluate the best fit of isotherm equations for the studied adsorption models to the experimental data, the chi-square test, χ^2, was used and it is given (Abdelwahab *et al.* 2013) by the following equation:

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

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

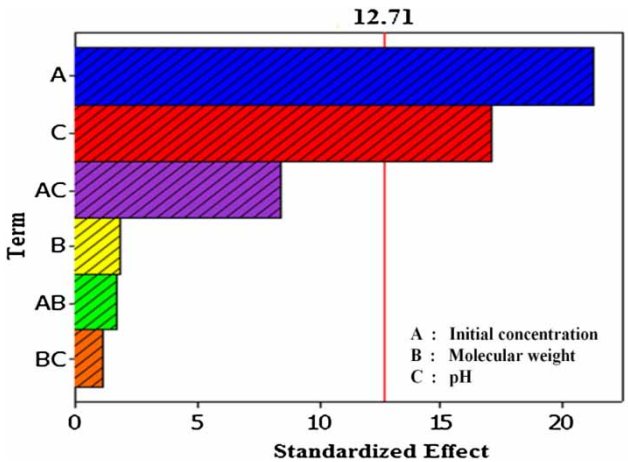

Figure 2 | Pareto chart of the effects.

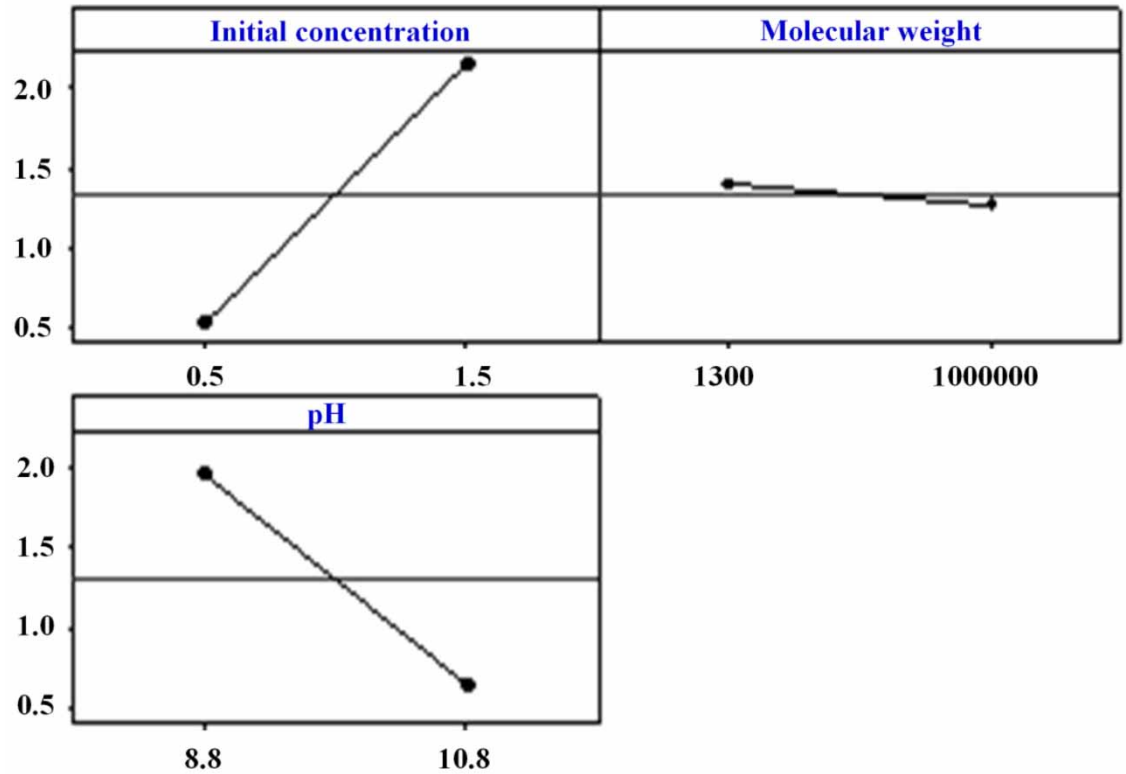

Figure 3 | Main effects plots for PEI adsorption.

