Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

A Kinetic and Thermodynamic Study of Silver Sorption onto Manganese Dioxide from Acid Solutions

Syed Moosa Hasany[a]; M. Mufazzal Saeed[a]
[a] NUCLEAR CHEMISTRY DIVISION, PAKISTAN INSTITUTE OF NUCLEAR SCIENCE AND TECHNOLOGY, ISLAMABAD, PAKISTAN

To cite this Article Hasany, Syed Moosa and Saeed, M. Mufazzal(1992) 'A Kinetic and Thermodynamic Study of Silver Sorption onto Manganese Dioxide from Acid Solutions', Separation Science and Technology, 27: 13, 1789 — 1800

To link to this Article: DOI: 10.1080/01496399208019447

URL: http://dx.doi.org/10.1080/01496399208019447

SEPARATION SCIENCE AND TECHNOLOGY, **27**(13), pp. 1789–1800, 1992

A Kinetic and Thermodynamic Study of Silver Sorption onto Manganese Dioxide from Acid Solutions

---

SYED MOOSA HASANY* and M. MUFAZZAL SAEED
NUCLEAR CHEMISTRY DIVISION
PAKISTAN INSTITUTE OF NUCLEAR SCIENCE AND TECHNOLOGY
P.O. NILORE, ISLAMABAD, PAKISTAN

Abstract

The batch kinetics of silver sorption at the tracer level onto manganese dioxide along with the thermodynamic parameters from dilute nitric and perchloric acid solutions are described. The values of ΔH, ΔS, and ΔG found from both acid solutions are similar. The sorption equilibrium constant, K_C, has been calculated at different temperatures between 288 and 308 K. Tests of different isotherms have shown that the sorption data fit very well to the Freundlich and Dubinin–Radushkevich (D-R) models at different temperatures. The thermodynamic data indicate the endothermic nature of silver sorption onto the oxide. The sorption capacity in the 0.23–0.77 mmol/g range and a mean free energy of sorption of about 11.5–15.4 kJ/mol have been found by using the D-R approach. The values of B and the correlation factor (r) have been determined by using the D-R isotherm. These values are comparable with those reported earlier for other sorption systems.

Key Words: Kinetics; Thermodynamics; Silver; Sorption; Manganese dioxide; Acid solutions

INTRODUCTION

Sorption of soluble metallic species by clays, oxides, and other colloidal materials is one of the important means of controlling the soluble metal concentration in heterogeneous systems. The sorption of silver on manganese dioxide from aqueous solutions was studied earlier in this laboratory (*1*) from the analytical and radiochemical points of view. However, its kinetics and thermodynamics have not been reported. This paper reports our results in detail about the kinetic and thermodynamic investigations of silver sorption onto manganese dioxide carried out in dilute nitric or perchloric acid solutions as a function of equilibration time, silver concentration, and temperature.

---

*To whom correspondence should be addressed.

EXPERIMENTAL

Manganese dioxide supplied by B.D.H. (Microanalytical Reagent, Product No 11015), 10–20 mesh, black in color, was used as such as an adsorbent. Its surface area, pore diameter, porosity, and skeletal density have been measured and were reported earlier (*2*). All the other chemicals used were of Analar grade, and all the solutions used were prepared in doubly distilled and deionized water. The preparation of ^{110}Ag tracer used in this study was described elsewhere (*1*).

Batch sorption experiments are carried out by shaking a known amount of adsorbent (usually 50 mg) with 4.5 cm^3 of 0.01 mol/dm^3 perchloric or nitric acid solution having a 8.9×10^{-6} mol/dm^3 silver concentration (except where otherwise specified) in a vibrating temperature controlled (±0.1°C) Gallenkamp Thermostirrer-100 model BKL 235 water bath. The shaking vials and electrolyte containing silver were kept in a water bath for at least 1 hour to attain a controlled temperature before the sorption studies were made. At the end of predetermined intervals, the contents of the shaking vials were centrifuged for 3 min. An aliquot (1 cm^3) of supernatant was analyzed radiometrically. The amount of silver sorbed at any given time was calculated by the difference in the activities of the aliquots drawn before and after sorption. The general procedure and apparatus used were described before (*3*). All experiments were performed at least in triplicate, and the results are reproducible within an experimental error range of ±2 to 5%.

