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Separation Science and Technology

Publication details, including instructions for authors and subscription information:
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To cite this Article Hasany, Syed Moosa , Najamuddin and Ikram, M.(1997) 'Uptake of Traces of Selenite by Manganese Dioxide from Aqueous Solutions', Separation Science and Technology, 32: 12, 1945 — 1957

To link to this Article: DOI: 10.1080/01496399708000747

URL: http://dx.doi.org/10.1080/01496399708000747

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SEPARATION SCIENCE AND TECHNOLOGY, **32**(12), pp. 1945–1957, 1997

Uptake of Traces of Selenite by Manganese Dioxide from Aqueous Solutions

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ABSTRACT

Sorption of selenite onto manganese dioxide has been investigated with respect to shaking time, concentration of sorbent and sorbate, nature of electrolyte, and influence of cations and anions. The sorption of other metal ions has been studied using optimal conditions selected for maximum sorption of selenite. The surface area, average pore diameter, porosity, and solid phase density of the sorbent have been measured. The sorption data followed only the Dubinin–Radushkevich (D–R) sorption isotherm among all the isotherms tested. The sorption capacity of 51.2 $\mathrm{nmol \cdot g^{-1}}$ and a constant β related to sorption energy have been estimated to be -0.007521 $\mathrm{mol^2 \cdot kJ^{-2}}$. The sorption energy is found to be 8.15 $\mathrm{kJ \cdot mol^{-1}}$. The kinetics of the sorption follows the Lagergren equation in the initial stages. The first-order rate constant, k', was evaluated to be 0.498 $\mathrm{min^{-1}}$ and of intraparticle diffusion rate 3.06×10^{-5} $\mathrm{mol \cdot g^{-1} \cdot min^{-2}}$. Among all the anions and cations tested, only carbonate, Fe(III), and citrate reduced the sorption significantly. The sorption data for other metal ions showed that Te(IV) can be separated from ions showing higher degree of sorption; especially Se(IV), As(III), Sb(V), and Eu(III). It can be concluded that manganese dioxide may be used for the separation of certain metal ions, their preconcentration from very dilute solutions, and for decontamination and treatment of industrial effluents.

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INTRODUCTION

Selenium, its alloys, and its compounds are used in solar cells, storage batteries, rectifiers, xerography, laser technology, infrared photography, the glass and ceramic industry, drugs, special medicines, pigments, rubber, lubricating oils, and greases (1). Excess amounts of selenium are toxic and cause damage to some body tissues and organs when absorbed through skin, inhaled, or ingested. The deleterious effects of selenium on humans and animals have been documented (2). Environmental pollution can be minimized by removing toxic and harmful substances from industrial effluents before they are discharged into the biosphere.

Metal oxides have been used as sorbents for a number of metal ions including toxic elements (3, 4). The sorption behavior of toxic elements on the surface of manganese dioxide has been investigated (5–10). The sorption of some toxic elements, namely cadmium (11), mercury (12), and antimony (13), has been studied in our laboratory. This paper reports the results of a study undertaken to examine the sorption of selenite ions onto manganese dioxide from aqueous solutions. The objective of this investigation was to optimize all parameters influencing the sorption of the metal ion on the oxide surface and to test its efficacy for the removal of selenite from aqueous solutions.

EXPERIMENTAL

Reagents and Radiotracers

Manganese dioxide, a microanalytical reagent of B.D.H. (Product 11015), black in color and of 10–20 mesh, has been used as a sorbent. The surface area, porosity, average pore diameter, and solid phase density of the oxide have been reported (14). ^{75}Se ($t_{1/2}$ = 120.4 d) was prepared by irradiating specpure selenium sponge in the PARR-I research reactor of this institute at a thermal flux of 2×10^{13} $n \cdot cm^{-2} \cdot s^{-1}$ for 5 hours. The isotopic abundance of ^{74}Se is 0.9%, and its absorption cross section for thermal neutrons is 51.8 barns. The irradiated selenium sponge was dissolved in 5 mL of concentrated nitric acid and then evaporated to dryness. One milliliter of concentrated nitric acid was added and again heated to dryness. The dissolved radioselenium was finally stored in 20 mL of deionized water. The specific activity of this solution was 2.84 $\mu Ci \cdot mL^{-1}$. Radioselenium is present as selenite (SeO_3^{2-}) ions in dilute nitric acid solution. All other tracers used in this study were produced by irradiating their metals or appropriate compounds in the same reactor. Their radiochemical purity was checked by gamma spectrometry. All the chemicals used in this investigation were of analytical or of equivalent grade, and all the solutions were made in doubly distilled deionized water whose conductance and pH were 4 μS and 6.8, respectively.

