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Sorption Behavior of Microamounts of Zinc on Titanium Oxide from Aqueous Solutions

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Abstract

The adsorption of microamounts of zinc on titanium oxide, prepared and characterized in this laboratory, has been studied in detail. Zinc adsorption has been found to be dependent on the pH of the aqueous solution, amount of oxide, and zinc concentration. Maximum adsorption is from pH 10 buffer. EDTA and cyanide ions inhibit adsorption significantly. The adsorption of other elements under optimal conditions has also been measured on this oxide. Sc(III) and Cs(I) show almost negligible adsorption. Zinc adsorption follows the linear form of the Freundlich adsorption isotherm:

$$\log C_{Ads} = \log A + (1/n) \log C_{Bulk}$$

with $A = 0.48$ mol/g and $n = 1$. Except at a very low bulk concentration (3×10^{-5} mol/dm^3), the Langmuir adsorption isotherm is also linear for the entire zinc concentration investigated. The limiting adsorbed concentration is estimated to be 0.18 mol/g.

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INTRODUCTION

Zinc is an essential element for animals and plants. It is needed in plants in small amounts, and its deficiency in plants hampers the healthy development of leaves and causes several diseases. Growing plants depend on the nutritional supply of essential elements from soil (*1*). Zinc is available for plants in soil solution and in soil solid phase (*2*). To correlate soil response toward zinc, it is necessary to study its adsorption in detail on soils or on their constituents. The adsorption of a number of elements on titanium oxide (*3–9*), one of the constituents of soils (*10*), has been studied, but no detailed study about the adsorption of zinc on titanium oxide has been cited except a few sketchy reports (*11*, *12*). However, adsorption of zinc on a number of oxides such as cerium oxide (*13*), zirconium oxide (*14*), aluminum oxide (*15*), tin oxide (*16*), antimony oxide (*17*), iron oxide (*18*), and manganese dioxide (*18–22*) has been studied. The present communication deals with the adsorption of zinc in microamounts from aqueous solution on titanium oxide, prepared and characterized in this laboratory.

EXPERIMENTAL

Reagents and Radiotracers

Preparation of Titanium Oxide

Titanium oxide was prepared as reported (*5*) by neutralizing a 1.6-mol/dm^3 titanium trichloride solution in 6.4 mol/dm^3 hydrochloric acid (250 cm^3) with 1 mol/dm^3 ammonium hydroxide added in small portions. The reaction mixture was stirred continuously up to 48 h. The titanium oxide thus formed was allowed to settle down overnight, and the supernatant was decanted. The precipitates were suspended in doubly distilled deionized water and stirred for 7 h, then allowed to settle down overnight and the supernatant was again decanted. This procedure was repeated 5 times. The precipitates were finally filtered and washed several times with water. The precipitates were dried in air for 3 days and then in a vacuum desiccator for 2 weeks over calcium hydroxide to constant weight. Later, it was ground and sieved to 200 mesh.

^{65}Zn tracer was prepared by irradiating specpure zinc metal (Johnson & Matthey) in the PARR-1 research reactor of this institute and then dissolved in nitric acid. The final concentration of nitric acid in stock solution was 0.027 mol/dm^3. All other tracers used were produced locally, and their radiochemical purity was checked by gamma spectroscopy. All solutions were made from doubly distilled deionized water and analytical reagents. The composition of the buffer solutions used in this study was given earlier (*23*).

Instrumentation

The instruments used for BET surface area, pore size distribution and skeletal density, and spectrophotometric measurements are given elsewhere (*24*). Thermogravimetric measurements were made with a Stanton Redcroft thermorecording balance model TG 750 at a heating rate of 5°C/min. Differential thermograms were obtained at a heating rate of 10°C/min using alumina as a comparison standard. Infrared spectra were recorded on potassium bromide pellets on a Perkin-Elmer 580 IR spectrometer with a sodium chloride prism. Powder x-ray diffractional patterns were taken on a x-ray diffractometer model D-Max II Rigaku, Japan, with a copper target at a wavelength of 1.5405 Å. The wavelength dispersive x-ray fluorescence spectrometer used was Rigaku model 3134. Inductively coupled plasma emission spectroscopic (ICP-ES) measurements were made with a computerized optical emission spectrometer Model 3580 from Applied Research Laboratories, Switzerland. The instruments used for pH (*23*) and radiometric (*24*) measurements were described before.

Procedure

Distribution coefficients (K_D) were determined radiometrically by using the batch technique at room temperature (23 ± 2°C). A solution (4.5 cm^3) of an appropriate electrolyte having a specified concentration of zinc or other element was shaken with a known amount of titanium oxide for a given time and then centrifuged for phase separation. The initial and final activities of the radiotracer solution were assayed, and K_D values were estimated in the usual manner (*25*). All measurements were the average of at least triplicate runs.

RESULTS AND DISCUSSION

Characterization of Titanium Oxide

Infrared spectra of titanium oxide prepared in the laboratory show four absorption bands, the first between 2800 and 3700 cm^{-1} with maxima at 3150 and 3430 cm^{-1}; the second between 1300 and 1700 cm^{-1} with maxima at 1400, 1560, and 1655 cm^{-1}; the third between 380 and 900 cm^{-1} with a maximum at 640 cm^{-1}; and the fourth between 250 and 380 cm^{-1} with maxima at 330 and 360 cm^{-1}. The first band is characteristic of interstitial or free water and the hydroxyl group, the second of interstitial water, and the third of the Ti—O group (*26*). Similar absorption bands with maxima at 1400 (*26*, *27*), 1550 (*26*), 1650 (*28*), and 3440 cm^{-1} (*27*) have been observed in other hydrous oxides.

