
RESEARCH ARTICLES

MANGANESE(II) ADSORPTION STUDIES ON ALUMINIUM OXIDE AND IRON(III) OXIDE BY NEUTRON ACTIVATION ANALYSIS

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ABSTRACT

Adsorption of manganese(II) ion on aluminium oxide and iron(III) oxide at various temperatures was studied. The amount of adsorbed and excess ions in the solution at equilibrium were determined by neutron activation analysis (NAA) using Cf-252 as the neutron source. The influences of electrolytes on the isotherms of adsorption were also investigated. Adsorption isotherms of manganese(II) ion on aluminium oxide were found to follow the Langmuir adsorption isotherm with the ions being more adsorbed at higher temperature. Adsorption on iron(III) oxide, however was found to follow the adsorption isotherm with less of adsorption than on aluminium oxide. Some electrolytes such as calcium chloride and ammonium chloride had some effect on the adsorption.

INTRODUCTION

Adsorption in dispersed systems has been widely investigated. Many techniques have been used to measure the uptake of ions from solution, for example the deposition of mercury on gold by coulometry¹ and the impregnation of iodide on charcoals by flow injection analysis². Few experiments have been carried out via radiochemical method such as the adsorptions of Na⁺, Ca²⁺, Ba²⁺ and Cl⁻ on titanium dioxide³, Cd²⁺, Cu²⁺, Pb²⁺ and Ni²⁺ on iron(III) oxide⁴ and the adsorption of Eu³⁺ on iron(III) oxide and iron(III) hydroxide⁵. These were studied using the radiotracer method. In this present work, adsorption studies of manganese(II) ion on aluminium oxide and iron(III)oxide were done by neutron activation analysis (NAA). This method offers some important advantages over other analytical techniques, which make it worthwhile to look for an extension of its application. Attractive features are the sensitivity of the method for many elements, negligible matrix effects during irradiation and counting. In addition, after activation, the method is not subject to interference by (non-radioactive) contamination and often a number of elements can be determined simultaneously⁶. More importantly, this technique provides true adsorption on adsorbent, whereas other techniques only apparent adsorption could be followed.

In this work, manganese(II) determination has been carried out by neutron irradiation of samples using Cf-252 as a neutron source. Then the γ -ray activity from the Mn-56 at energy of 846 keV was measured by a NaI(Tl) detector. The activity of the radionuclide produced is a direct measure of the quantity of the target element present in the irradiated sample.

The activity (A) of the radioactive nuclide is proportional to the neutron flux and the weight of the element to be determined⁶. Furthermore it also depends on the properties of target-nuclide and radioactive product nuclide. At the end of the irradiation time t_1 , the activity is given by

$$A = \frac{a \cdot W \cdot N_A \cdot \phi \cdot \sigma (1 - e^{-\lambda t_1}) e^{-\lambda t_2}}{M} \quad (1)$$

where

- a = abundance of the target nuclide in the mixture of stable isotopes of the element concerned
- W = weight of the element (g)
- N_A = Avogadro's number
- ϕ = neutron flux ($n \text{ cm}^{-2} \text{ sec}^{-1}$)
- σ = activation cross-section of the target-nuclide (cm^2)
- λ = $\ln 2 / t_{1/2}$ ($t_{1/2}$ = half-life of the radioactive product nuclide (s))
- M = atomic weight of the element concerned
- t_1 = irradiation time (s)
- t_2 = cooling time

Taking into account that parameters a, N_A , σ , and M are equal when sample and standard are compared, the following equation is obtained:

$$\frac{R_s f_s}{W_s \cdot e^{-\lambda t_s}} = \frac{R_x f_x}{W_x \cdot e^{-\lambda t_x}} \quad (2)$$

where W_x and W_s are weights of the element in sample and standard respectively

R_x and R_s are respective count - rates of sample and standard

f_x and f_s are respective relative flux factors

t_x and t_s are times after the end of the irradiation at which sample and standard are counted.

If f_x equals to f_s and t_x equals to t_s Eq.(2) can be reduced to:

$$\frac{W_x}{W_s} = \frac{R_x}{R_s} \quad (3)$$

Therefore, the amount of element in sample could be determined.

