

Ion Exchange Studies of Cerium (III) on Uranium Antimonate

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Ion exchange of cerium on uranium antimonate (USb) from nitric acid medium was studied. The distribution coefficient of ~19,000 mL/g was obtained for ion exchange of cerium in 0.1 M nitric acid and it decreased with increase in the concentration of nitric acid. Rapid ion exchange of cerium in the initial stages of equilibration followed by the establishment of equilibrium occurs after one hour. Ion exchange data were fitted into both Langmuir and Freundlich adsorption models using non-linear regression. The enthalpy change accompanied by ion exchange of cerium was determined by the temperature variation method. The performance of the ion exchanger under dynamic condition was assessed by following a breakthrough (BT) curve and the BT curve was fitted using Thomas equation.

1. Introduction

Radioactive liquid wastes are generally composed of major quantity of non-radioactive component contaminated with minor amounts of hazardous gamma emitting radionuclides such as ¹³⁷Cs, ⁹⁰Sr, ¹⁵⁴Eu, ¹⁴⁴Ce etc. Separation and concentration of the radioactive components from a large volume of radioactive waste minimize the volume of the radioactive fraction that is to be safeguarded for long time. Major gains achieved by the isolation of radioactive fission products are the reduction in occupational exposure, minimal radiation degradation to structural materials and chemicals used, low secondary waste generation, and reduction in the cost of disposal. Further, the other larger fraction of treated component can be either disposed or handled without serious hazards.

It is well recognized that only inorganic exchangers/sorbents can withstand to very high radiation dose levels without much degradation and they also exhibit unprecedented selectivity for fission products.¹⁻⁴ Several inorganic sorbents were found suitable for the separation of chemically toxic and radiotoxic metal ions from various waste streams.¹⁻⁴ Recent reviews by Clearfield² and Lehto and Harjula⁴ describe about the latest developments in inorganic sorbents and their applications to the treatment of nuclear waste. They have also indicated that not many sorbents are effective in the separation of fission products especially strontium from acidic liquid wastes and have suggested the need to develop new inorganic sorbents to accomplish these tasks. Thus, we have prepared several inorganic sorbents in the recent past and evaluated for the removal of fission products especially ¹³⁷Cs, ⁹⁰Sr, and ¹⁵⁴Eu from acidic streams.⁵⁻¹⁰

Hydrous antimony oxides and binary metal antimonates are excellent candidates for the separation of fission products especially divalent strontium-90 and trivalent rare earths from acidic waste streams.¹¹⁻¹⁴ Several insoluble binary metal antimonates containing titanium,¹²⁻¹⁴ zirconium,¹⁵ tin¹⁶ etc. were synthesized and the ion exchange properties of them were reported. In addition, it was shown that the pyrochlore structure of antimonates could be tuned to the desired ion exchange selectivity by substituting various cations such as W⁶⁺, Nb⁵⁺

into the framework of the parent compound.¹² Antimonates were also studied for the chromatographic separation of a mixture of metal ions of identical charge, separation of trivalent actinides from lanthanides, and for the separation of fission products.¹⁴ But so far, to the best of our knowledge, antimonate-containing uranium has not been evaluated for the uptake of fission products. However uranium based inorganic ion exchangers such as uranium phosphate were indeed reported by Pekarek and Veseley¹⁷ and studied for the sorption of various metal ions.

Thus, we have prepared uranium antimonate (USb) and studied the sorption of cesium, strontium, and europium.^{9, 10} Selectivity of USb was found to be in the order Eu³⁺ > Sr²⁺ > Cs⁺ and the rate of sorption of europium on USb found to be controlled by the diffusion of europium in the solid phase (diffusion coefficients (D_i) = $\sim 10^{-8}$ cm² s⁻¹). Sequential chromatographic separation of ¹³⁷Cs, ⁹⁰Sr, and ¹⁵⁴Eu from nitric acid medium was also performed.¹⁰ In this paper we report the ion exchange properties of cerium on USb. Effect of various parameters such as time, temperature, concentrations of nitric acid, and metal ion on the distribution coefficient was reported. The performance of the sorbent under dynamic condition was assessed by following the breakthrough curve up to the entire range (i.e. $C/C_0 = 1$), where C is the effluent radioactivity at various intervals of time and C_0 is the initial radioactivity of the feed.

2. Experimental

Materials. Potassium pyroantimonate (KSb(OH)₆) and uranyl nitrate were obtained from E. Merck. ¹⁴⁴Ce radioisotope was separated from the spent fuel solution by the procedure described in Reference 18. All the other chemicals and reagents were of analytical AR grade.

