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## Adsorption Properties Of Hydrous Titanium-Zirconium Mixed Oxide Heated To Different Temperatures

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### ABSTRACT

Hydrous oxides as well as mixed oxides are promising materials, among other types of inorganic ion-exchangers, for the removal of radioactive elements from waste solutions. Characterization, ion exchange property, thermal stability were studied for two synthetic hydrous titanium-zirconium mixed oxides. These oxides mainly consist of metal ions having both large(titanium), small(zirconium) ionic potential. The structural features, surface area, thermal stability of the prepared samples were investigated through the study of their physicochemical properties using appropriate techniques such as IR, X-ray, thermal analyses(TGA & DTA), surface area by nitrogen adsorption(BET). The results of the physicochemical properties prove that both the prepared samples are virtually amorphous, possess high surface areas with a large number of exchange sites(OH, H<sub>2</sub>O). These exchangers possess a high cation exchange capacity, are expected to be anion exchangers since hydrous zirconium oxide has an amphoteric character. Equilibria measurements showed high affinity to Cs<sup>+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup>, Eu<sup>3+</sup>. Thermal stability of the hydrous oxides indicated high resistance towards high temperatures up to 400°C where the oxide retained some of its capacity, especially in case of Eu<sup>3+</sup>. The exchange sites available at relatively high temperature are probably surface H<sub>2</sub>O groups.

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### KEYWORDS

Ion exchange;  
Sorption;  
Cs<sup>+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup>, Eu<sup>3+</sup> Ions;  
Titanium-zirconium;  
Hydrous;  
Mixed oxides.

### INTRODUCTION

In the last decades, inorganic ion-exchangers have occupied a strong position among ion exchange materials. They have numerous applications in the fields of nuclear energy, chemical engineering. Inorganic ion-exchangers are expected to have higher radiation, thermal stability compared with organic resins<sup>[1-6]</sup>. In ad-

dition, the inorganic ion-exchangers resist, to a large extent, the drastic conditions of acidity or basicity. Separation of radioactive nuclides from radioactive waste is the method applied for management of low, intermediate radioactive waste, using various kinds of inorganic ion-exchange materials<sup>[7,8]</sup>.

Inorganic ion-exchange materials are classified into heteropoly acids, ferrocyanides, hydrous metal

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oxides, natural clays, zeolites. Hydrous metal oxides are one of the important, promising materials for use in liquid waste treatment<sup>[9]</sup>. Furthermore, hydrous metal oxides are simple to be prepared, each has unique feature. Studies on preparing, characterizing hydrous oxides are necessary as the ion exchange mechanism has not yet been fully demonstrated<sup>[9]</sup>. Also, development, synthesis of new oxides such as mixed oxides<sup>[5,9,10]</sup> to gather more than one feature is an important goal.

The study of the structural features, thermal stability of hydrous oxides is very important from sorption behavior point of view. The effect of heat treatment of hydrous oxides in air, water at high pressure have been studied by many authors<sup>[11,5,12,13]</sup>.

Hydrous titanium oxide is one of the most attractive inorganic ion exchangers<sup>[5,10,14]</sup>, has been used for adsorption of uranyl ions, other elements<sup>[15-17]</sup>. It has titanium ions of large ionic potential, is expected to have a high affinity for both the transition metal ions, titanium. Hydrous zirconium oxide is an amphoteric ion exchanger containing small ionic potential, possesses large anion exchange capacity<sup>[5]</sup>.

This study is an attempt to prepare two samples of hydrous titanium-zirconium mixed oxides, in different media, to assess their applicability for the removal of important radio nuclides, such as Cs<sup>+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup>, Eu<sup>3+</sup> for the treatment of liquid waste. The effect of the structural features, thermal stability of the prepared sample on sorption behavior will be evaluated through this work.

## EXPERIMENTAL

### Synthesis of hydrous titanium-zirconium mixed oxides

All chemicals used throughout the study were analytical grade reagents. Hydrous titanium-zirconium mixed oxides are designated as HTZO(I), HTZO(II). They were obtained by precipitation with NaOH, NH<sub>4</sub>OH, respectively, from metal chloride solutions, following the procedure of<sup>[9]</sup>.

