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$_2 \cdot n$H$_2$O [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

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 ($E_\gamma = 204$, 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 ($\equiv AlOH$) 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 ($\equiv AlOH$) 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:

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

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 β of Tc(IV)–HA complexation was taken from [14]. The linear additive modeling for metal ion sorption in presence of HA was carried out
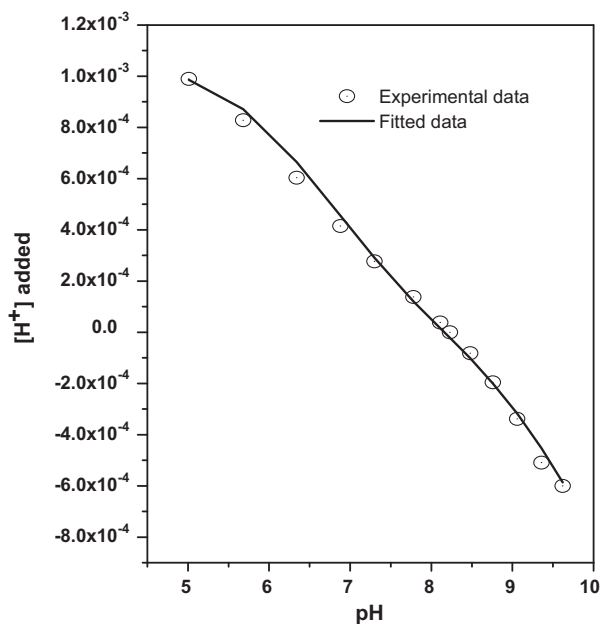
Fig. 1. Potentiometric titration of alumina and SCM fitting of the sorption data.

Fig. 2. Zeta-potential potential measurement of alumina as function of pH.

following the modification by Samadfam et al. [15] according to which K_d for the ternary system is given by:

$$K_d = \frac{K_d^0 + (V/W)f_{HA}\beta_2[HA]}{1 + (1 - f_{HA})\beta_1[HA]} \qquad (2)$$

Where K_d^0 is the distribution coefficient for the sorption of Tc(IV) on alumina in absence of HA and f_{HA} is the fraction of mineral bound HA. β_1 and β_2 are the stability constants for Tc(IV) complexation with HA when present in dissolved and sorbed state, respectively. V and W are the volume of the suspension and weight of the alumina powder. In order to take into account the change in the β value between Tc(IV) and mineral bound HA from that in aqueous solution, the β_2 value was varied in step of 0.1 unit so as to obtain the best fit with the experimental data of the ternary system.

2.2.1. Surface complexation modeling

Potentiometric titration data of alumina suspension was fitted into a model based on 2-pK approach for surface protonation/deprotonation and constant capacitance model for electrostatics [16] in the non-linear least square-fitting program FITEQL. Constant capacitance value of $1.2\,F/m^2$ was used throughout the FITEQL calculations. In modeling Tc(IV) sorption on alumina, surface protonation/deprotonation constants obtained from the above fitting was kept constant.

During the modeling of ternary Tc(IV)–HA–alumina sorption, $\log K$ for the sorbed species formed in binary systems, namely, HA–alumina, and Tc(IV)–alumina were kept fixed. For optimization procedure of the ternary system, the competition of Tc only between the sorbed and dissolved HA was considered. Tc(IV)
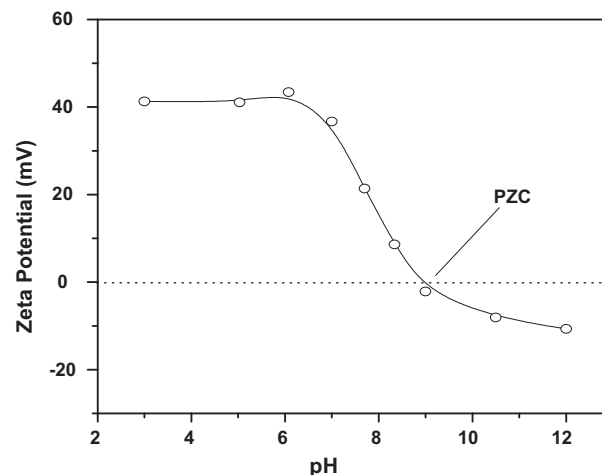
sorption on alumina over the studied pH range was very small and strong binding characteristics of Tc(IV)–HA system justifies this assumption in the ternary system modeling.

