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Effect of humic acid on sorption of technetium by alumina

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ABSTRACT

Sorption of technetium by alumina has been studied in absence as well as in presence of humic acid using $^{95}Tc^m$ as a tracer. Measurements were carried out at fixed ionic strength (0.1 M $NaClO_4$) under varying pH (3–10) as well as redox (aerobic and reducing anaerobic) conditions. Under aerobic conditions, negligible sorption of technetium was observed onto alumina both in absence and in presence of humic acid. However, under reducing conditions (simulated with $[Sn(II)] = 10^{-6}$ M), presence of humic acid enhanced the sorption of technetium in the low pH region significantly and decreased at higher pH with respect to that in absence of humic acid. Linear additive as well as surface complexation modeling of Tc(IV) sorption in presence of humic acid indicated the predominant role of sorbed humic acid in deciding technetium sorption onto alumina.

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1. Introduction

^{99}Tc is one of the long lived fission products having half life 2.11×10^5 years and cumulative fission yield of 6.16% in the thermal neutron induced fission of ^{235}U. During the reprocessing of the spent nuclear fuel, most of the technetium is concentrated in the high level waste (HLW), though it may also get into different streams of the reprocessing scheme [1]. The radionuclides present in the HLW are immobilized in a suitable glass matrix, which after an interim sub-surface storage of a few decades may ultimately be buried in a deep geological repository. Due to the decay heat of the radionuclides and/or the natural processes, such as, earthquakes, volcanic eruptions, corrosion of over-packs, etc, the radionuclides might get into the surrounding near field (engineered barriers) and ultimately in the far field (biosphere), thereby, leading to risk of exposure to public at large. In recent past colloid assisted migration has been observed as an important pathway for the migration of radionuclides in the biosphere [2,3]. These colloidal particles are inorganic as well as organic particles and coupling of radionuclides speciation onto these particles in geochemical transport code could lead to realistic assessment of radionuclides migration in aquatic environment [4].

Technetium exhibits rich redox sensitive chemistry with valence state ranging from −1 to +7. Under oxidizing conditions technetium is stable in the anionic form (TcO_4^-), which makes it less reactive towards various components of the aquatic environment and hence is highly mobile [1]. Under reducing conditions, Tc(VII) gets reduced to lower oxidation states, mainly to Tc(IV), which may exist as TcO^{2+}, $TcO(OH)^+$ or $TcO(OH)_2$ depending upon pH in absence of complexing agent [1]. Distribution and mobility of technetium in environment has been observed to be significantly influenced by the presence of reducing agents. Byegard et al. [5] carried out the laboratory and field studies on reduction and sorption of Tc(VII) on magnetite in synthetic and natural ground water from Stripa mines and corroborated the enhanced sorption in case of natural ground water to the presence of Fe^{2+} ions. Enhanced sorption characteristics of ^{99}Tc onto bentonite material in presence of different Fe(II)-based additives under anaerobic conditions was attributed to the reduction of the pertechnetate anion to its lower oxidation state in the form of insoluble $TcO(OH)_2$ or $TcO_2{\cdot}nH_2O$ [6].

Humic substances have been found to significantly influence radionuclide migration, depending upon the interaction affinity among radionuclides, humic substances and mineral surfaces. Humic substances (HS) are naturally occurring polyfunctional high molecular weight complexants and have strong interaction with metal ions as well as solid surfaces. In solution under neutral pH conditions, Tc(IV) is mainly associated with HS enhancing solubility up to the order of 2×10^{-6} M [7]. Evidence for the aggregation of Tc(IV) colloids with humic substances has been obtained in EXAFS and XANES studies [8,9]. Artinger et al. [10] carried out extensive

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studies on humic colloid mediated transport of Tc(IV) in Gorleben ground water and found the presence of humic substances enhancing the transport rate of Tc(IV). Humic and Fulvic acid (HA and FA), the two most abundant components of humic substances, are chemically heterogeneous compounds having different types of functional groups at different proportions and configurations. Conceptually, there are several ways in which humic acid may affect the speciation of metal ions on surface. It can form strong aqueous phase complexes with the metal ions, thereby competitively diminishing the metal ion sorption and precipitation. Alternatively, sorption of HA/FA to mineral surfaces may modify the surface characteristics and changes the metal retention behaviour of the surface.

The objective of the present study is to investigate the effect of HA on the sorption of technetium by alumina under normal atmospheric and reducing conditions. For this purpose, we have employed $^{95}Tc^{m}$, the gamma emitting radioisotope of technetium (E_{γ} = 204, 582 keV) as a tracer, thereby achieving lower concentrations (10^{-12} M) of technetium. Alumina was chosen as the model mineral oxide as it is the aluminol sites (≡AlOH) of alumina which dominate the sorption characteristics of naturally occurring aluminosilicate based clays, and various aluminium based solids (boehmite, bayerite, gibbsite, etc.). Linear additive modeling has been carried out to delineate the effect of HA on Tc(IV) sorption onto alumina and surface complexation modeling (SCM) has been done to identify the surface species responsible for this effect in the ternary system of Tc(IV)–HA–alumina.

