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INORGANIC ION EXCHANGER BASED ON TIN OXIDE FOR HEAVY METALS SEPARATION

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ABSTRACT

In present work it was studied the behavior of three different tin mixed oxides for the separation of Ga from waste. The results are analyzed in terms of synthesis and characterization of the inorganic ion exchanger using differential thermogravimetric analyses X-ray powder diffraction, XRD, granulometric distribution analyses scattering electronic microscopy and infrared spectra. In terms of adsorption, experiments for determination of the percent extraction (%E) and the weight distribution ratios of gallium ($Dw_{Ga^{3+}}$) and isotherm equilibrium measurements were done. The results showed that these inorganic ion exchangers are good materials for recovery of this heavy metal.

1. INTRODUCTION

Many selective inorganic ion exchange materials have been synthesized during the last four decades and found many applications in the areas of separation technology, ion exchange catalysis, and nuclear industry [1-3]. Synthetic and natural inorganic ion exchangers and adsorbents offer definite advantages over well-known and traditionally used organic resins to the extent that their chemical properties, radiation and thermal stability, resistance to oxidation and selectivity to certain ions are concerned, as described in the literature [4-5]. Inorganic ion exchangers are a vast field for study and materials of ever-higher selectivity are required to treat the large amounts of nuclear waste and environment remediation around the world. Some inorganic ion exchangers such as zeolites, sodium titanates, titanosilicates and hexacyanoferrates are in use at nuclear sites today. Inorganic ion exchangers with magnetic properties also are used in nuclear facilities and in water treatment station nowadays [6-8]. Otherwise gallium is an industrially useful metal and its separation from other metals from Group 13 such as aluminum and indium is very important. Use of gallium as GaAs increase rapidly for higher speed operation and information processing systems due to GaAs has a signal transmittance speed about five times faster than silicon [9]. It also processes better optical properties and radiation hardness than silicon due to its energy band structure. Accordingly this statements, various research activities utilizing these properties of GaAs, which it possible exemplifies as super computers, lasers, satellite communications, astronautics and military purposes etc, are actively in progress worldwide [10]. In these processing of GaAs production, the final yield is often only less than 15% and the remainder of GaAs is wasted as scrap. It is, therefore, very important to recycle the gallium metal from GaAs scrap because this metal is a relatively rare element of importance in the high technology industry and radiomarkers fabrication [11]. Another source of gallium become to the bauxite Bayer processing were gallium is extracted from alkaline solution containing relatively high amounts of aluminum [12]. Wherein Brazil aluminum production is an important process in the economy, and tons of aluminum are produced, this country also

could turn out to be a significant gallium producer. Gallium also is a useful radiomarkers in wars instead cancer disease in medicine diagnostic. In this work we have studied the behavior of three inorganic ion exchangers for separation and purification of gallium from waste.

2. EXPERIMENTAL SECTION

2.1. Synthesis of inorganic ion exchangers – Composite tin(IV) oxide silicon oxide was prepared by neutralizing a mixed solution of tin(IV)chloride and a solution (30%) metasilicate with ammonium hydroxide using two different concentrations of tin(IV) in final composition. In the first experiment (A) 10.00grams of tin metal were dissolved in concentrated chloridic acid forming tin(II)chloride. For obtain the Tin (IV)chloride hydrogen peroxide was added, them to the solution was add to 100grams of a metasilicate solution(30%w/w) and neutralized with ammonium hydroxide. In the second experiment (B) 30.00grams of tin was used instead 10 grams. From obtain exchanger based on yttrium/tin oxide, solution of tin chlorine and yttrium chlorine was mixed and precipitated by ammonium hydroxide. The precipitated of all processes were aged in liquor for 48 hours. The reaction product was thoroughly washed with distillated water for the removal of chloride traces. Precipitates were dried in air followed by heat until 110^{o}C for ammonium ion removal and convert each exchanger into the hydrogen form on the cationic sites. (see Fig. 1).

