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

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To cite this Article Hasany, Syed Moosa , Habib-Ur-Rehman and Rashid, Asma(1989) 'Adsorption of Microamounts of Silver on Manganese Dioxide from Acid Solutions', Separation Science and Technology, 24: 15, 1363 — 1375
To link to this Article: DOI: 10.1080/01496398908050657
URL: http://dx.doi.org/10.1080/01496398908050657

SEPARATION SCIENCE AND TECHNOLOGY, 24(15), pp. 1363-1375, 1989/90

Adsorption of Microamounts of Silver on Manganese Dioxide from Acid Solutions

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Abstract

Adsorption of microamounts of silver on manganese dioxide from nitric and perchloric acid solutions has been studied and optimized with respect to shaking time, concentrations of electrolyte, adsorbent, and adsorbate. Maximum adsorption (>99.5%) has been achieved from 0.01 mol/dm^3 acid solution using 50 mg oxide at 10^{-5} mol/dm^3 silver concentration after 30 min shaking. The adsorption decreases with increasing concentration of acid and adsorbate from both the acids. The presence of a 10^4-fold greater concentration of cyanide, thiocyanate, thiosulfate, and Pb(II) than silver reduces the adsorption drastically. The adsorption of silver follows the Freundlich adsorption isotherm over the entire concentration range investigated from 9.27×10^{-6} to 2.92×10^{-3} mol/dm^3 with a value of A = 49 mmol/g and $1/n$ = 0.93. Moreover, the Langmuir adsorption isotherm is also valid except at the lowest and highest concentrations. The values of the limiting adsorption concentrtion (C_m) have been found to be 1 mmol/g and of the equilibrium constant for adsorption 87 dm^3/mol at 23 ± 2°C.

INTRODUCTION

In recent years the adsorption properties of oxides and hydroxides have been widely studied (*1–3*) because of their superior thermal and radiation

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stability. These materials have wide application in industry and chemistry. They are used for the conditioning of moderator and coolant water in pressurized water reactors, for the separation of uranium and plutonium from fission products, for the production of pure radioactive nuclides, for the decontamination of intensive radioactive fields, and for the radiochemical separations in activation analysis. They are employed for water treatment, for water purification and desalination, and for the removal of corrosion products and ionic impurities from high temperature water. These compounds are applied in the determination of heavy metals in gasoline and other hydrocarbons and impurities in highly pure materials. They are also used in hydrometallurgy, food technology, partition chromatography, metal recovery, and in industrial waste treatment (*1*).

In our laboratory, manganese dioxide has been studied for its adsorption characteristics for a number of metal ions (*4–12*). In continuation of these studies, the present communication illustrates the results of the adsorption of silver in trace amounts on manganese dioxide from acid solutions.

EXPERIMENTAL

^{110}Ag tracer was prepared by irradiating specpure silver metal in the PARR-I reactor of this institute at a thermal flux of 2×10^{13} n cm^{-2}/s for 4 days. The irradiated metal was dissolved in a very small portion of concentrated nitric acid and then evaporated to dryness. The residue was later dissolved in deionized water. Other tracers used were prepared by irradiating specpure metals or their appropriate compounds. Their radiochemical purity was checked by gamma spectroscopy.

Manganese dioxide, BDH microanalytical reagent (11015), 10–20 mesh, black in color, was used as an adsorbent. Its surface area, pore diameter, porosity, and skeletal density have been measured and reported earlier (*10*). All the chemicals used in this investigation were of Analar grade, and all the solutions were made in doubly distilled deionized water.

The details of the experimental procedure and the method for the computation of distribution coefficient (K_D) and percent adsorption are given elsewhere (*8*). The measurements of K_D were carried out at 23 ± 2°C. The results are the average of at least triplicate runs and the precision in most cases is ±5%.