Thermogravimetric analysis indicates that titanium oxide starts losing water at a low temperature (35°C), and a substantial weight loss with respect

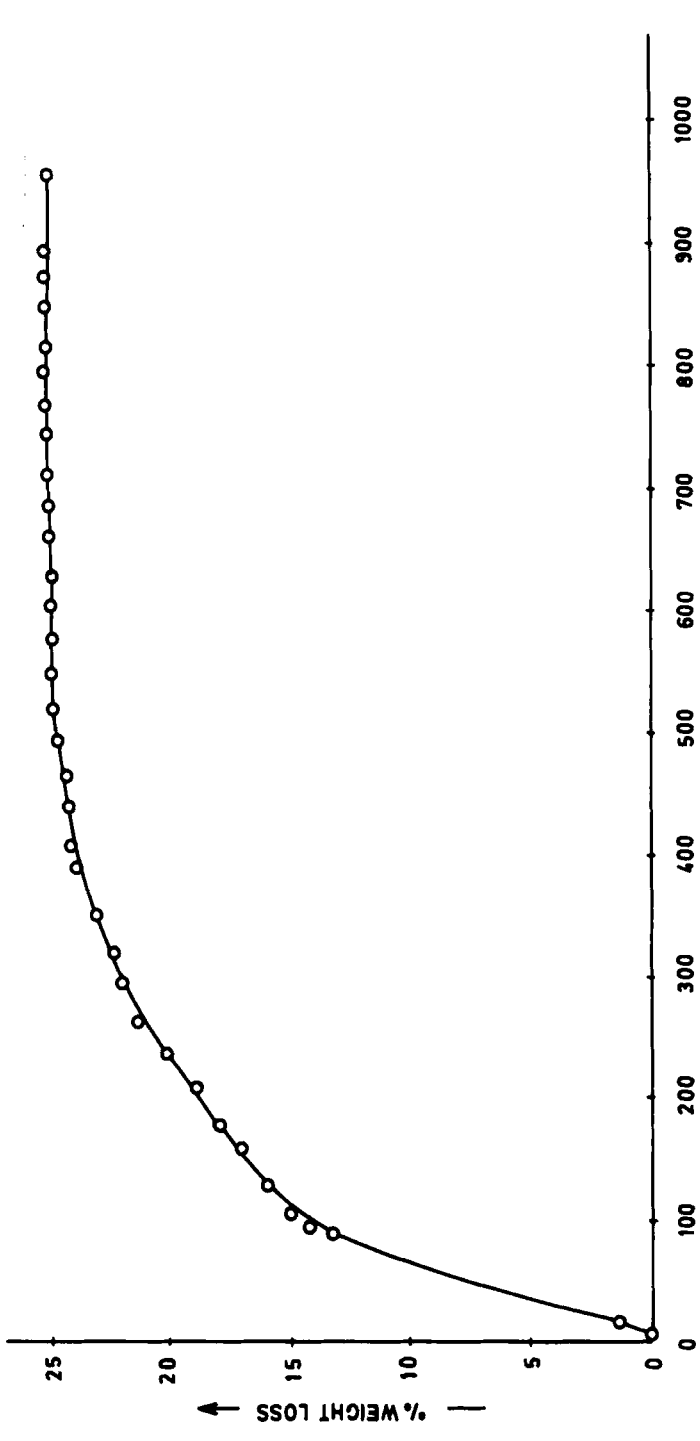

FIG. 1. Thermogravimetric analysis of titanium oxide.

to the initial weight is noticed at around 100°C (13.4%) (Fig. 1). The weight loss between 200 and 400°C is much less, the total loss reaching about 24%. This is of the same order of magnitude as reported for hydrous titanium oxide (*26*). No significant weight loss is observed beyond 400°C up to 900°C (1.2%). It can be concluded on the basis of earlier observations that up to 200°C the weight loss may be due to the removal of the interstitial or free water. At higher temperatures, 200–400°C, chemically bound water is lost. The last part of the curve shown in Fig. 1 may indicate anhydrous phase equilibrium or loss of chloride traces present in the sample. Figure 2 shows the differential thermogram of the oxide. This shows two distinct peaks between 105 and 210°C, and from 270 to 350°C. This thermogram is in agreement with the results of thermogravimetric analysis.

The x-ray diffraction spectra of titanium oxide show no significant peak. However, small peaks at $2\theta = 24$, 31, 48, 55, and 63° indicate that the structure is neither completely amorphous nor crystalline in nature. From these results it may be interpreted that the sample has a disordered phase. The x-ray fluorescence analysis indicates no impurity present in the sample except traces of chloride ions whereas ICP-ES results reveal 46.08% titanium in the sample. On the basis of these data, the oxide has the formula $TiO_2 \cdot 1.4H_2O$ or $TiO_{1.9}(OH)_{0.2} \cdot 1.3H_2O$.