RESULTS AND DISCUSSION

The kinetic studies were carried out from 0.01 mol/dm^3 nitric or perchloric acid solution at a silver concentration of 8.9×10^{-6} mol/dm^3 and at temperatures of 30 and 35°C. The electrolytes and their concentrations were selected in view of our earlier results where high K_D values were obtained for silver sorption onto manganese dioxide from the same electrolytes (*1*). The equilibration time was varied from 1 to 30 min, and the amount of silver sorbed after each interval of time is plotted in Fig. 1. The sorption increased with time up to 10 min and then remained constant in all cases, indicating that equilibrium is achieved in the system within 10 min. The adsorption dynamics is quite significant because it describes the solute uptake rate which in turn controls the residence time of adsorbate uptake at the solid–liquid interface. It is clear that sorption of silver is rapid in the initial stages and gradually decreases with the progress of sorption until an equilibrium is established. This indicates that the sorption of silver takes place in two distinct stages, a relatively fast one followed by a slower one.

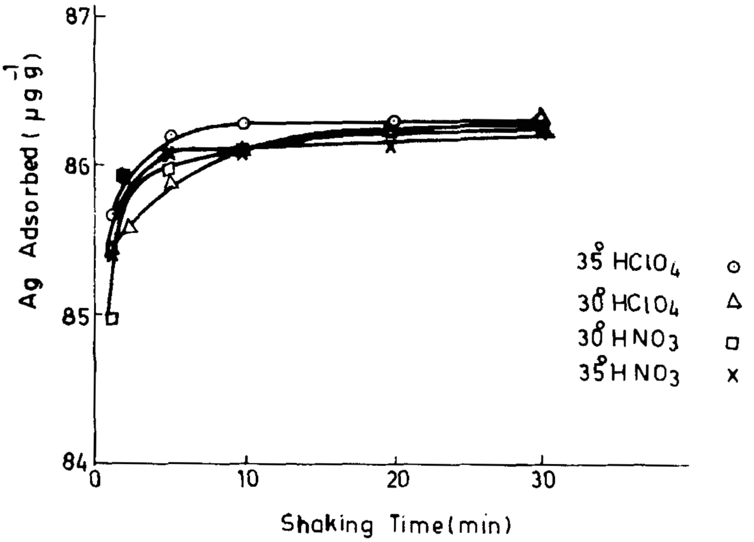

FIG. 1. Amounts of silver sorbed onto manganese dioxide from 0.01 mol/dm^3 acid solution vs time.

The sorption of silver from acidic solution onto manganese dioxide can be considered as a reversible reaction with an equilibrium between two phases.

$$A + Ag \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A\text{—}Ag \tag{1}$$

the overall rate constant, K', and the rate constant for adsorption, k_1, and desorption, k_2, of the reaction can be calculated by using the following equations:

$$K' = k_1(1 + 1/K_C) = k_1 + k_2 \tag{2}$$

and

$$K_C = k_1/k_2 = C_{Be}/C_{Ae} \tag{3}$$

where C_{Be} is the equilibrium concentration of silver on the adsorbent, C_{Ae} is the equilibrium concentration of silver in solution, and K_C is the equilibrium constant:

$$C_{Ae} = C_{A0}(1 - F_e) \tag{4}$$

and

$$C_{Be} = C_{A0}F_e \tag{5}$$

where C_{A0} is the initial concentration of silver in solution and F_e is the fractional attainment of sorption at equilibrium. Substituting the values of C_{Be} and C_{Ae} in Eq. (3) from Eqs. (4) and (5), K_C becomes

$$K_C = F_e/(1 - F_e) \tag{6}$$

The values of K_C, k_1, and k_2 can be determined by using Eqs. (2) and (3).

The amount of silver sorbed at time t is plotted against $\sqrt{t}$ in Fig. 2. According to the Weber and Morris (*4*) equation:

$$q_t = k_d\sqrt{t} \tag{7}$$

The slope of the straight line of q_t vs $\sqrt{t}$ yields the value of k_d, the rate constant of intraparticle transport. The plots of q_t vs $\sqrt{t}$ shown in Fig. 2 for all cases are neither linear nor do they pass through the origin. It appears that in no case is the Weber and Morris Equation (Eq. 7) followed by the sorption system.