2.2. Characterization of inorganic ion exchangers(IIE) – The IIE were characterized by thermal analyses, X-ray powder diffraction, granulometric analyses, scanning electronic microscopy and infrared spectroscopy as followed description:

Thermal analyses Differential thermogravimetric analyses (DTA) curves were obtained in a NETZSCH STA 409C using aluminum crucibles with 17.800mg and 19.000mg (synthesis 1 and 2) of samples, under dynamic synthetic air atmosphere (40 mL·min^{-1}) and heating rate of 10 K·min^{-1} in the temperature range from 19 to 1000 ^{o}C and 17 to 1000 ºC (synthesis 1 and 2) The thermogravimetric (TG) curves were obtained with a thermobalance model NETZSCH STA 409C in the temperature range 19 to 1000 ^{o}C and 17 to 1000 ºC respectively to synthesis 1 and 2, using aluminum crucible with 17.800mg and 19.000mg (synthesis 1 and 2) of samples, under dynamic synthetic air atmosphere (40 mL·min^{-1}) and heating rate of 10 K ·min^{-1}.

X-ray powder diffraction, XRD. XRD pattern of mixed oxides were recorded in a Phillips, type MPD-1880 X-ray diffractometer (CuKα radiation, λ=1.5418 nm) with 2θ range between 2.5 to 80 in order to determine average crystallite size from the X-ray diffraction line broadening measurements by using the Scherrer formula [13]:

$$d = \frac{0.94\lambda}{\Delta(2\theta)\cos\theta} \quad (1)$$

Where: λ is the X-ray wavelength, Δ(2θ) is width at half height and θ is diffraction angle.

Granulometric distribution analyses were performed using a Cilas particulate analyzer model 1064 and sodium pyrophosphate (0.05% weight per volume) as a dispersant agent.

Scanning electronic microscopy was obtained in a microscopy Philips XR-30 using sputtering technique using gold as covering materials.

Infrared spectra were measured at room temperature in a Bomen MD 102 spectrometer in spectral ranges of 4,000 – 400cm^{-1}. It was applied KBr pellet technique for obtention of inorganic ion exchanger infrared spectra

2.3. Adsorption Experiments

Determination of the percent extraction (%E) and the weight distribution ratios of gallium-67 (Dw_{Ga}^{3+}). The adsorption of gallium ion by inorganic ion exchange from nitric hydrochloric acid and basic solutions was measured by contacting a know volume (usually 2mL) of a solution held the spike of Ga-67 with a known weight of resin in a vial. The exact ratio of aqueous phase volume (mL) to resin weight (g) was varied as necessary to produce a measurable decrease in the concentration of metal ions in aqueous solution by a single contact with the resin. The mixing of the IIE and each aqueous phase was performed using a Downer Mix. The stirring rate was chosen to produce a suspension of the resin in aqueous phase. The percent uptakes (%E) of Ga^{3+} by the IIE were calculated from the following equation [14]:

$$\%E = [(I_b - I_a)/ I_b]x100 \quad (2)$$

where I_b and I_a are the concentration off metal ion in the bulk solution and after extraction, respectively.

Weight distribution ratios (Dw) were calculated from the following equation [14]:

$$Dw = \frac{\frac{I_O - I_S}{W}}{\frac{I_S}{V}} \quad (3)$$

where I_b and I_a are the concentration of metal ion before and after extraction, respectively, W is the weight of resin (g) and V is the volume of aqueous phase (mL).

Ion exchange Isotherm equilibrium measurements were performed equilibrating approximately 0.05g of adsorbent in H^+ form with 2.0mL solution containing various molar concentrations of Ga, a spike of Ga-67 . The desired pH was obtained adding NH_4OH in the solution.

Radioassay of Ga-67:- gallium isotope radioassay was done by measuring the gamma activity of the sample with a NaI(Tl) scintillation counter Ortec type. In all experiment it was used analytical grade reagents.

3. RESULTS AND DISCUSSION

The inorganic ion exchangers SnSiO were synthesized from two batch experiments B1 and B2 using the same precipitation method and different mass of tin chloride that gave two different composition of mixed oxide. $SnO_2Y_2O_3$ was synthesized following the same methodology exchanging Si by Y as showed in Fig. 1.

