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KINETICS OF NITROSO R-SALT SORPTION ON AMBERLITE IRA 402 RESIN

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ABSTRACT

The sorption of nitroso R salt from aqueous solution by ion exchange resins, such as AMBERLITE IRA 402 (Cl^- form) , is described. The experimental data have been analyzed by using the sorption kinetics for a first-order and pseudo-first order kinetic reaction models. The sorption rate constants according to these kinetic models have been calculated.

Keywords: Nitroso R-Salt, Chelating Resin, Ion-Exchange Kinetics, Sorption Rate Constant

1.Introduction

In the last years, the selective and quantitative retention of metal ions has been involving a great number of chelating sorbents.This studied sorbents are including inorganic materials (silicagel, kieselgur, controlled-pore glass) and organics (cellulose, dextran, polymeric resins, fibrous materials, foamed plastics) [1-4].

The chelating resin posses functional groups chemically bound (grafted groups) to an organic matrix and these active goups can form chelates with metal ions. However, only a few types of chelating resins are produced commercially and the use of resins such as these is limited by the difficulty of synthesis and their high cost.

The above mentioned disadvantages can be eliminated by preparing a complexing resin (ion exchanger modified with chelating reagent), by ion-exchange sorption of a chelating reagent on a conventional ion exchanger [5,6]. All these applications imply a knowledge of kinetic properties of a given system.

The present study deals with the sorption kinetics of nitroso-R salt from aqueous solutions on strongly basic anion-exchanger AMBERLITE IRA 402.

The kinetics of nitroso R-salt sorption has been caried out to understand the behavior of this ion-exchange resin. So that, to quantify the changes in the sorption of nitroso R-salt with time, an appropiate kinetic model is required.

For this purpose two models were tested: first and pseudo-first order kinetic models [8,9].

2. Experimental

2.1. Reagents

All solutions were prepared with demineralized water (electrolytic conductivity $\gamma = 0{,}70...1{,}20 \mu S / cm$ and pH=5.7- 6.2) and all chemichals were of analytical-reagent grade.

The chloride form of a commercially available strongly basic anion exchange resin AMBERLITE IRA 402 type 1 (Rohm and Haas,France) was used for preparing the chelating resin. The physical properties and specifications for strongly basic anion-exchang resin AMBERLITE IRA 402-Cl are presented in table 1.

Nitroso R-salt (NRS), (disodium 3-hydroxy-4-nitroso-2,7-naphthalenedisulfonat), produced by Fluka AG Switzerland Germany, was used as a chelating reagent for the preparation of the modified resin.

Standard working solutions were freshly prepared by the appropiate dilution of $5\cdot10^{-3}$ M NRS stock solution with demineralized water.

Table 1. *Physical properties and specifications for strongly basic anion- exchange resin AMBERLITE IRA 402.*

Polymer matrix structure	Polystyrene cross-linked with divinylbenzene-gel
Physical form and appearance	Clear golden spherical beads
Functional groups	Type 1 ; $-N^{+}(CH_3)_3$
Ionic form (as shipped)	Cl^- form
Shipping Weight	610-680 g/l (Cl^- form)
Screen size:(U.S.Standard Screen)	16-50 mesh wet
Mean diameter (μm)	620-770
Uniformity coefficient	1.6
Specific gravity (moist Cl^- form)	1.063-1.093
Moisture retention (Cl^- form)	50-56 %
Swelling ($Cl^- \rightarrow OH^-$)	30%
Exchange capacity (Cl^- form)	3.70 meq/g
Operating temperature (Cl^- form)	max. 60 ^{0}C
pH range stability (OH^- form)	0-13

2.2. Apparatus

A UV-VIS Specord 205 (Analytik Jena AG, Germany) double-beam spectrophotometer equipped with two pairs of 1 cm path length glass cuvettes was used for the absorbance measurements.

An AG-3 (ITM, Romania) magnetic stirrer with top hot plate and speed control was used for this experiments.