The main objective of this work is to obtain information about the adsorption of manganese (II) ion on aluminium oxide and iron (III) oxide. In general, oxides of metal such as aluminium oxide (Al_2O_3), silica (SiO_2) etc. have been commonly used as adsorbents.⁸⁻¹⁰ Aluminium oxide, with specific surface area of $100\text{-}200 \text{ m}^2/\text{g}$, is commonly used in column chromatography. Iron (III) oxide (Fe_2O_3) is red-brown in colour, rhombic or cubic crystalline in morphology, and soluble at a pH below 3.50. The oxides of Al_2O_3 and Fe_2O_3 exist in two forms which are distinguished as the α and γ form. The structures most commonly found for Al_2O_3 and Fe_2O_3 are the corundum ($\alpha\text{-Al}_2\text{O}_3$) and haematite ($\alpha\text{-Fe}_2\text{O}_3$) respectively. The radioisotope method was employed to measure the amount of strongly adsorbed ions on the solid surface in dispersed systems. This method was based on the measurements of solid activity from sediments. The influence of electrolytic substances such as potassium chloride, calcium chloride and ammonium chloride on the adsorption isotherms has also been studied.

MATERIALS AND METHODS

Chemicals

All chemicals used were of analytical grade. Deionized water was used. A stock solution with a concentration of 1 g/dm^3 (1000 ppm) of Mn(II) ion was prepared from manganese(II) sulfate obtained from Matheson Coleman & Bell (Ohio, U.S.A.). Aluminium oxide (pH 9.0, 100 mesh) was purchased from Fluka (Buchs, Switzerland). Iron (III) oxide (M&B, England) was sifted with a 100-mesh sieve. Calcium chloride was obtained from BDH (Poole, England). Both ammonium chloride and potassium chloride were obtained from Merck (Darmstadt, Germany).

Measurements

Standards were prepared for each irradiation. Pure Al_2O_3 and Fe_2O_3 powder were weighed out into plastic vials and exact volumes of the standard solutions of manganese(II) were added and then evaporated onto these powder.

Suspensions of the metal oxides in manganese(II) solution were prepared¹¹⁻¹² with stirring at temperatures of 10, 30 and 50°C for about one hour. The suspensions were then filtered through $0.45 \mu\text{m}$ membranes with vacuum suction. The sediments were then packed in polyethylene bottles and consequently irradiated for 6 hrs by a Cf-252 neutron source with a thermal neutron flux of $10^5 \text{ n cm}^{-2} \text{ s}^{-1}$.

By comparison with the standards, photopeak measurements of Mn-56 at energy of 846 keV were detected using a Berthold NaI(Tl)-scintillation counter (Germany). The flow chart showing main steps in the measurement is shown in Figure 1. Electrolytic substances with a concentration of 0.30 mol/dm^3 , such as potassium chloride, calcium chloride and ammonium chloride, were added to the manganese(II) solution before mixing with the metal oxides in order to study their effects on the adsorption isotherms.

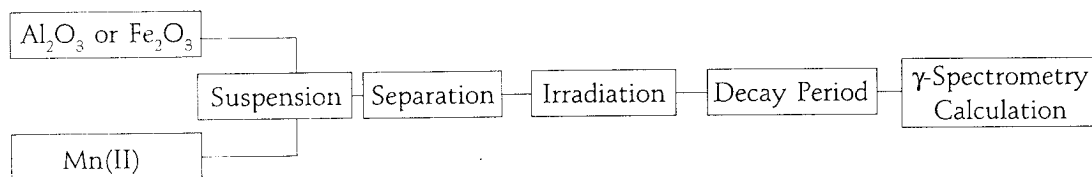


Fig.1 Flow chart of the main steps involved in adsorption measurements.

RESULTS AND DISCUSSION

In general, inorganic ions are adsorbed on the surface of metal oxides by electrostatic and chemical forces¹⁵. These ions are located in the Inner Helmholtz Plane (IHP) of the electrical double layer. Adsorption of Mn (II) on Al_2O_3 (pH 9.0) from the solution of manganese(II) sulfate at the various temperatures were studied via neutron activation analysis. The amount of adsorbed Mn(II) ion on Al_2O_3 surface were obtained through the activity of gamma radiation of Mn-56 at energy of 846 keV. An advantage of radiometric method is its good repeatability in counting. In this experiment, all measurements were done in triplicate and the counts obtained were almost the same, and not significantly different. Figure 2 shows the adsorption isotherm of Mn(II) ion on Al_2O_3 surface at 10, 30 and 50°C, respectively. Those isotherms were characterized by the fact that they tend monotonically to the limiting adsorption. At

higher, temperature there was more amount of Mn (II) coverage on Al_2O_3 surface. Linear Langmuir plots¹² (Figure 3) is of the form:

$$\frac{C}{X} = \frac{C}{k_1} + \frac{1}{k_1 k_2} \quad (4)$$

where C is the equilibrium concentration of Mn(II) ions in the solution in mol/dm^3 , X is the adsorbed amount of Mn(II) (mol/g of adsorbent), k_1 is the maximum adsorption (mol/g) and k_2 is a constant related to the energy of adsorption. At 10, 30 and 50°C the maximum adsorption of Mn (II) on Al_2O_3 were found to be 71.9, 74.1 and 78.7 $\mu\text{mol/g}$, whilst the values of k_2 were obtained to be 7.70, 9.70 and 2.30 $\text{dm}^3/\mu\text{mol}$, respectively.

