

COMPARATIVE STUDY OF INORGANIC ION EXCHANGERS TO BE USED IN AQUEOUS EFFLUENT

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ABSTRACT

An important class of adsorber is the inorganic ion exchangers (IIE) that are developed to improve separation processes, due to their high selectivity, concentration and removal metallic ions in solutions. The IIE's present high capacity of exchanging with fast kinetic, they are better than organic resins with relation to thermal stability and they resist to chemistry attack, temperature variation and radiation. In this work it was made a comparative study between two inorganic exchangers prepared by different synthesis routes. The oxide made up of SnO₂/TiO₂ was synthesized by neutralization of tin chloride (IV) and titanium chloride (III) mixed solution and the exchanger based on manganese and potassium that was prepared by a manganese and potassium oxalates mixed in the proportion of 6% and 60% mass compositions of potassium oxalate in the bulk. The exchangers were characterized by thermal analysis, X-ray powder diffraction, infrared spectroscopy and scanning electron microscopy (SEM). To the exchangers adsorption study, cadmium was used, because of their large range of applications that include nuclear industry. The exchangers revealed to be effective, with adsorption percentages around 100% in the pH range studied (1-13) to SnO₂/TiO₂ IIE and for exchangers based on potassium/manganese pH9 is the best one for both potassium concentrations.

1. INTRODUCTION

The cadmium is one of the metals with a great degree of toxicity and it has been spilt in the environment for the development of agro-industrial, metallurgic, chemical industry activities and also for process of the garbage incineration.

The inorganic ion exchangers (IIE) normally present high capacity and fast speed exchange and are better than organic resins, moreover they are chemical and radioactive steady. IIEs also present high selectivity for different ions that might suffer modifications by chemical transformation or crystallographic composition from the exchanger material. The ion exchangers' properties could be affected by the method and conditions of synthesis. [1]

Oxides precipitated from aqueous systems, also called hydro oxides, are an important class of synthetic inorganic ion exchangers used in the separation technology, catalytic application and chemical processes like in the cycle of nuclear fuel. Oxides of tetravalent elements are, in the great majority, amphoteric exchangers. [2] The manganese oxides possess a favorable selectivity of exchange for some metals due to its crystalline structure. The α -MnO₂ group presents tunnel structure, which four pairs of octahedrons manganese chains form the frame and the tunnel might be filled by ion Ba²⁺ (holandite), Pb²⁺ (coronadite), Na⁺ (manjiroite) and K⁺ (criptomelane).

The mixed oxides exchangers, as the $\text{SnO}_2/\text{TiO}_2$, belong to a class of developed adsorbents to improve processes of ion separation. Some of them are formed as precipitated others as gels that are washed, dried and triturated before use.

2. EXPERIMENTAL SECTION

2.1. Synthesis of Inorganic Ion Exchangers

The exchangers based on manganese oxide were prepared through the manual mixture of the oxalates of manganese and potassium in an agate mortar, until homogenization and it was burned at 530°C during 8 hours. After this stage the exchangers were washed with acid nitric 1 mol L^{-1} for carbonate removal, followed by washing with distilled water until pH 7, dried in heater at 80°C until constant weight and it was stored in a dessecator.

The compose oxide of $\text{SnO}_2/\text{TiO}_2$ was prepared by neutralization of a mixing solution of tin (IV) chloride, titanium (III) chloride with ammonia solution in a reactor type batch. To this solution it was added hydroxide of ammonium until neutralization, pH 7. The molar compositions of the metals in solution were of 0.25mol Sn, 0.03mol of Ti and 3.85×10^{-4} mol of Eu. The particles were aged in the solution liquor for 48h. The precipitated was very thin therefore it was opted to the migration of chloride ions using cellophane membranes where the gradient used for the separation was the difference in concentration of chloride ions in solution. For analytical control of chloride ions it was made a test with AgNO_3 . After removal of chloride ions, the material was dried at 110°C in a heater.