The best isotherm was that with the highest regression coefficient, R^2, and lowest chi-square statistic χ^2. Obtained values are given in Table 4.

As seen from Table 4, the Langmuir model describes the best fit to the experimental data.

SURFACE MODIFICATION OF THE AFN MEMBRANE

Factorial design study

The modification of the AFN membrane by the adsorption of PEI on its surface was determined as a function of the several parameters such as: initial PEI concentration, pH solution and molecular weight of the PEI. To investigate the influence of these parameters an experimental design methodology by means of a full factorial design (2^3) has been adopted.

The objective of the factorial design was to find parameters that have a significant influence on the adsorption of PEI on the surface of the AFN membrane. In this study a full factorial design of the type 2^3 was used to investigate the influence of three parameters on the surface modification of the AFN membrane. These factors were: initial PEI concentration (X_1), molecular weight of the PEI (X_2) and solution pH (X_3).

The factorial levels of the coded factor are presented in Table 5.

The different data have been analyzed with MINITAB software. The relative importance of the various investigated factors and their interactions are illustrated in the Pareto chart of the effects (Figure 2). The vertical line in the chart

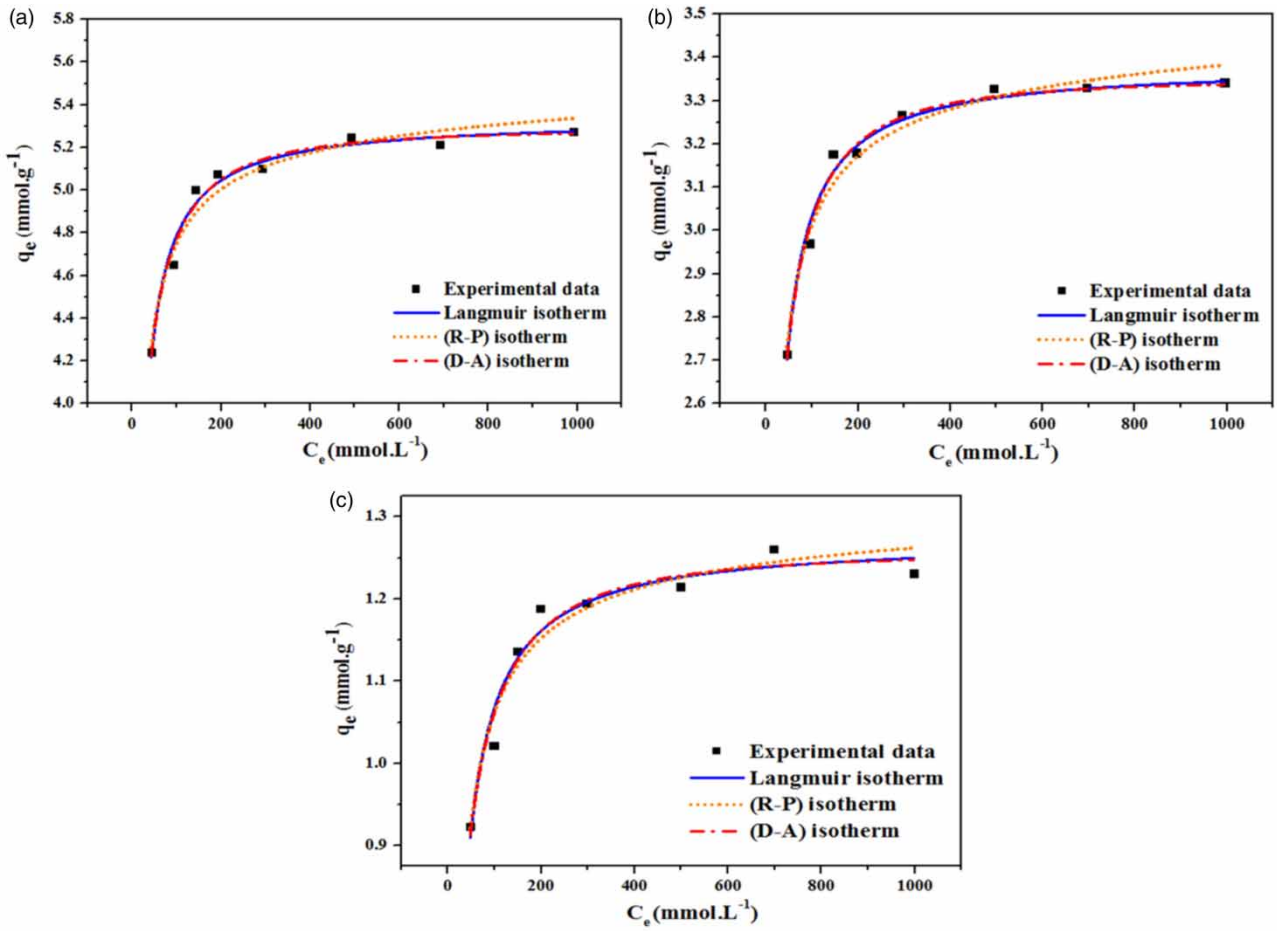

Figure 4 | Experimental data and adsorption isotherms determined by non-linear regression of fluoride (a), nitrate (b) and sulfate (c) ions onto modified AFN membrane at 298 K.

indicates minimum statistically significant effect at a 95% confidence level.

According to the Pareto chart, the initial concentration and the pH seem to be highly influent on the experimental response since the absolute values of their coefficients are higher than the t value ($t = 12.71$, for $\alpha = 0.05$).

The main effects of each parameter on the adsorption amount of PEI are given in Figure 3.

It can be seen that the initial concentration of PEI is the most important variable on the adsorbed amount of PEI and has a positive effect. The effect of pH factors is negative, it means that increasing pH value of PEI solution leads to a decrease in the amount of PEI adsorbed on the AFN membrane. The effect of the molecular weight is very negligible.

