QUÍMICA

MODIFICATION OF AMBERLITE IRA 400 (CL⁻) BY INCORPORATING ALIZARIN S AND SODIUM MORPHOLYLDITHIOCARBAMATE (MORDTC) RESPECTIVELY

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ABSTRACT

A chelating sorbent was obtained by incorporating Alizarin S and Sodium Morpholyldithiocarbamate (MorDTC) respectively in Amberlite IRA 400 (Cl⁻). Structural characteristics were studied by X-Ray Powder Diffraction (XRD), Optical Microscopy (OM), Differential Scanning Calorimetry (DSC) and Adsorption Techniques. The pH of optimal retention pH of MorDTC in Amberlite IRA 400 (Cl⁻) was obtained (pH 8-9). For Alizarin S an optimal retention is achieved even at pH 1-2. The sorption capacity of the resin without modification is 0.575 mmol g^{-1} .

KEYWORDS

Amberlite IRA-400 (Cl⁻), Alizarin S, Sodium Morpholyldithiocarbamate (MorDTC), physico chemical characterization.

INTRODUCTION

The importance of chelating sorbents in analytical chemistry has risen substantially in recent years. Sorption methods are characterized by the

simplicity of their implementation. They are convenient for the concentration of metals from any, including large volumes of solution, and are easily combined with different methods of element determination. Owing to these advantages, the methods of concentration by sorption are successfully used in analytical chemistry (Zolotov, Yu.A. et al).

Concentration and separation with the help of chelating sorbents is characterized by high selectivity and effectiveness which assure an increase in sensitivity and reliability of the subsequent determinations of elements by different chemical, physicochemical and physical methods (Myasoedova, G.V. et al).

An extensive literature on ion-exchange resins and non-polar sorbents modified with chelating ligands (Myasoedova, G.V. et al) has been reported. The main advantage they offer is the possibility to control their capacity and selectivity of sorption by the appropiate choice of loading ligand. For this purpose, XAD copolymer (Yang, X.G. et al., Yang, X.G. et al., Yang, X.G. et al), actived carbon (Dogan, M. et al.), ion exchange resins (Abe, M.M. et al., Sengupta, B. et al., Chwastowska, J. et al., Chwastowska, J. et al.) chelating resins (King, J.N. et al.) and various polymers (Hoshi, S. et al.) have been used.

Extensive studies on different supports by incorporating diethyldithicarbamate (DTC) group have been reported (Myasoedova, G.V.et al., Miyazaki, A. et al., Van Berckel, W.W. et al., Yamagami, E. et al., Murthy, R.S. et al., Van Berckel,W.W.,et a.l). These studies are based on the formation of very stable neutral complexes of DTC with all transition metal ions and many representative metal ions also. Such complexes show high hydrophobic characteristic and therefore very low water solubility (Cao et al.).

MorDTC is a dithiocarbamate with properties similar to DTC. It synthesis and characterization were done by Cao et al (Cao et al). MorDTC coordinates with divalent metals producing too very stable neutral complexes. Stability of their complexes is the same as NaDTC (Sastri,V.S. et al).
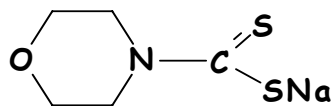
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Fig. 1. Structure of MorDTC

Two reagent were used in the present report: MorDTC and Alizarin S. This latter compound forms very stable complexes in strongly acidic solution with zirconyl ions (Pareissakis,G et al), Al(III) (Seth,R.L et al) Cu(II) (Sangal,S.P), Ni(II) (Brajter, K), etc. To our knowledge this is the first report on the use of MorDTC or Alizarin S as chelating agents immobilized in Amberlite IRA 400 (Cl⁻). The goal of this report is to study the modification that take place in Amberlite IRA 400 (Cl⁻) by MorDTC and Alizarin S.

