Equilibrium sorption isotherms for nitrate on resin Amberlite IRA 400

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ABSTRACT

The adsorption isotherms of nitrate on resin Amberlite IRA 400 at various pH, in the range 2–12, were experimentally determined by batch tests. The experimental data have been analysed using the Langmuir, Freundlich, Redlich–Peterson and Sips isotherms models. In order to determine the best fit isotherm, two error analysis methods were used to evaluate the data: the regression correlation coefficient, and the statistic Chi-square test. In the range of pH tested, the Sips model was found to give the best fit of the adsorption isotherm data. The maximum adsorption capacity can be deduced from the obtained correlation coefficients and was found to decrease for increasing pH.

1. Introduction

Several nitrogenous compounds, including ammonia, nitrite and nitrate are frequently present in drinking water [1]. Nitrates can cause several environmental problems. Nitrates and phosphates can stimulate eutrophication where pollution is caused in waterways by heavy algal growth, as both are rate-limiting nutrients for the process. A high concentration of nitrate-nitrogen in drinking water leads to the production of nitrosamine, which is related to cancer, and increases the risks of diseases such as methemoglobinemia in newborn infants [2,3].

Several methods that serve to reduce nitrates in drinking water were developed. The use of biological reactor seems to be the most promising technique in the treatment of high nitrate concentrations. However, maintaining biological processes at their optimum conditions is difficult, and the problems of contamination by dead-bacteria have to be solved to make such processes satisfactory for a safety use in drinking water treatment. Adsorption is a useful process for in situ treatment of underground and surface water, primarily due to it's easy of use [3].

Adsorbent resins are considered to be the most promising method owing to their chemical stability and ability to control surface chemistry [4].

The study of the adsorption equilibrium allows the estimation of the material capacity to adsorb various molecules [5]. Analysis of the isotherm data is important to develop equations to describe the results with accuracy and which could be used for design purposes [6]. The representation of adsorption isotherm can be based on models involving two or three parameters.

The most common isotherms applied in solid/liquid system are the theoretical equilibrium isotherm, Langmuir [7], the best known and most often used isotherm for the sorption of a solute from a liquid solution; the Freundlich isotherm [8], the earliest known relationship describing the adsorption equation; and the Redlich–Peterson isotherm [9], the earlier presented containing three parameters.

Linear regression was frequently used to determine the most appropriate model to fit adsorption isotherms and parameters were in general optimised by means of the least squares method. However, transformations of non-linear isotherm equations to linear forms implicitly alter their error structure and may also violate the error variance and normality assumptions of standard least squares [10]. In recent years, several error analysis methods, such as the error sum of squares, a hybrid error function, Marquardt's percent standard deviation, the average relative error and the sum of absolute errors have been used to determine the best-fitting isotherm [11,12]. In this study, a comparison of linear regression and Chi-square analysis of four isotherms, Langmuir, Freundlich, Sips and Redlich–Peterson were applied to the adsorption of nitrate on Amberlite IRA 400.

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Nomenclature

A	constant in the Redlich–Peterson isotherm (l/g)
b	the adsorption energy or the adsorption equilibrium constant (cm^3/mg)
B	constant in the Redlich–Peterson isotherm (l/mg)
C_0	initial concentration in solution (mg/l)
C_e	equilibrium concentration (mg/l)
k_f	Freundlich's constant related to the sorption capacity
m	mass of adsorbent (g)
n	Freundlich's constant related to the sorption intensity of a sorbent
q_0	maximum adsorption capacity (mg/g)
q_e	adsorption capacity at equilibrium (mg/g)
V	volume of solution (l)

Greek symbols

β	the degree of heterogeneity in the Redlich–Peterson isotherm
γ	the dissociation parameter in the Sips model

2. Materials and methods

2.1. Pre-treatment of resin

Before use, the resin was washed in distilled water to remove the adhering dirt and then dried at 50 °C. After drying, the resin was sieved to obtain a particle size range of 0.3–0.8 mm.