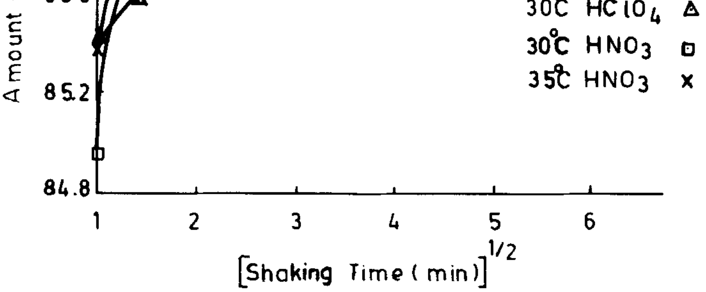

FIG. 2. Amount of silver sorbed onto manganese dioxide from 0.01 mol/dm^3 acid solution vs (time)$^{1/2}$.

The Lagergren equation (5)

$$\log (q_e - q_t) = \log q_e - (K'/2.303)t \tag{8}$$

was also tested by plotting log $(q_e - q_t)$ against time, where q_e and q_t are the amounts of silver sorbed at equilibrium and at time t'. K' is the overall rate constant. Only the data at 30°C from the perchloric acid solution follows the Lagergren equation in the silver sorption system, and this plot is shown in Fig. 3. From the slope of the linear plot, the value of K' at 30°C is computed to be 0.14 min^{-1}. The values of Bt, which is a mathematical function of $q_t/q_e = F$, can be calculated for each value of F as shown by Reichenburg (6):

$$F(1 - 6/\pi^2)e^{-Bt} \quad \text{or} \quad Bt = -0.4977 - \ln (1 - F) \tag{9}$$

and are plotted vs time for nitric acid and perchloric acid media at 30 and 35°C. A linear plot of Bt against time (Fig. 3) is obtained from perchloric acid solution at 30°C, but this straight line does not pass through the origin as observed by others (7). This may indicate that a particle diffusion mechanism is not operating and does not control the kinetics of silver sorption on the oxide. This conclusion was substantiated earlier by the fact that the

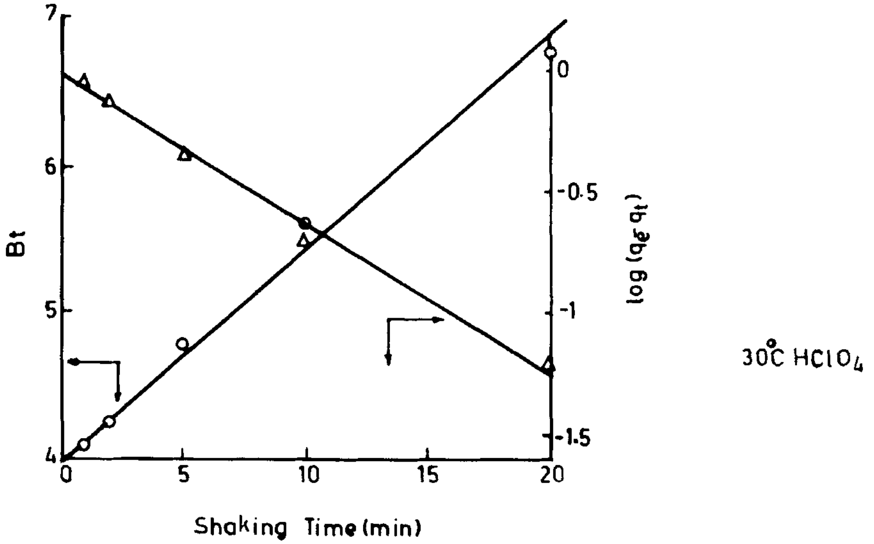

FIG. 3. Plots of overall rate constant and Bt vs t' of silver sorption from 0.01 mol/dm^3 perchloric acid solution at 303 K.

data do not fit into the Weber and Morris equation. The sorption of silver from acid solution on porous manganese dioxide may involve three steps (*10*): bulk transport of silver in solution, film transfer involving diffusion of silver through a hypothetical film boundary layer, and the diffusion of silver within the pore volume of manganese dioxide and/or along the pore–wall surfaces to an active sorption site. The actual sorption of solute on interior surface sites is generally considered to be very rapid, and hence it is not a rate-determining step. Therefore, film and intraparticle transport may be the steps controlling the rate of sorption from acid solutions. Because K_D decreases with increasing silver concentration, film diffusion does not seem to control the rate of sorption. This is in conformity with what has been observed experimentally.