2. Experimental

^{95m}Tc was produced by $^{96}Mo(p,2n)$ nuclear reaction using the 22 MeV proton beam from the BARC-TIFR Pelletron accelerator at Mumbai. The beam current on target was 200 nA. The MoO_3 target in the form of a pellet of thickness 200 mg/cm^2 was bombarded for 24 h by the proton beam. After the bombardment, the MoO_3 target was dissolved in dil. NaOH and technetium was radiochemically separated by solvent extraction with methyl ethyl ketone (MEK). The organic phase was passed through an alumina column to remove traces of molybdenum. The effluent was evaporated to dryness and subsequently dissolved in 0.1 M NaCl to form the stock solution. Concentration of technetium in the stock solution was 10^{-10} M.

γ-alumina powder from Degussa India Ltd. was used as obtained. The particle surface area determined by N_2 gas based BET analysis, was found to be 203 m^2/g. Zeta potential of the alumina suspension in 0.01 M $NaClO_4$ was measured at varying pH values using a Malvern zeta analyzer based on dynamic light scattering (DLS). Site density (≡AlOH) and surface hydrolysis constants of surface sites were determined by titrating alumina suspension (strength 7.5 g/l in 0.1 M $NaClO_4$) in N_2 environment with 0.1 M HCl and NaOH solutions and fitting the titration data using FITEQL V. 4.0 software [11]. pH was measured using a pH meter (Lab India) calibrated with buffer solutions of pH 4.00, 7.00 and 9.00 (Merck). The solutions were continuously stirred during titrations and N_2 gas was purged through the solutions for 30 min before titration was started to remove any dissolved CO_2. HA (ACROS Co., Sodium salt) was characterized for its pK_a values by potentiometric titration and fitting the titration data using FITEQL in discrete site model having 3-sites (HL_i; i = 1–3) for proton affinity [12]. In this titration, the pH of the HA solution in distilled water (0.1 M NaCl + 0.04 g HA) was brought to 2.97 by addition of little amount of 0.1 M HCl and then this solution was forward titrated with the successive addition of 0.2 ml of the base (0.02 N NaOH + 0.08 M NaCl) up to nearly 10 ml. Total proton exchange capacity (PEC) of HA was determined following standard Baryta method [13]. All the other chemicals used in the experiment were of analytical grade and procured from the local suppliers.

2.1. Sorption experiments

Alumina suspensions (5 g/l) were prepared in 0.1 M $NaClO_4$ and kept in polypropylene tubes. The pH of the suspensions (10 ml) was adjusted using dilute HCl and NaOH solutions. Prior to pH adjustment the suspensions were allowed to equilibrate for 2 h. Eight samples having varying pH in the range from 3 to 10 were prepared. Two sets of experiments (corresponding to oxidizing and reducing conditions) were carried out and in each set the sorption of technetium on alumina was measured both in absence as well as in presence of HA. In the first set, the aerobic condition was maintained. For binary Tc–alumina sorption, 100 μl of $^{95}Tc^{m}$ stock solution was added to each of the suspensions which were then kept for equilibration in a shaker for 24 h. In ternary Tc-HA–alumina sorption, the alumina suspension was equilibrated first with HA (2 mg/l) for 48 h and subsequently $^{95}Tc^{m}$ was added and equilibrated in the suspension for next 24 h. After equilibration, pH of the suspensions was measured and two 1 ml aliquots from each tube were taken for gamma activity measurement of ^{95m}Tc to obtain the initial activity (A_0). The gamma activity was measured using a well type 3″ × 3″ NaI(Tl) detector coupled to 1024 channel analyzer. The remaining 8 ml of the suspensions were centrifuged by a high speed centrifuge at 16,000 rpm (rcf 27476 g) for 45 min and two 1 ml aliquots from the supernatant were taken for measurement of activity (A) left in the liquid phase. The percentage sorption was calculated from the measured activity data before and after phase separation as:

$$\%\,\text{sorption} = \left[\frac{A_0 - A}{A_0}\right] \times 100 \qquad (1)$$

The second set of experiments was carried out under reducing conditions which were managed by adding 100 μl of $SnCl_2$ solution (10^{-4} M) in each suspension and purging dry N_2 gas before keeping the samples for equilibration. The reduced state of technetium was confirmed by solvent extraction procedure using tetra phenyl arsonium chloride in chloroform. Negligible extraction of technetium to the organic phase negated the presence of Tc(VII). It was assumed that sorption of Tc(IV) on alumina is not be affected by Sn^{2+} (10^{-6} M) as the HA concentration and the concentration of surface sites on alumina is much in excess over the Sn^{2+} concentration. Sorption studies under reducing condition were carried out using the same procedure as described above for the aerobic conditions.

Humic acid sorption on alumina was separately studied over pH 3–10 in 0.1 M $NaClO_4$. 2 mg/l HA was equilibrated with the alumina suspension at different pH for 48 h. Subsequently the suspensions were centrifuged at 10,000 rpm (rcf 10733 g) for 30 min and the absorbance of the supernatant solutions was measured at 254 nm using UV–Visible spectrophotometer (JASCO) [13]. Percentage sorption was determined from the absorbance of the initial HA solution (2 mg/l) at 254 nm and that of the supernatant solutions after equilibration using similar equation as (1).

2.2. Modeling of sorption data

Linear additive modeling of Tc(IV) sorption data in ternary system was carried out using the binary system K_d value for interaction between Tc(IV) and alumina, HA and alumina and stability constant of Tc(IV)–HA complex. The data for $\log \beta$ of Tc(IV)–HA complexation was taken from [14]. The linear additive modeling for metal ion sorption in presence of HA was carried out

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