2.2. The resin characteristics

The main characteristics of the Amberlite IRA 400, an anion exchange resin gel type, are given in Table 1.

2.3. Nitrate solutions

The stock solution of NO_3^- used in this study was prepared by dissolving an accurate quantity of KNO_3 in distilled water. A range of dilutions, 1–26 mg/l, was prepared from the stock solution. The pH of the aqueous solutions of NO_3^- was approximately 6.8 and did not change significantly with the dilution.

2.4. Sorption equilibrium

Equilibrium experiments at 22 °C were carried out by contacting 0.5 g of resin with 200 ml of nitrate solutions at different initial concentrations. The solutions were placed in flasks and stirred at a constant agitation speed of 400 rpm for 3 h. Preliminary tests showed that the adsorption was complete after 1 h. Experiments

Table 1
Characteristics of Amberlite IRA 400 ion exchange resin

Polymer matrix	Polystyrene DVB
Functional group	—N^+R_3
Ionic form	Cl^-
Exchange capacity	2.6–3 eq kg^{-1} of dry mass
Appearance	Yellow to golden spherical beads, translucent
Effective size	0.3–0.8 mm
Water retention	42–48%
Visual density in wet state	0.66–0.73 g/ml
True density in wet state	1.07–1.10 g/ml

Information provided by the manufacturer (Merck, Darmstadt, Germany).

were mainly carried out without initial adjustment of the pH. To determine the effect of pH onto adsorption performances, the pH was adjusted using 1N NaOH and 1N HCl solutions.

The concentration of residual nitrate ions was determined spectrophotometrically according to the Rodier protocol [13]. The adsorption capacity at equilibrium q_e (mg/g) was obtained as follows:

$$q_e = (C_0 - C_e)\frac{V}{m} \tag{1}$$

where C_0 and C_e are the initial nitrate concentration and the concentration at equilibrium; V is the volume of solution and m the mass of adsorbent.

3. Result and discussion

3.1. Effect of solution pH

Adsorption can be expressed as the separation of substances of one phase accompanied by their attraction to the surface of an adsorbing phase. This transfer process takes place until equilibrium conditions are reached. The correlation of the isotherm data by theoretical or empirical equations is required for a practical use. Adsorption isotherms at 22 °C in 1N HCl or 1N NaOH are shown in Fig. 1. The isotherm data were treated according to isotherm equations with two and three parameters.

Different pH values were obtained by using different amounts of HCl in the protonation step or NaOH. The variations of the percentage removal vs. pH followed a bell-shaped curve (Fig. 2). The adsorption was maximum at pH 6.8 and low beyond 12. Below pH 2, the adsorption became negligible. Increasing pH to 12.45 allowed the desorption of nitrate without losing the effectiveness of the resin, and the lower values of removal in alkaline conditions were probably due to competing OH^- ions.

An explanation for getting bell shaped curve (Fig. 2) can be given based on the surface characteristics of Amberlite IRA 400. The mechanism is based on the formation of an amine group, similarly to the mechanism proposed by Roberts and Taylor [14,15] for polyaminated chitosan resins:

The $RCH=N+R3'$ group reacts with water in two steps:

firstly with OH^- : $RCH=N^+R_3' + OH^- \rightarrow RCH(OH)-NR_3'$

then with H^+ : $RCH(OH)-NR_3' + H^+ \rightarrow RCH(OH)-NH^+R_3'$

$RCH(OH)-NH^+R_3'$ contains an amine group, which is particularly reactive and able to retain anions. Water is involved in this
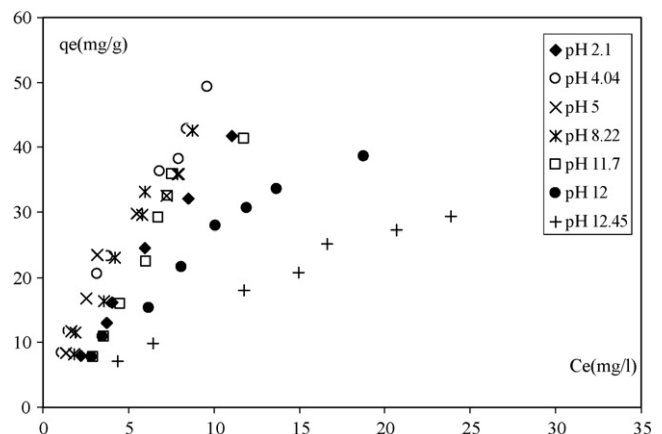

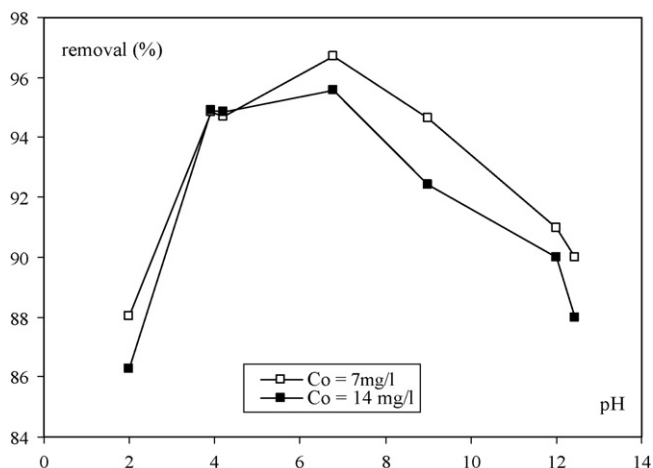**Fig. 1.** Adsorption isotherms for nitrate at 22 °C and at various pH.

Fig. 2. % Removal vs. pH for two different initial nitrate concentrations.

Fig. 3. Linear expression of the Langmuir equation (Eq. (3)) (lines: calculated data) for the adsorption of nitrate (symbols: experimental data) onto Amberlite IRA 400 at various initial pH.

Fig. 4. Langmuir equation obtained by using the non-linear (Eq. (2)) and linear methods (Eqs. (3) and (4)) for the adsorption of nitrate at various initial pH.

mechanism, which was therefore optimal at neutral pH, as shown in Fig. 2.

3.2. Langmuir isotherm

One of the most common isotherm models is the Langmuir model. According to this model, a single adsorbate is retained in only one molecular layer. The Langmuir isotherm model can be expressed as:

$$q_e = \frac{q_0 b C_e}{1 + b C_e} \quad (2)$$

where q_e is the adsorption capacity at equilibrium, C_e is the equilibrium concentration, and q_0 and b are the Langmuir constants related to the maximum adsorption capacity and the adsorption energy, respectively. Maximum adsorption capacity q_0 represents the monolayer coverage of sorbent with sorbate and b represents the enthalpy of adsorption. Four different types of linearization can be used for the Langmuir isotherm [16]; the widely used linear expressions are Eqs. (3) and (4):

$$\frac{1}{q_e} = \frac{1}{b q_0} \frac{1}{C_e} + \frac{1}{q_0} \quad (3)$$

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

Non-linear regression and graphical methods by plotting $1/q_e$ vs. $1/C_e$ and C_e/q_e vs. C_e were used to evaluate the two Langmuir's parameters.