The X-ray powder diffractions shown different behavior for the three inorganic ion exchangers studied, B1 and B2 and $SnO_2Y_2O_3$ see Fig. 2. The precipitated from the solution that has 10grams of thin chloride, A, is amorphous and no shape line is observed but a broad bands characteristic of glass is present. In the second composition where it was used 30 grams of thin chloride, B, shape lines from cassiterite structure are present 27.11(110) and 35.52 (101). Crystallite size founded were obtained using a Scherrer formulae (1) and it was founded 141, 80 and 5 nm as crystallite diameter for inorganic ion exchangers **SnO_2/SiO_2** A, B and **SnO_2/Y_2O_3** respectively. [13]

Scanning electronic micrographs in Fig. 2 show that the agglomerates obtained for the three exchangers present heterogeneous particle size distribution morphology. The exchanger B shows particles with form tending to spherical and the size of agglomerates are close to 200μm. For A exchanger agglomerates smaller than 200μm are a dominant phase although the forms of them loose the spherical aspect. For SnO_2/Y_2O_3 exchanger it was possible observe that the grain sharper remains irregular at SEM micrography and show agglomerated size almost less than 200nm.

The granulometric distribution analysis (Figure not showed) of the IIE A varies from 0.1 to 250μm, with a larger incidence of particles in approximately 100 μm.For B exchanger material, a smaller variation was observed in the granulometric distribution analysis (0.2 to 180μm), with larger incidence in size particles with approximately 80μm diameter.

TG/DTG/TGA thermograms (Figure not showed) of three exchangers studied and the results shown that the decomposition occurs quite similar.Inorganic Ion Exchanger A showed a 16.23% weight loss between 25 to 320 °C (three events), wich was attributed to dehydration of the interstitial water and hydroxyl's decomposition . For the IIE B 32.73% of weight loss were obtained in 25 to 400°C (three events).

The infrared spectra of the inorganic ion exchanger studied, are represented in the Fig. 3. The spectra shows broad bands in the region of 3491, 3156, 3003 and 2788(A) and 3458, 3189, 3003 and 2801(B)cm^{-1} attributed to the νO-H of different type of water and in ~1644(B1)e 1636(B) cm^{-1} attributed to the δH-O-H. The broad absorption bands in the region of 972(A) was shifted for1081cm^{-1}in (B) exchanger and they were attributed to ν Si-O-Si_{syn}. The large bands at around 700 (A) and 678cm^{-1} (B) were attributed to ν (Sn-O-Sn) of SnO_2 in crub live phase and the bands at 584 (A) and 592 (B) cm^{-1} were attributed to a convolution of the (δ Si-O-Si) and ν (Sn-O) bands of the SnO_2 [15] SnO_2/Y_2O_3 showed wide band that appear at approximately 3400 cm^{-1} corresponding to the (OH vibration that was ascribed to the physisorbed water in the matrix and it intensity decrease with thermal heating. The angular stretching of H_2O molecule appears at approximately 1628 cm^{-1}. It is necessary to mention that broad vibration bands located at approximately 620 cm^{-1} is associated with $\delta_{O\text{-}Sn\text{-}O}$ and the band in approximately 960 cm^{-1} is attributed to $\nu_{Sn\text{-}O}$. [15]

The infrared spectra of the exchangers agree with the results of thermal analyses that show more than one type of water in the inorganic ion exchangers.

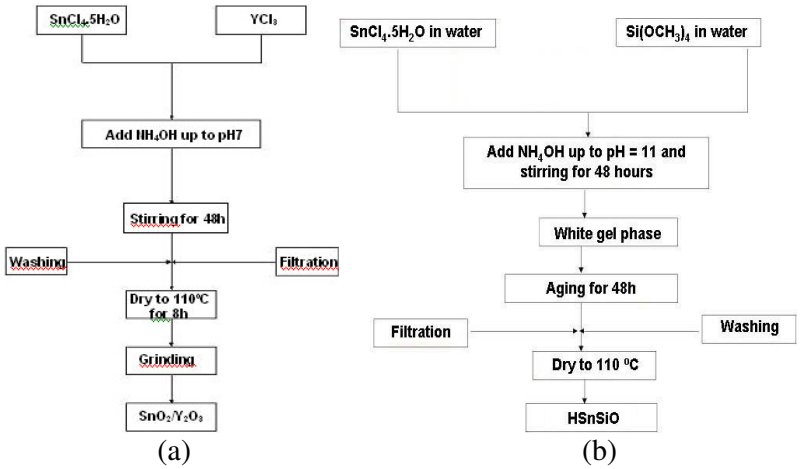


Figure 1. Flow sheet diagram for obtention of inorganic ion exchange. a) SnO_2/Y_2O_3 b) SnO_2/SiO_2 (A) c) SnO_2/SiO_2 (B)