Another parameter, the initial concentration of silver in solution, that influences its sorption has been investigated in the 6.39×10^{-5} to 1.01×10^{-3} mol/dm^3 range by using 10 minutes of shaking time at 30 and 35°C from both acid solutions at a V/m ratio of 90 cm^3/g by using 50 mg of the oxide. In all four sets the sorption of silver decreases with an increase in its initial concentration in solution. The distribution of silver between the solid–liquid interface at equilibrium has been applied to different adsorption isotherms. The Langmuir adsorption isotherm was tested by plotting C_S/C_{Ads} vs C_S, where C_S and C_{Ads} are the concentrations of silver in solution and on the oxide at equilibrium. The plots did not yield straight lines, thus showing that the sorption of silver does not obey Langmuir adsorption isotherm. Although the Freundlich adsorption isotherm is usually regarded as empirical, this adsorption isotherm is applied by drawing a plot of log C_{Ads} vs log C_S. The sorption of silver followed the Freundlich adsorption isotherm over the entire concentration range investigated. These plots are shown in Fig. 4. The fitting of the data to the Freundlich isotherm suggests that sorption is not restricted to one specific class of sites and assumes surface heterogeneity. From the slope and intercept of the plots, the Freundlich parameters (A and $1/n$) are quantified for nitric and perchloric acid solutions at 30 and 35°C. These values are listed in Table 1 and are comparable with the values reported for other sorption systems (*8–10*). The slope of the Freundlich isotherm for all cases is less than 1, indicating a concentration-dependent sorption of silver on manganese dioxide.

The sorption data were tested for another adsorption isotherm, the Dubinin–Radushkevich (*11*) (D-R). The D-R isotherm is more general than the Langmuir isotherm and assumes there is a very small subregion of sorption surface that is uniform in structure and energetically homogeneous. The D-R equation is

$$X = X_m e^{-B\epsilon^2} \tag{10}$$

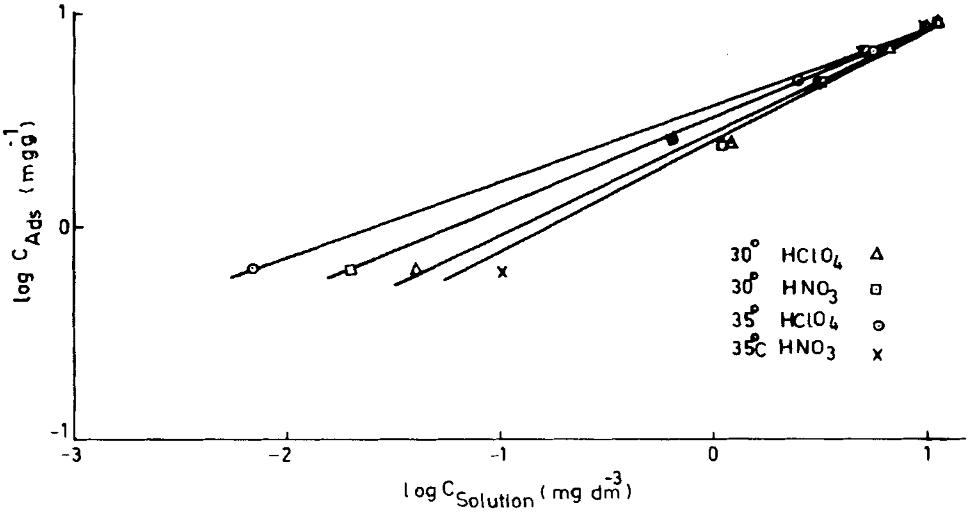

FIG. 4. Freundlich sorption isotherm of silver onto manganese dioxide from 0.01 mol/dm^3 acid solutions.