RESULTS AND DISCUSION

In view of our earlier experience (*7–9*), the initial adsorption of microamounts of silver was studied on 50 mg of manganese dioxide as a function of the shaking time (1–120 min) from nitric and perchloric acid solutions at fixed acid concentrations of 0.01, 0.1, 1, and 3 mol/dm^3. The concentration of silver was kept constant at 9.27×10^{-6} mol/dm^3 throughout these studies except where otherwise specified. The results are recorded graphically in Figs. 1 and 2. From both media the adsorption increases with increasing shaking time, sharply in the initial stages, and attains equilibrium in 30 min. This trend is valid for all the concentrations used and is independent of the nature of the acid. The shapes of the shaking time variation curves are quantitatively different but qualitatively almost the same for both acid solutions of different concentrations. The adsorption increases in the order 0.01 > 0.1 > 1 > 3 mol/dm^3 at all shaking times. However, for shaking times above 10 min, the distribution coefficients from 1 mol/dm^3 nitric acid solutions are somewhat higher than the values at corresponding shaking times from 0.1 mol/dm^3 nitric acid solutions. This type of anomaly was also noticed for the adsorption of hafnium on manganese dioxide from perchloric acid solutions (*12*). Because maximum adsorption has been achieved from 0.01 mol/dm^3 acid solution after 30 min shaking, these conditions were selected for further studies.

It may be possible that in the initial stages the surface coverage is too low and the adsorptive species accumulate rapidly at the adsorbent surface and occupy active sites, resulting in a higher uptake in the early shaking time. As a consequence, some portion of the active adsorbent sites may be blocked with the passage of time, hence the rate becomes slower and reaches equilibrium when the surface becomes almost saturated.The time required to accomplish equilibrium, i.e., 30 min, demonstrates that adsorption of silver is similar to that of physical adsorption and involves fast processes.

Another parameter that controls adsorption is the amount of adsorbent. This was varied from 10 to 300 mg for both acids. The results are shown in Fig. 3. In both acid media the distribution coefficient first increases with an increase in the amount of the adsorbent, attains a maximum at 50 mg, and then begins decreasing with a further increase in the amount of oxide. Throughout use of the entire amount of manganese dioxide provided, the K_D values obtained from perchloric acid are higher