Langmuir model parameters and statistical fits of experimental data to the above equation are given in Table 2. They showed that amongst the several available linear expressions, the non-linear
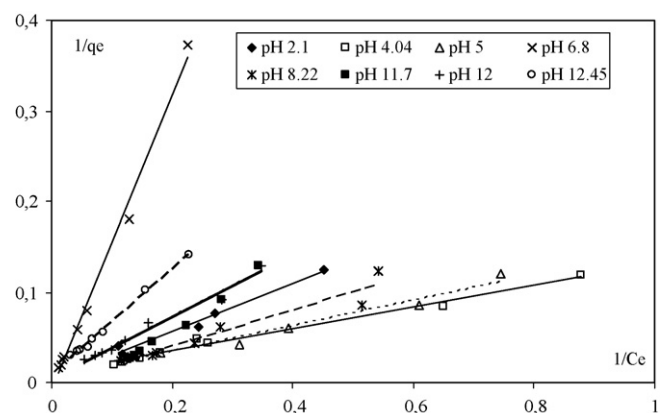
regression represented the most suitable method to determine the parameters. Constants q_0 and b, as well as the regression correlation coefficient R^2 of Eqs. (3) and (4) differed. Linearization affected significantly the values of the Langmuir's parameters. Eq. (3) (Fig. 3) gave high values of R^2 but the parameters q_0 and b were negative, showing that validation of this kind of model cannot be based on the criterion R^2. The large difference between the results given by Eqs. (3) and (4) can be attributed to the absence of chemical mechanism of adsorption given by the Langmuir isotherm [17].

Fig. 4 shows experimental data adjusted to the Langmuir model obtained by using linear and non-linear methods. The isotherm

Table 2
Non-linear and linear Langmuir isotherm parameters

pH	Langmuir model								
	Non-linear regression (Eq. (2))			Linear regression (Eq. (3))			Linear regression (Eq. (4))		
	R^2	b (cm³/mg)	q_0 (mg/g)	R^2	b (cm³/mg)	q_0 (mg/g)	R^2	b (cm³/mg)	q_0 (mg/g)
2.10	0.963	0.041	123.1	0.963	0.016	238.1	0.179	<0	<0
4.04	0.987	0.048	147.8	0.956	0.105	78.74	0.376	0.046	147.0
5.00	0.967	0.098	85.24	0.971	0.051	138.8	0.807	0.085	92.6
6.80	0.982	0.006	161.4	0.993	<0	<0	0.228	<0	<0
8.22	0.970	0.036	169.5	0.933	<0	<0	0.020	0.006	833.3
11.70	0.893	0.022	205.0	0.988	<0	<0	0.934	<0	<0
12.00	0.982	0.031	108.9	0.978	0.015	192.3	0.637	0.022	140.8
12.45	0.985	0.029	71.55	0.970	0.022	80.00	0.501	0.015	104.1

Fig. 5. Linear form of the Freundlich equation (Eq. (5)) (lines: calculated data) for the adsorption of nitrate (symbols: experimental data) onto Amberlite IRA 400 at various initial pH.
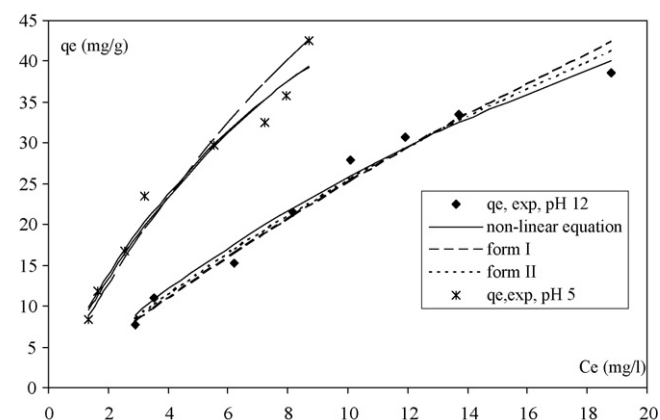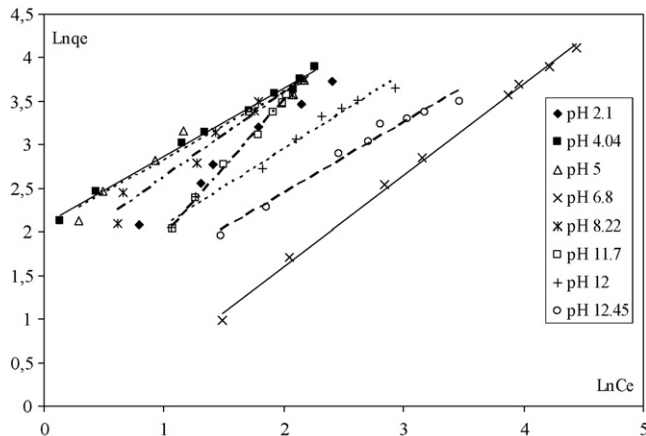
parameters obtained by using the non-linear method gave the best fitting.