Into 100mL of 0.24M TiCl<sub>4</sub> solution, prepared by diluting liquid TiCl<sub>4</sub> with distilled water, mixed with 4gm ZrOCl<sub>2</sub>, 100mL of 0.5M NaOH solution were

added at an average rate of 2mL./min with continuous stirring. The pH value at precipitation was about 13. The precipitate was left overnight in the mother liquor then by decanted. The precipitate was uniformly dispersed into distilled water, filtered through a buchner funnel under suction. The precipitate was washed several times with distilled water until the pH approached a constant value of about 10. It was then air dried at 55°C. The solid material was immersed in hot water to break it down into different particle sizes which were dried again at 55°C, stored in a desiccator over saturated NH<sub>4</sub>Cl solution.

The same procedure was followed using 50% NH<sub>4</sub>OH instead of NaOH to compare the effect of the precipitating media on the sorption behavior of the samples.

### Samples characterization

X-ray analysis for both HTZO(I), HTZO(II) at room temperature, 200, 800°C were carried out using the Shimadzu X-ray diffractometer model XD-D1, with Ni filtered CuK<sub>α</sub> radiation.

IR analysis for both samples heated at room temperature, at 800°C was performed using a fully automatic infrared pomen, hartman spectrometer, model MB157, Canada.

The spectra were scanned over the frequency range 400-4000cm<sup>-1</sup>.

The specific surface areas, for the two samples heated at room temperature, 800°C, were determined using a Nova 3200, version 6.08 high speed gas sorption analyzer. The samples were degassed under vacuum before measuring adsorption.

Thermogravimetric analysis(TGA), differential thermal analysis(DTA) were carried out for both samples, HTZO(I), HTZO(II). Shimadzu TGA-50, Shimadzu DTA-50 systems with platinum cell were used for measurement of TGA, DTA respectively. The TGA, DTA measurements were done up to a temperature of 800°C, with a heating rate of 10 °C/minutes in a nitrogen atmosphere, using α-Al<sub>2</sub>O<sub>3</sub> as reference.

### Measurement of ion exchange capacity

The capacities listed here in meq/g for the two exchangers were measured by repeated equilibration

of 0.001M chloride solution of metal ions ( $\text{Cs}^+$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Eu}^{3+}$ ) at  $V/m=100$  (5mL solution/0.05g solid) for the two exchangers, with 0.01M metal ion concentration for sample HTZO(II) only. The contact time for all equilibrations was 24 hours. These solutions were tagged with tracers ( $^{137}\text{Cs}$ ,  $^{60}\text{Co}$ ,  $^{65}\text{Zn}$ ,  $^{154}\text{Eu}$ ), the pH adjusted to 9 for  $\text{Cs}^+$  ion, 4.5 for the other cations. The  $\gamma$ -activity was measured, using a single channel ortec EG, G scaler connected to a well type Na(Tl) scintillation head.

### Heat treatment of exchanger

Portions of the two exchangers in H-form were heated in air to a constant weight at constant heating temperatures. After cooling, the samples were immersed in water overnight, then dried to constant weight in a desiccator containing saturated  $\text{NH}_4\text{Cl}$  solution.

## RESULTS AND DISCUSSION

### Infrared analyses

Infrared spectra for HTZO(I) prepared in NaOH medium at room temperature,  $800^\circ\text{C}$  are shown in figure 1. HTZO(I) consist of strong broad adsorption b,s around  $3400$ ,  $1600\text{cm}^{-1}$  due to the presence of structural hydroxyl groups, of adsorbed, molecular water present in the structure. Ignition of sample to  $800^\circ\text{C}$  results in a change in IR pattern (Figure 1 curve b), where both b,s become very weak but do not disappear. At  $800^\circ\text{C}$ , a compound formation between  $\text{TiO}_2$ ,  $\text{ZrO}_2$  may take place. The moderately strong b, at  $1400\text{cm}^{-1}$  is due to the presence of some  $\text{CO}_3^{2-}$  ions formed during the preparation of mixed oxide due to adsorption of  $\text{CO}_2$  by exchanger<sup>[18]</sup>. In addition, there are some weak inflections around  $500\text{cm}^{-1}$  due to the metal-oxygen (M-O) stretching vibration<sup>[19]</sup>. These inflections are clearly seen at  $800^\circ\text{C}$ , figure 1 curve b.