where X is the amount of silver sorbed; X_m is the maximum amount of silver that can be sorbed on the oxide, i.e., sorption capacity; B is a constant related to the energy; and ϵ (Polanyi potential) $= RT \ln (1 + 1/C)$, where R is the gas constant in kJ·mol^{-1}·K^{-1}, T is the absolute temperature in degrees Kelvin, and C is the concentration of silver in solution at equilibrium. The D-R isotherm can be linearized as

$$\ln X = \ln X_m - B\epsilon^2 \tag{11}$$

If ln X is plotted against ϵ^2, a straight line should result. The D-R plots of ln X vs ϵ^2 are given in Fig. 5. The linear plots indicate that the D-R

TABLE 1
Freundlich Parameters of Silver Sorption onto Manganese Dioxide from 0.01 mol/dm^3 Acid Solutions

Temperature (K)	Electrolyte	$1/n$	A (μmol/g)
303	Perchloric acid	0.49	26.7
308		0.37	36.1
303	Nitric acid	0.42	30.7
308		0.53	26.1

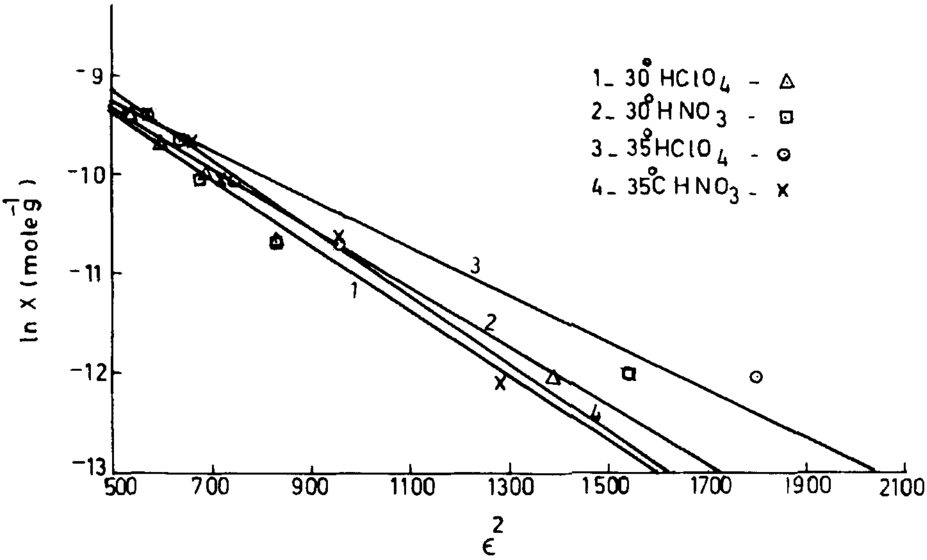

FIG. 5. Dubinin–Radushkevich (D-R) isotherm of silver sorption onto manganese dioxide from 0.01 mol/dm^3 acid solutions. 1: Perchloric acid at 303 K. 2: Nitric acid at 303 K. 3: Perchloric acid at 308 K. 4: Nitric acid at 308 K.

isotherm is followed for silver sorption. This isotherm yields the values of B and X_m and the mean sorption energy change, i.e., E, for a mole of silver sorbed (*12*):

$$E = 1/\sqrt{-2B} \tag{12}$$

on the oxide from Eq. (12), using the value of B from Eq. (10). Linear regression analysis using paired values of ln X and ϵ^2 resulted in the derivation of X_m, B, E, and the correlation factor (r). The correlation factor is a statistical measure of how well the data points fit the regression line. These D-R parameters, evaluated for silver sorption on manganese dioxide, are tabulated in Table 2 for both acid solutions at 30 and 35°C.

The values of E obtained through regression and from the slopes of the D-R plots shown in Fig. 5 are similar. The values of B, E, X_m, and r obtained for silver sorption are comparable with the corresponding values reported for the sorption of Cs on mylonite (*8*) and basalt (*9*), and of U on basalt (*9*) and granite (*10*). The maximum sorption capacity of 0.23–0.77 mmol/g is computed from the D-R equation. This value is comparable

TABLE 2
Dubinin–Radushkevich (D-R) Parameters of Silver Sorption onto Manganese Dioxide from 0.01 mol/dm^3 Acid Solutions

