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Role of magnetite and humic acid in radionuclide migration in the environment

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ABSTRACT

Sorption of ^{137}Cs, ^{90}Sr, ^{154}Eu and ^{141}Ce by magnetite has been studied at varying pH (4 to 11) in the presence and absence of humic acid. The sorption studies have also been carried out at varying ionic strength (0.01 to 0.2 M $NaClO_4$) and humic acid concentration (2 to 20 mg/L). Percentage sorption of ^{137}Cs and ^{90}Sr was found to be pH dependent, with the sorption increasing with increasing pH of the suspension. At any pH, the percentage sorption of ^{90}Sr was higher than that of ^{137}Cs. The results have been explained in terms of the electrostatic interaction between the positively charged metal ions and the surface charge of the magnetite which becomes increasingly negative with increasing pH. On the other hand, ^{154}Eu and ^{141}Ce were found to be strongly sorbed by the magnetite at all pH values, with the sorption being independent of pH. The strong sorption of trivalent and tetravalent metal ions suggests the role of complexation reactions during sorption, apart from the electrostatic interactions. However, in the case of ^{141}Ce surface precipitation of Ce(III) formed by reduction of Ce(IV) in the presence of magnetite cannot be ruled out. Presence of humic acid (2 mg/L) was found to have negligible effect on sorption of all metal ions.

1. Introduction

The high level waste (HLW) generated from the reprocessing of spent nuclear fuel contains long lived radionuclides such as, ^{90}Sr (29 y), ^{129}I (1.57×10^7 y), ^{137}Cs (30 y), ^{135}Cs (2×10^6 y), ^{99}Tc (2.1×10^5 y) as well as minor actinides. The HLW is proposed to be buried in the deep geological repository after vitrification in a suitable matrix, e.g., borosilicate glass, synroc, etc. However, with time these radionuclides may leach out from the waste form and be released into the natural environment thereby contaminating it. Besides this, the environment is also contaminated due to nuclear testing, re-entry and disintegration process of nuclear powered satellites, uranium mining and nuclear weapons. The most important point concerning the safety of geological disposal is to maintain and evaluate safety measures to counteract the possibility of radionuclide affecting the humans and environment through ground water. Extensive studies are being conducted worldwide to investigate the migration behaviour of these long lived radionuclides in the aquatic environment, which is important for the performance assessment of the deep geological repository.

Colloids are known to enhance the migration of radionuclides in ground water (Kersting et al., 1999). The colloid facilitated transport of radionuclides may be further affected by the presence of humic substances in ground water, as they have strong tendency to complex the metal ions (Choppin, 1999). The ground water in the vicinity of granitic rocks is expected to contain magnetite colloids. It is therefore of interest to study the role of magnetite in migration of long lived radionuclides in aquatic environments. Very few studies have been carried out on the sorption of radionuclides by

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magnetite. Literature reports exist on the sorption of long lived radionuclides, such as ^{137}Cs, ^{133}Ba and ^{152}Eu by magnetite (Catalette et al., 1998), sorption of Yb(III), Ni(III) and Cs(I) by magnetite (Marmier et al., 1999), and that of uranium (VI) by colloidal magnetite (Missana et al., 2003) in the pH range of 6–8.

Humic acid (HA) has been found to strongly influence the sorption of Eu(III) by silica (Fairhurst et al., 1995), and alumina (Wang et al., 2006). However, studies on the effect of humic acid (HA) on sorption of long lived radionuclides by magnetite colloids are rare. With this in view we synthesized colloidal sized magnetite powder and investigated the sorption behaviour of ^{137}Cs, ^{90}Sr, ^{154}Eu and ^{141}Ce, representing monovalent, divalent, trivalent and tetravalent metal ions respectively. Synthesized magnetite is an iron oxide containing both Fe^{2+} as well as Fe^{3+} in an inverse spinel structure with cubic packing of O_2^- ions. The distribution of Fe^{2+} and Fe^{3+}in the crystal structure can be written as $[Fe^{3+}]_{tetrahedral}\,[Fe^{2+}\,Fe^{3+}]_{octahedral}\,O_4$, with Fe^{2+} ions occupying half the octahedral sites and the Fe^{3+} ions distributed evenly at octahedral and tetrahedral sites (Allen et al., 1974a). ^{154}Eu was used as a representative of trivalent minor actinides, such as, americium and curium, while ^{141}Ce was used as an analogue of tetravalent actinides, namely, plutonium and thorium. The sorption studies were carried out at varying pH, ionic strength and HA concentration so as to understand the mechanism of the underlying sorption phenomena.