EXPERIMENTAL PART
Apparatus
- Measurements of pH were made with a Pracitronic pH meter MV 88 with a combined glass electrode.
- UV-Visible spectra of the reagent (Alizarin S or MorDTC) were recorded on a Ultrospic III (Pharmacia- LKB) spectrophotometer.
- X Ray Powder Diffraction Pattern of each resin were registered on a Phillips PW-1710 X Ray Diffractometer with filtered Cu radiation with Ni (λ=1,54178 Å). Diffractional field researched between $0.056 <\sin \theta/\lambda>0.566$ Å^{-1}. This is related with the range between 5 to 60 degree(2φ).
- Mettler Differential Scanning Calorimeter with a scanner velocity of 10 °C min^{-1} at temperature between 50-250 °C range was used for thermal study of the resin.
- External morphology studies were carried out with a Leika Wild M10 Stereo Microscope joined with a Sony CCD/RGB Video Chamber connecting to a PC and with a target for prosecuting of EYE GRABBER.
- Adsorption Isotherms were recorded with a classical instrument which consist in a vacum microburete with liquid adsorbate (Guerasimov, I).

Chemical Reagents

All solutions were prepared from analytical reagent grade chemicals using ultrapure water with resistivity 18 MΩcm, which was obtained by means of a Milli-Q water purification system (Millipore, Betford, USA). Most metal salts were purchased from Merck.

- Amberlite IRA-400 (Cl$^-$), styrene-DVB (bencene divinyl) copolymer, (Fluka reagent) density (wet) apparent 0.70 g/ml, true 1.11 g/ml. Effective size 0.40-0.50 mm. Moisture contents 42-48 %, pH range 0-14. Maximum operating temperature: 60 ^{o}C (OH), 77 ^{o}C (Cl$^-$). Total exchange capacity a) meq/g (dry) 3.8, meq/ml (wet) 1.4 (Cátalogo Chemika-Biochemika).

- Alizarin S (Merck p.a.). The work solution was prepared dissolving the appropriate mass of reagent in ultrapure water.

- MorDTC was supplied by Laboratory of Bioinorganic Chemistry, Faculty of Chemistry, Havana University, Cuba. The work solution was prepared dissolving the appropriate mass of the reagent in ultrapure water.

Preparation of chelating sorbent

Amberlite IRA 400 (Cl$^-$) was immersed in ultrapure water during several days. Alternative treatment with 0,1 mol/L NaOH and 0,1mol/L HCl was performed. After the filtration, the resin was washed with water until pH 7 and was dried on filter paper at room temperature. The resulting material was then ground and sieved to a particle size of 0.4-0.5 mm (Bello E). The resin was then treated with the chelating agents in the following way.

a) 50 mg of Amberlite IRA 400 (Cl$^-$) were added to 5 mL 1.10^{-3} mol/L solution of Alizarin S in water using continuous stirring during 30 min. Afterwards it was filtered off, washed with ultrapure water and dried at 110 ^{o}C for 30 min.

b) 500 mg of Amberlite IRA 400 (Cl$^-$) were added to 25 mL 1.10^{-4} mol/L solution of MorDTC in water with pH 8-9, using continuous stirring during 30 min. Afterwards it was filtered off, washed with ultra pure water and dried at room temperature on filter paper.

Influence of the pH on the reagent retention

1) Amberlite IRA 400 (Cl$^-$) loaded with Alizarin S.
   50 mg of Amberlite IRA 400 (Cl$^-$) were added to 5 mL 1.10^{-3} mol/L Alizarine solutions in a pH range from 1 to 10 using continuous

stirring during 30 minutes. Afterwards the solutions were filtered off, the resins washed with ultrapure water and the final volume made up to 50 mL with ultrapure water.

2) Amberlite IRA 400 (Cl⁻) loaded with MorDTC.
   Was employed the same procedure described in the case of Alizarin S. The differences were: mass resin 500 mg and pH range 6-8.

Influence of the resin mass on the sorption of the reagents

For both reagents the resin mass used was between 0,2 and 1,0 g. The procedure followed was the same one described in previous paragraphs.

Study of external morphology by optical microscopy

This study was done employing Amberlite loaded with Alizarin S or MorDTC and without modification. The experiments were carried out with stirring time of 30 and 45 min. Diameter and area of particles was measured employing IMAGELL software. This system was used by digital prosecution and for morphologic analysis of images.

X Ray diffraction study

These experiments were carried out employing Amberlite IRA 400 (Cl⁻) without modification and with this reagent loaded with MorDTC and Alizarin S.