2.2. Characterization

The exchangers were characterized by thermal analysis, X-ray powder diffraction, infrared spectroscopy and scanning electron microscopy (SEM). The study of adsorption of the metal cadmium was made by spectrophotometric method with ditizone as colorimetric agent. [3]

3. RESULTS AND DISCUSSION

3.1 Thermal Analysis

FIGURE 1 show thermal analyses of Mn/K oxide and four events of mass loss could be identified. In the first stage was observed a mass loss of 19.32% ($115\text{-}152^\circ\text{C}$) and 12.68% ($25\text{-}121^\circ\text{C}$) for potassium content of 6% and 60% respectively and it was attributed the salts dehydration. For the DTG it was observed that this lost occurs in a stage for the 6%K content and in two stages for the 60%K content. This is due to dehydration that occurs in distinct temperatures and to different tipe of water of the salts hydrated. A second event of mass loss was 33.53% ($467\text{-}561^\circ\text{C}$) and 23.57% ($291\text{-}335^\circ\text{C}$) for IIE 6% and 60% respectively; it was attributed to the anidric oxalates decomposition. The third stage of mass loss was 2.23% ($467\text{-}562^\circ\text{C}$) and 4.78% ($573\text{-}629^\circ\text{C}$) for 6% and 60% content respectively; it was attributed to the successive losses probably due to reduction of the MnO_2 to MnO_3 or Mn_3O_4 and the

decarbonization of the K_2CO_3 . The fourth stage of mass loss was attributed to the transition from Mn_3O_4 to MnO with mass loss of 0.35% (1070-1100°C) and 14.48% (732-877°C) for IIE 6% and 60% respectively. The DSC showed endothermic character with the first mass loss occurring in two events for both potassium content and the second occurring in one event for the 6% content and in three events for the 60% potassium content.

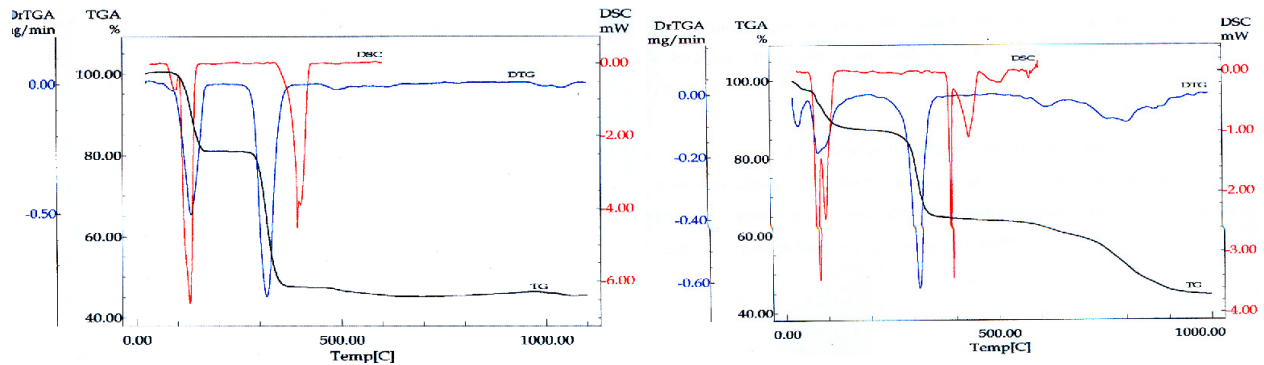


Figure 1. TG/DTG and DSC curves to IIE of manganese with 6% and 60% of potassium.