3. Results and discussion

3.1. Alumina and Humic acid characterization

Alumina surface sites can be represented by $\equiv$AlOH, which is formed by the dissociative hydroxylation of unterminated Al–O bonds on alumina surface [17]. Protonation/deprotonation of $\equiv$AlOH sites can take place in one of the following ways:

$$\equiv AlOH + H^+ \rightarrow AlOH_2^+ \quad (K_1) \qquad (3)$$

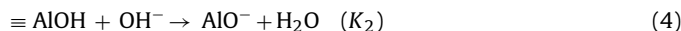$$\equiv AlOH + OH^- \rightarrow AlO^- + H_2O \quad (K_2) \qquad (4)$$

Fig. 1 shows the titration curves for the acid and base leg of the titration of alumina along with their fitting in FITEQL. Surface site acidity constants (pK_1 and pK_2) and total number of surface sites are given in Table 1. These are in agreement with the literature data for alumina [18]. Fig. 2 shows the zeta potential of alumina as a function of pH. The pH_{PZC} was found to be 8.9, which is within the range of pH_{PZC} values for alumina in the literature [18]. Higher pH_{PZC} indicates the positive surface charge of alumina upto pH 9 which may contribute to the electrostatic attraction of negatively charged species like pertechnetate towards alumina surface.

Modeling of HA potentiometric data (Fig. 3) was done in the FITEQL employing 3-sites discrete model description of HA. Table 2 gives the modeling result. Three pK_a (3.60, 5.89 and 8.12) values obtained in this study compare well with the literature [19] where three values have been referred to carboxyl group, amine groups and phenol groups, respectively. PEC of HA was found to be 5.67 meq/g.

3.2. Sorption experiments

Fig. 4 shows the sorption data of Tc(VII) on alumina both in absence and presence of HA under aerobic conditions. The data

Table 1
Details of potentiometric titration of alumina suspension and SCM fitting.

Log K ($\equiv$AlOH + H$^+$ $\leftrightarrow$ $\equiv$AlOH$_2^+$)	7.2 ± 0.2
Log K ($\equiv$AlOH $-$ H$^+$ $\leftrightarrow$ $\equiv$AlO$^-$)	-9.1 ± 0.1
Alumina concentration	7.5 g/l
Ionic strength	0.1 M NaClO$_4$
Specific surface area	203 ± 5 m^2/g
Specific capacitance	1.2 F/m^2
Surface sites ($\equiv$SOH)	1.022×10^{-3} mol/l
WSOS/DF[a]	29.5

[a] Weighted sum of squares divided by degree of freedom.

Table 2
Surface complexation modeling of the humic acid titration data assuming discrete site model of HA.

Ligands	Amount of ligands, (M)	Log K	WSOS/DF
HL$_1$	5.107×10^{-4}	-3.60	7.39
HL$_2$	3.715×10^{-4}	-5.89	
HL$_3$	2.108×10^{-4}	-8.12	
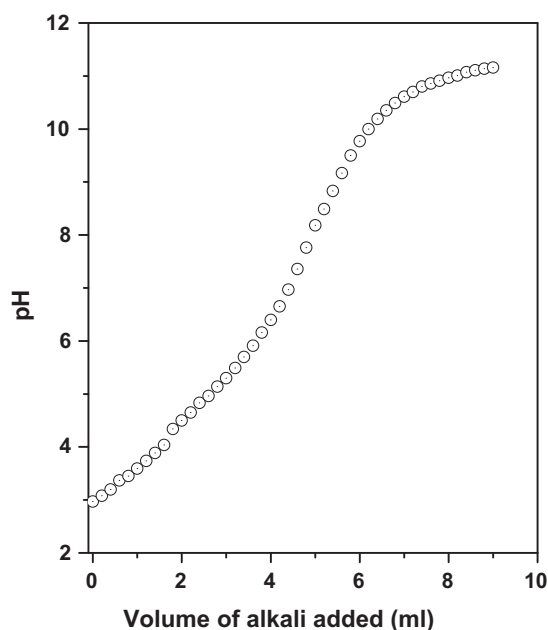
Fig. 3. Potentiometric titration data for humic acid.