In the case of Alizarin S the concentration of the solution was 1.10^{-3} mol/L and the samples were prepared with and without stirring.

In the case of MorDTC the concentration of the solution was varied from $0,25.10^{-4}$ to 1.10^{-4} mol/L with a stirring time of 30 min.

The samples were ground in an agate mortar and the loose powder was pressed into a diffractometer sample holder. The X ray diffraction pattern was collected using Ni filter CuKα radiation ($\lambda= 1.54178$ Å) on Philips PW 1710 diffractometer operated at 40 Kv and 30 mA. The alignment of the diffractometer was checked by using a silicon external standard from National Institute of Standards and Tecnology NIST-SRM- 6406 with cell parameter a=5.430940 (35) Å at 25 °C (Pomés, R). The powder pattern was recorded at 25°C from 5 to 60° (2θ)

using an angular step $0.02^{°}$ and counting time of 5 s and processed by XPAS program (Singh, B et al).

The reported peak heights and positions were extracted by fitting Pearson VII type functions to the diffraction maxima. The position of the first peaks were input in the program for least square unit cell refinement LSCCLT (Garvey,R.).

Study by Differential Scanning Calorimetry
Experiments were carried out employing the resin without modification and resin loaded with Alizarin (1.10^{-3} mol/L) or MorDTC (1.10^{-4} mol/L) at a stirring time of 30 min.

RESULTS AND DISCUSSION
Influence of the pH on the reagent retention
The percentages of retention were calculated in all cases and the results obtained are shown in fig. 2.
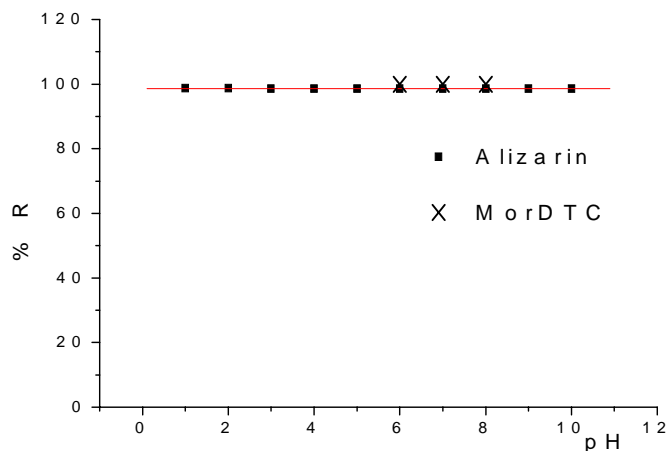

Fig. 2. Study of the retention pH of Alizarin and MorDTC.

In the case of Alizarin S retention is independent of pH in the investigated range. However in the case of MorDTC reagent retention is possible at pH more than 6 because of decomposition of this reagent at acid pH values. In fig. 3 and 4 is shown that characteristic bands of the reagent disappeared and additionally a strong band of CS_2 is

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observed around 210 nm. The selected pH values were: 2 for Alizarin S (this is the resulting pH of Alizarin S aqueous solutions) and 8 for MorDTC.
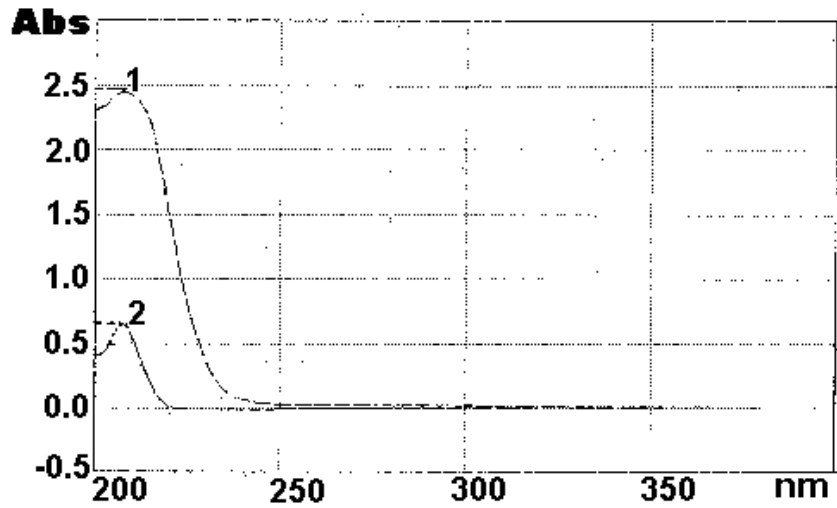