Instruments

The instruments used for measurement of surface area, porosity, pore size, solid phase density measurements, radiometric assay, gamma spectrometry (14), and pH (12) have been listed earlier.

Procedure

The radiotracer and dynamic batch techniques used for sorption have been given in detail along with equations to compute R_d (distribution ratio) and percent sorption (12). The experimental procedure for sorption measurement is similar to what has been described earlier (13). The sorption measurements were carried out at 23 ± 2°C at least in triplicate, and the results are the average values and the precision in most cases is ±3%. The concentration of selenium was kept at 2.39×10^{-3} M and that of manganese dioxide at 50 mg throughout this study except otherwise specified. Usually a 10 to 25 μL solution of radioselenium was added to 5 mL of the sorptive medium. After thorough mixing of radioactivity, a 0.5-mL aliquot was withdrawn to determine the initial activity. The counts per minute were always between 12,600 and 31,500 per mL. This corresponds to a statistical error of ±0.89 to ±0.56%. The remaining 4.5 mL solution was shaken with 50 mg of the oxide for a definite time interval. After separating the solid and liquid phases by centrifiguation, another aliquot of 0.5 mL was taken to measure the final activity. By comparing the initial and final activities, the extent of sorption can be estimated.

RESULTS AND DISCUSSION

In addition to other factors, the presence of H^+ and OH^- ions acting as potential-determining ions signifies the potential at the surface of sorbent, and thus the surface charge on the oxide/H_2O interface depends on the pH of the sorptive medium. Therefore, sorption of selenite (2.39×10^{-3} M) onto manganese dioxide (50 mg) has been investigated as a function of pH of aqueous solutions covering the pH range from 1 to 10 using 15 minutes of shaking time. The selections of 50 mg of manganese dioxide and 15 minutes of shaking time were made based on our earlier experience (15, 16) where the maximum sorptions were obtained for europium and silver on the same oxide under similar conditions of equilibration time and sorbent dosage. The results are given in Table 1, both in terms of distribution ratio and percent sorption along with the composition of buffer

TABLE 1
Sorption of Selenite (2.39×10^{-3} M) onto Manganese Dioxide (50 mg) from Buffer Solutions of Different pHs

pH	R_d ($cm^3 \cdot g^{-1}$)	% Sorption
1[a]	1.07×10^5	99.8
4[b]	1.62×10^4	99.4
5.6[b]	1.89×10^5	99.9
7[c]	1.26×10^2	69.8
10[c]	3.86×10	30.0

[a] 0.1 M (sodium perchlorate + perchloric acid).
[b] 0.1 M (sodium acetate + acetic acid).
[c] 0.1 M (sodium hydroxide + boric acid).

solutions. It is evident that variation in the pH of the sorptive solution produces a significant difference in the distribution ratios of selenite, especially in the alkaline range (pH > 7). The PZC (point of zero charge) of manganese dioxide is reported in the 2.8–4.5 range (17–19). At low pH values (<PZC) the surface becomes positive and has a tendency to accumulate negatively charged selenite ions. As a result, the uptake of selenite is maximum in the acidic region. In alkaline solution at pH > PZC, the oxide possesses a negative surface charge. Hence, as the sorptive solution becomes more basic, smaller amounts of negatively charged selenite ions are sorbed. The maximum sorption of selenite is achieved at a pH close to 7. Therefore, for all subsequent measurements, deionized water of pH 6.8 was chosen as the sorptive medium in which the maximum sorption of selenite (>99.9%) was recorded. The pH of deionized water after adding radioselenium (10–25 μL) was found to be in the 3.9 to 3.5 range. The dependence on pH of the sorption of selenite ions on the oxide surface is presumably due to an exchange mechanism which involves the sorption of traces of selenite ions and the simultaneous release of H^+ or OH^- ions from the surface.