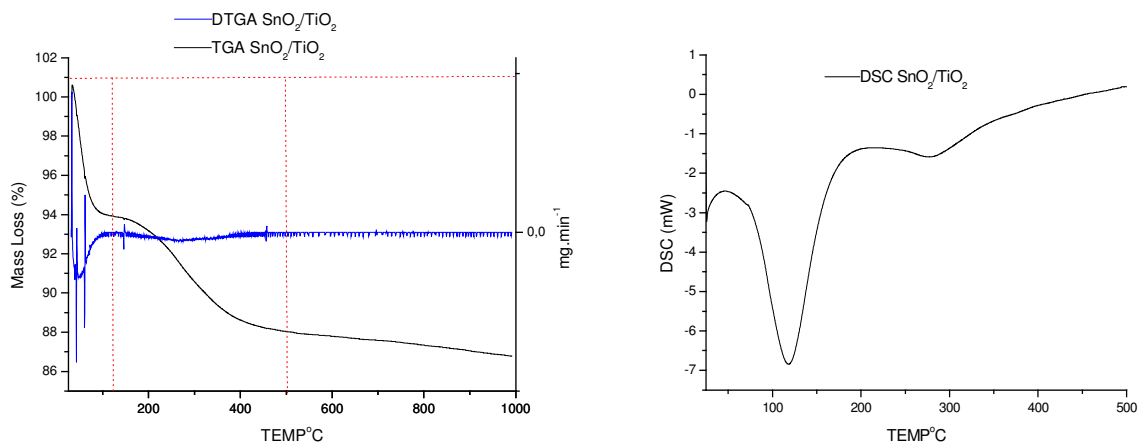


Figure 2. TG/DTG and DSC curves to IIE SnO_2/TiO_2

The FIGURE 2 shows the TG, DTG and DSC curves to IIE SnO_2/TiO_2 . It is possible observe two events of mass losses which were attributed to the dehydration and the loss of crystallization water together with losses of hydroxyl ions respectively. These losses occur in the interval at 31.54 – 132.89°C (6.1183%) and 131.63 – 492.90°C (5.8289%). The exchanger presented good thermal stability. It showed DSC curve events in 118.86°C (- 1381.94 mJ) and in 283.23°C (- 183.44 mJ). It is evident the endothermic character of the process of H_2O loss and crystalline rearrangement of the studied system.

3.2 X-ray powder diffraction

The X-ray powder diffraction had indicated that the exchanger with 6% of potassium has three different composites: bixbiite (Mn_2O_3) in 2θ : 23.1; 32.9 and 55.1 (ICDD-PDF 41-1442); manganite ($\text{MnO}(\text{OH})$) in 2θ : 26.1; 37.2 and 51.2 (ICDD-PDF 41-1379) and criptomelane ($\text{KMn}_8\text{O}_{16}$) in 2θ : 12.7; 18 and 28.7 (ICDD-PDF 41-1348). In the exchanger with 60% of potassium it was observed that the characteristic lines of diffraction did not confirm the presence of the criptomelane and there are some phases not identified by the database ICDD-PDF. The mixed oxide $(\text{Ti},\text{Sn})\text{O}_2$ presented anastase structure [4] with lines of diffraction in 2θ : 27.25 (TiO_2) (JCPDS 34-0180), 52.35 (Ti_2O_3) (JCPDS 12-0754) and 34.4 (SnO_2), 38.2 (SnO_2) (JCPDS 41-1445).

3.3 Scanning Electron Microscopy (SEM)

The micrographs of the IIE (figure not showed) indicated that the IIEs are in the form of agglomerations with homogeneous surfaces and are distributed by heterogeneous form with different sizes and formats.

3.4 Infrared Spectroscopy

The infrared spectra, FIGURE 3, shows broad bands in the region of 3400 cm^{-1} for all studied exchangers, attributed to the stretching νOH of the water and hydroxyl linked in different metals and a band in the region of $1625\text{-}1636\text{ cm}^{-1}$ attributed to the angular deformation δHO of the hydration water.

For the exchangers based on manganese oxide the band that appears in the region of 2300 cm^{-1} in the spectrum of IIE 6% was attributed to CO_2 . The bands in the region of $1350\text{-}1500\text{ cm}^{-1}$ can be attributed to OH groups linked manganese directly or probably the carbonate impurity. The bands that also appear in the region $1100\text{-}1300\text{ cm}^{-1}$ can be attributed to OH group linked manganese ($\delta_{\text{Mn-OH}}$) [5] or hydronium ions, because the exchangers were washed with acid solution. The bands in the region $800\text{-}500\text{ cm}^{-1}$ are characteristics of the stretching $\nu\text{Mn-O}$.

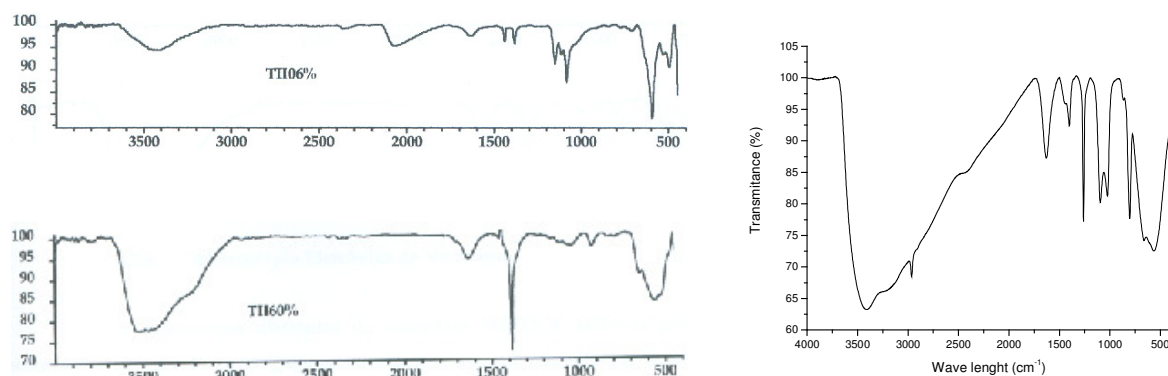


Figure 3. IR spectra to IIE of manganese and tin oxide respectively.