Fig. 3. UV spectra of MorDTC solutions pH=5.
1. Solution of MorDTC $(1.10^{-4}$ mol/L).
2. Solution of MorDTC $(1.10^{-4}$ mol/L) after contact with Amberlite.

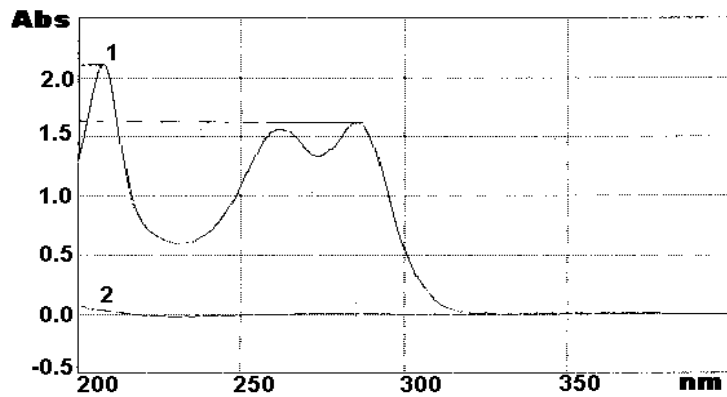Fig. 4. UV spectra of MorDTC solutions pH=8.
1. Solution of MorDTC $(1.10^{-4}$ mol/L).
2. Solution of MorDTC $(1.10^{-4}$ mol/L) after of contact with Amberlite.

Influence of the resin mass on the sorption of the reagents

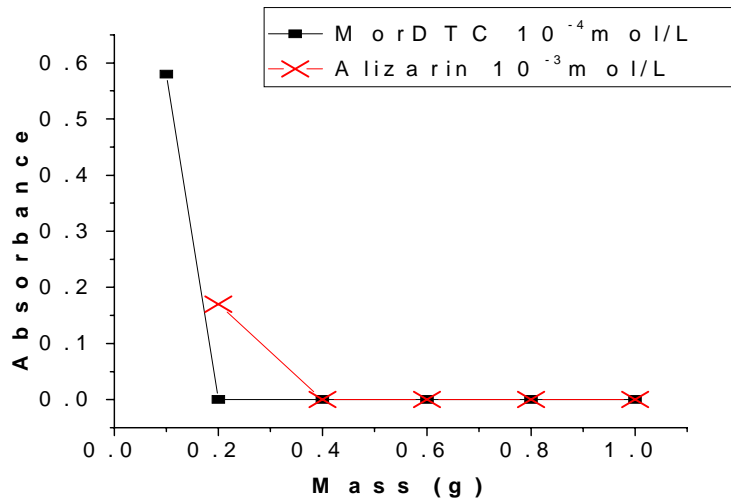As can be seen in fig. 5 there is a maximum retention of both reagents from 0,2 to 1,0 g of the resin.

Fig 5. Influence of resin mass in the sorption of the reagents.

Optical Microscopy

The results of the external morphological studies are shown in table 1.

Table 1. Variation of the resin particle size (mm). Microscope LEIKA ($n=50$ $\alpha=0,05$).

	$\bar{x} \pm t\alpha\ S/n^{1/2}$	S	S_r (%)	t_{exp}
Amberlite without modifier	0,534 ± 0.013	0.047	8.8	-
Amberlite + MorDCT Stirring time (45 min)	0,494 ± 0,013	0.045	9.1	4.37
Amberlite + Alizarin Stirring time (15 min)	0,494 ± 0,010	0.034	6.8	4.49

t_{tab} (0,05;98)=1,98

As can be observed both reagents have produced a decrease of around 7% in the particle diameter, probably because of the introduction of the reagents in the pores of the resin.