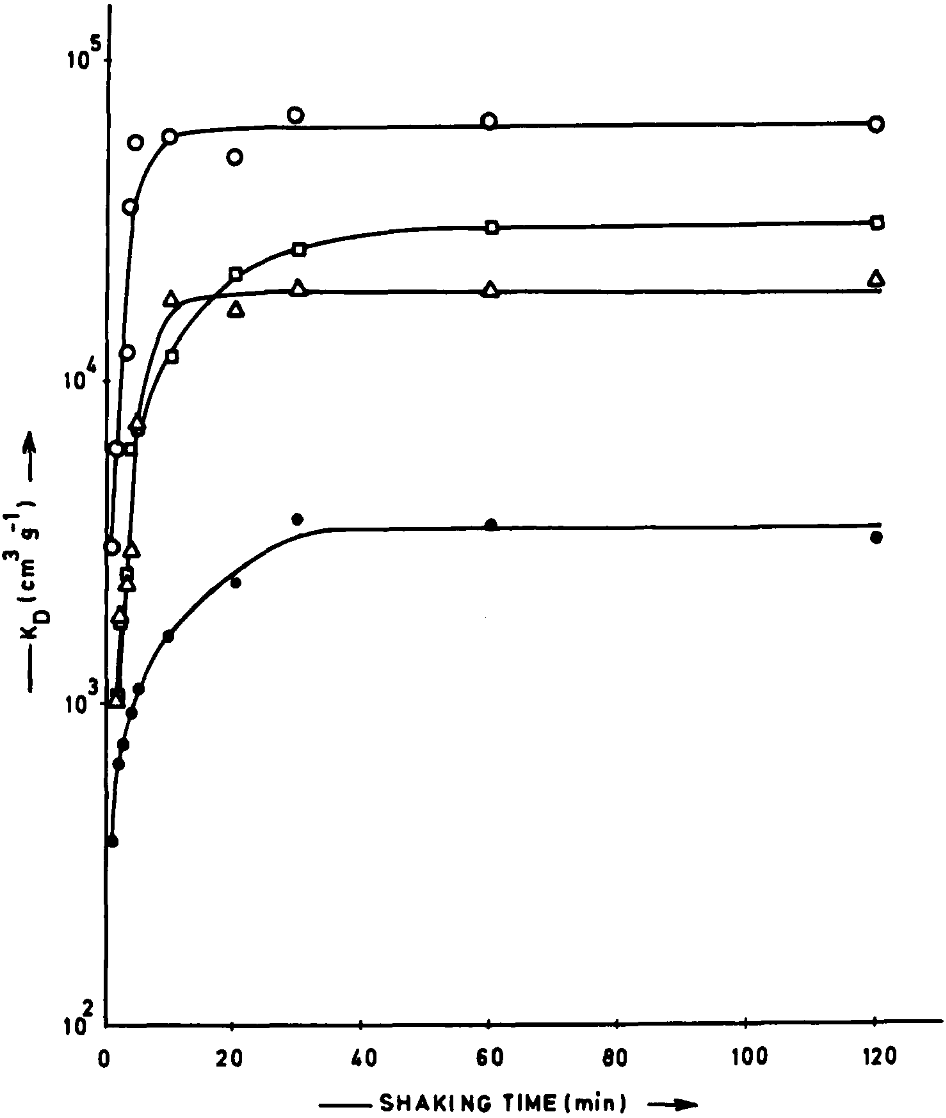

FIG. 1. Adsorption of 9.27×10^{-6} mol/dm^3 silver on 50 mg manganese dioxide from (○) 0.01, (△) 0.1, (□) 1, and (●) 3 mol/dm^3 nitric acid solutions as a function of shaking time.

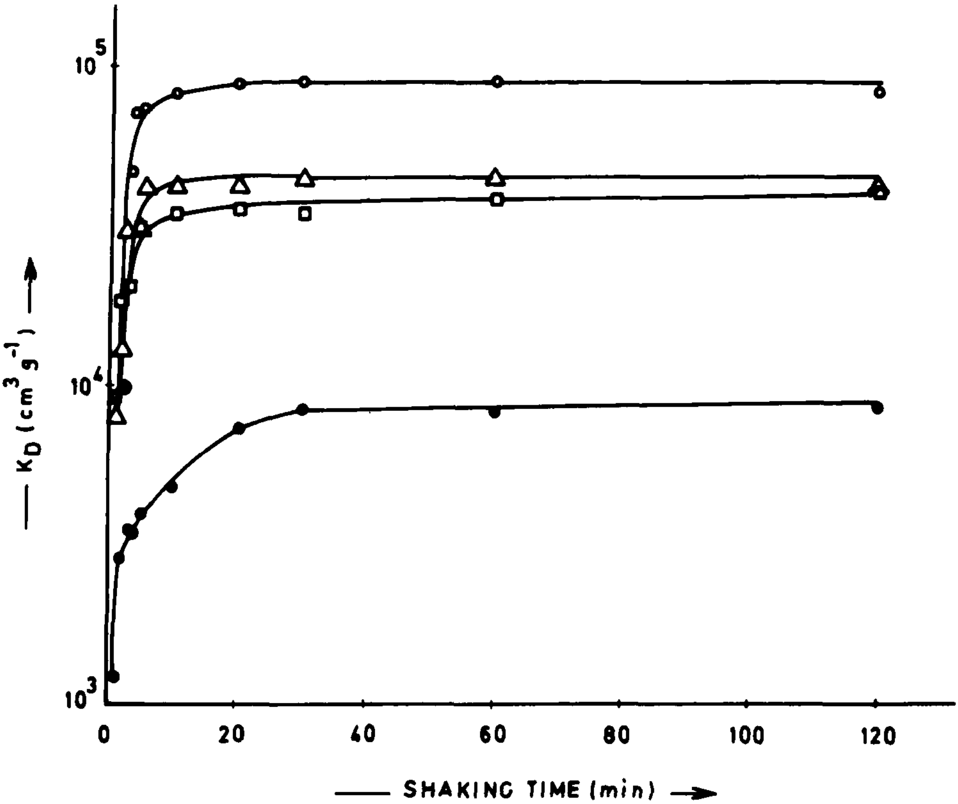

FIG. 2. Adsorption of 9.27×10^{-6} mol/dm^3 silver on 50 mg manganese dioxide from (○) 0.01, (△) 0.1, (□) 1, and (●) 3 mol/dm^3 perchloric acid solutions as a function of shaking time.

than the corresponding values from nitric acid solutions. The optimum amount of oxide, i.e., 50 mg, was used in all further experiments. A similar trend for the adsorption of cobalt (*4*), strontium (*5*), cesium (*6*), cadmium (*7*), and zirconium (*10*) on manganese dioxide in relation to its amount was observed in our earlier studies, and maximum adsorption was noted on 50 mg of the oxide for cobalt (*4*), cadmium (*7*), and zirconium (*10*).