Figure 2 represents IR spectra of HTZO(II) prepared in  $\text{NH}_4\text{OH}$  medium, heated at room temperature,  $800^\circ\text{C}$ . The b,s are more or less similar to the b,s for the sample prepared in NaOH medium with very few differences. The IR spectra of the two samples, prepared in NaOH or  $\text{NH}_4\text{OH}$  media (Figure 1, 2) indicate that the structure of mixed HTZO remained

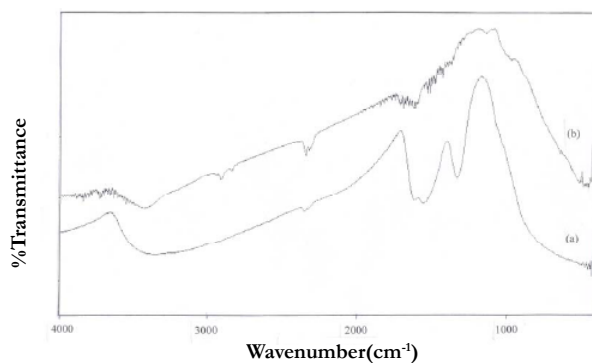


Figure 1 : Infrared spectra of HTZO (I) at room temperature (a) and at  $800^\circ\text{C}$  (b)

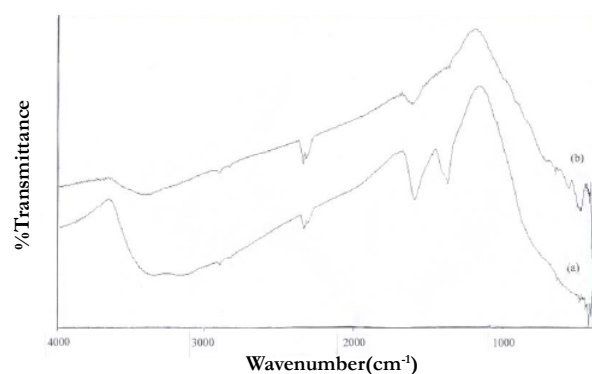


Figure 2 : Infrared spectra of HTZO(II) at room temperature (a) and at  $800^\circ\text{C}$  (b)

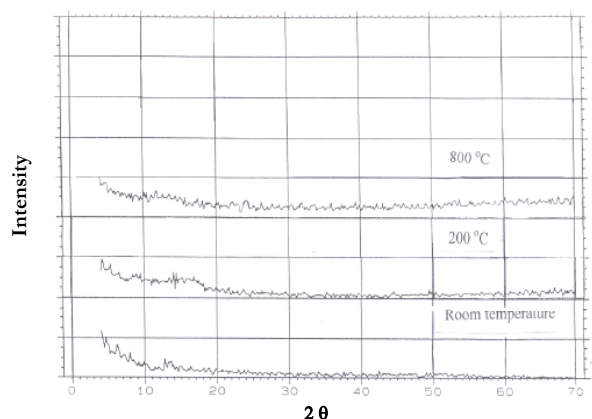


Figure 3 : X-ray diffractograms of HTZO(I) at different heating temperatures

practically unaltered. The structure of HTZO has the same structure whether precipitated with NaOH or  $\text{NH}_4\text{OH}$ . Thus, it is considered as a potential adsorbent in the treatment of radioactive waste.