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Study by X Ray Diffraction

Amberlite IRA 400 (Cl⁻) is completely amorphic. As it react with Alizarin S the amorphism is diminished and characteristic peaks, superposed with bands of the Amberlite, appear in the X-ray diffraction pattern (fig. 5). These maxima are found at 4.42, 3.40 and 3.37 A^o respectively. These peaks and the crystalinity does not depend on weather Allizarin S is incorporated with or without agitation.

When the resin is modified with MorDTC, the agitation time is very important in the appearance of diffraction maxima of the crystalline phase. The highest diffraction maxima were found for 30 and 45 min of stirring during the preparation of the resin. The amorphism decreased in 40% for 40-45 min stirring.

These maxima appeared at 2.72 and 2.07 A^o as can be observed in fig. 6. These results were obtained for 10^{-4}mol/L solutions of MorDTC. For more diluted solutions the observed effect is less intense.

The differences observed between MorDTC and Alizarin S indicate that the latter in faster incorporated to Amberlite.
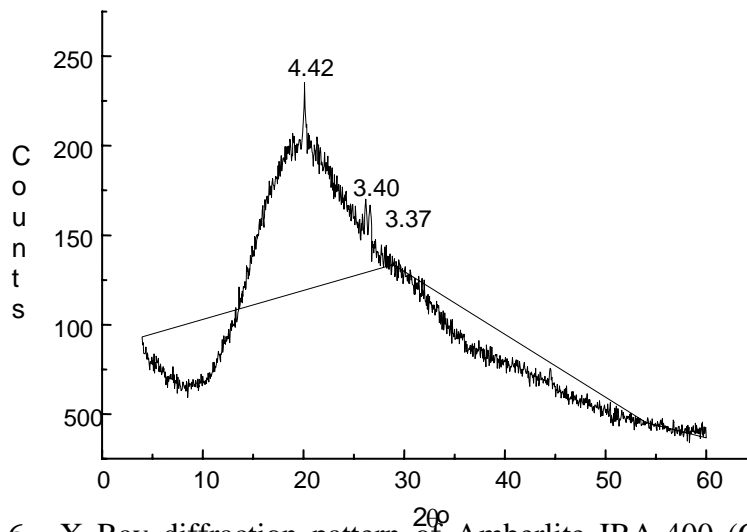

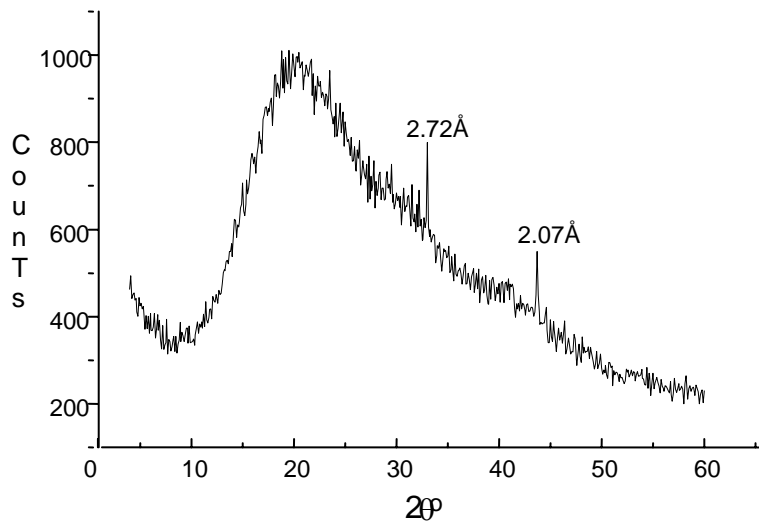Fig. 6. X Ray diffraction pattern of Amberlite IRA-400 (Cl⁻) with Alizarin S.

Fig. 7. X Ray Powder Pattern of Amberlite with MorDTC.

