A Study of Adsorption of Zr (IV) on Manganese Dioxide

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Abstract

The adsorption of zirconium, on manganese dioxide from nitric acid solutions has been studied as a function of shaking time, concentration of electrolytes, concentration of adsorbate and temperature effects (25- 90°C).

Four hours of shaking was appropriate to ensure that the adsorption plateau was reached and the adsorption of zirconium decrease with an increase in nitric acid concentration. The limiting adsorption capacities at 3 molar nitric acid was 0.2 Zr per mole of MnO_2. Working at elevated temperature was in favour of the adsorption phenomena.

Introduction

It is possible to reduce significantly the decontamination load on a solvent- extraction process by partially removing certain of the difficulty separated fission products in appropraite "head- end" steps preceding solvent extraction.

Zr is one of the elements most difficult to separate in the solvent-extraction processes, head end development has largely directed at methods for removing this element from uranium. The strong adsorption of some metals by certain sorbent is used to effect their removal.

In recent years, investigations have devoted much effort to the search for new sorbents and further study of the properties of known sorbents for the purpose of selective extraction of radioactive isotope from various solutions.

Various metal oxides have been used successfully as sorbent for the separation process. Active manganese dioxide may be a useful subject of investigation from this point of view. Some of the first investigators who used it for the extraction of certain radioactive elements were khlopin and Balandin (1). They proposed it for the isolation of microamounts of radioactive strontium and cesium from aqueous solutions. Manganese dioxide, has also been used for the adsorption of a variety of elements including toxic elements (2).

Other laboratory studies have shown that manganese dioxide adsorption can also be applied to the removal of protactinium from solution of thorium and uranium- 233 (3).

In recent years, a few practical applications of the adsorbing properties of manganese dioxide have been proposed, such as radium elemination from liquid effluents in the uranium industry and monitoring of sea water for radioisotopes released by nuclear reactors (4- 9).

Continued research into techniques for removal of radionuclides would appear to be potentially beneficial.

Experimental

Preparation of manganese dioxide: Many forms of manganese dioxide are known, non- stoichometric composition and hydrated compounds depending on the method of preparation and drying temperature.

The manganese dioxide used in this work was prepared by adding dropwise $KMnO_4$ solution (21.3 grams of $KMnO_4$ per litre) to $MnSO_4$ solution (71.4 grams of $MnSO_4$ per litre) heated to about 90°C, the resulting MnO_2 was washed, dried at 60°C and then sieved the fraction between 100- 170 mesh was used (10).

Kinetics study experiments: The kinetics study for the radioisotope was done by shaking in a test tube 7.5 millilitre of 3M nitric acid containing 5 micro litre of the zirconium isotope with 0.05 grams of manganese dioxide prepared as described in previous sections. The shaking was done for different time intervals ranging from 15 minutes to 7 hours. After the end of the shaking time, the test tubes were centrifuged for 10 minutes at about 2000 rev/min. Using centaur-2 centrifuge. One millitre of the supernatent solution was taken for counting using NaI detector coupled to a single channel analyser. The adsorption percent was then calculated.

For the adsorption kinetics of uranium, a 26 gu/ 1 in 3M HNO_3 was equilibrated with MnO_2 for 15 min. to 7hrs.

The uranium solution remaining in the aqueous phase was analysed potentiometrically using Davis and Gray method (11).

Effect of nitric acid concentration on adsorption ability of MnO_2: Nitric acid molarity between 1 and 4 were used. The experimental technique is as that described in pervious sectiona. Shaking time equal to 4 hours was found to be appropriate. The radioisotope studied was Zr- 95. The experiments were conducted first on trace level then a carrier was added to the system as $(Zr(NO_3)_4$.

Uranium concentration equals to 26 g u/1 was used to study the effect of different concentration of nitric acid on the adsorption ability of MnO_2.

Adsorption with MnO_2 at different temperatures: The adsorption behaviour of MnO_2 at different temperatures was studied. The temperatures chosen were 40, 50, 60, 70, 80 and 90°C. A thermostated water bath was used throughout the work. In a test tube containing 7.5 ml 3M nitric acid, 5 micro litre of Zr tracer and 0.05g MnO_2 were shaken for 4 hours at a fixed thermostated temperature. Then 1 millilitre of the supernatent solution was taken for counting as stated in sections before.