The BET surface area, as determined by adsorbing nitrogen, was found to be 92 m^2/g. The porosity was estimated to be 0.66 cm^3g, and the average pore size diameter 37 nm. The skeletal density was computed to be 1.37 g/cm^3. The solubility of titanium oxide thus prepared was checked by shaking the oxide with 4.5 cm^3 of all the electrolytes used in adsorption studies for 2 h. Titanium was measured spectrophotometrically (*29*) by

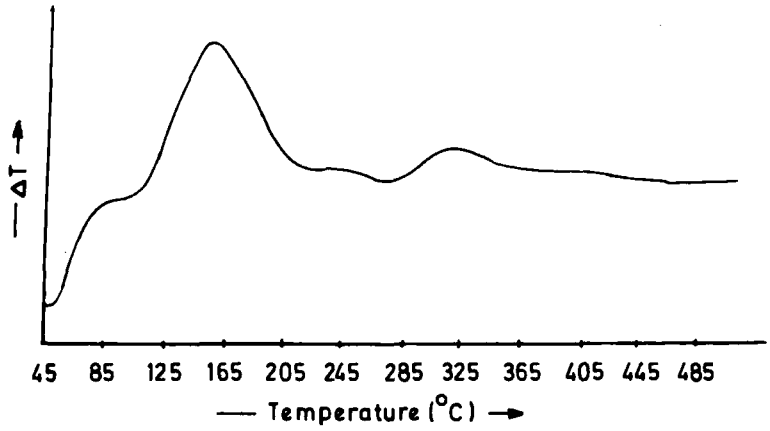

FIG. 2. Differential thermogram of titanium oxide.

using chromotropic acid as a chromogenic reagent in a supernatant solution. Titanium was not detected in any sample. The detection limit of this method is 40 ng/cm^3.

Adsorption Studies

The adsorption of zinc (6.12×10^{-5} mol/dm^3) from 0.01 mol/dm^3 solutions of perchloric acid, nitric acid, and hydrochloric acid has been studied on 50 mg of titanium oxide as a function of shaking time (1 to 60 min) to test whether adsorption equilibrium between adsorbate and adsorbent has been established. This low acid concentration of electrolytes was selected in view of our experience where higher distribution coefficients (K_D) have been obtained at low acid concentrations in the case of zirconium (*24*) and europium (*30*) adsorption on manganese dioxide. The results are shown in Fig. 3. In all three acid solutions in the initial 5 min, the adsorption increases with increasing shaking time and attains a constant value at around 10 min. In general, the distribution coefficients are in the order perchloric acid > hydrochloric acid > nitric acid. The adsorption of germanium on different adsorbents from perchloric acid was always found

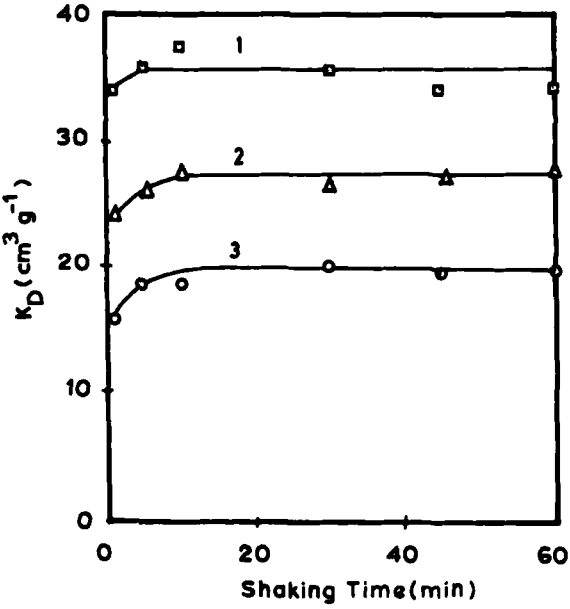

FIG. 3. Adsorption of zinc (6.12×10^{-5} mol/dm^3) on titanium oxide (50 mg) from 0.01 mol/dm^3 solution of 1) perchloric acid, 2) hydrochloric acid, and 3) nitric acid as a function of shaking time.

higher than its adsorption from nitric acid of equal molarity (*31*). At equilibrium the maximum distribution coefficient (K_D) corresponds to 29.2, 23.2, and 18.2% adsorption from the three acid solutions, respectively. The concentration of zinc was kept constant at 6.12×10^{-5} mol/dm^3 throughout these investigations except where specified.

Because of the low distribution coefficient (<37 cm^3/g), it was obviously not considered feasible to investigate further the adsorption of zinc in detail from acid solutions. Therefore, buffer solutions of pH 4, 7, 10, and 12 covering acidic and alkaline regions were employed to determine the adsorption equilibrium from 1 to 420 min. The results are given in Fig. 4. From pH 4, 7, and 12 buffer, K_D increases with an increase in shaking time and attains a constant value in 30 min whereas from pH 10 buffer solution the equilibrium was established within 2 min and K_D remained constant throughout the entire time duration investigated. After equilibrium, the adsorption of zinc was found to be in the order from pH 10 > 12 > 7 > 4. Although from pH 4 to 10 the K_D value increases in the order of 10^2, the percent adsorption changes only from 83.6 to 99.9%.

In view of these results, it was considered worthwhile to investigate the adsorption of zinc on 50 mg titanium oxide as a function of initial pH (1 to 10). Because hydrogen and hydroxyl ions are potential-determining ions for most adsorbents, their concentration in an electrolyte can affect adsorption very substantially. Ten minutes shaking time was used for this study. The results are depicted in Fig. 5. The distribution coefficient increases with increasing pH and attains a maximum value of the order of 10^5 cm^3/g at pH 10. A steep rise was observed between pH 2 and 6. The K_D values obtained at pH 2 and 4 were of the same order of magnitude as reported earlier (*11*). As maximum adsorption was achieved from pH 10 buffer solution, this electrolyte was used in all subsequent measurements. A spontaneous change in the nature of a trace element in solution may alter the adsorption. Therefore, a change in the pH alters the nature of the zinc species and consequently affects the adsorption.