Study by Differential Scanning Calorimetry

The DSC determinations gave the possibility to study how the chelating agents could affect the water release from the resin. A strong release was observed at 125° C for the untreated resin. This effect was attenuated when Alizarin S was incorporated without agitation. When Alizarin S and MorDTC were incorporated with agitation no defined release of water was observed at 125° C. This behavior might be explained due to the large porous volume of the original resin as was shown previously by Optical Microscopy. This results were confirmed in the study of water adsorption shown in fig. 8.
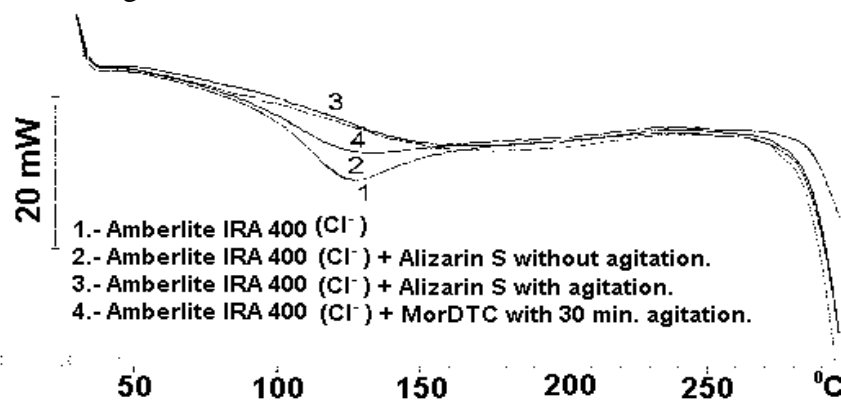

1.- Amberlite IRA 400 (Cl⁻)
2.- Amberlite IRA 400 (Cl⁻) + Alizarin S without agitation.
3.- Amberlite IRA 400 (Cl⁻) + Alizarin S with agitation.
4.- Amberlite IRA 400 (Cl⁻) + MorDTC with 30 min. agitation.

Fig. 8. DSC studies for water absoption in the Amberlite with and without modification.

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Water adsorption study

The samples were activated at 300 ^{o}K and 0,13 Pa during 15 hours. The volume-filling model of Dubinin (Bering, B.P et al) was applied to the experimental isotherm. The obtained results have shown linear range. Maximum adsorption (Na), characteristic energy (Ec) as well as micropore volume were obtained from the intercepts and the slopes of the linear range of graphics (see fig. 9, 10, 11).
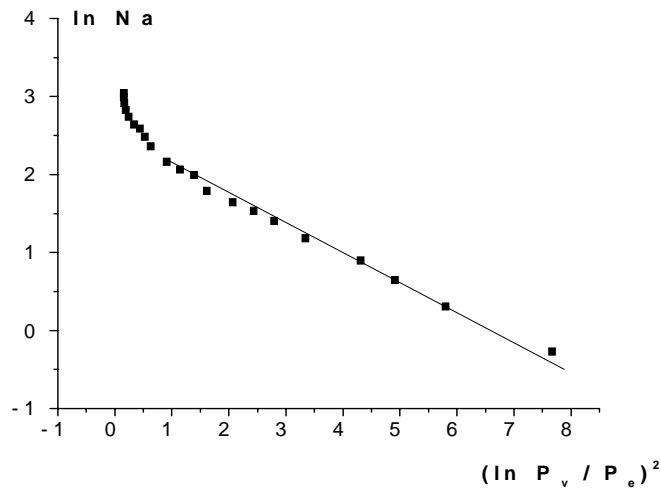
Fig. 9 Adsorption isotherm of water in Amberlite IRA 400 (Cl$^-$) in Dubinin Coordinates. (M$_1$). Pe: equilibrum pressure. Pv: vapor pressure.
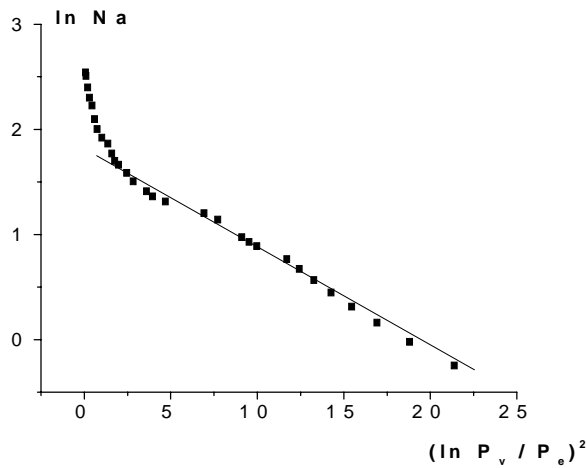
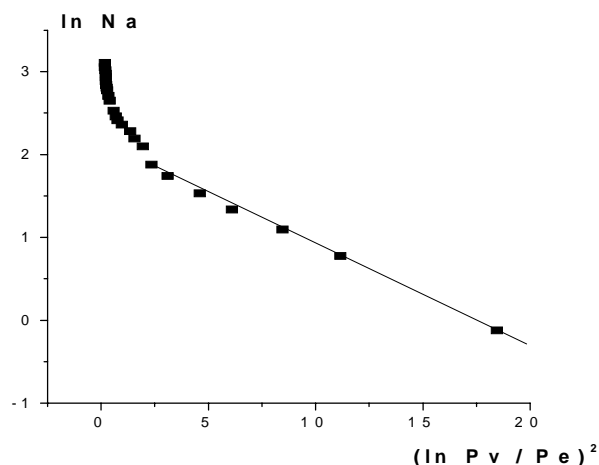Fig. 10 Adsorption isotherm of water in Amberlite IRA 400 (Cl$^-$)+ MorDTC (stirring).