The adsorption of silver on the oxide was checked in relation to its own concentration in the range from 9.27×10^{-6} to 2.92×10^{-3} mol/dm^3 from

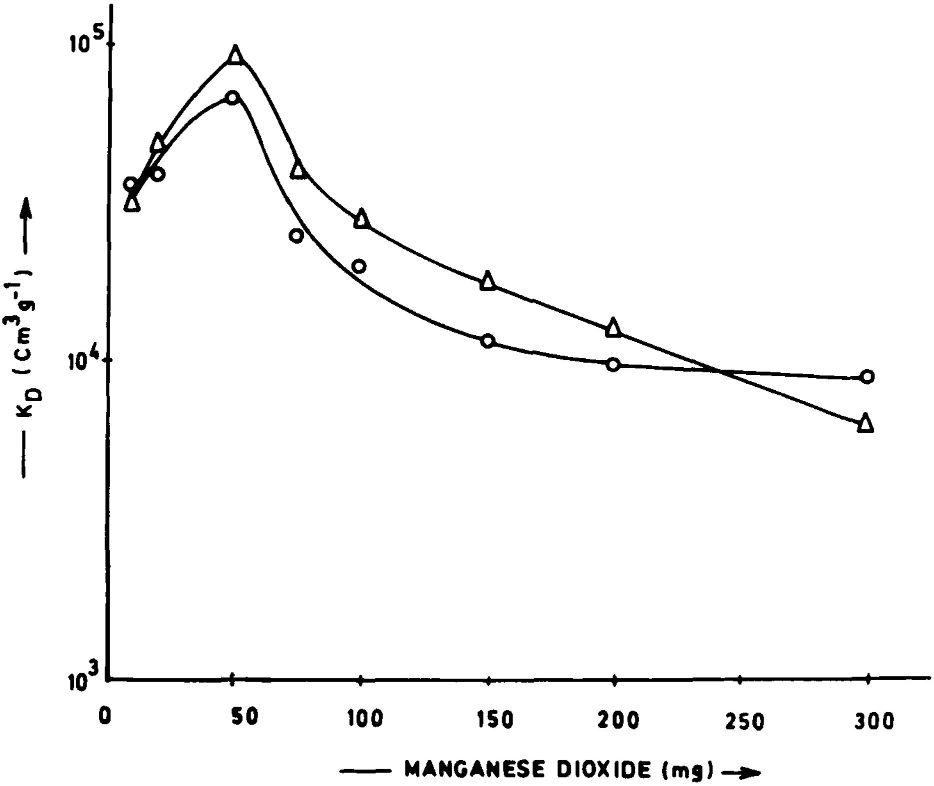

FIG. 3. The dependence of silver adsorption on the amount of manganese dioxide from 0.01 mol/dm^3 nitric acid (O) and perchloric acid (Δ) solutions.

both acid solutions. The results are given in Fig. 4. It is evident that from both media the distribution coefficient increases with a decrease in the concentration of adsorbate over the entire concentration range investigated. This can be interpreted in terms of the reduction of the relative number of active sites as the concentration of silver is increased. Similar trends were noticed in the case of strontium (*5*), cadmium (*7*), and zirconium (*10*) adsorption on manganese dioxide. This increase of adsorption with an increase in dilution of the investigated system may be due to the availability of a lesser number of adsorptive species at lower concentrations for a relatively equal number of surface-active sites. In general,