Fig. 5. Sorption profiles of Tc(IV) on alumina both in absence as well in presence of humic acid (2 mg/l) Fit lines are surface complexation modeling of sorption data of the binary and ternary system.

show negligible sorption of TcO_4^- on alumina at all the pH values in both the cases. Though the zeta potential of alumina is positive at pH < 9, negligible sorption of negatively charged species, TcO_4^- at all the pH values indicates that the electrostatic factors are not important in the sorption phenomena in the present case. This may be due to the bulky nature of TcO_4^- anions and the steric factors may be responsible for the negligible interaction between $\equiv Al-OH_2^+$ and TcO_4^- species. As HA does not complex Tc(VII), the sorption of HA on alumina does not affect the sorption of Tc(VII) on alumina either. The above results therefore corroborate the expected high mobility of Tc(VII) in aquatic environment. Our studies on sorption of Tc(VII) on hematite [20] showed similar results.

In the presence of reducing agent (Sn^{2+}), TcO_4^- is reduced to Tc(IV), which is present as TcO^{2+}, $TcO(OH)^+$ or $TcO(OH)_2$, depending upon the pH of the solution. The solubility of TcO_2 is found to be
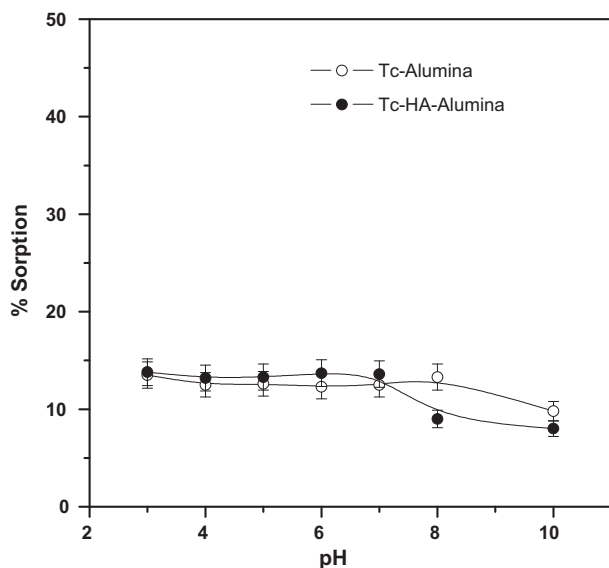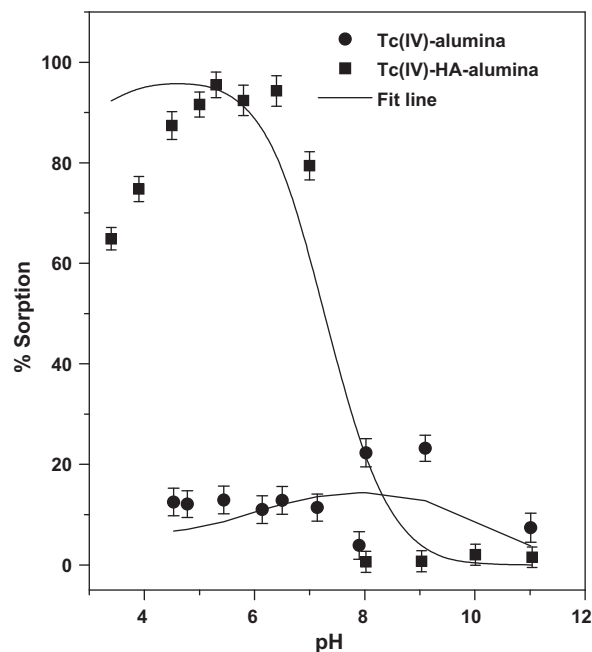

Fig. 4. Sorption of Tc(VII) on alumina (in 0.1 M $NaClO_4$) over pH 3–10 in absence as well as in presence of HA.