Fig.11. Adsorption isotherm of water in Amberlite IRA 400 (Cl⁻)+ Alizarin (stirring time 15min) in Dubinin coordinates. (M_3)

Maximum adsorption and micropore volumes are arranged in the following order $M_1 > M_3 > M_2$ (Table 2). These results indicate that the introduction of the reagents in the resin diminishes the pore volume, probably due to that part of the resin pores are blocked by the reagents. There is good agreement between this behavior and those obtained by Optical Microscopy (see tab 1). By the other hand according to Dubinin (Dubinin,M.M., et al) ($Ec \sim 1/r$), this relation indicate that the reduction of pore radius in the case of modified resins, is probably determined for deposition of reagent in the pore walls.

Table 2. Maximum adsorption values (N_{max}), characteristic energy (Ec) and micropore volume (Vmp) of the different resin samples obtained from the adsorption isotherms applying Dubinin model.

Samples	$N_{a.}$ (mmol/g)	Ec (j/mol)	Vmp (cm^3/g)
M_1	12.9	3928	0.23
M_2	6.34	8007	0.11
M_3	8.35	7131	0.15

CONCLUSIONS

Amberlita IRA 400 (Cl⁻) coated with Alizarin S and Sodium Morpholyldithiocarbamate (MorDTC) respectively was caracterized employing different techniques, like X-Ray Powder Diffraction (XRD), Optical Microscopy (OM), Differential Scanning Calorimetry (DSC) and Adsorption Techniques.

The combination of XRD, OM, DSC and Adsorption Techniques indicated that the modification process of Amberlite IRA 400 (Cl⁻) resin with Alizarin S or MorDTC reagents could take place by inclusion of them in this resin by a chemical-sorption mechanism. The introduction of these reagents in Amberlite IRA 400 (Cl⁻) resin have produced a volumetric contraction and consequent diminution of the pore size. This sorbent can be applied to the analysis of natural samples considering that in the case Alizarin, retention is independent of pH in the investigated range, however for MorDTC reagent the retention only is possible at pH more that 6.

RESUMEN

Se reporta la obtención de un sorbente quelatante mediante la incorporación de Alizarina S y del Morfolilditiocarbamato de sodio (MorDTC) a la Amberlita IRA 400 (forma cloruro). Se reportan las características estructurales del sorbente que se estudiaron mediante Difracción de Rayos X de polvos (DRX), Microscopía Optica (MO), Calorimetría Diferencial de Barrido (DSC) y Técnicas de Adsorción. Se determinó que para el MorDTC, el pH óptimo de retención en la Amberlita IRA 400 (forma cloruro) estaba entre 8 y 9. En el caso de la Alizarina S, la retención es óptima a pH tan bajos como 1-2. La capacidad de sorción de la resina sin modificación es de 0.575 mmol g⁻¹.

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