Another parameter, the amount of adsorbent which influences the adsorption, was varied from 5 to 500 mg. The distribution coefficient registers an enhancement with an increase in the amount of titanium oxide, attains a maximum value around 10 mg, and then starts decreasing with a further increase in the amount of adsorbent (Fig. 6). Therefore, 10 mg titanium oxide was used in further experiments. The trend of the variation of K_D with that of the amount of the adsorbent is almost identical with the trend that was observed in the cases of zirconium (*24*) and mercury (*25*) adsorption on manganese dioxide. Although the distribution coefficient varies by a factor of 10^2 from 5 to 500 mg of the oxide, the percent adsorption of zinc always remains >99.9%.

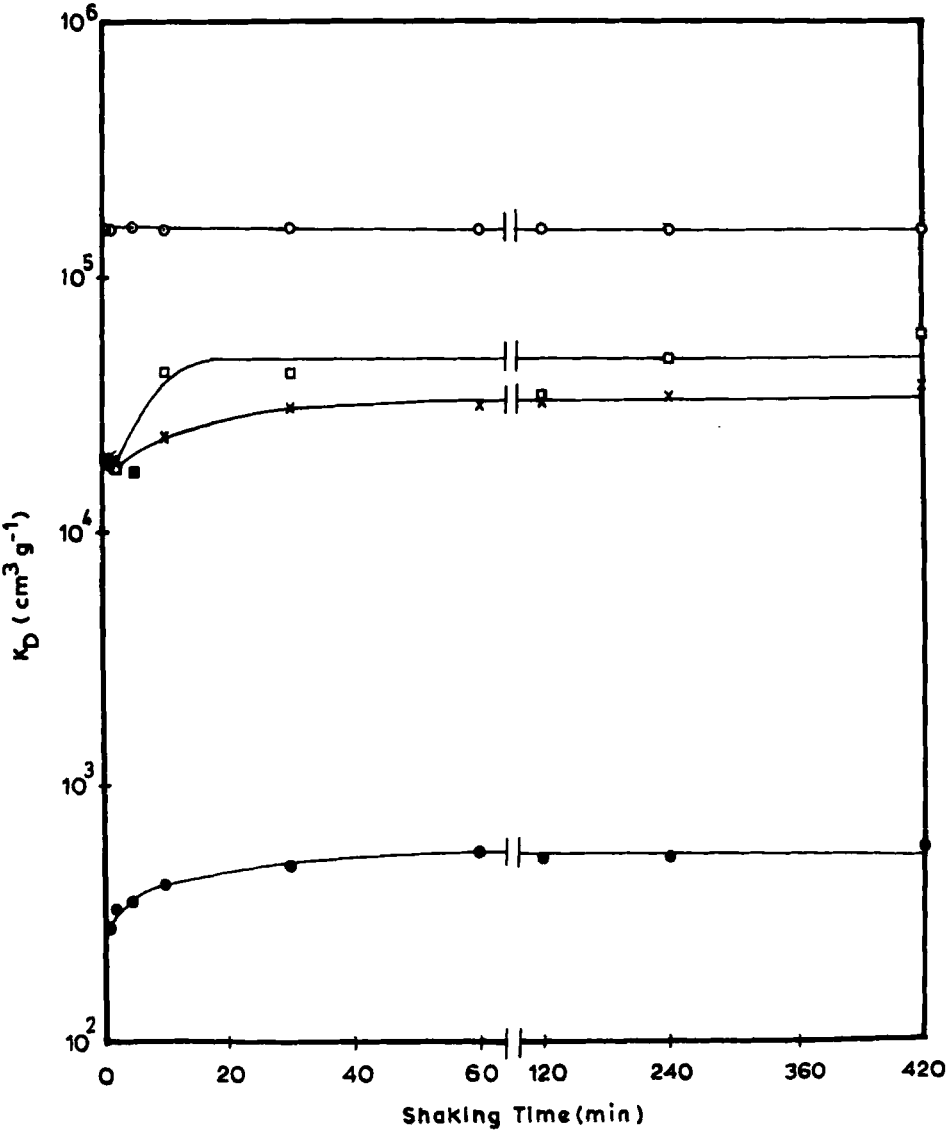

FIG. 4. Adsorption of zinc (6.12×10^5 mol/dm^3) on titanium oxide (50 mg) from buffers of pH 4 (●), 7 (×), 10 (○), and 12 (□) as a function of shaking time.