3.3. Freundlich isotherm

The empirical model was shown to be consistent with exponential distribution of active centres, characteristics of heterogeneous surfaces. The amount of solute adsorbed, q_e is related to the concentration of solute in the solution, C_e, as following:

$$q_e = k_f C_e^{1/n} \tag{5}$$

The constants in the Freundlich isotherm are determined by linear regression, by plotting $\ln q_e$ vs. $\ln C_e$ (Fig. 5), as well as by non-linear regression.

Table 3 shows the linear and non-linear Freundlich adsorption isotherm constants, k_f and n, and the regression correlation coefficients, R^2. Based on the R^2 values, the non-linear form of the Freundlich isotherm appeared to produce a reasonable model for adsorption. The non-linear isotherm constants were not very different from those of the linear regression, indicating non-significant difference between both analytical methods. The linearization of the Freundlich model gave only one linear form. The value of n close to 1 indicated that adsorption was favourable.

The Freundlich adsorption isotherm gives an expression encompassing the surface heterogeneity, and the exponential distribution of active sites and their energy. This isotherm does not predict any saturation of the sorbent by the sorbate, thus infinite surface coverage is predicted mathematically, indicating a multilayer adsorption on the surface [18].
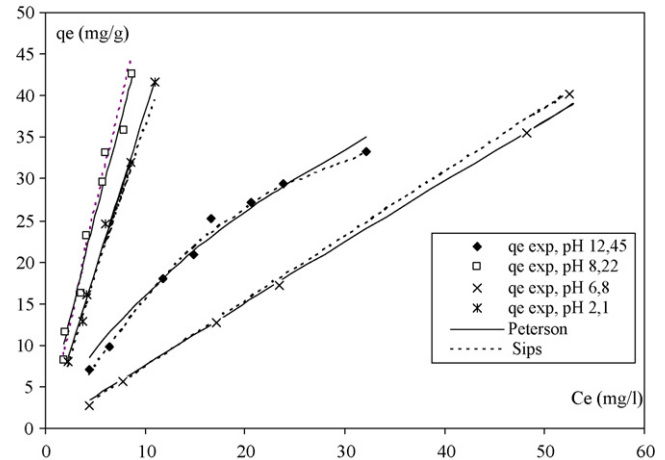

Fig. 6. Sips (Eq. (7)) and Redlich–Peterson (Eq. (6)) isotherms for nitrate adsorption onto Amberlite IRA 400 at 22 °C and various pH.

3.4. Redlich–Peterson isotherm

$$q_e = \frac{A C_e}{1 + B C_e^{\beta}} \tag{6}$$

The Redlich–Peterson equation involves three parameters A, B and β ($0 < \beta < 1$). A and B are constants, and β is the degree of heterogeneity. When coverage is very low, Eq. (6) becomes linear and leads to the Henry's Law. For high coverage, Eq. (6) can be assimilated to the Freundlich equation [5], since the ratio A/B and $(1 - \beta)$ corresponded to the parameters k_f and $1/n$ of the Freundlich isotherm (Eq. (5)). For $\beta = 1$, it can be assimilated to the Langmuir equation [19], A/B is numerically equal to the monolayer capacity (Q_0) and B is the sorption equilibrium constant.