The influence of the amount of manganese dioxide on the sorption of selenite was also studied from 10 to 500 mg while keeping the selenite concentration (2.39×10^{-3} M) and shaking time (15 minutes) constant. Figure 1 displays the distribution ratio of selenite versus the dosage of the oxide. The R_d value increases with an increase in the amount of sorbent and attains a maximum value at around 50 mg. Apparently 50 mg of the oxide is sufficient to achieve maximum sorption of selenite (>99.9%). A decrease in R_d values is registered beyond 50 mg of the oxide, while the

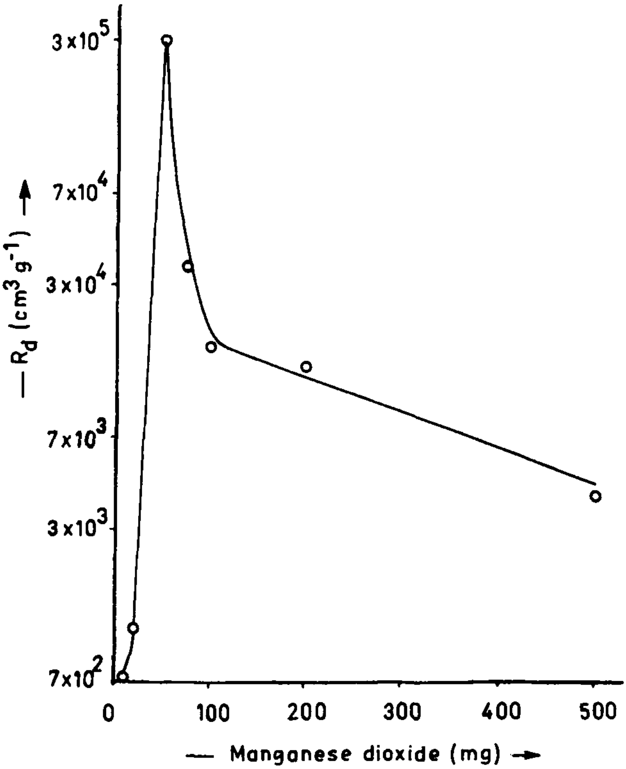

FIG. 1 The dependence of R_d for selenite (2.39×10^{-3} M) sorption from deionized water onto manganese dioxide on its dosage.

percent sorption remains almost constant (>99.6%) up to 500 mg of the oxide used. In further experiments, 50 mg of the oxide was used. The trend of R_d versus the dosage of the sorbent is similar to what was observed for zirconium (14), silver (16), cobalt (20), and cesium (21) sorption onto manganese dioxide from aqueous solutions.

The distribution of microamounts of selenite between the oxide and the aqueous solution (i.e., deionized water) was studied over a tenfold selenite concentration ranging between 3.59×10^{-4} and 3.59×10^{-3} M. The results are shown in Fig. 2. A strong dependence of selenite sorption on its concentration is noticed. The uptake of selenite by the oxide increases with an increase in its concentration in terms of R_d values. A similar trend is also observed in the sorption of zirconium on the same oxide when the

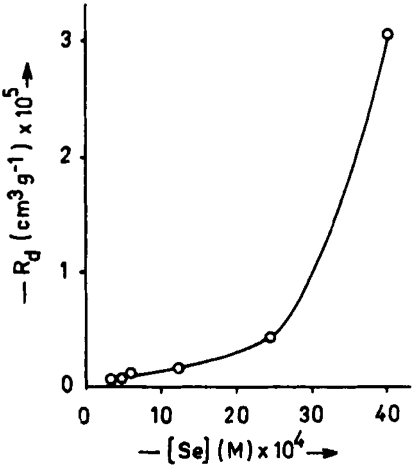

FIG. 2 Variation of selenite sorption on 50 mg of manganese dioxide from deionized water with its concentration.

zirconium concentration was varied up to 2×10^{-4} M (14). The percent sorption of selenite remained ≥98% throughout the entire concentration range investigated.