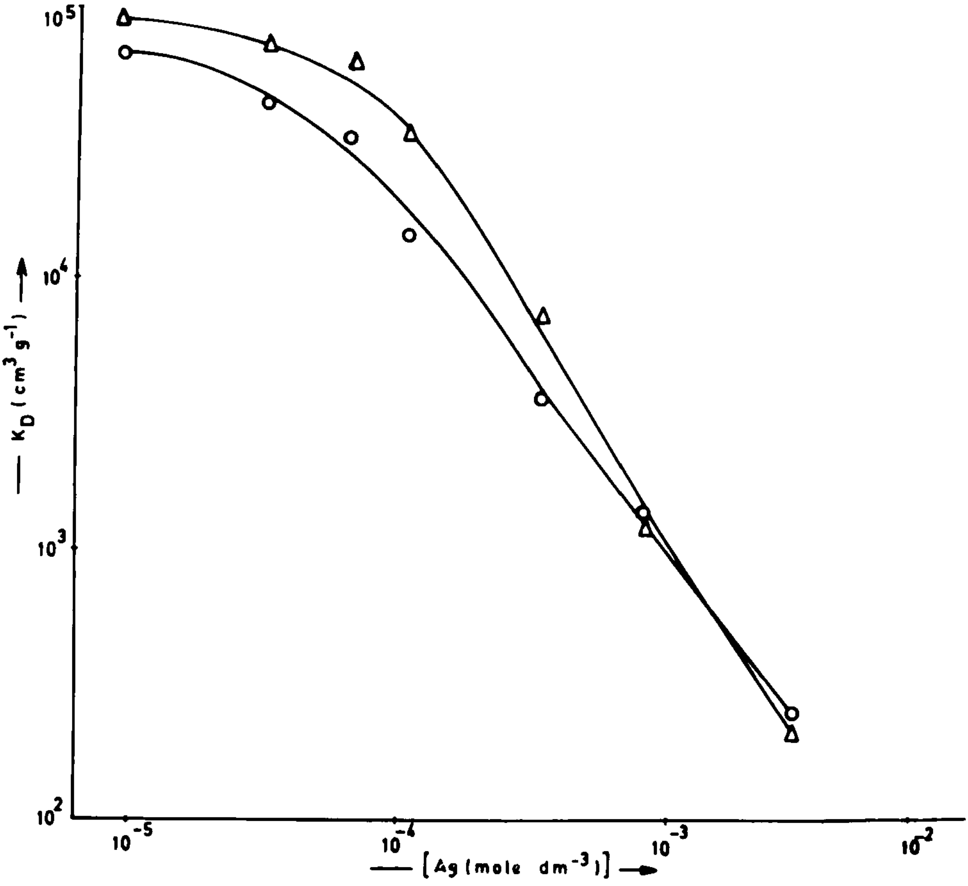

FIG. 4. The relationship between the distribution coefficient of silver and its concentration from 0.01 mol/dm^3 nitric acid (○) and perchloric acid (△) solution using 50 mg manganese dioxide.

correspondingly higher adsorption has been noticed from perchloric acid solution than from nitric acid solutions as observed earlier in the case of adsorption dependence upon the amount of adsorbent. The relationship between adsorbed and bulk concentration was tested in the linear form of the Freundlich adsorption isotherm:

$$C_{\text{Ads}} = AC_{\text{Bulk}}^{1/n} \tag{1}$$

where C_{Ads} is the adsorbed concentration in mol/g, C_{Bulk} is the bulk concentration in mol/dm^3, and A and n are characteristic constants for the adsorption system. To check the validity of the Freundlich adsorption isotherm, log C_{Ads} was plotted against log C_{Bulk} and a straight line was obtained (Fig. 5). This indicates that the uptake of silver on manganese dioxide follows the Freundlich adsorption isotherm over the entire concentration of silver investigated from both solutions, which is often valid for physical adsorption. The values of $1/n = 0.93$ and $A = 49$ mmol/g were