Therefore, to modify the studied membrane, the initial concentration and the pH of the PEI solution were fixed, respectively, at the highest value (1.5 g.L^{-1}) and the lowest value (pH = 8.8). A similar finding has been reported by Amara & Kerdjoudj (2007), they found that the modification of anion exchange membrane is more effective at high concentration and a low pH of the polyelectrolyte solution.

Adsorption study on the modified AFN membrane

Equilibrium adsorption isotherms of Langmuir, D-A and R-P models established for the adsorption of fluoride, nitrate and sulfate ions using the modified AFN membrane are given in Figure 4.

The different adsorption parameters along with regression coefficients (R^2) and chi-square statistic χ^2 obtained from the non-linear regression have been evaluated and compiled in Table 6.

Based on the values of the regression coefficient (R^2) and the chi-square test χ^2 obtained for the three studied anions, the experimental results of the adsorption of fluorides, nitrates and sulfates on the modified AFN membrane fitted well with the D-A model. The adsorption energies, E, determined from this model are between 8 and 16 kJ.mol^{-1}, which indicates that the adsorption of fluoride, nitrate and sulfate ions on the modified AFN membrane is an ion exchange process.

To better illustrate the efficiency of the surface modification on the adsorption capacity of the AFN membrane, results were presented with the best fit modelled line both for the modified and the unmodified membrane as given in Figure 5.

Table 6 | Langmuir, D-A and R-P parameters determined from nonlinear regression for the adsorption of F^-, NO_3^- and SO_4^{2-} on the modified AFN membrane

Model parameters	Cl^-/F^-	Cl^-/NO_3^-	Cl^-/SO_4^{2-}
Langmuir			
q_0 (mmol.g^{-1})	5.34	3.38	1.27
K_L (L.mol^{-1})	86.62	86.20	51.48
R^2	0.978	0.982	0.959
χ^2	3.33×10^{-3}	0.99×10^{-3}	0.63×10^{-3}
D-A			
q_0 (mmol.g^{-1})	5.28	3.35	1.25
E (kJ.mol^{-1})	9.49	9.45	8.33
n_D	2.80	2.82	2.61
R^2	0.980	0.985	0.964
χ^2	3.65×10^{-3}	0.97×10^{-3}	0.68×10^{-3}
R-P			
A	0.62	0.39	0.08
B	0.13	0.13	0.07
β_{RP}	0.98	0.98	0.98
R^2	0.963	0.962	0.952
χ^2	6.68×10^{-3}	2.47×10^{-3}	0.90×10^{-3}