### X-ray analysis

Figures 3, 4 represent the X-ray analysis of the

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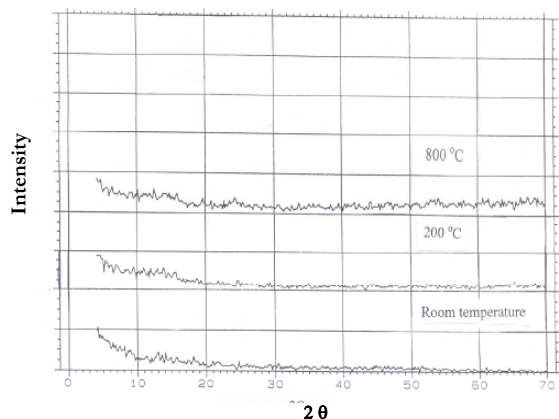


Figure 4 : X-ray diffractograms of HTZO(II) at different heating temperature

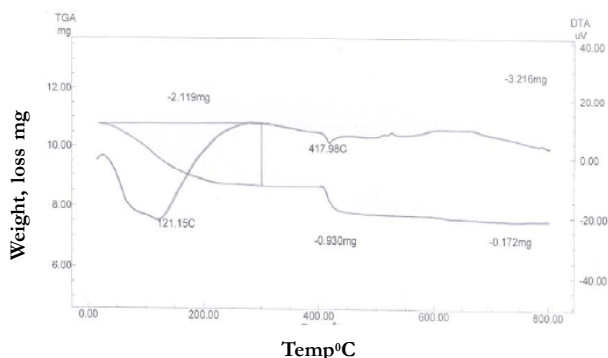


Figure 5 : Thermogravimetric(TGA) and differential thermal analysis(DTA) of HTZO(I)

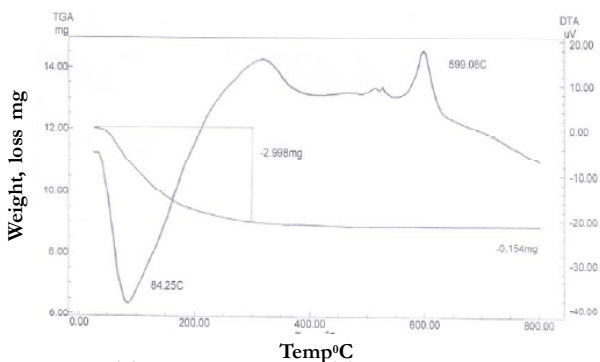


Figure 6 : Thermogravimetric(TGA) and differential thermal analysis(DTA) of HTZO(II)

TABLE 1 : Specific surface area for both HTZO(I), HTZO(II) at room temperature, at 800°C

| Sample   | $S_{BET}$ , $m^2/g$ |        |
|----------|---------------------|--------|
|          | Room temperature    | 800°C  |
| HTZO(I)  | 187.984             | 10.251 |
| HTZO(II) | 408.589             | 18.192 |

mixed oxides HTZO(I), HTZO(II) respectively. It is clear that both samples are virtually amorphous. No peaks could be detected in their X-ray patterns

at any heating temperatures up to 800°C. These results are in agreement with previously published results of other researchers<sup>[20]</sup>. Also, Zou, Lin<sup>[21]</sup> have found that the XRD patterns of the pure TiO<sub>2</sub> or ZrO<sub>2</sub> exhibit tetragonal phase structure for heat treatment at 450°C, the pattern of the titania exhibits the reflection peaks of the anatase phase. Moreover, they have been reported three other mixed titanium- zirconium mixed oxides with different ratios, they found that the XRD patterns were in amorphous form. Zr<sup>4+</sup> or Ti<sup>4+</sup> ions in the mixed Ti-Zr oxides may inhibit the crystallite size growth<sup>[22]</sup>.

### Surface area measurement

The specific surface area obtained by nitrogen adsorption ( $S_{BET}$ ) gives the area of all exposed surfaces which the N<sub>2</sub> molecules can reach (micropores, mesopores, macropores).  $S_{BET}$  is obtained by applying the BET method<sup>[23]</sup>, is expressed in m<sup>2</sup>/g by the equation:

$$S_{BET} = \frac{V_m}{M_v} AN$$

where  $M_v$  is the molecular weight of nitrogen,  $V_m$  is the monolayer capacity,  $A$  is the cross-sectional area occupied by one adsorbate molecule in Å (16.2 Å),  $N$  is Avogadro's number.