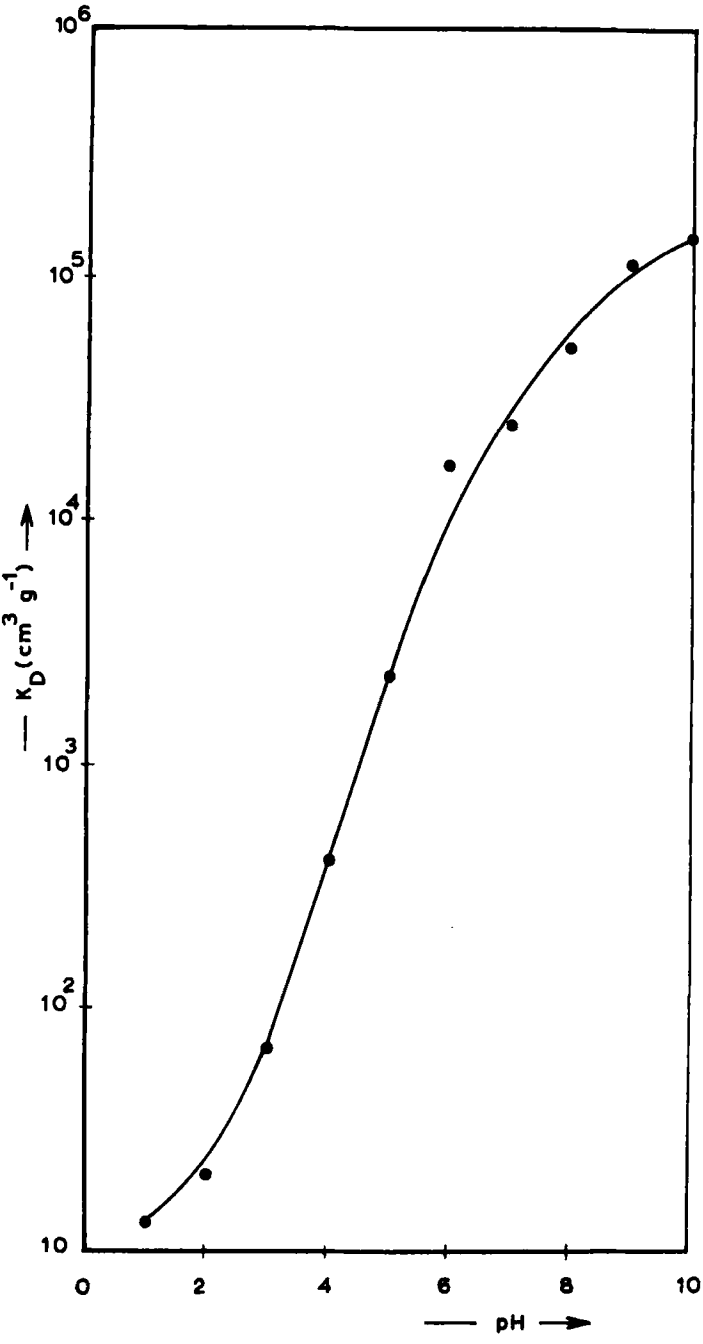

FIG. 5. Distribution coefficient of zinc (6.12×10^{-5} mol/dm^3) on titanium oxide (50 mg) as a function of pH.

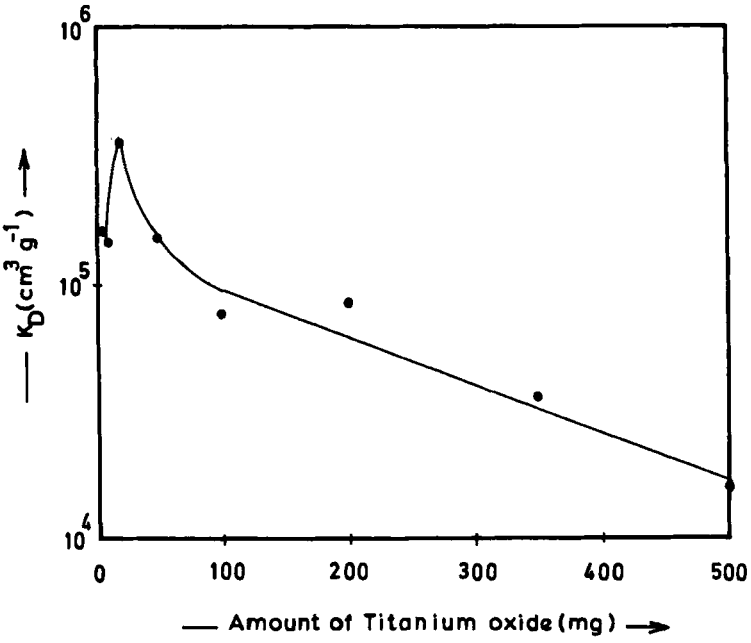

FIG. 6. The dependence of zinc (6.12×10^{-5} mol/dm^3) adsorption on the amount of titanium oxide from pH 10 buffer solution.

The influence of zinc concentration on its adsorption from pH 10 buffer was also investigated in the range from 3×10^{-5} to 10^{-3} mol/dm^3 under optimum conditions. The results are recorded in Fig. 7. The distribution coefficient first increases with increasing zinc concentration and attains a maximum at 10^{-4} mol/dm^3 concentration. Beyond this concentration the K_D starts decreasing with a further increase in zinc concentration. This pattern is similar to what has been observed in our studies of zirconium (*24*) and mercury (*25*) adsorption on manganese dioxide. The relation between zinc adsorption and its concentration was subjected to the linear form of the Freundlich adsorption isotherm:

$$\log C_{Ads} = \log A + (1/n) \log C_{Bulk}$$

where C_{Ads} is the adsorbed concentration of zinc in mol/g of the oxide, C_{Bulk} is the bulk concentration of metal in mol/dm^3, and A and n are characteristic constants related to a specific adsorption system. The plot of log C_{Ads} vs log C_{Bulk} is linear throughout the entire bulk concentration of zinc studied (Fig. 8). From the slope of Fig. 8, the value of n was estimated to be unity and that of A to be 0.48 mol/g.

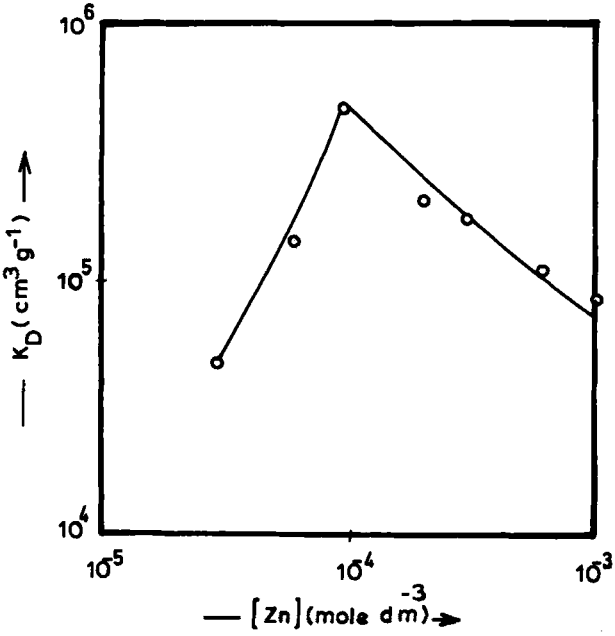

FIG. 7. The influence of zinc concentration on its adsorption on titanium oxide (10 mg) from pH 10 buffer solution.