Preparation of Uranium Antimonate. Uranium antimonate was prepared by the procedure described elsewhere.⁹ Briefly it involves drop wise addition of 200 mL of 0.05 M uranyl nitrate to a hot solution of 200 mL of 0.1 M potassium pyroantimonate. The precipitate thus obtained was heated to 60°C for about 12 hours and allowed to age in the mother liquor overnight. It was then filtered, washed thoroughly with distilled water and dried at 60°C. This dried product was ground, sieved and converted to H⁺ form by passing 1 M nitric

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acid into a column packed with the particles of USb. The H⁺ form of USb was then washed with distilled water till pH of the effluent was neutral, which is subsequently used for all the ion exchange studies.

Ion Exchange Studies. Variation of distribution coefficient (K_d , mL/g) of cerium with the concentration of nitric acid was studied by equilibrating 0.05 g of the sorbent (USb) with 10 mL of the solution containing nitric acid (varied from 0.1 M to 2.0 M) spiked with ¹⁴⁴Ce radioactive tracer. After 6 hours of contact, an aliquot was taken from the supernatant and the radioactivity was measured using well-type NaI(Tl) scintillation detector. The distribution coefficient was calculated using eq 1

$$K_d = \frac{A_i - A_f}{A_f} \left(\frac{V}{m} \right) \quad (1)$$

where A_i and A_f are the radioactivity per mL of an aliquot before and after equilibration, respectively. V (in mL) and m (in g) are the volume and mass of the sorbent taken for equilibration, respectively.

The rate of uptake of metal ions from nitric acid was studied, at 300 K, by contacting 0.05 g of the sorbent with 10 mL of the solution containing 0.1 M nitric acid, 10 mg/L of Ce (III) ion spiked with ¹⁴⁴Ce tracer. At various intervals of time, shaking was stopped and aliquot was drawn from the supernatant. From the measurement of activity at a time t , the metal ion exchanged was calculated. Similar experiment was performed when the concentration of cerium was increased to 100 mg/L.

Cerium ion exchange isotherm was obtained by equilibrating, at 300 K, 0.05 g of the sorbent with 10 mL of the solution containing 0.1 M nitric acid and the varied amounts of cerium ion (from 10 mg/L to 1000 mg/L) spiked with ¹⁴⁴Ce tracer. After 6 hours, shaking was stopped and the activity of supernatant was measured as described earlier. From the initial and final activity, the amount of cerium exchanged by the USb was calculated.

Effect of temperature on the distribution coefficient of cerium on USb was studied by equilibrating 0.05 g of the sorbent with 10 mL of 0.1 M nitric acid solution containing 200 mg/L of cerium ion spiked with ¹⁴⁴Ce tracer. After 6 hours of contact between sorbent and solution, the distribution coefficient was measured as described above. Similar experiments were performed at various temperatures from 300 K to 323 K.

Column Studies. Breakthrough experiment was performed by packing a slurry containing 1.0 g of the sorbent into a column of radius 0.25 cm provided with sintered disc at the bottom. The column was conditioned with nearly 10 bed volumes of 0.1 M nitric acid. The feed solution composed of 1.1×10^{-3} M cerium (III) ion spiked with ¹⁴⁴Ce tracer in 0.1 M nitric acid.

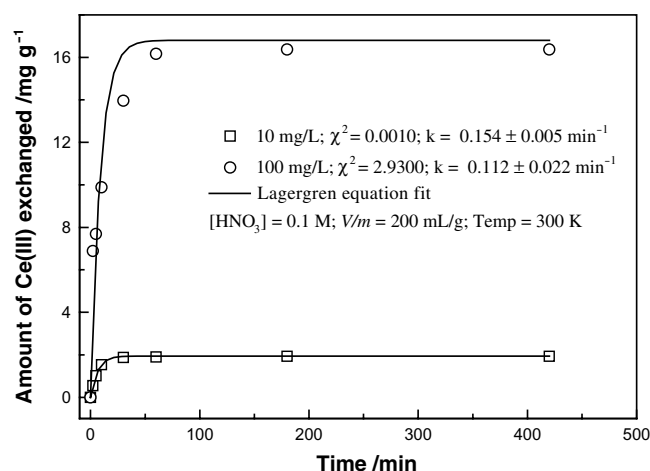


Figure 1. Uptake of Ce³⁺ by USb from 0.1 M nitric acid.