3.5. Sips isotherm

$$q_e = \frac{q_0 b C_e^{\gamma}}{1 + b C_e^{\gamma}} \tag{7}$$

In the Sips model, q_e and C_e are the adsorption capacity at equilibrium and the equilibrium concentration, q_0 represents the maximum adsorption capacity, b the adsorption equilibrium constant and γ the dissociation parameter. If $\gamma = 1$, the Sips model reduces to the Langmuir model.

The experimental data were fitted to the Redlich–Peterson and Sips equations by applying non-linear regression analysis. Fig. 6 shows the equilibrium plot for various initial pHs. Both equilibrium models were in agreement with experimental equilibrium data. The calculated isotherm constants were given in Table 4, and showed that the two models gave similar regression correlation coefficients,

Table 3
Non-linear and linear Freundlich isotherm parameters

pH	Freundlich model (Eq. (5))					
	Non-linear regression			Linear regression		
	R^2	n	k_f	R^2	n	k_f
2.10	0.992	1.04	3.54	0.974	0.78	5.14
4.04	0.995	0.78	8.01	0.962	0.80	7.45
5.00	0.963	0.77	7.77	0.962	0.77	7.77
6.80	0.998	1.05	0.62	0.998	1.05	0.62
8.22	0.965	0.98	5.21	0.965	0.98	5.21
11.70	0.944	1.29	2.19	0.995	1.55	1.50
12.00	0.979	0.87	3.35	0.978	0.87	3.35
12.45	0.978	0.81	2.26	0.960	0.83	2.06

Table 4
Redlich–Peterson and Sips isotherms parameters

pH	Redlich–Peterson model (Eq. (6))				Sips models (Eq. (7))			
	R^2	A	B	β	R^2	q_0 (mg/g)	b (cm^3/mg)	γ
2.10	0.993	6.44	0.66	0.02	0.993	75.6	0.031	1.51
4.04	0.991	12.90	0.70	0.37	0.996	109.0	0.077	0.91
5.00	0.967	8.73	0.13	0.90	0.966	123.0	0.060	1.01
6.80	0.999	1.85	1.31	0.03	0.999	291.0	0.002	1.11
8.22	0.971	8.32	0.44	0.23	0.970	166.0	0.027	1.21
11.70	0.891	5.05	0.22	0.10	0.982	126.0	0.006	2.03
12.00	0.975	4.47	0.21	0.55	0.988	60.8	0.033	1.36
12.45	0.976	2.80	0.17	0.64	0.993	45.9	0.021	1.39

irrespective of the experimental pH. Therefore, the more adequate model cannot be chosen on the basis of the comparison of the regression coefficients as the sole criterion. In view of the comparison of both models, one additional criterion that can be considered was the statistic test.

3.6. Adsorption isotherm comparison

Based on the linear regression correlation coefficient R^2, the four equilibrium models matched experimental data. Table 5 shows that the average correlation coefficient decreased in the following order: 0.984 for the Sips model, 0.976 for the Freundlich model, 0.970 for the Redlich–Peterson model and 0.966 for the Langmuir isotherm model. High R^2 values for the Redlich–Peterson isotherm indicated an approximation of equilibrium data to Henry's law at low initial concentrations and an approximation to the Freundlich isotherm at high concentrations [20]. As discussed above, comparison of isotherm models cannot only be based on the comparison of the correlation coefficients as the sole criterion. In addition, experimental data were also analysed by means of the Chi-square test to compare the models.

The statistic Chi-square test, namely the sum of the squares of the differences between experimental and calculated data divided by the corresponding calculated data [16], is given by the following mathematical statement:

$$\chi^2 = \sum \frac{(q_{e,exp} - q_{e,cal})^2}{q_{e,cal}} \qquad (8)$$

where $q_{e,exp}$ and $q_{e,cal}$ are the experimental and calculated equilibrium capacity (mg/g). χ^2 increased for an increasing difference between calculated and experimental data [21].