Determination of capacity of adsorbent: This was investigated at 3M nitric acid with 7×10^{-4} mole of MnO_2 and different moles of zirconium. The limiting adsorption capacities for zirconium was found.

Results and Discussion

The results of the kinetics studies experiments are drawn in figs (1, 2) for zirconium and uranium. Adsorption variation with time was fast in the initial stages but then proceeds slowly and attains equilibrium after four hours of shaking for zirconium, while one hour shaking was quite enough to attain equilibrium for uranium.

Adsorption of Zr on manganese dioxide was studied as a function of nitric acid concentration (1- 4M). The results are given in fig. (3). Adsorption decrease with an increase in electrolyte concentration being 70% for zirconium from one molar nitric acid solution which reduces to 25% for four molar nitric acid. A similar behaviour was noted by Hasany, S. M. (12) working on strontium and Kozawa, A.;

(13) and Gabano, J. P. (14) working on zink this led them to the conclusion that adsorption may be explained by a mechanism involving prior hydrolysis of the metal to give a hydrolysis product which is hydrolytically adsorbed. Thus, higher acid concentrations would tend to suppress the hydrolysis of zirconium ; therefore, very low adsorption of the zirconium metal would take place from highly acidic solutions.

Another parameter that influences adsorption is the concentration of the metal ion itself in solution. The adsorption of the metal ion on manganese oxide measured in both trace and macro amounts (by adding measured quantities of $Zr(NO_3)_4$). The limiting adsorption capacity for zirconium was found from the plot in fig. 4 to be equal to 0.2 mole/ mole MnO_2, which is a high capacity.

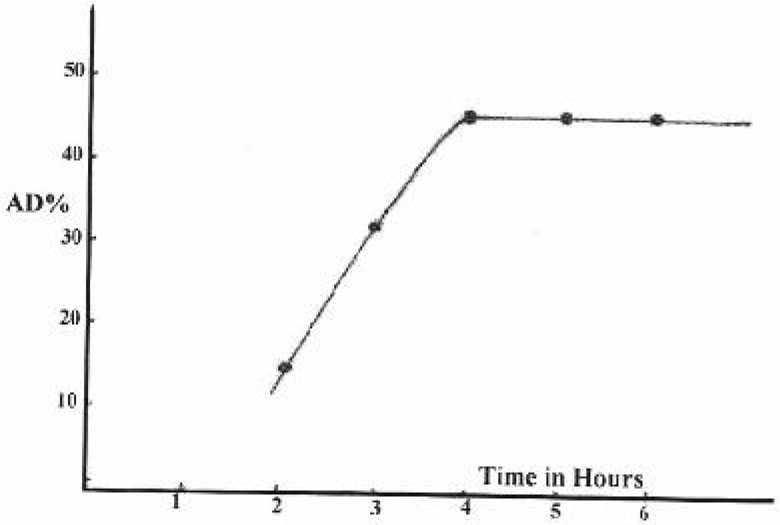
Temperature influence on the adsorption phenomena for zirconium was studied from 25°C up to 90°C, the plots in fig. (5), show a remarkable increase in percent adsorption of zirconium. No considerable change in percent adsorption was observed for uranium fig. (6).

For all cases the percent adsorption for uranium was around 4%. Thus, one can conclude from this study that zirconium adsorption on manganese dioxide can be achieved with limited loss in uranium concentration under the optimum experimental conditions specified.

References

1. Pushkarev, V. V.and Tkachenko, E. V. (1962) Radiokhmiya, 4:49.
2. Biglocca, C. (1974) Anal. Chem, 39:1634.
3. Stoller, R. (1978) Reactor Handbook, Interscience Publishers, Inc. New York.
4. Kurbatov, M. N.and Fu Chun-Ju, Kurbatou, T. D. (1984) J. Chem. Phys. 6:87.
5. Kurbatov, M. N. (1959) J. Chem. Phys., 19:258.
6. McKibben, J. M. (1984) Radiochem. Acta , 36:3.
7. Ruscueci, P.R. and Kowala, A. D. (2002) Journal of Reviews An Environmental Health, 3: 271.
8. Lindner, L. K. (2001) European Journal of Soil Science, 5: 473.
9. Rundberg, R. S. (2000) Soil Science Society Of America Journal 44: 26 .
10. Carla, B. (1967) Analytical Chem, 36:1635.