This was passed into a column at the flow rate of 0.20 mL/min. Various fractions of the effluent were collected until the ratio of effluent activity (C) to initial activity (C_0) equals to one. The ratio of C/C_0 , called as breakthrough, was plotted against the volume of the solution passed in to the column to obtain a breakthrough curve. Cerium was eluted with 5 M nitric acid at a flow rate of 0.1 mL/min and 1 mL fractions were collected for obtaining the material balance.

3. Results and Discussion

The rate of uptake of cerium on USb from 0.1 M nitric acid is shown in Figure 1. Rapid ion exchange was observed in the initial stages of equilibration followed by saturation occurs within three hours. The experimental data was fitted to Lagergren equation of the form

$$a_t = a_e (1 - e^{-kt}) \quad (2)$$

where a_t and a_e are the amount of cerium exchanged at a time t and equilibrium respectively and k is the Lagergren first order rate constant. Non-linear regression of the experimental data using eq 2 results in a rate constant of $0.154 \pm 0.005 \text{ min}^{-1}$ and $0.112 \pm 0.022 \text{ min}^{-1}$ for the exchange of cerium from 0.1 M nitric acid containing cerium of 10 mg/L and 100 mg/L respectively.

Plot of distribution coefficient (K_d) of cerium as a function of the concentration of nitric acid is shown in Figure 2. K_d values decreased from 18,943 mL/g to 6 when the concentration of nitric acid was increased from 0.1 M to 2 M. If the sorption of Ce³⁺ on USb involves ideal ion exchange mechanism as shown in eq 3, then the plot of $\log K_d$ against $\log [H_a^+]$ should result in a slope of -3 according to eq 6.



$$K = \frac{[Ce_s^{3+}][H_a^+]^3}{[Ce_a^{3+}][H_s^+]^3} \quad (4)$$

$$\log K_d = \log K + 3 \log [H_s^+] - 3 \log [H_a^+] \quad (5)$$

$$\log K_d = \log K' - 3 \log [H_a^+] \quad (6)$$

where the subscripts 'a' and 's' represent aqueous and sorbent phase respectively and K_d is defined by eq 1. Since the ion exchange reaction was carried out in trace level concentration of cerium ion, the magnitude of $[H_s^+]$ may be assumed as unaltered and hence K' is constant. Log-log plot for the sorption of cerium on USb is shown in Figure 2. A slope of -2.6 obtained is an indicative to the adherence to ideal ion exchange mechanism for the sorption of cerium on USb. A slight deviation from the theoretical slope of -3 could be due to the calculation

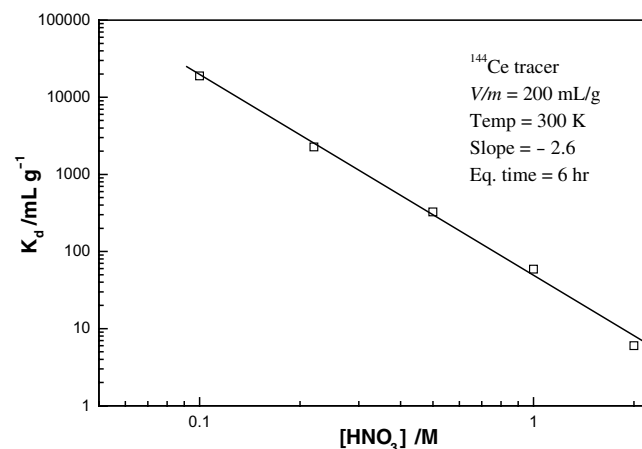


Figure 2. Variation of distribution coefficient of cerium (III) with $[HNO_3]$ on USb at 300 K.

based on concentration terms instead of activity used in eq 6. Similarly, log-log plot for the sorption of Cs⁺ on USb have resulted¹⁰ in a slope of -0.9 in accordance with ideal ion exchange mechanism, while considerable deviation from the expected value was observed¹⁰ for Sr²⁺ (slope = -1.6) and Eu³⁺ (slope = -2.4) sorption on USb.