2. Experimental

2.1. Reagents

Aldrich humic acid was used in the present study. Though Aldrich Humic acid has been found to be closer to soil humic acid with regard to its carbon content and hydro-phobicity, (Juhna et al., 2003), it has been used to simulate ground water (Dries et al., 2005). The commercially available reagent was purified by dissolution in water followed by addition of dilute HCl to precipitate humic acid. The step was repeated twice. The precipitate was filtered and dried under vacuum. All other reagents were of analytical grade and the solutions were prepared in Millipore water having resistivity of 18 MΩ cm.

The pH of suspensions was measured using LABINDIA pH meter (9908N108) which was calibrated using the standard buffer solutions (Merck).

3. Synthesis of magnetite

Equal amounts of two different iron salts $FeCl_3$ and $(NH_4)_2SO_4$ $FeSO_4.6H_2O$ were dissolved in distilled water separately and equal volume of each of the solution was mixed. Ammonia solution was added to the resultant solution with constant stirring at 80 °C for 2 h. The solution was aged for 1 h. After filtration the precipitate was cooled overnight and subsequently washed with distilled water followed by acetone. The precipitate was aged in the oven at 100 °C for 12 h and was ground in a planetary ball mill with a small quantity of acetone for 4 h and kept in the oven at 80 °C for 8 h.

4. Characterization

The magnetite powder was characterized for its crystal structure, particle size, zeta potential and concentration of surface sites. XRD spectra, recorded using the X ray diffractometer (DIANO) over the 2θ range of 10 to 60°, confirmed the cubic magnetite structure and size of the synthesized powder was found to be 12 nm (Scherer method). The surface area of the magnetite powder was determined using the BET surface area analyzer (SORPTOMATIC, 1990). Malvern instrument Zetasizer nano ZS was used for the determination of zeta potential of the magnetite colloids. The magnetite suspensions in water, having concentration of 1.0 g/L, were prepared at various pH ranging from 2 to 11. The ionic strength was maintained at 0.01 M using $NaClO_4$ solution.

Sorption of metal ions by the magnetite surface takes place via the protonated ($\equiv Fe{-}OH_2^+$) and deprotonated ($\equiv Fe{-}O^-$) surface sites. In order to determine the concentration of these surface sites, acid base titration of the magnetite suspension (300 mg/50 mL) in 0.1 M $NaClO_4$ was carried out with 0.1 M $HClO_4$ and 0.1 M NaOH. The blank electrolyte solution (0.1 M $NaClO_4$) was also titrated with standard acid and base. The methodology for determination of site density from the data on acid base titration of colloidal suspension is given elsewhere (Jain et al., 2007).

5. Preparation of ^{137}Cs, ^{90}Sr, ^{154}Eu and ^{141}Ce tracers

^{141}Ce, the short lived (30 days) isotope of cerium was used for the present study. 10 mg of CeO_2 was irradiated in APSARA reactor of Bhabha Atomic Research Center (neutron flux density $= 5\times10^{12}$ n cm^{-2} s^{-1}) for a time period of 6 h. Irradiated CeO_2 was dissolved in concentrated HNO_3. The solution was dried and then dissolved in dilute HNO_3. The tetravalent oxidation state of cerium in the stock solution was ascertained by measurement of its UV–Visible spectrum, which showed the absorption maximum at 309 nm representative of Ce(IV). 100 µL aliquots from this stock solution were added to the colloidal suspensions for sorption study. The concentration of Ce(IV) in the sorption samples was 7.5×10^{-8} M. In the case of ^{154}Eu, 5 mg of ^{153}Eu (96%, enrichment) as europium oxide was irradiated for one week in the high flux Dhruva reactor of Bhabha Atomic Research Center, Mumbai (neutron flux density $= 1\times10^{14}$ n cm^{-2} s^{-1}). The radiotracer stock solution was prepared in the same manner as that for ^{141}Ce. There was no special reason for using ^{154}Eu. The stock solution was used for perturbed angular correlation studies, and hence the same was used for the present work. The concentration of Eu(III) in the sorption samples was 2×10^{-9} M. No carrier added ^{137}Cs and ^{90}Sr were procured from the Board of radiation and isotope technology (BRIT), Mumbai, India. The concentration of Cs(I) and Sr(II) in the sorption experiments was 4×10^{-10} M. The radionuclidic purity of the radiotracers was monitored by gamma counting using HPGe detector (Eurysis Measures, France) coupled with 4096 channel analyzer.

6. Sorption study

Sorption of ^{137}Cs, ^{90}Sr, ^{154}Eu and ^{141}Ce by magnetite was measured by batch sorption method. Separate experiments