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Incidența minimă a suspiciunii / Minimum incidence of suspicion

p.84:18 – p.84:31	p.98:01s - p.98:22s
p.85:06 – p.85:11	p.98:06d - p.98:16d
p.85:24 – p.85:27	p.98:19d – p.98:26d
p.85:28 – p.85:31	p.99:02s – p.99:08s
p.86:Fig.6	p.99:Fig.1

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STUDIES REGARDING THE SORPTION OF NITROSO R-SALT ON AMBERLITE IRA 402 RESIN

Part II

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Abstract: The paper presents some peculiar aspects of ion exchange behaviour for a strongly basic anion exchange and sulphonic chelating agent. A chelating resin was prepared from AMBERLITE IRA 402 (Cl⁻) - a common strongly basic anion- exchanger, by treatment with Nitroso R-Salt (NRS).The sorption of NRS on resin and some properties of NRS -IRA 402 chelating resin have been studied.Some parameters of ion-exchange equilibrium as the distribution coefficients K_d , ion-exchange constant $K_{Cl^-}^{NRS}$, uptake percentage R (%) and apparent Gibbs free energy change (ΔG) have been calculated.

Keywords: strongly base anion exchanger, chelating sorbents, ion exchange capacity, ion-exchange isotherm, distribution coefficient, ion-exchange constant, apparent Gibbs free energy, uptake percentage, Nitroso R-salt.

I. 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) [1,2,3].

The chelating resin posses functional groups chemically bound (grafted groups) to an organic matrix and these active groups 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 sorption of a chelating reagent on a conventional ion exchanger.

Some authors suggest the treatment of conventional ion-exchangers with sulphoderivatives of organic complexing reagents [4,5,6,7]. In this way, the resin is equilibrated with solutions of sulfonic chelating reagent and immobilization of this reagent on the anion exchanger resin takes place by an ion exchange mechanism, due to affinity for strongly anion exchanger, affinity resulting from the presence of sulfonic groups. Also interactions between the anion exchanger matrix and aromatic rings of chelating reagent has a remarkable importance [4,8,9].

Thus, several chelate forming reagents: thoron [10], sulfosalicylic acid [11], chromazurol S [12], eriochrome black T [13], Nitroso R-salt [15], acid 8-hydroxyquinoline-5-sulfonic acid [14], Ferron (7-iodo-8-hydroxyquinoline-5-sulfonic acid) [1,20], Alizarin red S [6,16], chromotropic acid [6], zincon [17], SPADNS [18], sulfonated azo-dyes [19] have been immobilized on anionic resins.

In this paper we have presented a chelating resin prepared by the modification of a common anion exchange resin with Nitroso R-salt. The interaction between Amberlite IRA 402 (Cl⁻) anionit and NRS as a function of chelating reagent concentration, phases contact time, and hydrodynamical regim have been studied.

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 chemicals 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), having quaternary ammonium as the active groups was used for preparing the chelating agent-loaded resin. This type of resin is placed in a line for the demineralizing of water which is designed to supply feed water for high pressure boilers [21].

Prior to use, the resin was backwashed and rinsed with water as reported previously [22]. 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). Moisture content was 48.90 %.

The exchange capacity of the AMBERLITE IRA 402 resin was determined by converting a known amount of resin to the chloride form with an excess of 4 M HCl solution. After washing the resin thoroughly with demineralized water, chloride ions were eluted with 1 M NaNO₃ solution and determined by titration with a standard silver nitrate solution. The exchange capacity for anions was found to be 2.90 meq/dry resin (chloride form). The exchange capacity for the anion-exchange resin loaded with NRS was 1.70 mmole NRS/g of resin. When reaching saturation, the NRS-resin becomes brown. Chelating sorbent exhibits a good stability in acid medium (HCl). The NRS was partially eluted from resin even with 0.1-1 M HCl. At treatment with 0.3 M HCl solution, the released amount of NRS is not exceed 15%.

Nitroso R-salt (NRS), (disodium 3-hydroxy-4-nitroso-2,7-naphthalenedisulfonat), produced by Fluka AG Switzerland Germany, was used as the chelating reagent for the preparation of the chelating agent-loaded resin. Standard working solutions were freshly prepared by the appropriate dilution of $5 \cdot 10^{-3}$ M stock solution with demineralized water.