The change in the adequacy of the isotherm model from the Langmuir model for the adsorption on the unmodified AFN membrane to the D-A model for the adsorption on the modified membrane can be explained by the decrease of membrane homogeneity after modification. In fact, for the unmodified AFN membrane the better correlation between the experimental data and the Langmuir model fit can be explained by the high homogeneity of the membrane surface. This result is in agreement with the heterogeneity parameter β_{RP} deduced from the R-P model which is equal to 1. As seen in Table 6, the values of the heterogeneity parameters, n_D, determined from the D-A model, decreased ($n_D < 3$) for the modified AFN membrane, indicating a decrease in the homogeneity of the AFN membrane after surface modification by PEI.

The D-A constants q_0, which represent the maximum adsorption capacities, for the adsorption of F^-, NO_3^- and SO_4^{2-} on the modified AFN membrane, were compared with those obtained with the unmodified one deduced from the

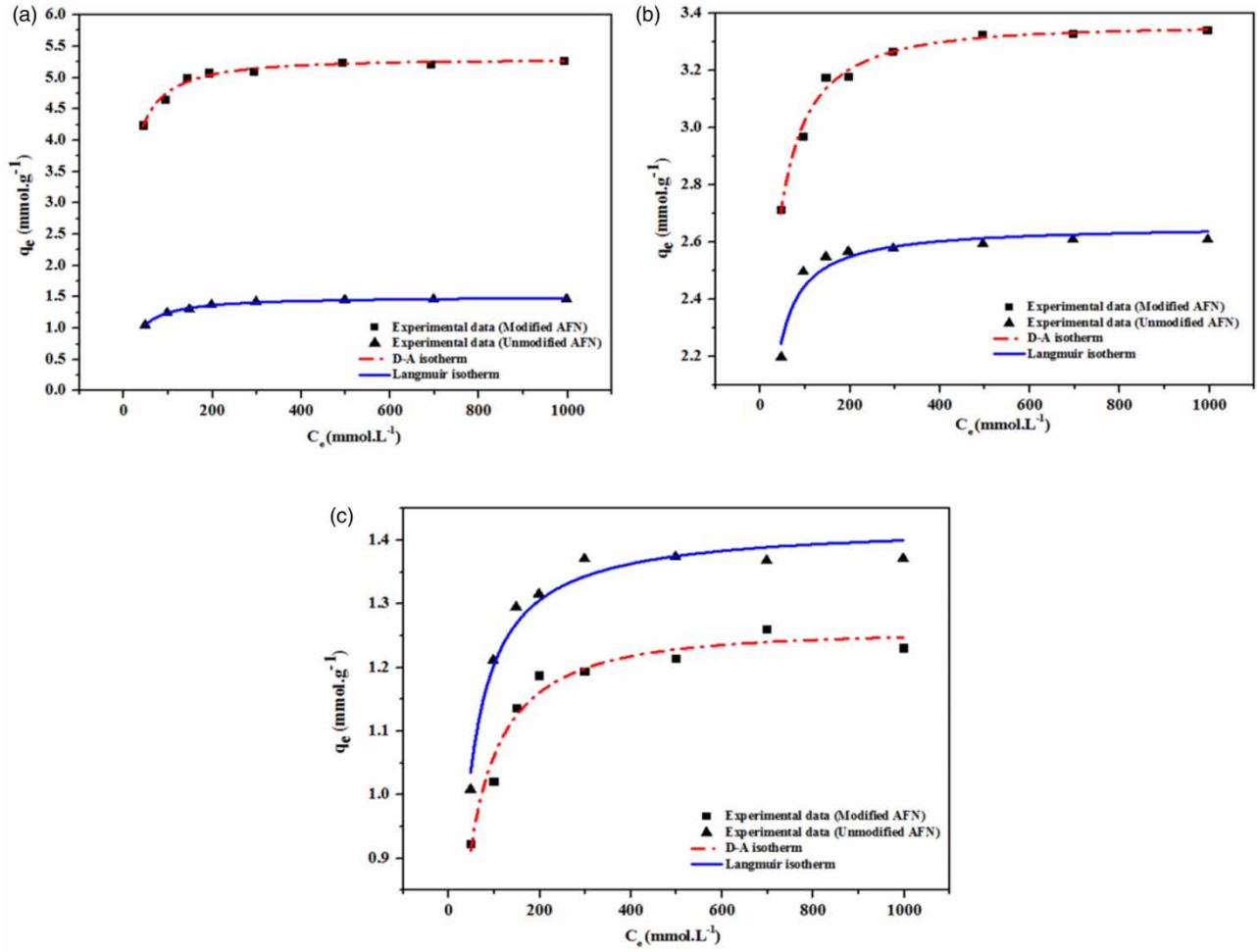

Figure 5 | Adsorption isotherms of fluoride (a), nitrate (b) and sulfate (c) ions on the modified and the unmodified AFN membrane at 298 K.

Langmuir fitting. In fact, for the unmodified membrane the maximum adsorption capacities were 1.51 mmol.g^{-1}, 2.66 mmol.g^{-1} and 1.42 mmol.g^{-1}, respectively, for the adsorption of F^-, NO_3^- and SO_4^{2-} ions. It is shown, from the results given in Table 6, that after surface modification of the AFN membrane the maximum adsorption capacities of fluoride and nitrate ions increase. The maximum adsorption capacity of sulfate on the unmodified membrane, however, is larger than that of the modified one.

For the modified AFN membrane, the E values determined from D-A model were found to be 9.49, 9.45 and 8.33 kJ.mol^{-1}, respectively, for fluorides, nitrates and sulfates. Results show that the affinity order is: $F^- > NO_3^- > SO_4^{2-}$. This finding can be attributed to the layer of the PEI formed in the surface of the membrane which plays a role of a repulsive barrier towards ions of high valences.