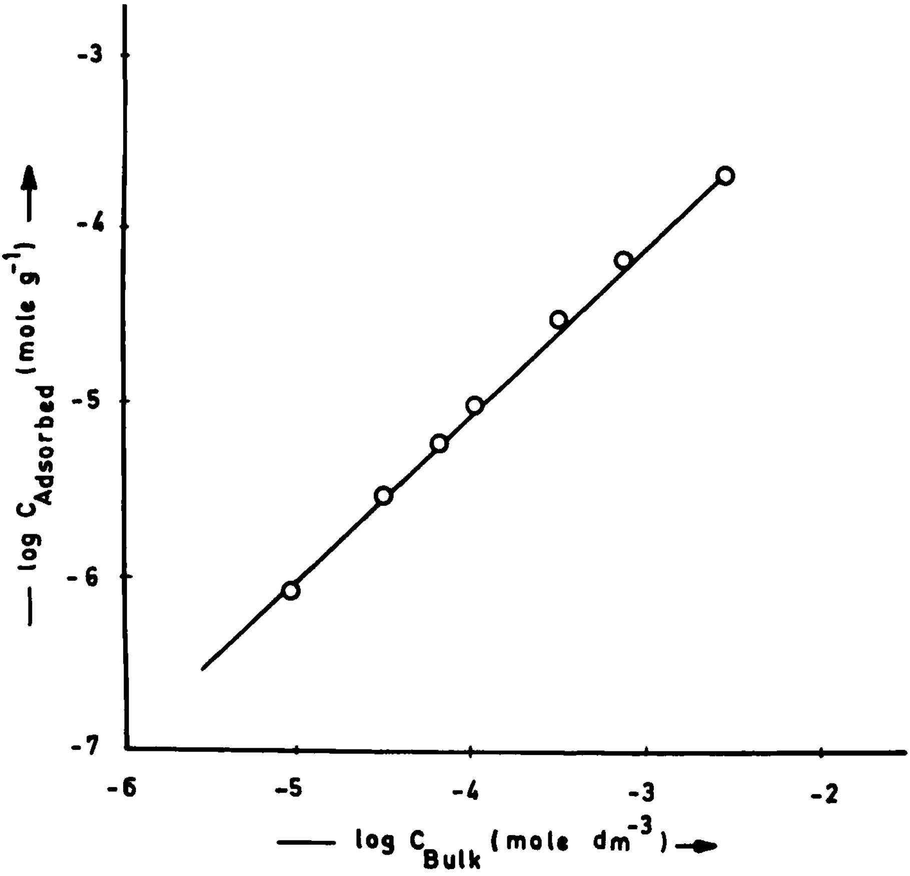

FIG. 5. Freundlich adsorption isotherm of silver on manganese dioxide from nitric or perchloric acid solution.

computed from the slope and intercept of the plot, respectively. These values are of the same order of magnitude as those reported earlier for the adsorption of zirconium on maganese dioxide from acid solutions (*10*). The value of $1/n$ is usually related to the nature and the strength of adsorption forces as well. Thus the higher fractional value of $1/n$ signifies that strong adsorptive forces are operative on the oxide surface. Moreover, a relatively higher value of A further confirms the higher affinity of silver for manganese dioxide. This higher affinity of silver may be due to its low hydration energy and/or its strong electrostatic interaction with adsorption sites as a result of its strong polarizability.

The applicability of the Langmuir adsorption isotherm for the present system has been tested in the form

$$\frac{C_{\text{Bulk}}}{C_{\text{Ads}}} = \frac{1}{KC_m} + \frac{C_{\text{Bulk}}}{C_m} \qquad (2)$$

by plotting ($C_{\text{Bulk}}/C_{\text{Ads}}$) vs C_{Bulk} (Fig. 6), where C_m is the limiting adsorbed concentration in mol/g and K is the equilibrium constant for adsorption