2.2. Apparatus

A UV-VIS Specord 205 (Analytik Jena AG, Germany) double-beam spectrophotometer equipped with a pair 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 the batch method.

2.3. Methods and analysis

2.3.1. Forming calibration curve of NRS.

Using Microsoft Excel, the plot of absorbance at $\lambda_{420 \text{ nm}}$ vs. concentration of nitroso R-salt for a series of standard solutions of known concentration (in the range 0...50 mg/l) generates a straight line according to Lambert-Beer Law: $A = 0.0073c - 0.0021$ ($R^2 = 0.9999$).

2.3.2. Ion-exchange isotherm. Effect of hydrodynamical regim.

Procedure a (batch method-static regim with intermittent stirring). A 1.0000 g portions of air-dried anion-exchange resin in chloride form were swollen and equilibrated with 100 ml of NRS solutions at different concentrations in a 500-ml glass-stoppered flask. Then, the mixtures were stirred intermittently and set aside for 24 h. After such treatment, the loaded resin beds were filtered off on a fritted-glass funnel, washed with demineralized water and the solution was collected in a 1000-ml volumetric flask. An appropriate volume of the filtrate was used for the determination of the amount of NRS by measurement of absorbance at 420 nm.

Procedure b (batch method-static regim with continuous stirring). A 1.0000 g of air-dried anion-exchange resin in chloride form were equilibrated with 500 ml of NRS solutions at different concentrations ($2 \cdot 10^{-4}$... $1.25 \cdot 10^{-3}$ M) in a 500-ml glass-stoppered flask. Then, the mixtures were stirred for 2 h by a magnetic stirrer. The loaded resin beds were filtered off on a fritted-glass funnel, washed with demineralized water and the solution was collected in a 1000-ml volumetric flask. The amount of NRS was determined by spectrophotometrically measurement at 420 nm

2.3.3. Effect of time at different initial concentrations on the sorption of NRS on Amberlite IRA 402(Cl)

A 1.0000 g of air-dried anion-exchange resin in chloride form were equilibrated with 500 ml of NRS solutions at different concentrations ($2 \cdot 10^{-4}$... $1.25 \cdot 10^{-3}$ M) in a 500-ml glass-stoppered flask. Then, the mixtures were stirred for 2 h by a magnetic stirrer. The amount of NRS was determined at adequate time intervals by spectrophotometrically measurement at 420 nm. This was done by extracting 2.5 ml of solution at each adequate time interval.

3. RESULTS AND DISCUSSION

The ion-exchange isotherm was obtained according to:

$$q_e = \frac{v(c_0 - c_e)}{m} \quad (1)$$

where q_e is the exchange capacity of NRS (at equilibrium or at time t), in mmoles/g; C_0 and C_e are the initial and equilibrium phase concentration of chelating reagent, respectively, in mmoles/ml; v is the volum of aqueous solution, in ml, and m is the weight of air-dried resin used, in g. The ion-exchange isotherms for sorption NRS on Amberlite IRA 402(Cl) resin were constructed using batch method.

3.1. Effect of time and hydrodynamical regim for sorption of NRS on Amberlite IRA 402(Cl)

Preliminary runs showed that the exchange reaction studied by static method with intermittent stirring was not completed even in 24 h.

Figure 1 shows that in case of intermittent stirring (24 hours), the time required for the resin saturation with NRS was about 5 days but only two hours were necessary for the sorption of about half of this amount.

Figure 2 shows the effect of the hydrodynamical regim - in case of continuous stirring, the sorption equilibrium is attained only after two hours of phase contact, and about of 20 min. were necessary for the sorption of about half of this amount. In both cases the sorption of the NRS reagent increases with the phases contact time.

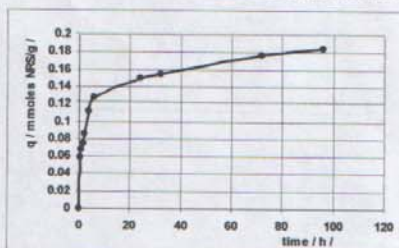


Fig.1. Effect of time on the sorption of NRS on Amberlite IRA 402-Cl. Batch method, intermittent stirring: $c_0 = 139.586$ mg/l; $m/v = 1/500$; $t = 25^\circ \text{C}$.