2.3. Methods and analysis

Prior to use, the resin was backwashed and rinsed with water as reported previously [7]. The resin was conditioned by consecutive treatments with 2M NaOH (250 ml solution/100 ml of resin) and 2 M HCl (250 ml solution/100 ml of resin) to remove organic and inorganic impurities and then was rinsed with demineralized water till Cl^- elimination, and air-dried at constant weight (96 hours).

2.3.1. Kinetic curves of the sorption of NRS on Amberlite IRA 402-Cl

Weighed amounts (1.0 g) of air-dried anion-exchange resin in chloride form were swallen and equilibrated with 500 ml of NRS solution with different initial C_0 concentrations, in a 500-ml glass-stoppered flask. Then, the mixtures were stirred for a predetermined period by a magnetic stirrer.

The amount of NRS was determined at adequate time intervals by spectrophotometrically measurement at 420 nm according to Lambert-Beer low.

This was done by extracting 2.5 ml of solution at each adequate time interval.

3. Results and Discussion

The kinetics of sorption describing the solute retention rate, which in turn governs the residence time of the sorption reaction, is an important characteristic which defines sorption effciency.

In this paper, the calculation of rate constants starts from the assumption that the overall ion-exchange process can be assimilated to a pseudo-first order reaction. This approximation is acceptable because the order of this above-mentioned reaction is slightly over 1 for most ion-exchange systems [8].The ion-exchange sorption of NRS on Amberlite IRA 402 resin was previosly analysed [5, 6].

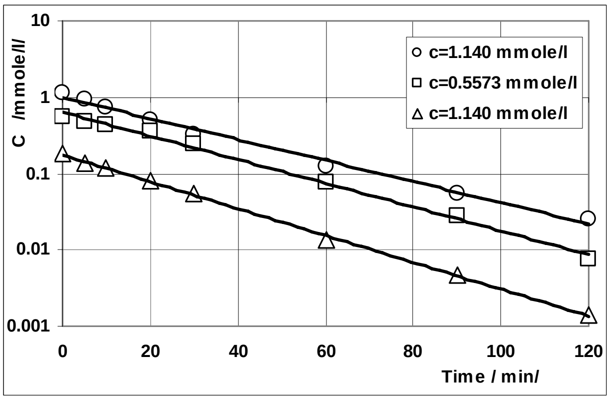

Fig.1.*The NRS concentration C of the external solution vs. time for different initial concentrations. Batch method: m/v=1 g/500 ml; stirring time τ = 2 h; t = 25 ^{0}C. Semi-logarithmic graph.*

The effect of time on NRS concentration C of the external solution, is shown in fig.1. The semi-logarithmic plot C = f (t) shows that the C varies linearly. From the point of view of formal kinetics, it suggests that the ion-exchange reaction could follow a first order reaction.

3.1. First order sorption kinetic model

The sorption of nitroso R salt from liquid phase to solid may be considered as a reversible reaction with an equilibrium state being established between two phases. A simple first-order reaction model [8-10] was used to correlate the rates of reaction, which can be expressed as:

$$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B$$

where k_1 is the forward reaction rate constant and k_2 is the backward reaction rate constant. If a is the initial concentration of NRS and x is the amount of NRS transferred from liquid phase to solid phase at any time t (expressed as concentration consumed in reaction), the rate can be expressed as:

$$\frac{dx}{dt} = \frac{-d(a-x)}{dt} = k(a-x) \qquad (1)$$

where C= a-x is the concentration of external solution at any time t and k is the overall reaction rate constant. Since k_1 and k_2 are the rate constants for the forward and reverse process (sorption and desorption), the rate can be expressed as:

$$\frac{dx}{dt} = k_1(a-x) - k_2x \qquad (2)$$

If x_e represents the concentration of NRS sorbed at equilibrium, then $k_1(a-x_e) - k_2x_e = 0$, because under these conditions:

$$\frac{dx}{dt} = 0 \quad \text{or} \quad K = \frac{x_e}{a-x_e} = \frac{k_1}{k_2} \qquad (3)$$

where K is the equilibrium constant. Now under equilibrium conditions, the rate becomes:

$$\frac{dx}{dt} = [k_1(a-x) - k_2x] - [k_1(a-x_e) - k_2x_e] \qquad (4)$$

The above equation is in the form dx/dt = k(a–x). Therefore,

$$(k_1 + k_2)t = \ln\frac{x_e}{x_e - x} \qquad (5)$$

$$\ln(1 - f_t) = -(k_1 + k_2)t = -kt \qquad (6)$$

where k is the overall rate constant and $ft = x/x_e$ is the fractional attainment of equilibrium of nitroso R salt. This was calculated by considering nitroso R-salt sorption on the resin in a given time range (2-3 hrs).

In the present study a concentration of nitroso R-salt in the range 0.1860 - 1.140 mmole/l was examined. Using the kinetic equations, the overall rate constant, the forward and backward rate constants were calculated.

As can be seen in fig.2, plotting ln (1− f_t) vs. t, a straight line passing through the orrigin is obtained.

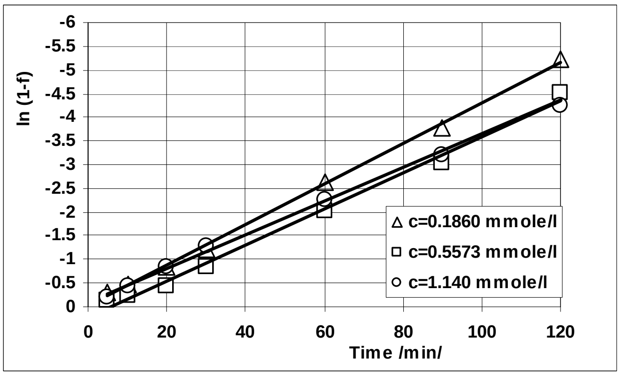

Fig.2.*First order kinetic plot for NRS sorption on Amberlite IRA 402.*

The overall rate constant k for a given concentration of NRS was calculated considering the slope of the straight line, and by using eq. (6) the equilibrium constant K and forward rate constants k_1 were calculated and are shown in table 2.

Table 2. *The first order reversible reaction parameters for NRS sorption on Amberlite IRA 402.*

Initial concentration, a (mmole/l)	Kinetic equation	Overall rate constant $k \cdot 10^{-3}$ (min^{-1})	Sorption rate constant $k_1 \cdot 10^{-3}$ (min^{-1})	Equilibrium constant K	Half time life $t_{1/2}$ (min)
0.1860	ln (1-f) = - 0.0427t-0.0291 R^2= 0.9985	42.70	42.61	464	16.26
0.5573	ln (1-f) = - 0.0380t-0.216 R^2= 0.9933	38.0	37.89	347.31	18.29
1.140	ln (1-f) = -0.0356t-0.0869 R^2= 0.9986	35.60	35.31	125.66	19.62

From table 2, it can be seen that the forward rate constants for the sorption of NRS are much higher than the backward rate constants, namely the desorption process.

The increasing of initial concentration of NRS (a) leads to the decreasing of the overall and forward rate constant, and to the increasing of the half time life $t_{1/2}$. The equilibrium constant, $K=k_1/k_2$, decreases with the increasing of a.

3.2. Pseudo-first order sorption kinetic model

The sorption kinetics may be described by a pseudo-first order reaction (Lagergren’s first order rate equation has been called pseudo-first order since 1998 [9] .