11. Davies, W. and Gray, W. (1964) Talanta, 11:1203.
12. Hasany, S. M. and Chaudhary, M. Y. (1981) International Journal of Applied Radiation and Isotopes, 32:899.
13. Kozawa, A. (1959) J. Electrochem. Soc., 16: 522.
14. Cabano, J. P. and Etienne, P. (1965) J. of Electrochem. Acta, 10: 947.



Fig(1) Variation of percent adsorption for Zr (from 3M HNO_3) with shaking time

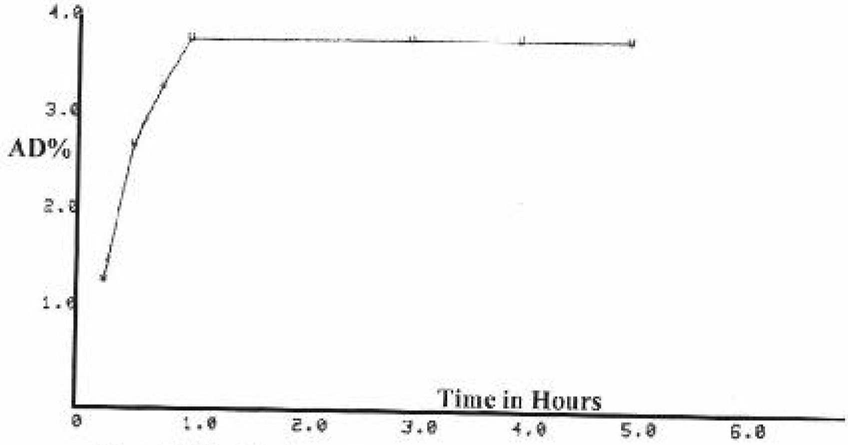


Fig (2) Variation of percent adsorption for Uranium (from 3M HNO_3) with shaking time.