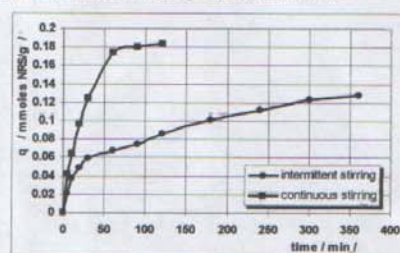


Fig.2. Effect of intermittent and continuous stirring on the sorption of NRS on Amberlite IRA 400-Cl. Batch method: $c_0 = 139.636$ mg/l; $m/v = 1/500$; $t = 25^\circ \text{C}$.

The ion-exchange isotherm obtained at different initial concentrations C_0 and at equilibrium time $t=2$ h is shown in fig. 3. It is obvious that the exchange capacity q increases with C_0 increasing.

After 2 hours, in the range of studied concentrations, 1.000 g resin reduces the initial concentration of NRS in solution in the range $2.550 \cdot 10^{-5} - 1.399 \cdot 10^{-6}$ M, giving a high sorption percentage.



Fig.3. Ion-exchange isotherm of NRS on Amberlite IRA 402-Cl. Batch method: $m/v=1$ g/500 ml; stirring time, $\tau = 2$ h; $t = 25$ °C.

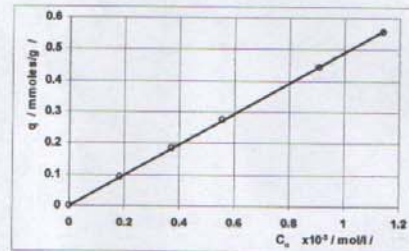


Fig.4. Effect of initial concentrations C_0 on sorption of NRS on Amberlite IRA 402-Cl. Batch method: $m/v=1$ g/500 ml; stirring time $\tau = 2$ h; $t = 25$ °C.

Figure 4 shows the effect of initial concentration C_0 on the NRS sorption on the resin: the sorption increases linearly with initial concentration C_0 : q (mmoles/g) = $0.4821 \cdot C_0$ (mol/l) + 0.0015 ; $R^2 = 1$.

The curves are typical of ion-exchange and show that the resin has a higher affinity for the NRS.

3.3. Effect of time at different initial concentrations on the sorption of NRS on Amberlite IRA 402(Cl)

Figure 5 shows that, for three concentrations, the sorption capacity of NRS increased with the initial concentration C_0 and phases contact time.

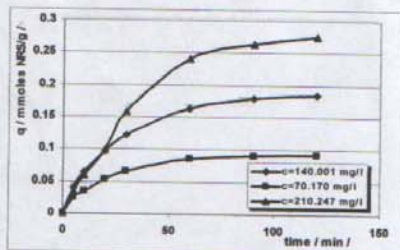


Fig.5. Effect of time and initial concentrations C_0 on sorption of NRS on Amberlite IRA 402-Cl. Batch method; $m/v=1$ g/500 ml; stirring time $\tau = 2$ h; $t = 25$ °C.

Effect of time on equilibrium concentration C_e is shown in fig.6. The semi-logarithmic plot $C_e = f(t)$ shows that the C_e varies linearly. The plot $C_e = f(t)$ describes an exponential curve: $C_e = a \cdot e^{-kt}$ (the plot is not represented). From the point of view of formal kinetics, it suggests that the ion-exchange reaction could follow a first order reaction.

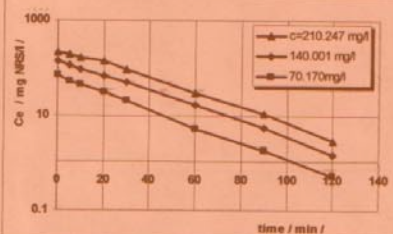


Fig.6. Effect of time on equilibrium concentration C_e . Batch method: $m/v=1$ g/500 ml; stirring time $\tau = 2$ h; $t = 25$ °C. Semi-logarithmic graph.