The differential equation is as follows:

$$\frac{dq_t}{dt} = k'(q_e - q_t) \qquad (7)$$

By integrating eq. (7) for boundary conditions t=0 to t=t and q*t*=0 to q*t*=q*t*, gives:

$$\log\left(\frac{q_e - q_t}{q_e}\right) = -\frac{k't}{2.303} \qquad (8)$$

which is the integrated rate law for a pseudo-first order (Lagergren kinetic rate equation), where q*e* is the amount of nitroso R-salt sorbed at equilibrium (mmole/g of resin), q*t* is the amount of nitroso R-salt sorbed at time t (mmole/g of resin) and k` is the equilibrium rate constant of pseudo-first sorption. In order to obtain the rate constants, the straight line plots of log (q*e*–q*t*) vs. t for different concentrations of NRS have been analysed.

The rate constants, k` , were calculated from the slope of these plots (Figure 3). Linear fits were observed for all initial concentrations, indicating that sorption reaction can be approximated to pseudo-first order kinetics. Constants k` have been calculated and summarized in table 3.

From table 3, it can be seen that the pseudo-first order rate constants k` for the sorption of NRS decreased with the increasing of initial NRS concentration .

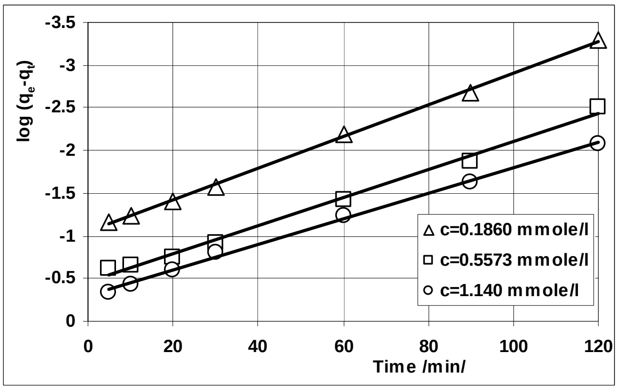

Fig.3.*Pseudo-first order kinetic plot for NRS sorption on Amberlite IRA 402.*

Table 3. *The pseudo-first order reaction parameters for NRS sorption on Amberlite IRA 402.*

Initial concentration, a (mmole/l)	Kinetic equation	Pseudo-first rate constant k` (min^{-1})
0.1860	log (qe-qt) = - 0.0186t-1,0446 (R^2= 0.9987)	$42.70 \cdot 10^{-3}$
0.5573	log (qe-qt) = - 0.0164t-0.4645 (R^2= 0.9938)	$37.77 \cdot 10^{-3}$
1.140	log (qe-qt) = -0.154t-0.2856 (R^2= 0.9984)	$35.46 \cdot 10^{-3}$

The values of the sorption rate constants k and k`, evaluated for the two kinetic models are practically identical and have the same size order as those in literature.

The ion-exchange process can be regarded as a mass transfer. Generally, the sorption rate is controlled either by a film-diffusion mechanism or particle diffusion mechanism.

The slower step controls the overall ion-exchange rate. In order to see which of these two processes is rate-determining a further analysis is necessary.

The NRS was initially sorbed by the exterior surface of resin.When the sorption of the exterior surface reached the saturation level, the NRS ions passed through the resin via the network and were sorbed by the interior surfaces.

When the NRS ions diffused into the pores of the resin, the diffusion resistance increased which in turn caused the diffusion rate to decrease.

The NRS functional groups of chelating resin have larger dimensions than the functional groups as classical exchanger and can hinder the diffusion of NRS ions into the center of the sorbent particle.

This could explain the decrease of sorption rate constans whereas the initial NRS concentration of the external solution increases.

4. Conclusions

In this paper it has been shown that Amberlite IRA 402 sorbent material can be used for the retention of Nitroso R-Salt from aqueous solutions. Kinetically, the sorption process was featured by applying two different models. Testing the system for the first and pseudo-first order kinetic equations, it was possible to determine the sorption rate constants.

Also, these results indicated that the first and pseudo-first order kinetic reaction models provided a good corellation of the experimental data for all initial concentrations.

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