Electrolyte	Temperature (K)	B (mol^2/kJ^2)	r	X_m (mmol/g)	E Regression (kJ/mol)	E Graphical (kJ/mol)
Nitric acid	303	−0.00259	0.9779	0.28	13.88	12.08
	308	−0.00379	0.9954	0.77	11.48	12.13
Perchloric acid	303	−0.00308	0.9884	0.38	12.74	12.25
	308	−0.00210	0.9847	0.23	15.41	14.37

with the values of 0.45 and 0.70 mmol/g for silver sorption on ceric tungstate (*7*) and on iron-zirconium mixed oxide (*13*) respectively. The mean free energy E is in the 11.5–15.4 kJ/mol range. The magnitude of E indicates the type of sorption involved, i.e., chemisorption or ion exchange. The value of E is in the 8 to 16 kJ/mol range expected for ion-exchange reactions (*14*). Hence, it is likely that silver sorbs on the oxide predominantly by ion exchange.

The sorption of silver was also studied as a function of temperature in the 15–35°C range from both acids. The concentration of silver was kept at 9.27×10^{-6} mol/dm^3, a shaking time of 30 min was employed, and the V/m ratio was kept at 90 cm^3/g. The value of K_D (distribution ratio) and K_C were evaluated by using Eq. (3). The values of K_D and K_C obtained at different temperatures are given in Table 3. For both acids, K_D and K_C increase with increasing temperature. This increase of silver sorption with

TABLE 3
Distribution Coefficient (K_D) and Equilibrium Constant (K_C) of Silver Sorption onto Manganese Dioxide from 0.01 mol/dm^3 Acid Solutions at Different Temperatures

Temperature (K)	Nitric acid K_D (cm^3/g)	Nitric acid K_C	Perchloric acid K_D (cm^3/g)	Perchloric acid K_C
288	18,363	204	25,060	278
293	24,425	271	31,522	350
303	48,197	535	67,468	750
308	50,109	557	74,422	827

a rise in temperature may be explained on the basis of thermodynamic parameters which have been calculated using the following relationships:

$$\Delta G = -RT \ln K_C \tag{13}$$

$$2.303 \log K_C = -\Delta H/RT + \Delta S/R \tag{14}$$

$$\Delta S = (\Delta H - \Delta G)/T \tag{15}$$

Plots of log K_D and log K_C vs 1/K are given in Figs. 6A and 6B, respectively. However, the values of ΔG, ΔH, and ΔS were calculated on the basis of the slope and intercept of the plot shown in Fig. 6B, and they are listed in Table 4. The computed ΔH value of 39.8–43.5 kJ/mol is of the same order of magnitude as reported for silver sorption on ceric tungstate (ΔH = 34.7 kJ/mol) (*7*) and of phosphate sorption on zirconium oxide (ΔH = 25 kJ/mol) (*15*). The negative values of ΔG indicate the spontaneous nature of silver sorption, and the positive values of ΔH show the sorption to be endothermic, with weak bonding between adsorbate and adsorbent. The positive entropy change may be at least partly brought about by a change in the hydration states of silver ions.

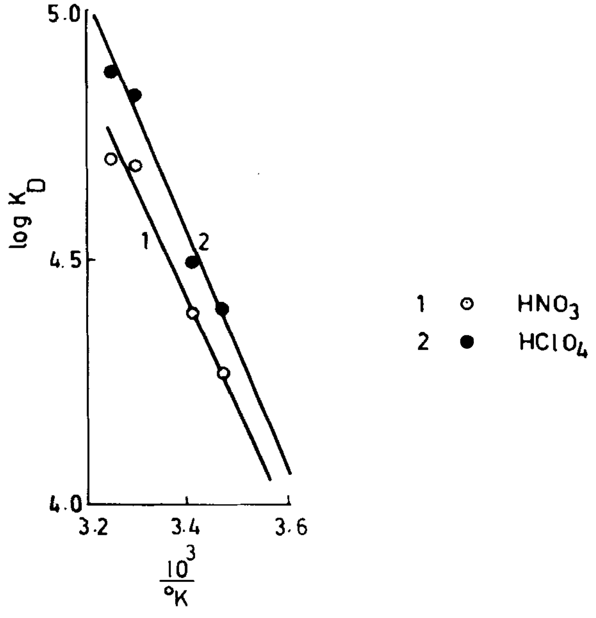

FIG. 6A. Distribution coefficient (K_D) vs 1/K from 0.01 mol/dm^3 acid solutions.