The effect of the contact time between sorbate (2.39×10^{-3} M) and sorbent (50 mg) or the kinetics of the sorption of selenite on the oxide was studied over a range of 1–60 minutes using deionized water as the sorptive medium. The sorbed concentration of selenite q_t (mol·g^{-1}) as a function of $\sqrt{t}$ is shown in Fig. 3. The uptake of selenite in the initial stages is quite rapid, with most being sorbed within the first 5 minutes (~98%). The rate of sorption becomes slower with the passage of time and reaches a constant value at about 20 minutes. According to the Morris–Weber equation (22):

$$q_t = k_d \sqrt{t} \qquad (1)$$

If this relationship holds good, then a linear plot would be obtained when q_t is plotted vs $\sqrt{t}$. Figure 3 shows that this is not the case. The slope of the initial curve of Fig. 3 gives a value of k_d, the intraparticle diffusion rate, as 3.06×10^{-5} mol·g^{-1}·min^{-2}. The kinetic data of selenite sorption on the oxide were tested with the Lagergren equation (23):

$$\log(q_e - q_t) = \log q_e - \frac{k' t}{2.303} \qquad (2)$$

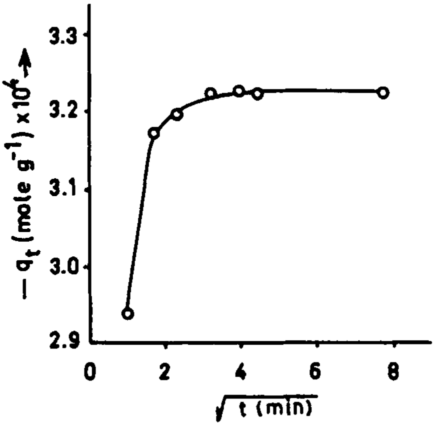

FIG. 3 The amount of selenite sorbed on manganese dioxide (50 mg) as a function of $\sqrt{t}$.

The plot of log ($q_e - q_t$) vs t is shown in Fig. 4, where q_e and q_t are the sorbed concentrations at equilibrium and at time t, and k' is the first-order rate constant. The slope of the initial curve gives the value $k' = 0.498$ min^{-1}. A plot of Bt vs t is shown in Fig. 5, where Bt is a mathematical function of different F values and can be expressed as

$$\mathrm{Bt} = -0.4977 - \ln(1 - F) \quad (3)$$

where F is the fraction sorbed at time t. The plot shown in Fig. 5 gives a straight line up to 15 minutes. In other words, it can be deduced that particle diffusion is the rate-controlling mechanism (24).

The concentration dependence study of selenite was further tested by applying different sorption isotherms: Langmuir, Freundlich, and Dubinin–Radushkevich (D–R). The data followed only the D–R isotherm which was tested in the following linearized form:

$$\ln C_{\mathrm{ads}} = \ln C_{\mathrm{m}} - \beta\epsilon^2 \quad (4)$$

where C_{ads} is the adsorbed concentration, C_{m} is the maximum sorption capacity of the sorbent, and ϵ is the Polanyi potential which can be expressed as

$$\epsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (5)$$

where R is the ideal gas constant in kJ·mol^{-1}·deg^{-1}, T is the absolute

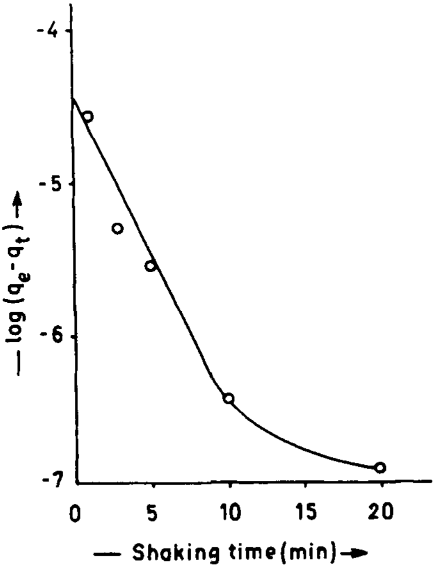

FIG. 4 Selenite sorption plot of log (q_e − q_t) vs shaking time.