Based on the statistic test, Table 5 shows at acidic pH (<6.8), a less significantly difference between Sips model and Redlich–Peterson model. At alkaline pH (above 11.70), the Sips isotherm exhibited lower χ^2 values than the Langmuir, Freundlich and Redich–Peterson isotherms. Average χ^2 values decreased in the following order: 1.87, 1.23, 1.09 and 0.81 for the Langmuir, the
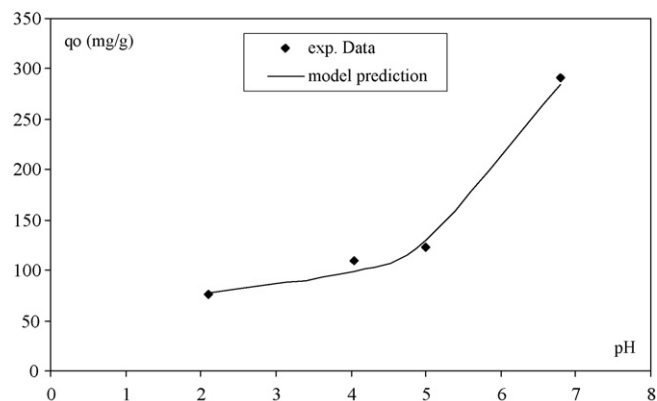

Fig. 7. Effect of pH on Amberlite IRA 400 maximum adsorption capacity (Eq. (9)).

Redlich–Peterson, the Freundlich and the Sips models, respectively. Based on the statistic Chi-square test, the Sips model appeared to lead to the better fit.

3.7. pH related empirical model

The functional groups or adsorption sites of resin Amberlite IRA 400 are influenced by the pH of the solution. Therefore, the maximum adsorption capacity obtained from Sips equation vary with the pH of the solution, while an influence of the pH influence on the adsorption equilibrium constant and the dissociation parameter was very difficult to derive from Table 4.

An empirical model was therefore proposed to represent nitrate adsorption data at different acidic pH, by introducing the maximum capacity as an exponential function of the pH in the Sips isotherm (Eq. (7)). The logistic function given below (Eq. (9)) was found to match experimental q_0 vs. pH data (Fig. 7):

$$q_0 = \exp(a + c\,\text{pH} + d\,\text{pH}^2) \qquad (9)$$

It should be noted that parameters a, c and d have no physical meanings. Experimental data obtained at different pH were fit-

Table 5
Comparison of non-linear regression coefficients R^2 and the statistic Chi-square test χ^2

pH	Langmuir		Freundlich		Redlich–Peterson		Sips	
	R^2	χ^2	R^2	χ^2	R^2	χ^2	R^2	χ^2
2.10	0.963	1.618	0.992	0.319	0.993	0.315	0.995	0.305
4.04	0.987	0.792	0.995	0.380	0.991	0.431	0.996	0.418
5.00	0.967	1.317	0.962	1.830	0.967	1.300	0.952	1.419
6.80	0.982	2.724	0.998	0.292	0.999	0.266	0.9996	0.288
8.22	0.969	1.586	0.965	1.472	0.971	1.432	0.970	1.774
11.70	0.893	5.571	0.944	2.000	0.891	4.258	0.982	1.118
12.00	0.982	0.787	0.979	1.160	0.975	1.038	0.988	0.646
12.45	0.985	0.544	0.976	1.175	0.976	0.849	0.993	0.251

Table 6
Tabulated χ^2 distribution for 29 degrees of freedom [22]

α	0.95	0.90	0.75	0.50	0.30	0.25	0.10	0.05	0.01	0.005
χ^2	42.6	39.1	33.7	28.3	3.66	23.6	19.8	17.7	14.3	13.1

ted by a non-linear regression method (using software package Levenberg–Marquardt) to optimise the three adjustable parameters (a, c and d), by minimisation of the sum of the deviation squares between experimental and predicted values. The optimised values were 4.577, −0.223 and 0.056 respectively and the regression correlation coefficient R^2 was high (0.994).