The results of specific surface area,  $S_{BET}$ , measurement are given in TABLE 1 for both HTZO(I), HTZO(II) at room temperature, at 800°C.

From TABLE 1, it is clear that the method of preparation has a large effect on the surface area of the investigated samples. Also, the specific surface area of the sample prepared in NH<sub>4</sub>OH medium is double that prepared in NaOH medium. Generally, the medium may affect the porous texture of the prepared gels<sup>[24,25]</sup>.

The higher surface area is obtained by using NH<sub>4</sub>OH as a precipitating agent. This may be reflected on the number of adsorption sites, hence on the exchange capacity which may increase with the increase in capacity<sup>[26]</sup>.

### Thermal analysis

The experimental data of the thermal analyses of HTZO(I), HTZO(II) samples are shown in figures 5, 6 up to a temperature of 800°C. For the two prepared samples, HTZO(I), HTZO(II), the TG



curves show a continuous loss in weight with increased temperature. The weight loss is obviously due to dehydration, its continuous nature is indicative of the absence of definite hydrates of the prepared samples.

The water content of the prepared hydrous oxides is determined from the weight losses of the samples heated at 800°C was 29.83% for HTZO(I), 27.8% for HTZO(II). Accordingly, the following empirical formulae for HTZO(I), HTZO(II) are given as  $\text{TiO}_2 \cdot \text{ZrO}_2 \cdot 4.8\text{H}_2\text{O}$ ,  $\text{TiO}_2 \cdot \text{ZrO}_2 \cdot 3.998\text{H}_2\text{O}$ , respectively. The data obtained from both thermogravimetric curves, the results of ignition loss are seem to be almost identical for the two prepared samples.

DTA represents the enthalpy change, endo-, exothermic, caused by any structural, chemical or phase change. The peak area is a measure of the heat of reaction, hence, also of the amount of the active substance. The main advantage of DTA over TG is that the measured heat change is not necessarily accompanied by a change in weight. Generally, endothermic peaks are indicative of dehydration, reduction, phase transformation, some decomposition reactions, while some other decomposition, crystallization reaction are exothermic.

The differential thermal analysis(DTA) curve of HTZO(I) given in figure 5 shows the expected endothermic peaks corresponding to the weight losses. The first one is a very large endothermic peak extending to a temperature of about 200°C, having a maximum at about 120°C, representing the dehydration process of weakly adsorbed water. It may also be due to loss of some surface OH groups(condensation)<sup>[27,28]</sup>. The second very small endothermic peak is observed at about 417°C, can be attributed to the beginning of transformation process. A very broad ill-defined exothermic peak is observed at about 600°C, may be attributed to the phase transition from amorphous to  $\text{Ti-ZrO}_4$  phase.

Few differences are detected for the DTA curve of HTZO(II) figure 6. The first very large endothermic peak has a maximum at about 85°C, extends to a temperature of about 200°C. It is followed by an overlapping exothermic broad peak with a maximum at about 320°C. This exothermic peak may be attributed to an early beginning of transformation pro-

cess. Also, a sharp exothermic peak at a temperature of 599°C may be attributed to the phase transition from amorphous to  $\text{T-ZrO}_4$ .

Taking into consideration the above-mentioned continuous water loss from the present HTZO(I) figure 5 or HTZO(II), that X-ray data proved that the samples were amorphous, we can say that we have mainly an amorphous hydrous titanium-zirconium oxide. Apart from the water molecules present as such in the hydrous oxide, OH groups are present on the surface. The overlapping exothermic peak in HTZO(II) has been disturbed by the endothermic effect due to removal of surface water, OH groups. This has probably resulted in the decrease of the size of this peak.

Corae et al.<sup>[29]</sup> have characterized  $\text{ZrMo}_2\text{O}_3$  through DTA, found that the temperature of the endothermic events, the crystallization of the trigonal phase were independent of solution stoichiometry. But from DTA curves in figures 5, 6 we can conclude that the surface structure is slightly different for the two samples. This is reflected in the different modes, extents of bonding of surface water, OH groups, which give rise to endothermic peaks located at different temperatures. Also, the differences in exothermic peak positions are due to differences in the temperature of crystallization<sup>[25]</sup>.