Ion exchange isotherm of cerium on USb is shown in Figure 3. The amount of metal ion loaded on to the solid phase increased with increase in the concentration of metal ion in aqueous phase, followed by saturation. The experimental data was fitted with non-linear Langmuir and Freundlich isotherms of the form given in eqs 7 and 8, respectively,

$$C_E = \frac{K_L b C_S}{1 + K_L C_S} \quad \text{(Langmuir equation)} \quad (7)$$

$$C_E = K_F [C_S]^\beta \quad \text{(Freundlich equation)} \quad (8)$$

where C_S is the amount of metal ion present in solution phase at equilibrium (mg/L), C_E is the amount of metal ion in the exchanger phase (mg/g), K_L (in L/mg) and K_F (in L/g) are the Langmuir and Freundlich adsorption constants, respectively, b is the apparent ion exchange capacity (mg/g) and β (0 < β < 1) is the measure of heterogeneous interaction of the Ce³⁺ with the sorbent. When β = 1, the sorbent is said to be homogeneous and all the sites are indistinguishable with respect to the energy of sorption. The Freundlich and Langmuir constants can be related to energy of adsorption¹⁹ and thus it was regarded as a measure of affinity of the metal ion towards the sorbent. It can be easily shown from eq 7 that at high values of C_S, the value of C_E approaches the magnitude of b. Thus b was found to be ~35 mg/g from Figure 3. The isotherm was fitted

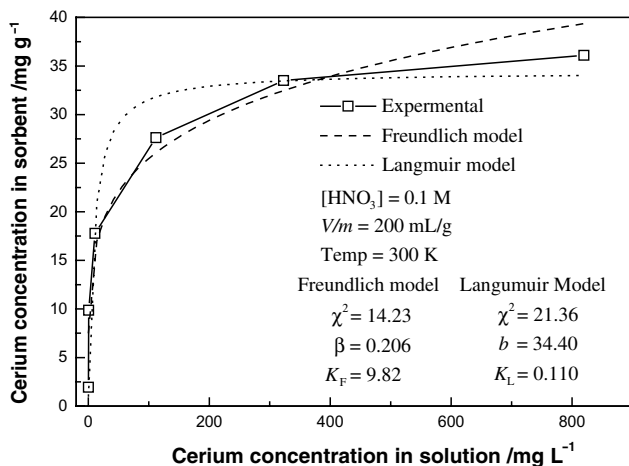


Figure 3. Variation of the amount of cerium in the solid phase with concentration of cerium in solution.

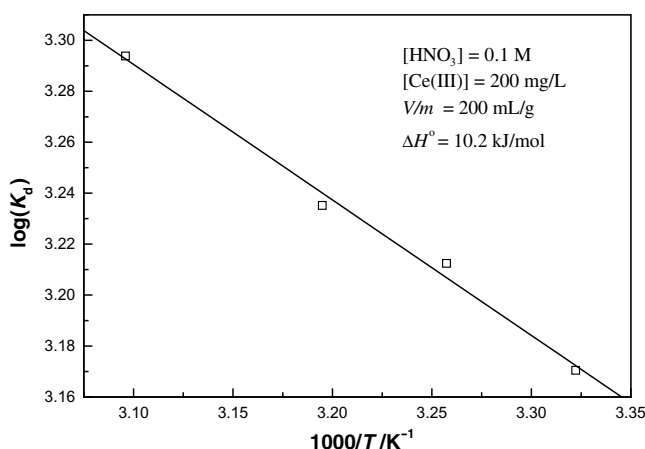


Figure 4. Plot of log K_d against 1/T for the ion exchange of cerium on uranium antimonate.

to eqs 7 and 8 using non-linear regression and the coefficients obtained are shown in Figure 3. From the χ² values of the fitting, it can be seen that the data were described better by Freundlich isotherm in the entire range. However, when the equilibrium concentration of cerium was less than 500 mg/L, the data adheres to Freundlich equation, above which, it follows Langmuir adsorption model in the high cerium concentration range.

The plot of logK_d against 1/T is shown in Figure 4 and the standard enthalpy change (ΔH°) accompanied by the sorption of cerium can be evaluated^{10, 20} using eq 9

$$\log K_d = \left[\frac{-\Delta H^\circ}{2.303 R} \right] \frac{1}{T} + \text{constant} \quad (9)$$

where R is the gas constant. From the slope of the linear fit shown in Figure 4, ΔH° was found to be 10.2 kJ/mol. The endothermicity observed for the ion exchange of cerium could be due to the requirement of the energy for dehydrating water molecules surrounding Ce³⁺ ion in the aqueous phase before sorption. ΔH° obtained for the ion exchange of Ce³⁺ is higher than the enthalpy observed¹⁰ for the sorption of Sr²⁺ (9.9 kJ/mol) on USb but lower than Eu³⁺ (32 kJ/mol) sorption.