The adsorption of Mn (II) ion on Fe_2O_3 was also studied at the same temperatures of 10, 30 and 50°C. The adsorption isotherms shown in Figure 4 exhibit smaller amounts of Mn(II) uptake on Fe_2O_3 than on Al_2O_3 surface at low concentration of Mn (II) but the uptake increases sharply at concentration above $10 \times 10^{-5} \text{ mol/dm}^3$. More adsorption also occurs at higher temperature. These indicate that the adsorption of Mn (II) ion on Al_2O_3 and Fe_2O_3 surfaces are both endothermic processes.

However, the adsorption isotherm of Mn (II) ion on Fe_2O_3 , as shown in Figure 4, increased gradually with concentration. The linear plot in Figure 5 indicates that the adsorption isotherms of Mn (II) ion on Fe_2O_3 surface followed the equation as follows

$$X = kC^{1/n}$$

$$\text{or } \log X = \frac{1}{n} \log C + \log k \quad (5)$$

where n and k are constants. At 10, 30 and 50°C the values of n obtained were 0.28, 0.30 and 0.32, whilst the values of k were found to be 2.51×10^{-12} , 2.00×10^{-11} and 3.16×10^{-10} , respectively.

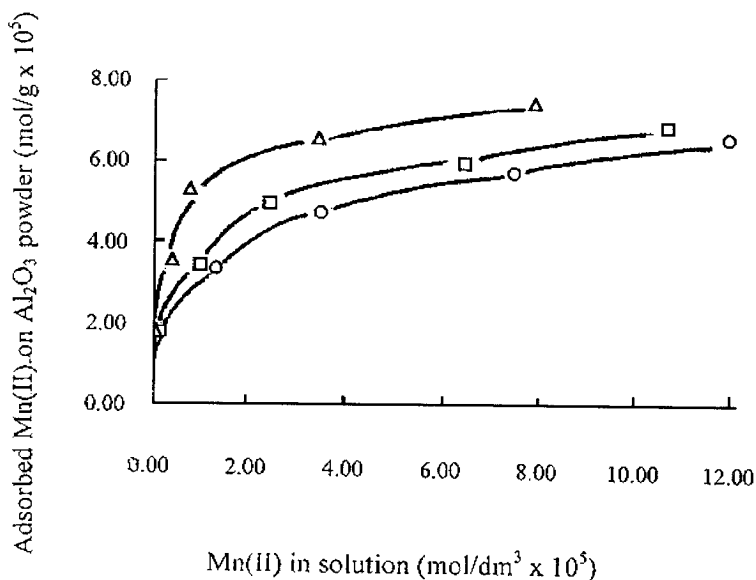


Fig.2 Adsorption isotherms of manganese(II) on Al_2O_3 at temperatures of 10°C (○), 30°C (□) and 50°C (△).

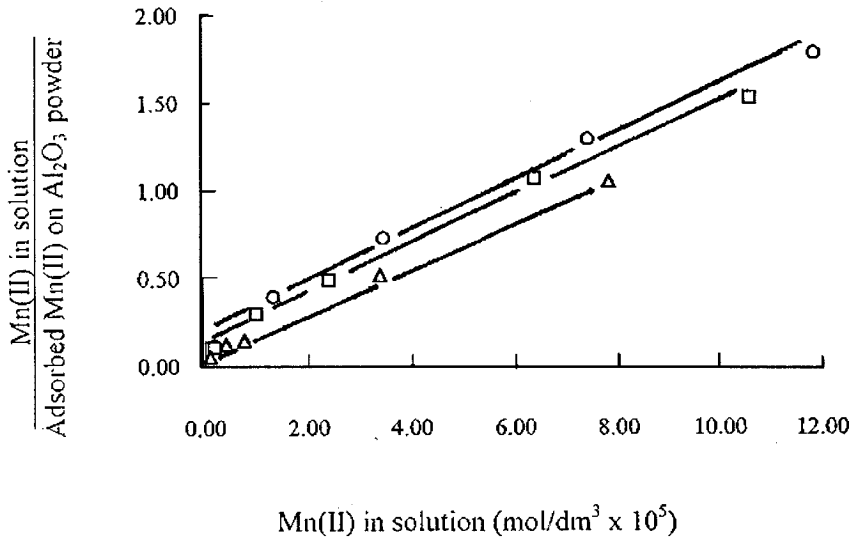


Fig.3 Langmuir plots of manganese(II) on Al₂O₃ at temperatures of 10°C (○), 30°C (□) and 50°C (△).