Desorption of fluoride from the modified AFN membrane

In order to study the possibility of the desorption of fluoride from the modified AFN membrane by nitrate and sulfate ions, adsorption equilibrium isotherms of Langmuir, D-A and R-P models were established for (F^-/NO_3^-), (F^-/SO_4^{2-}) and (NO_3^-/SO_4^{2-}) systems using the modified AFN membrane. All experiments were carried out at initial concentrations from 0.05 to 1 mol.L^{-1} and constant temperature of 298 K. The different adsorption parameters determined from the non-linear regression are illustrated in Table 7.

Table 7 | Langmuir, D-A and R-P parameters for (F^-/NO_3^-), (F^-/SO_4^{2-}) and (NO_3^-/SO_4^{2-}) systems determined by non-linear regression

Model parameters	F^-/NO_3^-	F^-/SO_4^{2-}	NO_3^-/SO_4^{2-}
Langmuir			
q_0 (mmol.g^{-1})	1.97	1.32	1.26
K_L (L.mol^{-1})	19.41	12.61	17.95
R^2	0.953	0.934	0.958
χ^2	6.01×10^{-3}	5.81×10^{-3}	2.16×10^{-3}
D-A			
q_0 (mmol.g^{-1})	1.87	1.22	1.19
E (kJ.mol^{-1})	6.06	5.32	6.06
n_D	2.69	2.78	2.53
R^2	0.974	0.976	0.964
χ^2	4.08×10^{-3}	2.54×10^{-3}	2.21×10^{-3}
R-P			
A	0.04	0.02	0.03
B	0.02	0.02	0.02
β_{RP}	0.98	0.96	0.97
R^2	0.941	0.914	0.948
χ^2	9.09×10^{-3}	9.02×10^{-3}	3.18×10^{-3}

For the modified AFN membrane in Cl^- form, the adsorption energies of NO_3^- and SO_4^{2-} were found to be 9.45 kJ.mol^{-1} and 8.33 kJ.mol^{-1}, respectively. As seen in Table 7, the values of the adsorption energies of NO_3^- and SO_4^{2-} on the same membrane in F^- form decreased. In fact, nitrate and sulfate ions are favorably adsorbed on the modified membrane in Cl^- form. These results show that the F^- anions previously exchanged on the modified AFN membrane are difficult to be removed by NO_3^- and SO_4^{2-} ions.