The Langmuir adsorption isotherm was also tested in the following form:

$$\frac{C_{\text{Bulk}}}{C_{\text{Ads}}} = \frac{C_{\text{Bulk}}}{C_{\text{Saturation}}} + \frac{1}{BC_{\text{Saturation}}}$$

where a plot of $C_{\text{Bulk}}/C_{\text{Ads}}$ vs C_{Bulk} was found to be a straight line (Fig. 9) except at very low zinc concentration (3×10^{-5} mol/dm^3). This indicates that the Langmuir adsorption isotherm is also followed by zinc adsorption with a deviation at low concentration. From the slope of the plot, the value of limiting adsorbed concentration at saturation was computed to be $C_{\text{Saturation}} = 0.18$ mol/g.

In order to understand the adsorption mechanism, it is necessary to ascertain the nature of the different species present in the aqueous solutions of different pHs. It is established that zinc can be present in solution either as divalent Zn^{2+} or in hydrolyzed $Zn(OH)^+$, $Zn(OH)_2$, $Zn(OH)_3^-$, and $Zn(OH)_4^{2-}$ forms. By using corresponding formation constants (*32*), the percent of each species present under certain pH conditions may be calculated. No hydrolysis of zinc takes place up to pH 6, and at pH 7 the dominant species of zinc would remain Zn^{2+} (99.33%). At pH 8 zinc will

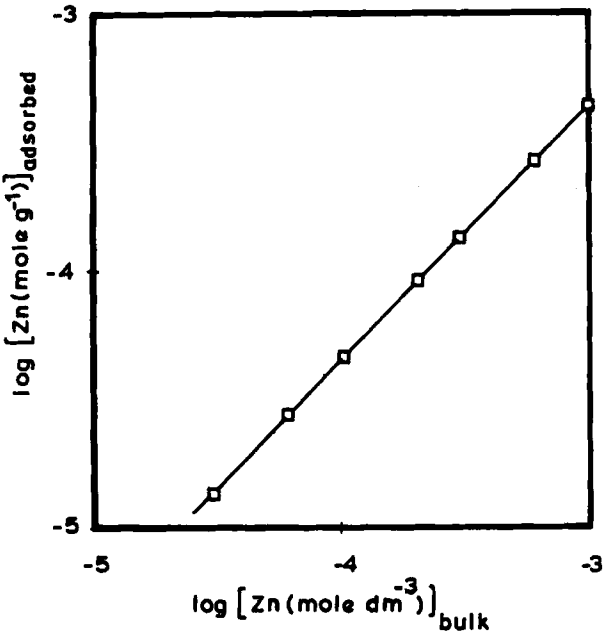

FIG. 8. Freundlich adsorption isotherm of zinc on titanium oxide.

be present as Zn^{2+} (93.67%), $Zn(OH)^{+}$ (2.91%), and $Zn(OH)_2$ (3.42%). In a solution at pH 9, the dominant species would be Zn^{2+} (59.66%), $Zn(OH)_2$ (36.99%), and $Zn(OH)^{+}$ (3.16%), whereas at pH 10 the major species would be $Zn(OH)_2$ (82.26%), Zn^{2+} (12.88%), and $Zn(OH)_3^{-}$ (4.10%). Moreover, at pH 12 the dominant species are expected to be

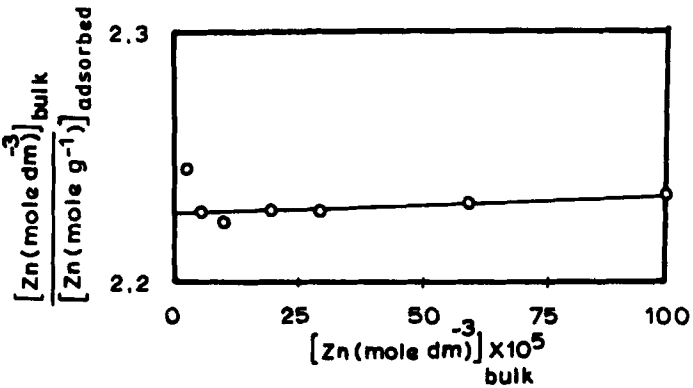

FIG. 9. Langmuir adsorption isotherm of zinc on titanium oxide.

$Zn(OH)_3^-$ (55.44%), $Zn(OH)_4^{2-}$ (27.79%), and $Zn(OH)_2$ (16.61%). At all pHs the polymeric species of zinc, namely $Zn_2(OH)^{3+}$ and $Zn_2(OH)_6^{2-}$ (*32*), would be very small. The maximum adsorption occurs at pH 10, where the maximal proportion of the neutral species, i.e., $Zn(OH)_2$, is obtained. This is in conformity with what has been envisaged (*33*). Moreover, advance hydrolysis may be one of the reasons why the pH dependence of adsorption of hydrolyzable zinc passes through a maximum at pH 10 and then decreases due to the increasing proportion of hydroxo anions.