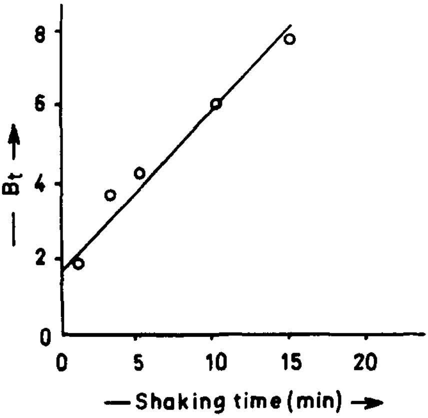

FIG. 5 The relationship of Bt and shaking time for selenite sorption on manganese dioxide.

temperature in kelvin, and C_e is the equilibrium concentration of selenite in solution. A plot of ln C_{ads} vs ϵ^2 gives a straight line as shown in Fig. 6. From the slope of this plot, the value of $\beta = -0.00752$ mol^2·kJ^{-2}, and from the intercept, the value of $C_m = 51.2$ n·mol·g^{-1} are evaluated for the selenite sorption system. The value of the correlation factor (γ) for linear regression analysis was found to be 0.9703. The value of β can be related to the sorption energy E by the following formula (25):

$$E = 1/\sqrt{-2\beta} \tag{6}$$

The value of the sorption energy is evaluated to be 8.15 kJ·mol^{-1}. This value is of the same order of magnitude as the heat of reaction usually found for ion-exchange processes or physical adsorption ($\leq$8 kJ·mol^{-1}), which could be attributed to the weaker bonding between selenite ions and the oxide surface (24).

The effect of various interfering or complexing anions and cations on the sorption has been assessed to evaluate the feasibility of using manganese dioxide as a scavenger for minute amounts of Se of nonradioactive as well as radioactive species of Se in natural or wastewater treatment. The anions were added in the form of their sodium or potassium salts, and the cations were included as their nitrates. The concentrations of these anions and cations were kept around $\sim10^{-2}$ M. The results are given in Tables 2 and 3. All the anions tested tend to reduce the R_d values, most significantly phosphate, citrate, and carbonate. The percent sorption of selenite in the presence of these anions is >82, ~73, and ≥44% respectively. The suppression of sorption in the presence of these ions may be explained as due to the competition for active sorption sites and on the basis of the

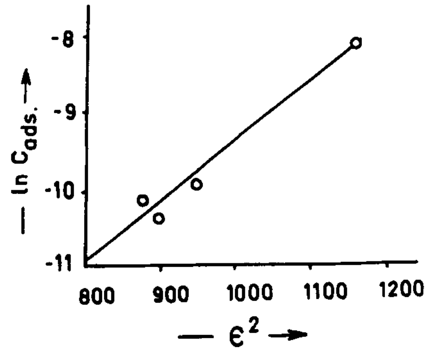

FIG. 6 Dubinin–Radushkevich (D–R) isotherm of selenite.

TABLE 2
The Influence of Anions on Sorption of Selenite (2.39×10^{-3} M) onto Manganese Dioxide (50 mg) from Deionized Water

Additional anions ($\sim 10^{-2}$ M)	R_d ($cm^3 \cdot g^{-1}$)	% Sorption
Nil	3.05×10^5	99.9
EDTA	9.41×10^3	99.0
Nitrate	5.95×10^3	98.5
Sulfite	3.71×10^3	97.6
Tartrate	2.68×10^3	96.7
Sulfate	2.36×10^3	96.3
Oxalate	1.71×10^3	95.0
Acetate	1.56×10^3	94.5
Thiosulfate	1.32×10^3	93.6
Perchlorate	1.10×10^3	92.4
Phosphate	4.14×10^2	82.1
Citrate	2.42×10^2	72.9
Carbonate	7.11×10	44.1

TABLE 3
The Effect of Cations on the Sorption of Selenite (2.39×10^{-3} M) onto Manganese Dioxide (50 mg) from Deionized Water