CONCLUSIONS

The adsorption of fluoride, nitrate and sulfate ions on the AFN membrane was studied. The suitability of the Langmuir, D-A and R-P adsorption models to the equilibrium data was investigated. Adsorption parameters were determined from non-linear regression. Results were found to best fit Langmuir adsorption isotherm. In order to improve the selectivity of the AFN membrane towards anions, modification of the surface of this membrane with PEI has been attempted. An experimental design methodology was adopted in this study to determine the optimal experimental conditions for the modification of the AFN membrane. Factorial design results showed that the main influent parameters for the adsorption of PEI on the surface of the membrane were the initial concentration and the pH of the PEI solution. Modified AFN membrane had higher adsorption capacities for fluoride and nitrate than the unmodified membrane, while the adsorption capacity for sulfate ions decreased after the surface modification of the membrane. According to these results it can be concluded that the modified AFN membrane is an effective adsorbent for the removal of fluorides from aqueous solutions.

REFERENCES

Abdelwahab, O., Amin, N. K. & El-Ashtoukhy, E.-S. Z. 2013 Removal of zinc ions from aqueous solution using a cation exchange resin. *Chem. Eng. Res. Des.* **91**, 165–173.

Amara, M. & Kerdjoudj, H. 2003 Modification of the cation exchange resin properties by impregnation in polyethyleneimine solutions: application to the separation of metallic ions. *Talanta* **60**, 991–1001.

Amara, M. & Kerdjoudj, H. 2007 A modified anion exchange membrane applied to purification of effluent containing different anions. Pre-treatment before desalination. *Desalination* **206**, 205–209.

Bae, B., Juang, Y., Han, W. & Shin, H. 2002 Improved brine recycling during nitrate removal using ion exchange. *Water Res.* **36**, 3330–3340.

Biesuz, R., Pesavento, M., Alberti, G. & Riva, F. D. 2001 Investigation on sorption equilibria of Mn(II), Cu(II) and Cd (II) on a carboxylic resin by the Gibbs-Donnan model. *Talanta* **55**, 541–550.

Chabani, M., Amrane, A. & Bensmaili, A. 2006 Kinetic modelling of the adsorption nitrates by ion exchange resin. *Chem. Eng. J.* **125**, 111–117.

Chabani, M., Amrane, A. & Bensmaili, A. 2009 Equilibrium sorption isotherms for nitrate on resin Amberlite IRA 400. *J. Hazard. Mater.* **165**, 27–33.

Chia-Hung, L., Jeng-Shiou, W., Hsin-Chieh, C., Shing-Yi, S. & Hoong Chu, K. 2007 Removal of anionic reactive dyes from water using anion exchange membranes as adsorbers. *Water Res.* **41**, 1491–1500.

Cortina, J. L., Miralles, N., Sastre, A. M. & Aguilar, M. 1997 Solid-liquid extraction studies of divalent metals with impregnated resins containing mixtures of organophosphorus extractants. *React. Fonct. Polym.* **32**, 221–229.

Dolar, D., Kosutic, K. & Vucic, B. 2011 RO/NF treatment of wastewater from fertilizer factory – removal of fluoride and phosphate. *Desalination* **265**, 237–241.

Dron, J. & Dodi, A. 2011 Comparison of adsorption equilibrium models for the study of Cl^-, NO_3^- and SO_4^{2-} removal from aqueous solutions by an anion exchange resin. *J. Hazard. Mater.* **190**, 300–307.

Du Preez, L. A., Odendaal, J. P., Maree, J. P. & Ponsonby, M. 1992 Biological removal of sulfate from industrial effluents using producer gas as energy source. *Environ. Technol.* **13**, 875–882.

Gohil, G. S., Binsu, V. V. & Shali, V. K. 2006 Preparation and characterization of mono-valent ion selective polypyrrole composite ion-exchange membranes. *J. Membr. Sci.* **280**, 210–218.

Guesmi, F., Hannachi, C. & Hamrouni, B. 2012 Selectivity of anion exchange membrane modified with polyethyleneimine. *Ionics* **18**, 711–717.

Guesmi, F., Hannachi, C. & Hamrouni, B. 2013 Modification of the AMX membrane surface: temperature dependence of anion exchange equilibrium. *Can. J. Chem. Eng.* **91**, 1465–1473.