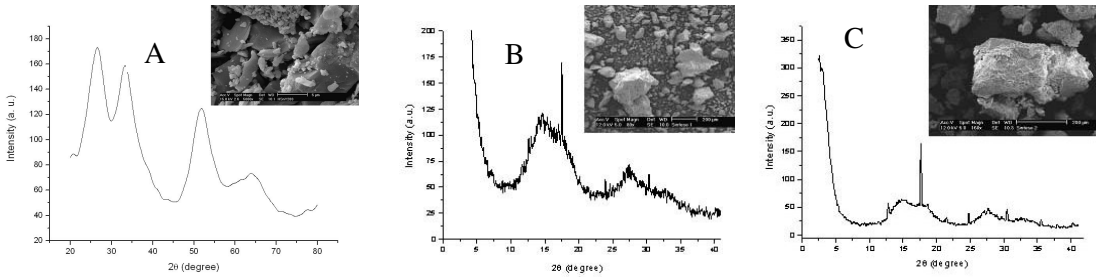


Figure 2. X ray powder diffraction and scanning electronic micrographies of tin mixed oxide. (a) SnO_2/Y_2O_3, (b) SnO_2/SiO_2(A), (c) SnO_2/SiO_2(B)

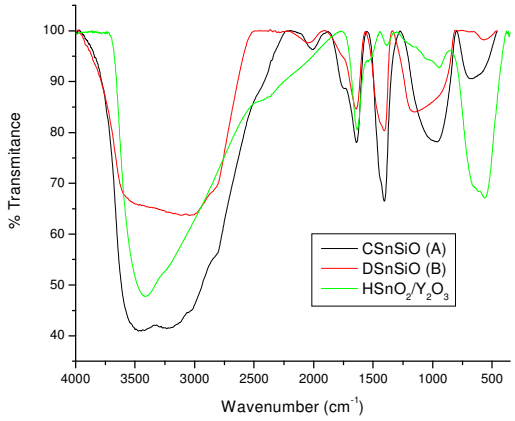


Figure 3. Infrared spectra of tin mixed oxide.

Galium exchanger

The M-OH- functional groups contained in the structure of hydrous oxides like SnO_2 show amphoteric reactions depending on the pH values of the solution and give rise to anion exchange in acid medium or cation exchanger in basic medium [14]. The sorption behavior of this mixed oxide seemed a practical way to find a suitable matrix for the sorption of the various gallium ions built in acidified solutions depending on pH value and Ga concentration [16, 17].

$$Ga^{3+} \xrightleftharpoons{\text{pH 3}} GaOH^{2+} \xrightleftharpoons{\text{pH 4}} Ga(OH)_2^{+} \xrightleftharpoons{\text{pH 5.3}} Ga(OH)_3 \xrightleftharpoons{\text{pH 8}} Ga(OH)_4^{-}$$

The stable species of the gallium in aqueous solution is the trivalent Ga^{3+}. However it is possible isolated gallium as monovalente and unstable divalente.

The metallic gallium is dissolved slowly in the acids minerals, but it is dissolved easily in regia water and in alkali solutions.

In the strongly alkaline aluminate solutions as it is the case of the Bayer liqueur (NaOH (4N)) the whole present gallium is in the gallate form, [Ga(OH)4] - [16-18] as showed in reaction above.

In Table 1 there are the results of % of extraction and Dw for the systems studied in pHs 8, 10 and 12. It is observed significant values of distribution ratios of the galium in the studied systems, and the pH conditions for the extraction of the same, change of system for system. The tin yttrium oxide has its great pH for extraction in 10, while the IIE A and B find their maxima in pH 12.

Table 1. Dw and %E of Ga-67 in the Inorganic ion exchangers in NaOH.

IEE	Dw	%E	Dw	%E	Dw	%E
pH	9	9	10	10	12	12
SnO_2/SiO_2A	3275.80	98.83	2693.45	98.72	6831.52	99.42
SnO_2/SiO_2B	1327.13	98.00	1276.23	97.76	1631.44	98.22
SnO_2/Y_2O_3	1320.54	97.90	3177.28	99.05	2032.63	98.43

Fig. 4 present Freundlich Isotherms from the IIEs studied and Cal [19] have been described the Freundlich equation as an empiric expression used for represent adsorption isotherms, when a linear behavior is present for the adsorption capacity and equilibrium concentration of adsorbed species in the equilibrium. Both as a logarithmic function as showed in the equation (4).