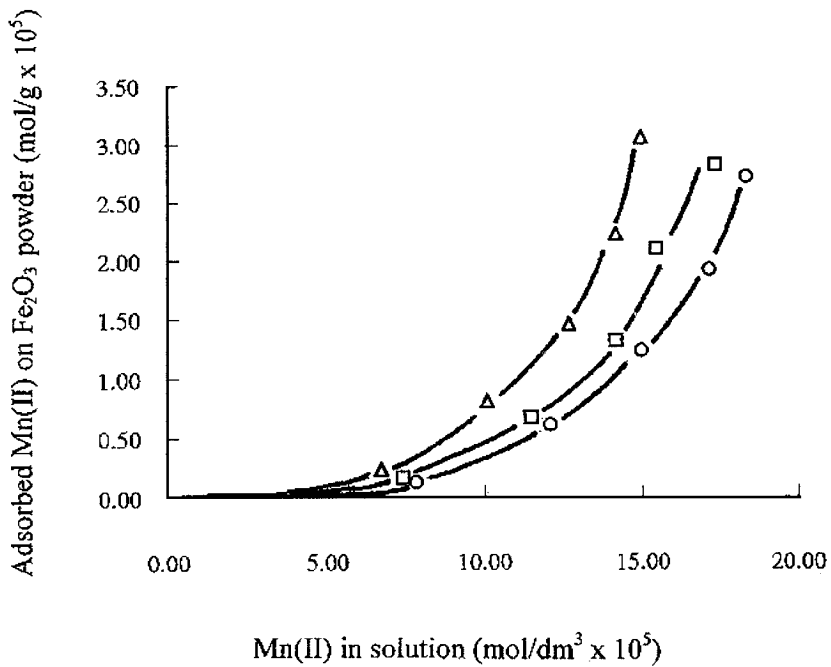


Fig.4 Adsorption isotherms of manganese(II) on Fe₂O₃ at temperatures of 10°C (○), 30°C (□) and 50°C (△).

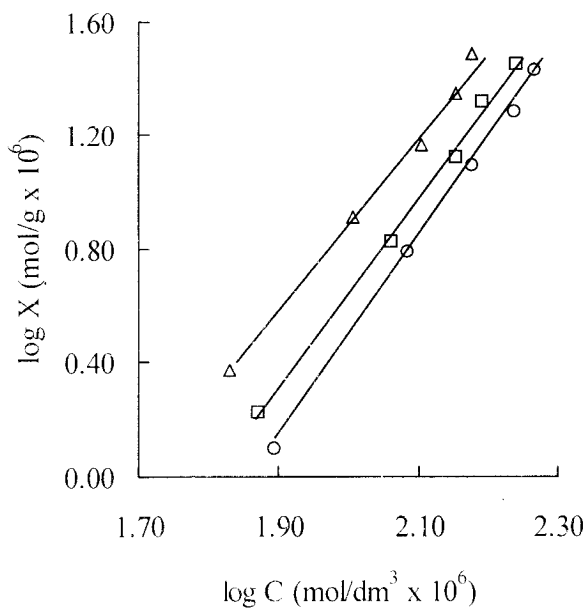


Fig.5 Linear plots of manganese(II) on Fe_2O_3 at temperatures of 10°C (O), 30°C (□) and 50°C (Δ).