Haghsheno, R., Mohebbi, A., Hashemipour, H. & Sarrafi, A. 2009 Study of kinetic and fixed bed operation of removal of sulfate anions from an industrial wastewater by an anion exchange resin. *J. Hazard. Mater.* **166**, 961–966.

Hannachi, C., Guesmi, F., Bouguerra, W. & Hamrouni, B. 2013 Adsorption of F^-, NO_3^- and SO_4^{2-} on AFN anionic membrane: kinetics and thermodynamics studies. *Am. J. Anal. Chem.* **4**, 501–509.

Hannachi, C., Guesmi, F., Missaoui, K. & Hamrouni, B. 2014 Application of adsorption models for fluoride, nitrate, and sulfate ion removal by AMX membrane. *Int. J. Technol.* **1**, 60–69.

Jeng-Shiou, W., Chia-Hung, L., Hoong Chu, K. & Shing-Yi, S. 2008 Removal of cationic dye methyl violet 2B from water by cation exchange membranes. *J. Membr. Sci.* **309**, 239–245.

Langmuir, I. 1918 The constitution and fundamental properties of solid and liquids – Part I. Solids. *J. Am. Chem. Soc.* **40**, 1361–1403.

Meenakshi, S. & Viswanathan, N. 2007 Identification of selective ion exchange resin for fluoride sorption. *J. Colloid Interface Sci.* **308**, 438–450.

Ranjana, A. 2012 Nitrate contamination in ground water samples of Gangapurcity town (Sawai Madhopur District) Rajasthan. *J. Chem. Bio. Phys. Sci.* **2**, 511–513.

Redlich, O. J. & Peterson, D. L. 1959 A useful adsorption isotherm. *J. Phys. Chem.* **63**, 1024–1026.

Sachin, N. M., Jayshri, V. P., Shilpi, K., Amit, B., Tapan, C. & Rajesh, B. B. 2011 Equilibrium isotherm and kinetic modeling of the adsorption of nitrates by anion exchange Indion NSSR resin. *Desalination* **276**, 38–44.

Samadi, M. T., Zarrabi, M., Sepehr, M. N., Ramhormozi, S. M., Azizian, S. & Amrane, A. 2014 Removal of fluoride ions by ion exchange resin: kinetic and equilibrium studies. *Environ. Eng. Manage. J.* **13**, 205–214.

Sata, T. & Mizutani, Y. 1979 Modification of properties of ion exchange membranes. VI. Electrodialytic transport properties of cation exchange membranes with an electrodeposition layer of cationic polyelectrolytes. *J. Polym. Sci. Polym. Chem.* **17**, 1199–1213.

Schoeman, J. J. & Steyn, A. 2001 Investigation into alternative water treatment technologies for the treatment of underground minewater discharged by Grootvlei Proprietary Ltd. into the Blesbokspruit in South Africa. *Desalination* **133**, 13–30.

Sehn, P. 2008 Fluoride removal with extra low energy reverses osmosis membranes: three years of large scale field experience in Finland. *Desalination* **223**, 73–84.

Serarols, J., Poch, J. & Villaescusa, I. 2001 Determination of the effective diffusion coefficient of Zn(II) on a macroporous resin XAD-2 impregnated with di-2-ethylhexyl phosphoric acid (DEHPA). Influence of metal concentration and particle size. *React. Fonct. Polym.* **48**, 53–63.

Solangi, I. B., Memon, S. & Bhanger, M. I. 2009 Removal of fluoride from aqueous environment by modified Amberlite resin. *J. Hazard. Mater.* **171**, 815–819.

Tehobanoglous, G. 1979 *Wastewater Engineering: Treatment Disposal Reuse.* 2nd edn. McGraw-Hill Inc., New York.

Vasiliu, S., Bunia, I., Racovita, S. & Neagu, V. 2011 Adsorption of cefotaxime sodium salt on polymer coated ion exchange resin microparticles: kinetics, equilibrium and thermodynamic studies. *Carbohydr. Polym.* **85**, 376–387.

Xu, X., Gao, B., Zhao, Y., Chen, S., Tan, X., Yue, Q., Lin, J. & Wang, Y. 2012 Nitrate removal from aqueous solution by Arundo donax L. reed based anion exchange resin. *J. Hazard. Mater.* **203–204**, 86–92.

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