The break through (BT) curve for the exchange of cerium on USb is shown in Figure 5. It can be seen from the figure that 1% BT, 50% BT, and 100% BT occur after passing 11 bed volumes (BV), 39 BV, and 83 BV of the feed solution, respectively. The ion exchange data under dynamic conditions was analyzed using Thomas equation²¹ of the form shown in eq 10, which has been widely used for describing BT curves.²²⁻²⁴

$$\frac{C_e}{C_o} = \frac{1}{1 + e^{(K_T(q_o m - C_o V))/Q}} \quad (10)$$

where,

- C_e = Cerium concentration in the effluent (mg/L) - Variable
- C_o = Cerium concentration in the feed (mg/L) = 154 mg/L
- K_T = Thomas rate constant (L min⁻¹ mg⁻¹)
- q_o = Maximum amount of cerium that can be loaded on USb (mg/g) under the specified condition
- m = Mass of the adsorbent (g) = 1.0 g
- V = Throughput volume (L)
- Q = Flow rate (L/min) = 0.2 × 10⁻³ L/min

Non-linear regression of the BT data using Thomas equation is shown in Figure 5. The fitting constants K_T and q_o for the ion exchange of cerium on USb under the specified conditions are found to be 9.3 × 10⁻⁵ L min⁻¹ mg⁻¹ and 7.6 mg/g, respectively. Marked difference of experimental capacity between dynamic absorption conditions, 7.6 mg/g, and batch experiments, 35 mg/g, could be due to the insufficient contact time given for

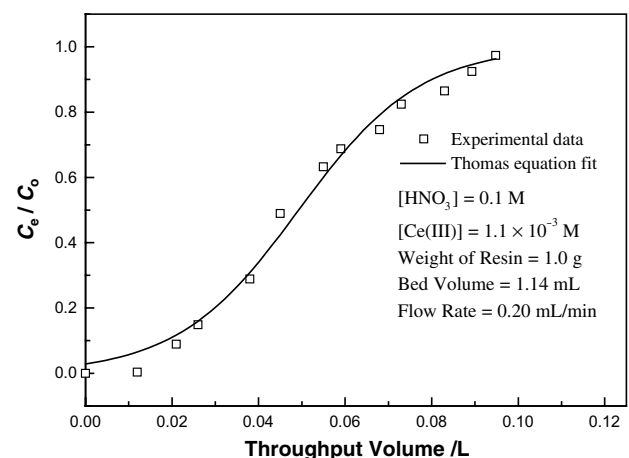


Figure 5. Break through curve for the ion exchange of cerium on USb fitted using Thomas model.

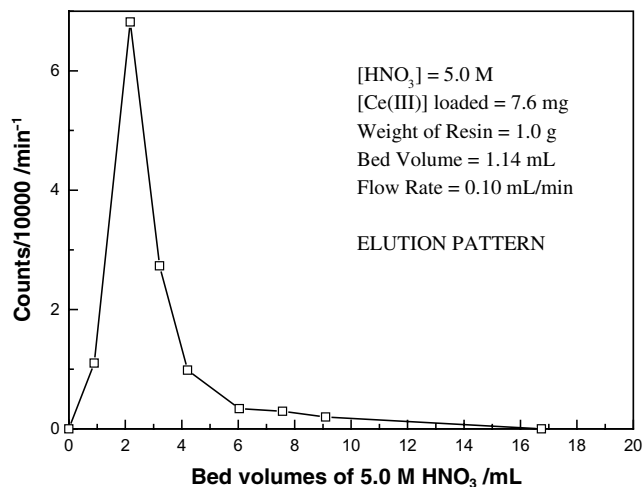


Figure 6. Elution pattern of cerium from USb with 5 M nitric acid.

the ion exchange of cerium on USb under dynamic conditions. The loaded cerium can be eluted using 5 M nitric acid and the elution pattern is also shown in Figure 6. More than 90% of cerium was eluted with in six BV and quantitative elution was observed with in 20 BV.