$\sim 10^{-8}$ M [14] which is much higher than the concentration of technetium used in the present study and hence surface precipitation can be ruled out. Fig. 5 shows the sorption data of technetium on alumina under reducing conditions. In the absence of HA, negligible sorption of Tc(IV) on alumina colloids was observed at all pH values. This can be explained in terms of the similar (positive) charge on the Tc(IV) species and on the alumina colloids in the pH range of 3–9. At higher pH, though alumina acquires a negative charge, technetium is predominantly present as neutral $TcO(OH)_2$ species thus explaining the negligible sorption even at pH > 9. Strong sorption characteristics of Tc(IV) was not observed in the present study as reported in the literature [21]. This could be attributed to the reduction and hydroxylation of technetium to $TcO(OH)^+$ and $TcO(OH)_2$ in the supernatant phases. These species have weak interaction with surface sites (cf Section 3.4). Tc(IV) studies in literature have been carried out mostly in presence of Fe(II) on surfaces where the approach of TcO_4^- to the Fe(II)–Fe(III) redox couple led to fixing of technetium onto the surface [22,23]. In the presence of HA, on the other hand, the data show almost 100% sorption of technetium on alumina. This can be explained as due to strong complexation of Tc(IV) by HA which in turn is strongly sorbed (Fig. 6) on alumina colloids at pH values <8. Wolfrum and Bunzl [24] observed increased sorption of Tc upon addition of Tc(VII) to peat suspensions when decreasing the dissolved oxygen concentration and attributed this effect to Tc(IV) incorporation in the organic matter. The literature reports [7,25] also indicate Tc(IV)–HS speciation as the predominant speciation of Tc(IV) in the aqueous phase, in presence of HA over the pH range investigated in the present study. When the pH is increased above 8, sorption of HA on alumina decreases drastically resulting in negligible sorption of Tc(IV) at higher pH values. Formation of neutral hydrolysed Tc species with dissolved humic acid further lowers the sorption percentage. These observations indicate that HA strongly influences the sorption of technetium on alumina colloids under reducing conditions. Lieser and Bauscher [26] studied the sorption of technetium on pyrite and magnetite and found low sorption of technetium in the pH range 3–9 under aerobic conditions. Under reducing conditions, the sorption ratio increased by four orders of magnitude. This enhances
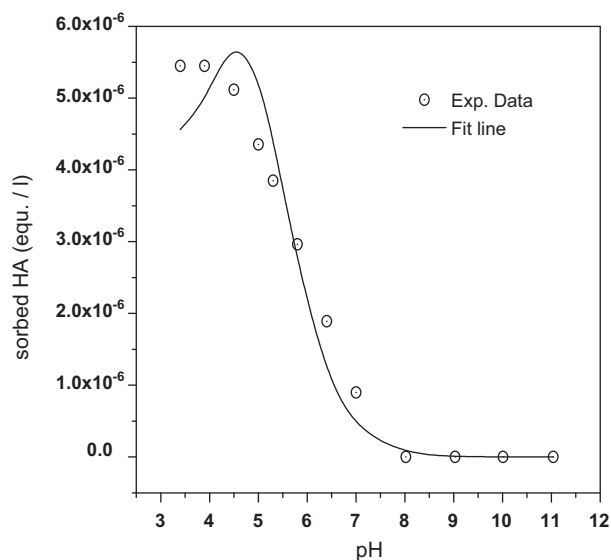
Fig. 6. Sorption of HA on alumina (in 0.1 M NaClO$_4$) over pH 3–11 and SCM fit of the sorption profile.

Table 3
Surface complexation modeling of binary and ternary systems.

Equilibrium reactions	Species optimized	Log K
Tc(IV)–alumina		
$\equiv$AlOH + TcO^{2+} → $\equiv$AlOTcO$^+$	$\equiv$AlOTcO$^+$	5.80
$\equiv$AlOH + TcO^{2+} + H$_2$O → $\equiv$AlOTcO(OH)	$\equiv$AlOTcO(OH)	−1.01
HA–Alumina		
$\equiv$AlOH + HL$_1$ → $\equiv$AlOHHL$_1$	$\equiv$AlOHHL$_1$	4.44
Tc(IV)–HA–Alumina		
$\equiv$AlOH + TcO^{2+} + HL$_1$ → $\equiv$AlOL$_1$TcO	$\equiv$AlOL$_1$TcO	6.79

5.3–6.9 with the maximum value corresponding to the quantitative sorption data. The literature studies have observed strong metal binding characteristics of mineral bound humic substances than in solution [27].