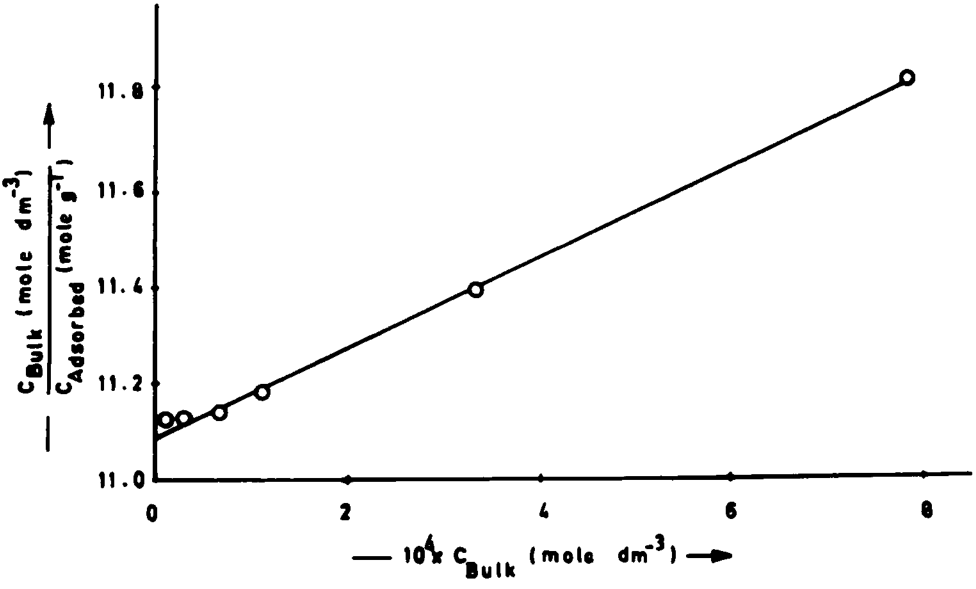

FIG. 6. Langmuir adsorption isotherm of silver on manganese dioxide from nitric or perchloric acid solution.

in dm^3/mol. The Langmuir adsorption isotherm is valid for silver adsorption in the intermediate range from 3.14×10^{-5} to 7.8×10^{-4} mol/dm^3. However, at the lowest and highest bulk concentrations of silver, the relationship is not applicable. Similar observations have been noted for the adsorption of zinc on titanium oxide from aqueous solutions (*13*). The values of C_m = 1 mmol/g and K = 87 dm^3/mol at 23 ± 2°C were determined from the slope and intercept of the linear plot shown in Fig. 6. The validity of the Langmuir adsorption isotherm over the intermediate range of concentration indicates monolayer coverage of silver on the outer surface of the adsorbent. Similar results for cobalt adsorption on alumina (*14*) and of zinc, cadmium, and thallium on manganese dioxide (*15*) have been reported.

The effect of various anions on the adsorption of silver was examined in the presence of their 0.1 mol/dm^3 concentration from both acid media. The results are listed in Table 1. All the anions tested reduce the adsorption to varying extents except molybdate from nitric acid solution. Small K_D values (<10 cm^3/g) were obtained in the presence of cyanide, thiosulfate, and thiocyanate ions where the adsorption in most cases examined is $<3\%$. Therefore, these anions ought to be removed from solutions from which silver adsorption has to be carried out. The strong complexes

TABLE 1

The Effect of Anions on the Adsorption of 9.27×10^{-6} mol/dm^3 Silver on 50 mg Manganese Dioxide from 0.01 mol/dm^3 Acid Solutions

	Nitric acid		Perchloric acid	
Additional anion[a] (~0.1 mol/dm^3)	K_D (cm^3/g)	% Adsorption	K_D (cm^3/g)	% Adsorption
Nil	6.69×10^4	99.8	8.99×10^4	99.9
Acetate	1.18×10^4	99.2	8.39×10^4	99.9
Ascorbate	3.43×10^3	97.4	2.80×10^3	96.9
Citrate	2.17×10^3	95.9	2.00×10^4	99.5
Cyanide	1.0	1.1	2.5	2.7
EDTA	7.68×10^3	98.8	7.19×10^3	98.7
Molybdate	7.88×10^4	99.9	3.17×10^4	99.7
Oxalate	6.34×10^3	98.6	2.20×10^4	99.6
Sulfide	1.78×10^4	99.5	1.05×10^4	99.1
Tartrate	9.62×10^3	99.0	2.94×10^4	99.7
Thiocyanate	7.4	7.6	2.1	2.3
Thiosulfate	2.2	2.4	6.2	6.5
Vanadate	4.54×10^4	99.8	3.11×10^4	99.7

[a] In the form of the sodium salt.

of silver with these anions have been reported in the literature (*16, 17*). A strong tendency to form complexes between silver(I) and cyanide ions has been reported, and anionic complexes like $[(Ag(CN)_n]^{1-n}$, where $n = 2$–4, have been postulated (*17*). Similar complexes of thiocyanate with silver having a composition of $[Ag(NCS)_n]^{1-n}$, where n may be 2 or 3, have been cited (*17*). Furthermore, thiosulfate ions form at least five complexes, $[Ag(S_2O_3)]^-$, $[Ag(S_2O_3)_2]^{3-}$, $[Ag_2(S_2O_3)_2]^{2-}$, $[Ag_3(S_2)_3O_4]^{5-}$, and $[Ag_2(S_2O_3)_6]^{10-}$, with silver (*17*). The reduction in adsorption may be attributed either to a low affinity of their silver complexes toward the oxide surface or to the displacement of silver ions adsorbed on the surface of the adsorbent by the anions themselves. The adsorption of anions on the surface of oxides has been reported by several workers (18–20).