4. Conclusions

Ion exchange of cerium from nitric acid medium on USb was studied as a function of various parameters. Rapid absorption in the initial stages of equilibration followed by the establishment of equilibrium occurs after one hour and the first order rate constant was found to be of the order of $1.2 \times 10^{-1} \text{ min}^{-1}$. K_d of 18,943 mL/g obtained for the ion exchange from 0.1 M nitric acid and it decreased with increase in the concentration of nitric acid. Slope ($= -2.6$) obtained from $\log K_d - \log [\text{HNO}_3]$ plot indicated that sorption of cerium by USb can be presumed to follow ideal ion exchange mechanism. Freundlich model seems to fit the ion exchange isotherm when the equilibrium concentration of cerium was less than 500 mg/L while Langmuir adsorption model was preferred in the later stage. From, non-linear regression of the experimental data using Langmuir equation, the apparent experimental capacity, b , was found to be 34.4 mg/g. The enthalpy change (ΔH°) accompanied for the ion exchange was found to be -10.2 kJ/mol , indicating that heat energy required for dehydrating water molecules surrounding Ce^{3+} for their entry in to USb. At 100% BT, the ion exchange capacity was found 7.6 mg/g for cerium, which was quantitatively eluted using 5 M nitric acid.

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References

- (1) A. Clearfield, *Inorganic Ion Exchange Materials*, (CRC Press, Boca Raton, FL, 1982).
- (2) A. Clearfield, *Solvent Extr. Ion Exch.* **18**, 655 (2000).
- (3) M. Abe, *Ion Exchange and Solvent Extraction*, edited by J. A. Marinsky and Y. Marcus, (M. Dekker, Inc., Vol. 12, New York, 1995), p. 381.
- (4) J. Lehto and R. Harjula, *Radiochim. Acta* **86**, 65 (1999).
- (5) J. S. Satyanarayana, V. N. Reddy, G. S. Murthy, and A. Dash, *Indian J. Chem. Tech.* **2**, 18 (1995).
- (6) J. S. Satyanarayana, G. S. Murthy, and P. Sasidhar, *Waste Management* **19**, 427 (1999).
- (7) J. S. Satyanarayana, V. N. Reddy, G. S. Murthy, and A. Dash, *J. Radioanal. Nucl. Chem. Lett.* **188**, 323 (1994).
- (8) S. S. Kumar, M. V. Sivaiah, K. A. Venkatesan, R. M. Krishna, G. S. Murthy, and P. Sasidhar, *J. Radioanal. Nucl. Chem.* **258**, 321 (2003).
- (9) M. V. Sivaiah, K. A. Venkatesan, R. M. Krishna, G. S. Murthy, and P. Sasidhar, *Colloids Surf. A: Physicochem. Eng. Aspects* **236**, 147 (2004).
- (10) M. V. Sivaiah, K. A. Venkatesan, R. M. Krishna, P. Sasidhar, and G. S. Murthy, *Radiochimca Acta* (in press).
- (11) M. Abe, *Inorganic Ion Exchangers And Adsorbents For Chemical Processing In Nuclear Fuel Cycle*, IAEA-TECDOC- 377, (International Atomic Energy Agency, Vienna, 1985), p.263.
- (12) T. Moller, A. Clearfield, and R. Harjula, *Micropor. Mesopor. Mater.* **54**, 187 (2002).
- (13) H. F. Aly and I. M. El-Nagger, *J. Radioanal. Nucl. Chem.* **228**, 151 (1998).
- (14) I. Yamagishi, Y. Morita, M. Kubota, and M. Tsuji, *Radiochim. Acta* **75**, 27 (1996).
- (15) J. Mathew and S. N. Tandon, *Can. J. Chem.* **55**, 3857 (1977).
- (16) R. Koivula, R. Harjula, and J. Lehto, *Micropor. Mesopor. Mater.* **55**, 231 (2002).
- (17) V. Pekarek and V. Vesely, *J. Inorg. Nucl. Chem.* **27**, 11512 (1965).
- (18) B. Saha, K. Swaminathan, C. R. Venkatasubramani, and P. R. Vasudeva Rao, *J. Radioanal. Nucl. Chem. Lett.* **214**, 17 (1996).
- (19) G. Sposito, *Soil Sci. Soc. Am. J.* **44**, 652 (1980).
- (20) K. A. Venkatesan, T. G. Srinivasan, and P. R. Vasudeva Rao, *Colloids Surf. A: Physicochem. Eng. Aspects* **180**, 277 (2001).
- (21) H. C. Thomas, *J. Am. Chem. Soc.* **66**, 1664 (1944).
- (22) T. Mathialagan and T. Viraraghavan, *Separation Sci. Technol.* **38**, 57 (2003).
- (23) Z. Aksu and F. Gonen, *Process Biochem.* **40**, 1 (2003).
- (24) T. Mathialagan and T. Viraraghavan, *J. Hazardous Mater.* **B94**, 291 (2002).