The low adsorption observed at pH 12 compared to that at pH 10 (Fig. 4) can be explained in terms of repulsion between the negatively charged species $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$ and negatively charged surface of the oxide, whereas there would be no repulsion between neutral $Zn(OH)_2$ and Zn^{2+} species and the oxide surface. Instead, there is an attraction between positively charged Zn^{2+} and the negatively charged oxide surface. The PZC of hydrous titanium oxide is 5.6–6 (*34*). This means that the oxide surface is positively charged below pH 6 and negatively charged above pH 6. Up to pH 6 there is specific absorption of Zn^{2+} ions on an oxide surface having OH^- and O^{2-} groups on its surface. However, at pH > 9 there is condensation of different hydrolyzed species formed on the oxide surface. Hydrolyzed cations show a strong tendency to be adsorbed on any available surface, perhaps due to their lower hydration. The hydroxyl group renders the complex more hydrophobic and stimulates the action of van der Waals forces or permits the formation of a hydrogen bond between hydrolyzed ions and some strongly electronegative atoms on the surface. The hydrolytic adsorption mechanism has also been proposed for the adsorption of zinc onto manganese dioxide (*35*).

The influence of various anions and cations on zinc adsorption has been examined under specific conditions where maximum adsorption of zinc has been noticed. The results are listed in Table 1. EDTA and cyanide drastically reduce the adsorption, whereas tartrate, molybdate, sulfate, fluoride, carbonate, and all the cations increase the distribution coefficient significantly. Except in the cases of EDTA and cyanide, the percent adsorption of zinc remains >99% in the presence of all the anions and cations tested. In general, substances which form strong complexes with the species undergoing adsorption can influence adsorption where such complexes are adsorbed more or less strongly. The decrease in the adsorption caused by EDTA and cyanide can be explained as being due either to a very low affinity between the complexes of zinc with these anions and the oxide or due to the adsorption of anions themselves on the surface of adsorbent, thus blocking the adsorption sites and making them inaccessible for zinc ions or replacing them from the surface. The strong complexes of zinc with EDTA and cyanide have been reported in the literature (*32*, *36*, *37*).

TABLE 1
The Influence of Additional Ions on the Adsorption of Zinc (6.12×10^{-5} mol/dm^3) on Titanium Oxide from pH 10 Buffer Solution

Additional ion ($\sim 10^{-2}$ mol/dm^3)	K_D (cm^3/g)	% Adsorption
Nil	1.54×10^5	99.7
EDTA	2	<1
Cyanide	16.9	3.6
Vanadate	0.81×10^5	99.4
Acetate	0.94×10^5	99.5
Ascorbate	1.27×10^5	99.6
Citrate	1.34×10^5	99.6
Phosphate	1.35×10^5	99.7
Oxalate	1.45×10^5	99.7
Iodide	1.56×10^5	99.7
Tartrate	1.99×10^5	99.8
Molybdate	2.30×10^5	99.8
Sulfate	2.64×10^5	99.8
Fluoride	4.70×10^5	99.9
Carbonate	4.77×10^5	99.9
Li(I)	4.16×10^5	99.9
Mg(II)	2.64×10^5	99.8
Sr(II)	2.25×10^5	99.8
Ca(II)	2.13×10^5	99.8

Moreover, the adsorption of anions on the oxide surfaces has also been cited (*38*, *39*). Similarly, the enhancement in the adsorption of zinc in the presence of certain anions can be due to stronger adsorption of corresponding zinc complexes on the oxide than the zinc ions themselves. The complexes of zinc with carbonate (*36*), tartrate (*32*, *36*, *37*), sulfate (*32*, *36*), and fluoride (*36*) are possible. The addition of cations like Cu(II), Cd(II), Co(II), Pb(II), Al(III), and Ce(III) has caused precipitation, therefore the results of zinc adsorption in their presence have not been recorded in Table 1. Changes in the adsorption behavior of zinc in the presence of anions or cations may also be explained as being due to changes in structure size of adsorbed colloids in the presence of foreign impurities.

To check the selectivity of the oxide, the adsorption of different elements from the periodic table was measured under optimal conditions. The results are listed in Table 2. It is clear that under specified conditions only Cs(I) and Sc(III) show almost negligible adsorption whereas all other cations except Ni(II) and Hg(II) have lower distribution coefficients than Zn(II). However, for most of the cations tested, the percent adsorption remains above 97%. Only trivalent thulium, terbium, gallium, arsenic, and samar-

TABLE 2
Adsorption of Other Metal Ions on Titanium Oxide Surface from pH 10 Buffer

Metal ion	K_D(cm³/g)	% Adsorption
Sc(III)	0.29	<0.1
Cs(I)	<1	0.2
Tm(III)	35	6.5
Tb(III)	4.63×10^2	48.0
As(III)	1.28×10^3	74.0
Ga(III)	2.88×10^3	86.5
Co(II)	4.43×10^3	89.7
Sm(III)	6.54×10^3	93.6
Hf(IV)	1.54×10^4	97.1
Ag(I)	1.83×10^4	97.6
Gd(III)	3.11×10^4	98.6
Dy(III)	3.50×10^4	98.7
Eu(III)	3.92×10^4	98.8
Cu(II)	7.29×10^4	99.4
Mn(II)	7.33×10^4	99.4
Zr(IV)	8.21×10^4	99.5
Zn(II)	1.54×10^5	99.7
Hg(II)	1.73×10^5	99.7
Ni(II)	5.85×10^5	99.9

ium and cobalt(II) exhibit lower percent adsorption. It is possible to separate Sc(III) and Cs(I) from Zn(II) and all other cations which have high K_D values. This oxide can also be used to preconcentrate Zn(II) and other cations like Ag(I), Cu(II), Ni(II), Mn(II), Hf(IV), Zr(IV), and rare earths by eluting them from the oxide column with a suitable eluant after their quantitative adsorption on the oxide surface. It is interesting to note that radiochemical separation of zinc and scandium is very important from the neutron activation analysis point of view because gamma energies of the ^{65}Zn (1115 keV) and ^{46}Sc (1121 keV) nuclides are too close to be separated easily by a multichannel analyzer.