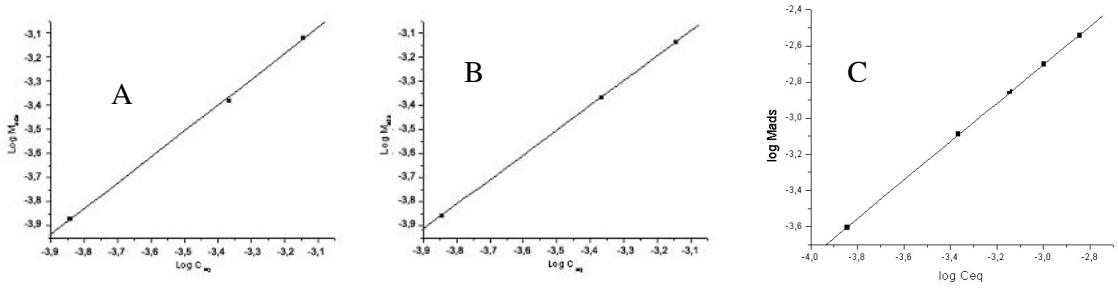


Figure 4. Freundlich Isotherms from the inorganic ion exchangers based on tin oxide

$$\text{Log } M_{ads} = \log K_F + 1/n \,.\, \log C_{eq} \qquad (4)$$

It is also considered that the K_F and 1/n are empirical constants and could be extracted from the above equation in the operation conditions.

In table 2 it is presented the behavior of – Freundlich Isotherms and it was observed that the studied materials present energetically homogeneous surfaces, the isotherms obey a linear equation with an inclination limits constant, in other words, the mass of gallium species adsorbed in the IIE are proportional to the concentration in the equilibrium

Table 2 – Freundlich Coefficients for the IIEs studied

IIEs	K_F	η	R
SnO_2/SiO_2A	1.7372	0.9334	0.9996
SnO_2/SiO_2B	1.2892	0.9682	1.0000
SnO_2/Y_2O_3	1.5300	0.9462	0.9994

The Free energy change of the ion exchange reaction per cation-equivalent, ΔG°could be calculated by the expression 5 [20]:

$$\Delta G^{o} = -(RT / Z_M Z_H) \ln K \tag{5}$$

Based on the calculation of Gibbs free energy, it can be concluded that the process of ion change, is spontaneous in the three synthesized IIE.

Table 3 Values of Thermodynamic parameters.

IIEs	Ga (g/L)	K_C	K	ΔG° (KJ/mol)
SnO_2/SiO_2A	0.01	8.48×10^{12}	1.15×10^{12}	-22,9334
	0.03	1.30×10^{12}	1.76×10^{11}	-21,3862
	0.05	2.96×10^{12}	4.01×10^{11}	-22,0654
SnO_2/SiO_2B	0.01	1.21×10^{13}	1.64×10^{12}	-23,2254
	0.03	2.49×10^{12}	3.37×10^{11}	-21,9210
	0.05	3.86×10^{12}	5.22×10^{11}	-22,2821
$SnO_2/Y2O3$	0.01	6.09×10^{12}	8.24×10^{11}	-22,6592
	0.03	1.25×10^{12}	1.69×10^{11}	-21,3525
	0.05	4.58×10^{12}	6.20×10^{11}	-22,4239

4. CONCLUSIONS

The synthesized tin mixed oxides showed good uptake properties for gallium separation the Sn/Si and Sn/Y substitution of the materials improved their metal uptake properties in basic solutions. The effects of increasing Sn concentration distribution coefficients (Kd) for gallium were almost identical for materials with Sn/Si. The effect of pH on the distribution coefficients was significant, a typical finding for hydrous metal oxides with their weakly acidic nature. An increase in the Kd values occurred with increasing equilibrium pH and excellent uptake of gallium was observed from solutions of basic pH. The gallium uptake from acidic solution was relatively low.

All of the IIE presented a percentage extraction above 90%, what shows that they possess a good efficiency in basic medium, and the IIE SnO_2/SiO_2A, in terms of retention capacity, is the most efficient (99 %E).

From Isotherms equilibrium curves, it was observed that the studied materials present energetically homogeneous surfaces, the isotherms obey a linear equation with an inclination limits constant, in other words, the mass of gallium species adsorbed in the IIE are proportional to the concentration in the equilibrium

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