The influence of cations representing different oxidation states and periodic groups on the adsorption of silver under optimal conditions has been tested. These results are cited in Table 2. Among the cations employed, only Zn(II) and Co(II) enhance the adsorption from perchloric acid, whereas all other cations tested suppress the adsorption, the most significant being Pb(II), Bi(III), and K(I). However, the percent adsorption remains above 97% in most cases, except in the presence of Pb(II) where >62% adsorption of silver has been obtained.

TABLE 2

The Influence of Cations on the Adsorption of 9.27×10^{-6} mo/dm³ Silver on 50 mg Manganese Dioxide from 0.01 mol/dm³ Acid Solutions

Additional cation[a] (~0.1 mol/dm³)	Nitric acid K_D (cm³/g)	Nitric acid % Adsorption	Perchloric acid K_D (cm³/g)	Perchloric acid % Adsorption
Nil	6.69×10^4	99.8	8.99×10^4	99.9
Na(I)	6.37×10^3	98.6	4.31×10^4	99.8
K(I)	3.00×10^3	97.1	7.58×10^3	98.8
Co(II)	1.52×10^4	99.4	9.36×10^4	99.9
Cu(II)	2.75×10^4	99.7	3.96×10^4	99.8
Zn(II)	1.12×10^4	99.2	1.00×10^5	99.9
Cd(II)	6.28×10^4	99.8	2.14×10^4	99.6
Pb(II)	1.44×10^2	61.5	1.58×10^2	63.7
Al(III)	1.69×10^4	99.5	2.30×10^4	99.6
Fe(III)	5.36×10^3	98.3	1.18×10^4	99.2
Bi(III)	3.51×10^3	97.5	1.57×10^3	94.6

[a] In the form of the nitrate.

TABLE 3
The Distribution Coefficient of Other Metal Ions on Manganese Dioxide from 0.01 mol/dm^3 Acid Solutions

	Nitric acid		Perchloric acid	
Metal ion	K_D(cm^3/g)	% Adsorption	K_D (cm^3/g)	% Adsorption
Zn(II)	16.2	15.2	24.8	21.6
Co(II)	1.75×10^2	66.1	2.39×10^2	72.7
Cd(II)	2.94×10^2	76.6	3.74×10^2	80.6
In(III)	3.44×10^2	79.3	3.06×10^2	77.3
Tb(III)	8.07×10^2	90.0	4.70×10^2	83.9
Nd(III)	1.32×10^3	93.6	8.26×10^2	90.2
Cr(III)	1.54×10^3	94.5	1.71×10^3	95.0
Sb(III)	3.15×10^3	97.2	3.64×10^3	97.6
Hg(II)	3.74×10^3	97.6	5.65×10^3	98.4
Eu(III)	3.84×10^3	97.7	3.58×10^3	97.5
Ce(IV)	3.97×10^4	99.5	1.79×10^4	99.5
Sn(II)	7.69×10^4	99.9	2.68×10^4	99.7

The adsorption of other metal ions under optimal conditions was measured from both acid media, and the results are summarized in Table 3. The distribution coefficient for each element is independent of the nature of the acid, and the K_D values are of the same order of magnitude in both acids. The adsorption of divalent Zn, Co, and Cd and of In(III) are somewhat low from both electrolytes, especially for Zn(II). The distribution coefficient of zinc from 0.01 mol/dm^3 nitric and perchloric acid solutions are of the same order of magnitude estimated for its adsorption on titanium oxide from the same media (*13*). The distribution coefficients of other elements investigated are in the range of 10^3 to 10^4 cm^3/g and their percent adsorptions are between 90 to 100%. It is concluded from these data that manganese dioxide can be used for the preconcentration of silver or other elements having high K_D values from dilute solutions which have their concentrations at trace levels, especially for the recovery of silver from photographic industry waste.

Acknowledgment

The assistance by the Reactor Operation Group in arranging irradiations is gratefully acknowledged.

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Received by editor January 19, 1989