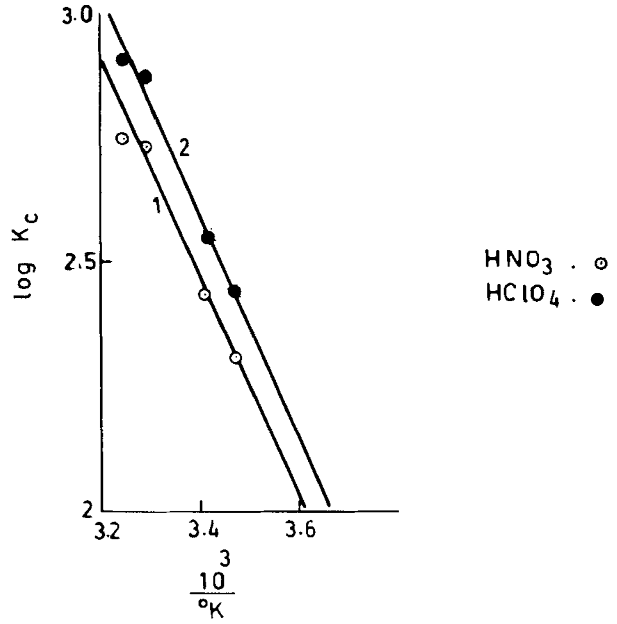

FIG. 6B. Equilibrium constant (K_C) vs 1/K from 0.01 mol/dm^3 acid solutions.

These findings are in accordance with the experimental observations. Since the sorption is endothermic, the amount of silver sorbed at equilibrium must increase with increasing temperature, because ΔG increases with an increase in solution temperature. The values of K_D and K_C given in Table 3 confirm these observations. The free energies (ΔG) estimated from the plots of K_C vs 1/K for both acids are of the same order of magnitude as those computed using D-R parameters.

The data are important for the recovery of silver from industrial effluents, especially in the photographic industry, and for its removal from wastewater.

TABLE 4
Thermodynamic Parameters of Silver Sorption onto Manganese Dioxide from 0.01 mol/dm^3 Acid Solutions

	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (J·mol^{-1}·K^{-1})
Nitric acid	39.8 ± 5.1	−15.5 ± 7.3	182.5 ± 17.2
Perchloric acid	43.5 ± 4.8	−16.4 ± 6.8	197.5 ± 16.0

REFERENCES

1. S. M. Hasany, H. Rehman, and A. Rashid, *Sep. Sci. Technol.*, *24*, 1363 (1989).
2. S. M. Hasany, E. Haq, and S. B. Butt, *Ibid.*, *21*, 1125 (1986).
3. S. M. Hasany and M. H. Chaudhary, *J. Radioanal. Nucl. Chem.*, *100*, 307 (1986).
4. W. J. Weber and J. C. Morris, *J. San. Eng. Div. ASEC*, *899*(SA2), 31 (1963).
5. S. Lagergren, *Bil. K. Sven. Vatenskapsakad. Handl.*, p. 24 (1898).
6. D. Reichenburg, *J. Am. Chem. Soc.*, *75*, 589 (1953).
7. E. M. Mikhail and N. Z. Misak, *J. Chem. Technol. Biotechnol.*, *39*, 219 (1987).
8. S. Aksoyoglu, *J. Radioanal. Nucl. Chem.*, *140*, 301 (1990).
9. L. L. Ames, W. R. A. McGarrah, and P. F. Salter, *Chem. Geol.*, *35*, 205 (1982).
10. S. Aksoyoglu, *J. Radioanal. Nucl. Chem.*, *134*, 393 (1989).
11. M. M. Dubinin and L. V. Radushkevich, *Proc. Acad. Sci. USSR, Phys. Chem. Sec.*, *55*, 331 (1947).
12. J. P. Hobson, *J. Phys. Chem.*, *73*, 2720 (1969).
13. S. K. Srivastava and C. K. Jain, *J. Radioanal. Nucl. Chem.*, *98*, 63 (1986).
14. F. Helfferich, *Ion Exchange*, McGraw-Hill, New York, 1962, p. 166.
15. D. R. Vissers, *J. Phys. Chem.*, *73*, 1953 (1969).

Received by editor November 18, 1991