For exchanger based on tin oxide the bands in the region 1026 cm^{-1} were attributed to the stretching $\nu\text{Sn-O}$ and in the region $662\text{-}564\text{ cm}^{-1}$ was related to the deformation $\delta\text{Sn-O-Sn}$ and the stretching $\nu\text{Ti-O}$ respectively.

3.5 Adsorption study of cadmium

The parameters of Cd^{2+} adsorption in this work were expressed in terms of distribution coefficients and efficiency of the adsorption. It was studied the influence of pH, time of contact and concentration in the adsorption of cadmium.

The influence of pH, showed in TABLE 1 was studied exchanging the pH from 1 to 9, it was analyzed 0.4 mL of a solution with $C_{\text{Cd}^{2+}} = 9.0 \times 10^{-5}\text{ mol L}^{-1}$ and mass of exchanger approximately 0.05 g. Contact time was 15 min for the exchanger based on manganese oxide and 10 min for the exchanger based on tin oxide. In relation to manganese IIE the potassium IIE contents 60% presented better results of adsorption and it was used in the other studies. The exchangers presented efficiency in the adsorption of cadmium with adsorption percentage near 100%, and in pH 9 all the exchangers studied in this work presented excellent adsorption.

Table 1. Influence of pH in the behaviour of retention of IIEs.

pH	IIE 6%K		IIE 60%K		IIE SnO_2TiO_2	
	Dw	%Ads	Dw	%Ads	Dw	%Ads
1	5	16.0	589	95.0	3981	99.3
2	7	19.0	741	96.0	4074	99.3
3	10	25.0	1950	99.0	16596	99.8
4	12	29.0	1288	98.0	2630268	100
5	24	45.0	1738	98.0	75858	100
6	18	40.0	1000	97.0	1513561	100
7	25	46.0	617	95.0	72443	100
8	66	70.0	1820	98.0	2041738	100
9	8912	99.7	23988	99.9	1288250	100

The influence of contact time presented in TABLE 2 was studied exchanging these contact times in the range of 5 to 30 minutes, for analysis with and established 0.4 mL of a solution with $C_{\text{Cd}^{2+}} = 9.0 \times 10^{-5}\text{ mol L}^{-1}$, pH 9 and mass exchanger approximately 0.05 g for all experiments. For both exchangers the time of 5 and 15 minutes presented high values of distribution coefficient. The exchanger based on manganese oxide had better values than the exchanger based on tin oxide.

Table 2. Influence study of contact time to IIEs.

Tempo (min)	IIE 60% K	IIE SnO₂TiO₂
	Dw	Dw
5	11220	10471
10	33884	4677
15	10233	10000
20	1778	3467
25	501	3020
30	331	2884

The influence of Cd²⁺ concentration, presented in table 3 was studied with Cd²⁺ concentration in the interval of $9.00 \times 10^{-5} - 1.50 \times 10^{-3} \text{ mol.L}^{-1}$, with contact time of 15min for the exchanger based on manganese oxide and concentrations of $9.03 \times 10^{-5} - 1.50 \times 10^{-3}$ with contact time of 10 min for the exchanger based on tin oxide, in pH 9; it was used 0.4 mL of the solution to the analysis and mass of exchanger of approximately 0.05 g. Both IIEs presented high values of Dw, but the exchanger based on tin oxide was more efficient in the studied concentrations. The exchanger based on tin oxide was better for lower concentrations while the exchanger based on manganese oxide was better for high concentrations.

Table 3. Influence study of Cd²⁺ concentration to IIEs.

[M] (mol.L⁻¹)	IIE 60% K	IIE SnO₂TiO₂
	Dw	Dw
9.03×10^{-5}	10233	1288250
4.03×10^{-4}	50119	621088
7.79×10^{-4}	103037	501187
1.50×10^{-3}	117490	794328

4. CONCLUSIONS

Both studied exchangers presented endothermic character, agglomerated form and heterogeneous sizes. Although the exchanger 6%K have been presented good retention in pH 9 it was to the capacity of exchanger with 60%K indicating that the increase of the potassium percentage improve the Cd²⁺ adsorption. The exchanger based on tin oxide present the best distribution coefficients in all ranger of pH studied indicating to be superior for all IIEs studied in this work.

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