### Capacity of HTZO(I), HTZO(II) at different heating temperatures

The effect of heat treatment, in air at different temperatures, on the ion exchange capacities of the samples for  $\text{Cs}^+$ ,  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Eu}^{3+}$ , is shown in fig-

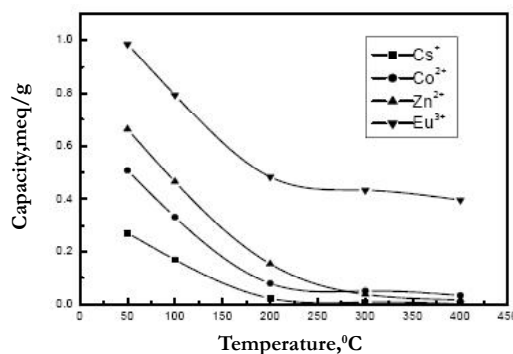


Figure 7: Effect of heating temperatures on the capacity of HTZO(I) for  $10^{-3}$   $\text{MCsCl}$  (■);  $\text{COCl}_2$  (●);  $\text{ZnCl}_2$  (▲) and  $\text{EuCl}_3$  (▼)

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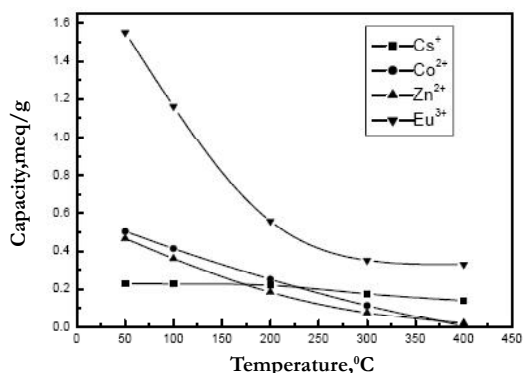


Figure 8 : Effect of heating temperatures on the capacity of HTZO(II) for  $10^{-3}$  M CsCl (■);  $\text{CoCl}_2$ (●);  $\text{ZnCl}_2$ (▲) and  $\text{EuCl}_3$ (▼)

ures 7-9. Figure 7 shows the effect of various heating temperatures on the ion exchange capacity of HTZO (I) for  $\text{Cs}^+$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Eu}^{3+}$  at  $10^{-3}$  M ion concentration. In case of  $\text{Eu}^{3+}$  uptake, this oxide retained about 50% of its original capacity to 200°C, then, the capacity decreased slightly from 200°C to 400°C. In case of  $\text{Cs}^+$ ,  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ , the exchanger lost most of its original capacity at 200°C, the capacity became zero at 400°C. Figure 8 shows a slightly different behavior for the effect of heating temperature on the ion exchange capacity of HTZO(II) for  $\text{Cs}^+$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Eu}^{3+}$  at the same  $10^{-3}$  M ion concentration. This hydrous oxide, HTZO(II), shows a relatively little effect of heating temperature except for  $\text{Eu}^{3+}$ . In case of  $\text{Cs}^+$  uptake, the exchanger lost less than 50% of its original capacity up to a temperature of 400°C. Moderate decreases were detected in capacities of  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$  up to 200°C then, the capacity sharply decreased at 400°C. The capacity of exchanger for  $\text{Eu}^{3+}$  decreased significantly with heating to up to 300°C to about 75% of its original capacity), remained the same at 400°C.