The following modified Sips model was then used to predict the adsorption isotherms at 22 °C and in a pH range from 2.1 to 6.8:

$$q_e = \exp(a + c\,\mathrm{pH} + d\,\mathrm{pH}^2)\frac{bC_e^n}{1 + bC_e^n} \tag{10}$$

Fig. 8 shows that the calculated isotherm profiles (Eq. (10)) matched experimental data recorded at 22 °C and at acidic pH. Only some discrepancies between calculated and experimental data can be found for pH 5 at high C_e values. Statistical validation of the modified Sips model was carried out by means of the χ^2 tests. For this purpose, calculated values of χ^2 were compared to tabulated values, and if $\chi^2_{cal} < \chi^2_{tab}$ the model was validated.

Empirical statistic χ^2 calculated from Eq. (8) ($\chi^2 = 13.16$) was compared to theoretical (tabulated) values of the distribution χ^2 (Table 6) with 29 degrees of freedom, by considering that the degrees of freedom corresponded to the number of experimental points minus one. A level of significance α of 0.01 was considered, leading to empirical values lower than the tabulated values, indicating that the difference between the theoretical and the experimental results was negligible. The modified Sips model gave therefore a good description of the experimental isotherms in the range of pH explored, i.e. from 2 to 6.8, with a high probability of 99%. The Average Absolute Deviation calculated by using Eq. (11) was 8.1% for a total number of 30 data points.

$$\mathrm{AAD} = \frac{1}{n}\sum_{i=1}^{n}\frac{\left|q_{e,\exp} - q_{e,cal}\right|}{q_{e,\exp}} \tag{11}$$
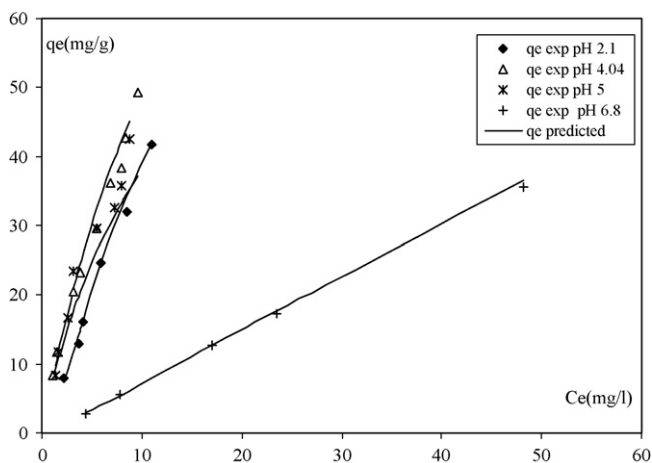

Fig. 8. Experimental and calculated (modified Sips model—Eq. (10)) adsorption isotherms of nitrate at various pH.

4. Conclusion

The following conclusions can be deduced from the above results:

- The isotherms of adsorption of nitrate on Amberlite IRA 400 at various pH were experimentally determined. The percentage removal after adsorption varied significantly with the initial pH of the nitrate solution. Irrespective of the pH of the solution, the equilibrium time of adsorption was about 1 h at 22 °C.
- The resin had a higher adsorption capacity at pH 6.8. Correlation equation was obtained to account for the effect of the pH on the maximum adsorption capacity of the resin.
- The mode of linearization had an effect on the estimation of the isotherm parameters of the Langmuir equation and the simulation precision.
- Many adsorption isotherm models fitted data quite well, but the Sips model was found to give the best fit of the adsorption isotherm data in a wide range of pH. The Sips model was modified by introducing an empirical equation that allowed to represent the effect of different initial pH on the maximum adsorption capacities.
- In case of several linear forms for an isotherm model, the correlation coefficient of the linear regression method was not an appropriate method of optimization to compare isotherm models.
- The non-linear Chi-square method provided the best satisfactory determination of experimental data.

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