REFERENCES

1. J. Janick, R. W. Schery, and F. W. Woods, *Plant Science: An Introduction to World Crops,* 2nd ed., Freeman, San Francisco, 1974, p. 327.
2. S. A. Barber, *Soil Nutrient Bioavailability,* Wiley, New York, 1984, p. 347.
3. P. Strohal and D. Nothig-Hus, *Mikrochim. Acta,* p. 899 (1974).
4. Yu. P. Novikov, V. M. Komarewsky, and B. F. Myasoedov, *Radiochem. Radioanal. Lett., 48,* 39 (1981).
5. L. Maya, *Radiochim. Acta, 31,* 147 (1982).
6. B. Venkataramani, A. R. Gupta, and R. Iyer, *J. Radioanal. Nucl. Chem., 96,* 129 (1985).
7. N. I. Ampelogova, *Radiokhimiya, 25,* 579 (1983).

8. K. Fujita, H. Yamashita, S. Takeuchi, and F. Nakajima, *J. Inorg. Nucl. Chem., 43,* 188 (1981).
9. M. Tsuji, M. Abe, and M. Orimo, *Bull. Chem. Soc. Jpn., 58,* 97 (1985).
10. C. A. Hampel and G. G. Hawley (eds.), *The Encyclopedia of Chemistry,* 3rd ed., Van Nostrand Reinhold, New York, 1973, p. 1013.
11. Y. Inoue and M. Tsuji, *Bull. Chem. Soc. Jpn., 51,* 479 (1978).
12. T. Sasaki, Y. Komatsu, and Y. Fujiki, *Sep. Sci. Technol., 18,* 49 (1983).
13. K. R. Kar, K. B. Pandeya, and A. K. Bhaduri, *J. Inorg. Nucl. Chem., 38,* 1211 (1976).
14. R. K. Srivastava, B. Pal, K. R. Kar, and K. B. Pandeya, *J. Inorg. Nucl. Chem., 41,* 1183 (1979).
15. R. T. Lawson and S. V. Evans, *Aust. J. Chem., 37,* 2137 (1984).
16. N. Jaffrezic-Renault, *J. Inorg. Nucl. Chem., 40,* 539 (1978).
17. M. Abe and K. Sudoh, *Ibid., 42,* 1051 (1980).
18. R. R. Gadde and H. A. Laitinen, *Anal. Chem., 46,* 2022 (1974).
19. C. Bigliocca, F. Girardi, J. Pauly, E. Sabbioni, S. Meloni, and A. Provasoli, *Ibid., 39,* 1634 (1967).
20. G. R. Doshi, T. M. Krishnamoorthy, V. N. Sastry, and T. P. Sarma, *Indian J. Chem., 11,* 158 (1973).
21. M. J. Gray and M. A. Malati, *J. Chem. Tech. Biotechnol., 29,* 135 (1979).
22. M. W. Rophael, W. E. Mourad, L. B. Khalil, and M. A. Malati, *J. Radioanal. Chem., 52,* 477 (1979).
23. S. M. Hasany and M. H. Chaudhary, *J. Radioanal. Nucl. Chem., 111,* 199 (1987).
24. S. M. Hasany, E. Haq, and S. B. Butt, *Sep. Sci. Technol., 21,* 1125 (1986).
25. S. M. Hasany and M. H. Chaudhary, *J. Radioanal. Nucl. Chem., 100,* 307 (1986).
26. C. Heitner-Wirguin and A. Albu-Yaron, *J. Inorg. Nucl. Chem., 28,* 2379 (1966).
27. N. Z. Misak and E. M. Mikhail, *Solv. Ext. Ion Exch., 5,* 939 (1987).
28. A. K. De and S. K. Das, *Sep. Sci. Technol., 13,* 465 (1978).
29. F. A. Lowenheim, F. D. Snell, and L. S. Ettre (eds.), *Encyclopedia of Industrial Chemical Analysis,* Vol. 19, Wiley-Interscience, New York, 1974, p. 115.
30. S. M. Hasany and M. H. Chaudhary, *Sep. Sci. Technol., 21,* 97 (1986).
31. S. Mirzadeh and M. Kahn, *Radiochim. Acta, 39,* 189 (1986).
32. J. Kragten, *Atlas of Metal-Ligand Equilibria in Aqueous Solutions,* Ellis Horwood, Chichester, 1978, p. 742.
33. N. D. Belenkov, Ju. V. Egorov, and V. D. Puzakov, *Radiokhimiya, 16,* 20 (1974).
34. R. O. James and T. W. Healy, *J. Colloid Interface Sci., 40,* 42 (1952).
35. M. Rashid and M. Ejaz, *Appl. Radiat. Isot., 37,* 501 (1986).
36. A. E. Martell and L. G. Sillen, *The Stability Constants of Metal-Ion Complexes,* Special Publication No. 25, The Chemical Society, London, 1970.
37. J. A. Dean, *Lange's Handbook of Chemistry,* 13th ed., McGraw-Hill, New York, 1985, p. 5-72.
38. A. K. De, S. K. Das, and P. Chakraborty, *J. Inorg. Nucl. Chem., 43,* 1909 (1981).
39. N. Z. Misak and E. M. Mikhail, *Ibid., 43,* 1903 (1981).

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