Additional cations ($\sim 10^{-2}$ M)	R_d ($cm^3 \cdot g^{-1}$)	% Sorption
Nil	3.05×10^5	>99.9
Ni(II)	3.45×10^5	>99.9
Zn(II)	1.50×10^4	99.4
Ag(I)	8.39×10^3	98.9
Ba(II)	8.17×10^3	98.9
Sr(II)	7.34×10^3	98.8
Pb(II)	7.21×10^3	98.8
Al(III)	6.52×10^3	98.6
Li(I)	6.36×10^3	98.6
Ca(II)	6.18×10^3	98.6
K(I)	6.05×10^3	98.5
Na(I)	5.46×10^3	98.4
Mg(II)	4.29×10^3	97.9
Fe(III)	1.24×10^2	57.9

formation of certain complexes which may not undergo sorption to the same extent on the oxide surface. The prior addition of these anions to the medium may also block the active sorption sites which otherwise would be available for sorption of selenite. SeO_3^{2-} appears to be displaced by anions like phosphate, carbonate, and citrate. Complexes of Se with carbonate, phosphate, and citrate have been reported in the literature (26, 27). Table 3 shows the results of selenite sorption in the presence of different cations. Only Ni(II) enhances the sorption whereas Mg(II) and Fe(III) cause a reduction in its sorption. No statistical difference was found for the percent sorption of selenite in the presence of the cations examined except in the presence of Fe(III). In general, sorption increases in the presence of cations due to the accumulation of a positive charge on the surface. These cations may reduce the repulsive charge between the oxide surface and the negatively charged selenite ions. The selenide of sodium and the selenite of Mg and Fe are reported in the literature (26). The reduction of selenite sorption in the presence of sodium, magnesium, and iron may be due to the formation of such complexes with selenite and their low affinity for the oxide surface as compared to selenite ions themselves.

The sorption of other metal ions was also measured on the oxide surface using conditions optimized for selenite sorption. The results are listed in Table 4 along with the separation factors with respect to selenite. The difference in the affinity of manganese dioxide for various metal ions can serve as a tool for the effective separation of these ions from aqueous solutions. All the species showed a lower affinity toward the oxide com-

TABLE 4

Sorption of Other Metal Ions onto Manganese Dioxide (50 mg) from Deionized Water

Metal ions	R_d ($cm^3 \cdot g^{-1}$)	Separation factor $R_d(Se)/R_d(M)$	% Sorption
Se(IV)	3.05×10^5	—	>99.9
As(III)	7.86×10^4	3.88	99.9
Sb(V)	1.12×10^4	27.23	99.2
Eu(III)	3.62×10^3	84.25	97.5
Mn(II)	2.83×10^3	107.77	96.9
Sc(III)	1.98×10^3	154.04	95.6
Sn(II)	8.36×10^2	364.83	90.2
Ag(I)	6.27×10^2	486.44	87.4
Ce(III)	5.74×10^2	531.36	86.2
Co(II)	2.82×10^2	1081.56	75.6
Hf(IV)	2.47×10^2	1234.82	73.3
Te(IV)	2.79×10^0	109319	3.0

pared to selenite, especially Co(II), Hf(IV), and Te(IV). As(III) and Sb(V) showed a higher affinity along with Se. This study provides data on the ability of manganese dioxide to remove Se(IV), As(III), and Sb(V) from aqueous solution, notably to preconcentrate these elements from their very dilute solutions. As a consequence of these measurements, it is seen that Se(IV), As(III), Sb(V), Eu(III), and Mn(II) can be separated from Te(IV).

On the basis of these data, some conclusions can be drawn. Manganese dioxide can be used for the separation of toxic substances like Se(IV), As(III), and Sb(V) from Te(IV). An oxide bed can be exploited to remove or preconcentrate these toxic species from their very dilute solutions. The accumulation of these metal ions on the oxide surface can be used to treat industrial effluents bearing these ions prior to their disposal. The oxide as a sorbent has useful applications in analytical, radio, and environmental chemistry as well as in liquid waste management from industries, and it can serve in pollution abatement studies.

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Received by editor September 24, 1996
Revision received January 1997