3.4. Simulation of sorption data with surface complexation model

In the ternary system Tc(IV)–HA–alumina, alumina was pree-quilibrated with HA before contacting with Tc(IV). Simulation of HA sorption on alumina carried out with 3-sites discrete model results for the humic acid proton affinity, provided outer sphere complex formed of HL$_1$ on alumina site ($\equiv$AlOHHL$_1$) as the major species responsible for HA sorption (Fig. 6). The log K value obtained for this species is 4.44. Surface complexation modeling of Tc(IV) sorption on alumina is shown in Fig. 5. The log K of the surface species $\equiv$AlOTcO$^+$ and $\equiv$AlOTcO(OH) responsible for Tc(IV) sorption were found to be 5.80 and −1.01, respectively. Binary systems (Tc–alumina, HA–alumina) data were kept fixed during the modeling of ternary system data (Fig. 5). Equilibrium reactions, species, and their formation constants optimized in modeling are given in Table 3. The sorption data of ternary Tc(IV)–HA–alumina system was best fitted with the $\equiv$AlOL$_1$TcO, with the optimized log K = 6.79. In the modeling study of Cu(II) and Pb(II) adsorption on kaolinite based clay minerals individually and in presence of humic acid, metal bridged ternary complex was found to reproduce the sorption data [19]. HA, being macromolecule, offers the possibility of formation of either the metal-bridged or ligand-bridged ternary complexes. In the present study pre-equilibration of alumina particles with HA indicates the greater possibility of formation of ligand-bridged surface complex of Tc(IV), which is validated with the successful modeling with both linear additive as well as surface complexation modeling.

4. Conclusion

Sorption of Tc(VII) by alumina under aerobic conditions is found to be negligible both in absence as well as in presence of HA. Under reducing conditions and in the presence of HA, technetium sorption increases and then decreases with pH in the range of 3–8 with the maximum sorption at pH 6. This has been explained in terms of the reduction of TcO$_4^-$ to Tc(IV), which is strongly complexed by HA, the latter being strongly sorbed on alumina at lower pH. The decrease in the sorption at higher pH values has been attributed to preferential existence of humic acid in the dissolved state and the interaction of hydrolysed Tc(IV) with this dissolved HA. Linear additive modeling of Tc(IV)–HA–alumina system indicates the predominant role of sorbed humic acid in defining technetium sorption. Outer sphere complex formed by HL$_1$ moiety of HA, on alumina site ($\equiv$AlOHHL$_1$) was found to be the major species responsible for HA sorption on alumina whereas Tc(IV) speciation as $\equiv$AlOL$_1$TcO determines the technetium sorption in Tc(IV)–HA–alumina system. The present study, thus, shows that humic acid strongly influences the sorption of technetium on alumina colloids under reducing conditions.

to still higher value in presence of conplexing agent, EDTA, at pH 7–8. Though the authors did not give an explanation for this enhancement, significant sorption of EDTA on the solid surfaces upto higher pH values could be attributed to this observation.

3.3. Simulation of sorption data with linear additive model

The sorption data in ternary system of Tc(IV)–HA–alumina is well explained by the linear additive model as shown by the fit line of Fig. 7. This indicates the predominant role of sorbed humic acid in Tc(IV) sorption. Variation in the log β_2 value in comparison to log β_1 (5.0) is shown in the inset of Fig. 7. It is worth mentioning that log β_1 value used in the calculation represents interaction of all soluble Tc(IV) species with HA. log β_2 value required for fitting the ternary system data varies over
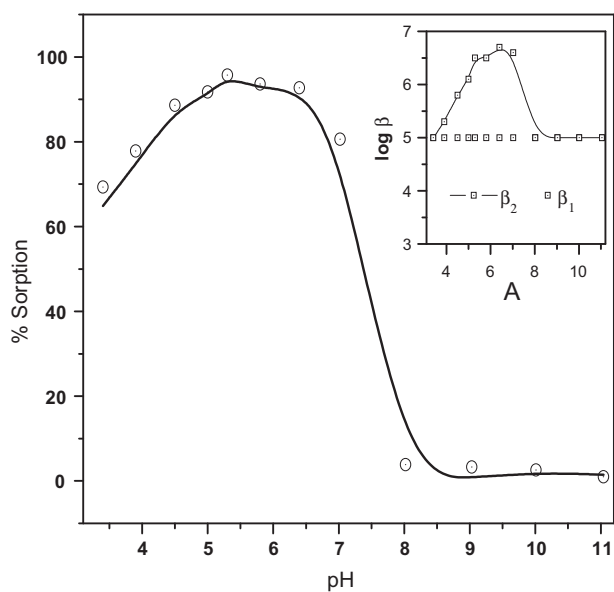

Fig. 7. Sorption of Tc(IV) on alumina (in 0.1 M NaClO$_4$) over pH 3–11 in absence as well as in presence of HA and linear additive modeling of the ternary system. In the inset: variation of log β_2 as a function of pH.

Acknowledgement

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