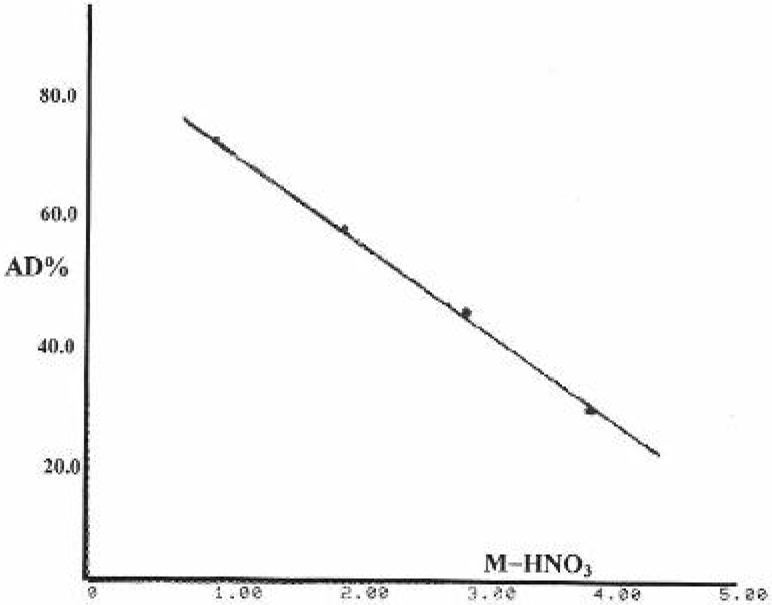


Fig (3) Percent adsorption of Zr as a function of nitric acid concentration

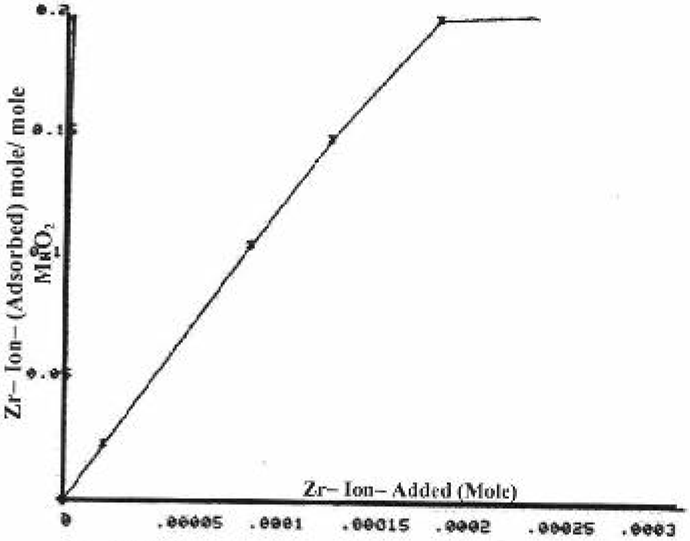


Fig (4) The limiting adsorption capacity of Zr metal on 0.05g MnO$_2$

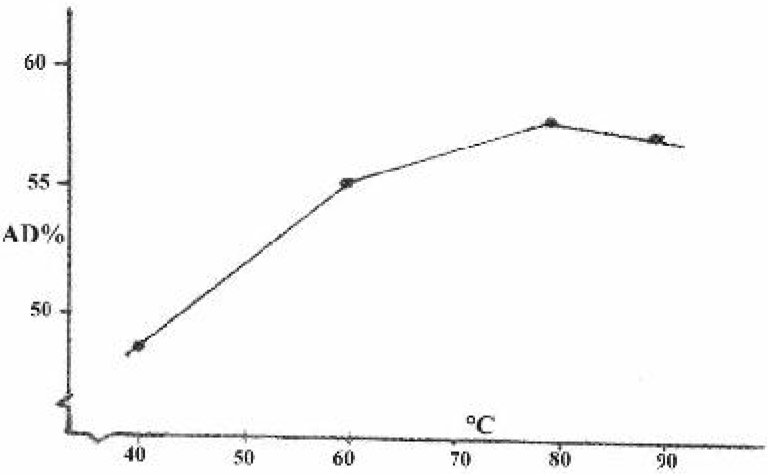


Fig.(5) Temperature influence on the percent adsorption of Zr.

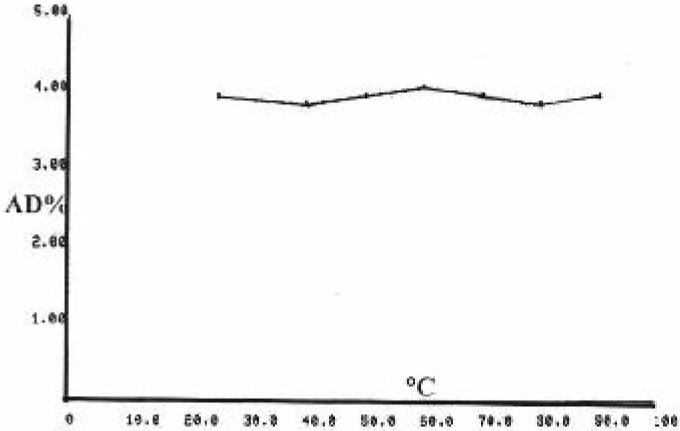


Fig (6) Temperature influence on the percent adsorption of Uranium in 3M HNO_3.

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دراسة امتزاز الزركونيوم (IV) على ثاني اوكسيد المنغنيز

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الخلاصة

امتزاز الزركونيوم (IV) على ثاني اوكسيد المنغنيز وفي وسط حامض النتريك تم دراسته بدلالة مدة الرج، تراكيز الحامض، المادة الممتزة فضلا عن درجات الحرارة، حيث وجد ان 4 ساعات من الرج هي ملائمة للوصول إلى حالة التوازن وان امتزاز الزركونيوم تقل بزيادة تراكيز حامض النتريك، كما تم ايجاد السعة الامتزازية الحدية لعنصر الزركونيوم في 3 مولاري حامض النتريك كما ان العملية الامتزازية تكون افضل في درجات الحرارة العالية (90مْ) عنها في درجة حرارة الغرفة..