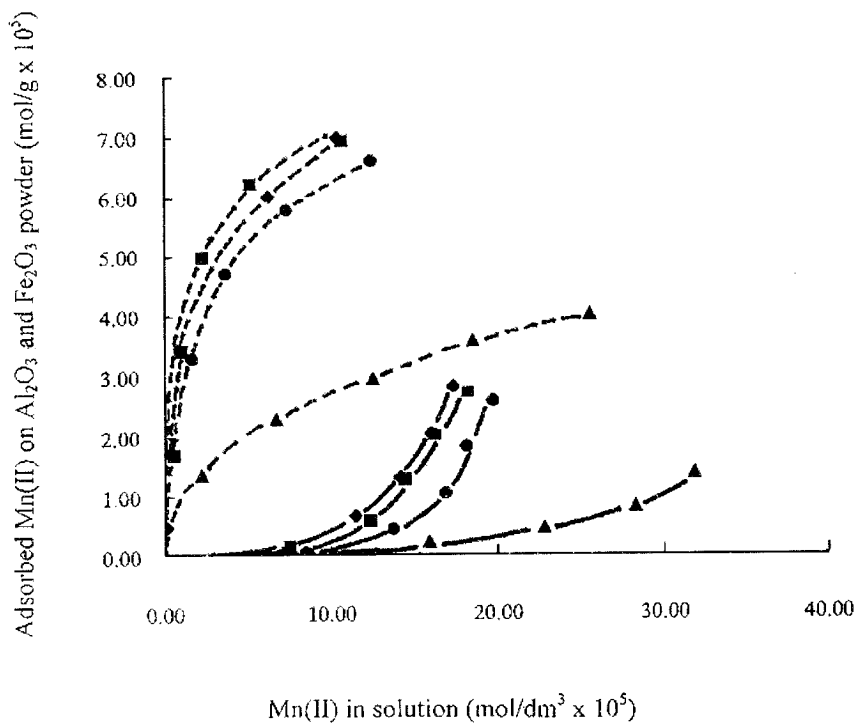


Fig.6 Electrolytic effects on the adsorption isotherms of manganese(II) on Al_2O_3 (dash line) and Fe_2O_3 (dark line): (◆) in H_2O , (■) KCl, (▲) CaCl_2 and (●) NH_4Cl solutions.

Figure 6 shows the effect of electrolytes on the Mn(II) adsorption on both Al_2O_3 and Fe_2O_3 surfaces at 10, 30 and 50°C. It was found that electrolyte CaCl_2 had a greater effect than NH_4Cl and KCl , respectively, on those adsorption isotherms of Mn (II) ion. An explanation for this is that the adsorbability of ions greatly depends on their valencies and size of ions. The higher the valency of the ion, the stronger the attraction by the oppositely charged species on microregions of a surface. Since the Ca^{2+} ion can be strongly adsorbed on the surface, it therefore decreases the amounts of adsorbed Mn^{2+} , whereas the NH_4^+ ion has less effect. The ionic radius also strongly affects its adsorbability. Among ions of the same valency, ions of the largest radius exhibit maximum adsorbability because of their great polarizability and capability of being attracted by a surface which consists of ions or polar molecules. Ions of smaller radius, on the other hand, are hydrated to a larger extent, thus hindering their ionic adsorption because their hydrate shell reduces electrical interaction. Therefore, NH_4^+ shows a small effect on the adsorption isotherms of Mn(II) whereas K^+ shows insignificant effect.

CONCLUSIONS

It can be concluded that both temperature and electrolytes affected the adsorption of Mn (II) ion on both aluminium and iron (III) oxides. Adsorption isotherms at temperatures of 10, 30 and 50°C on aluminium oxide were found to follow the Langmuir behavior. In contrast, the adsorption of Mn (II) ion on iron (III) oxide increased gradually with concentration. In addition, adsorption of Mn (II) ion was found to be greater at higher temperature on both aluminium oxide and iron (III) oxide of which more Mn(II) ion was uptaken on Al_2O_3 . The presence of certain electrolytes such as calcium chloride and ammonium chloride had significant effects on the adsorption isotherms, others such as potassium chloride did not.

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บทคัดย่อ

ได้ทำการศึกษาการดูดซับของแมงกานีส(II)ไอออนบนอะลูมิเนียมออกไซด์และไฮดรอกไซด์ ออกไซด์ที่อุณหภูมิต่างๆ โดยการหาปริมาณของไอออนที่ถูกดูดซับและที่เหลือในสารละลายที่สมดุล ด้วยเทคนิคนิวตรอนแอคติเวชัน (NAA) โดยใช้ ^{59}Fe เป็นแหล่งกำเนิดนิวตรอน และได้ศึกษาผลของอิเล็กโทรไลต์ที่มีอิทธิพลต่อไอโซเทอมของการดูดซับด้วย พบว่าไอโซเทอมของการดูดซับของแมงกานีส(II)ไอออนบนอะลูมิเนียมออกไซด์เป็นไปตามไอโซเทอมของแลงเมียร์ และเกิดได้ดีที่อุณหภูมิสูง ขณะที่การดูดซับบนไฮดรอกไซด์ (III) ออกไซด์เพิ่มอย่างช้าๆ ตามความเข้มข้นด้วยปริมาณการดูดซับที่น้อยกว่าบนอะลูมิเนียมออกไซด์ สารอิเล็กโทรไลต์ เช่น แคลเซียมคลอไรด์และแอมโมเนียมคลอไรด์ มีผลต่อไอโซเทอมของการดูดซับ