These results somewhat agree with those published by Inoue, Yamazaki<sup>[5]</sup>, where hydrous zirconium(IV) oxide lost about 20% of the original capacity for  $\text{Na}^+$  at a temperature of 70°C, hydrous titanium(IV) oxide was stable up to 80°C. The capacities of both oxides decreased significantly with heat treatment at temperatures higher than 150°C. Hydrous oxides, generally crystallized in the corresponding pure oxides, when they were heat-treated at a temperature of more than 400°C Inoue, Yamazaki<sup>[5]</sup>. Heating hydrous mixed

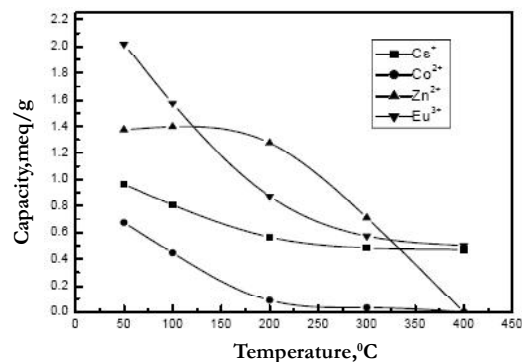


Figure 9 : Effect of heating temperatures on the capacity of HTZO(II) for  $10^{-2}$  M CsCl (■);  $\text{CoCl}_2$ (●);  $\text{ZnCl}_2$ (▲) and  $\text{EuCl}_3$ (▼)

oxide results in loss of most of the ion-exchange capacities. According to X-ray diffraction data of the heat-treated samples, the hydrous titanium(IV) oxide crystallized to a mixture of anatase, brookite at 623°C Inoue, Tsuji<sup>[30]</sup>. On the other hand, Petro et al.<sup>[11]</sup> studied surface characteristics of some hydrous oxides, the effect on their ion exchange behavior, deduced that the capacity may not be closely related with surface area, surface structure may be the more important factor<sup>[12]</sup>.

Figure 9 shows the effect of heating temperature at a different metal ion concentration,  $10^{-2}$  M, for HTZO(II). The exchanger generally shows a higher stability of  $\text{Zn}^{2+}$  capacity tends to be unchanged up to 200°C, then sharply decreases. It seems that bending vibration b<sub>s</sub> of the OH groups in HTZO(II) gel are quite important at 200°C<sup>[12]</sup>. The capacity of the exchanger for  $\text{Eu}^{3+}$  ion decreases to half its original value as the temperature increases from 50 up to 200°C. Even at 400°C the exchanger retained a considerable capacity. The b<sub>s</sub> corresponding to OH groups become very weak but do not disappear (as declared in IR) which means that surface OH, adsorbed H<sub>2</sub>O still act as exchange sites at 400°C. On the other hand, the exchanger lost about 40% of its original capacity of  $\text{Cs}^+$  at the heating temperature 200°C, most of the capacity of  $\text{Co}^{2+}$ . The capacities of  $\text{Cs}^+$ ,  $\text{Co}^{2+}$  change a little for heating at 200-400°C. Following Inoue, Yamazaki<sup>[5]</sup> who have studied thermal stability of some hydrous metal oxides, we propose that a part of the bound water is recovered when the sample is immersed in water af-

ter heat treatment at 400°C.

## CONCLUSION

The present work is concerned with a study of the sorption properties of two samples of hydrous titanium-zirconium mixed oxides as inorganic ion exchanger for the removal of radioactive nuclides such as Cs<sup>+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup>, Eu<sup>3+</sup>. The structure, surface characteristics of the prepared samples were evaluated by various physicochemical methods of analysis. X-ray analysis showed an amorphous nature of the prepared samples even at 800°C. Infrared indicated that both HTZO(I), HTZO(II) are mainly composed of hydrous titanium-zirconium oxide where the b,s of water molecules, surface OH groups were located in the IR spectra. The nominal BET surface areas are equal 187.984, 408.58 for HTZO(I), HTZO(II) respectively. Thermal analysis gave the empirical formulae TiO<sub>2</sub>.ZrO<sub>2</sub>.4.8H<sub>2</sub>O for HTZO(I), TiO<sub>2</sub>.ZrO<sub>2</sub>.3.998 H<sub>2</sub>O for HTZO(II).

Also, the study indicated that both samples possess thermal stability up to 400°C where were the oxides retained some of its capacity. We can conclude that hydrous titanium-zirconium mixed oxides may be considered as a potential adsorbent in the treatment of radioactive wastes.

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