Comparative Adsorption of Eu(III) and Am(III) on TPD

Journal:	*Environmental Science: Processes & Impacts*
Manuscript ID:	EM-ART-05-2015-000240.R1
Article Type:	Paper
Date Submitted by the Author:	23-Jun-2015
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Environmental Impact

The behaviors of adsorption/desorption of Eu(III) were widely investigated as an analogue to actinides as an example of Am(III) adsorption at solid/water interface, due to the similar ionic radius of Eu^{3+} to the trivalent actinides ions. More evidence and discussion on whether the behaviors of Eu(III) and Am(III) are the same or not are necessary. The comparative adsorption of Eu(III) and Am(III) on TPD was studied at various factors, for example, pH, TPD dose, the presence of FA, and the ion strength in this manuscript to check the comparative adsorption mechanisms between Eu(III) and Am(III). Our findings confirmed the similar adsorption mechanism, however there are still obvious differences between the characteristics of Eu(III) and Am(III) in some special cases, for example, the complex ability with organic matters and adsorption affinity to solid surface. It is very important to the evaluation of actinides' behaviors in environment through analogy.

Comparative Adsorption of Eu(III) and Am(III) on TPD

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Abstract: Comparative adsorption behaviors of Eu(III) and Am(III) on thorium phosphate diphosphate (TPD), i.e., $Th_4(PO_4)_4P_2O_7$, have been studied using batch approach and surface complexation model (SCM) in this study. The results showed that Eu(III) and Am(III) adsorption increased to a large extent with the increase in TPD dose. Strong pH-dependence was observed in both Eu(III) and Am(III) adsorption processes, suggesting that the inner-sphere complexes (ISCs) were possibly responsible for the adsorption of Eu(III) and Am(III). Meanwhile, the adsorption of Eu(III) and Am(III) decreased to a different extent with the increase in ion strength, which was possibly related to the outer-sphere complexes and/or ion exchange. In the presence of fulvic acid (FA), the adsorption of Eu(III) and Am(III) got a large enhancement mainly due to the ternary surface complexes of TPD-FA-Eu^{3+} and TPD-FA-Am^{3+}. SCM showed that one ion exchange ($\equiv S_3Am/Eu$) and two ISCs ($\equiv(XO)_2Am/EuNO_3$ and $\equiv(YO)_2Am/EuNO_3$) seemed more reasonable to quantitatively describe both adsorption edges of Eu(III) and Am(III). Our findings obviously showed that Eu(III) could be a good analogue to study actinides' behaviors in practical terms. However, one should be kept in mind that there are still obvious differences between the characteristics of Eu(III) and Am(III) in some special cases, for instance, the complex ability with organic matters and adsorption affinity to solid surface.

Keywords: Eu(III), Am(III), Adsorption, TPD, SCM, FA

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Introduction

How to safely and acceptably manage the radioactive waste possibly released from nuclear weapon tests and nuclear power plant accidents, for example, Chernobyl and Fukushima catastrophes, has become one of the most pressing problems facing the world nowadays due to their high radioactivity, high toxicity, high mobility, and long half-life in environment. Adsorption/desorption is the most important reaction controlling the fate of radioactive and toxic nuclides in environmental medium. [1-4]

^{241}Am is α and γ-active nuclide (half-life $t_{1/2}$□ = 485 a), which is closely associated with plutonium. ^{241}Am is mainly generated by the β-decay of ^{241}Pu.[5] Since Am is one of the most toxic elements in the radioactive waste, the knowledge of its sorption behaviors then becomes more and more attractive and important. In some previous papers, distribution coefficient (K_d) of Am(III) on red earth, natural hematite, alumina and silica has been investigated using batch approach.[6, 7] The results showed that the presence of fulvic acid (FA) and humic acid (HA) can enhance Am(III) adsorption on natural hematite, alumina, and soil, however a negative influence of Am(III) adsorption on silica was observed in the presence of HA. Actually, the understanding on the speciation and adsorption mechanism of Am(III) at solid/water interface are still scarce due to its extreme high radioactivity and toxicity, which makes the experiment much more difficulty and dangerous.

Generally speaking, Eu(III) has been often taken as a homologue for trivalent actinides ions as like Am(III) and Cm(III), because the ionic radius of Eu^{3+} is almost the same for all the trivalent actinide ions, which results in the similar physical and chemical characteristics.[1, 8-12] Therefore, the behaviors of Eu(III) on oxide mineral, clay, granite, and soil was widely adapted to extrapolate the transport behaviors of Am(III) and other actinides.[13-18] For example, the adsorption of Eu(III) on attapulgite was strongly dependent on pH and ionic strength, and independent of temperature. In the presence of FA/HA, Eu(III) sorption was enhanced at $pH < 4.0$, decreased at pH range of 4.0-6.0, and then increased again at $pH > 7.0$. Extended X-ray absorption fine structure (EXAFS) analyses indicated that pH can strongly affect the interaction between HA and Eu(III), and that different complex species also formed for the different addition sequences of HA and Eu(III) to attapulgite suspension.[15]

As well known, phosphate minerals with very sparing solubility and strong complexation ability to radionuclides are potential candidates as host materials or engineered barrier additives. Some of them, like apatite and monazite, are stable through a geological scale. Moreover, it has been proven that thorium phosphate diphosphate (TPD) owns simultaneously phosphate and diphosphate groups, which are the two different sites contributing to the adsorption behaviors of radionuclides. [19-20] Therefore it is benefit for us to compare the adsorption behaviors of Eu(III) and Am(III). In this work, the adsorption behaviors of Am(III) and Eu(III) on TPD were studied using both batch and modeling approaches to confirm whether adsorption mechanisms of Eu(III) and Am(III) are indeed similar or not. The proposals of this work are: (1) to study the effects of experimental conditions on the adsorption of Eu(III) and Am(III) on TPD surface; (2) to compare the adsorption isotherms of Eu(III) and Am(III) ; (3) to estimate the adsorption species of Eu(III) and Am(III) on TPD using surface complexation model (SCM); (4) to confirm whether Eu(III) can be used as an analogue to Am(III) or other actinides.

Experimental

TPD was prepared strictly as following the previous literatures.[8, 9, 22] Prior to experiment, TPD was stirred with distilled water for 24 hours, and then washed with distilled water until a constant electric conductivity reached. Thus washed TPD was dried at 120 ^{o}C for 5 hours, passed through a 0.125 mm mesh sieve; finally was kept in glass dish placed into desiccator. The synthesized TPD has been confirmed by XRD patterns (data not shown) and the surface area of N_2-BET was about 1.3 m^2/g.

The stock solution of ^{241}Am(III) was a generous of gift from the Institute of Modern Physics, Chinese Academy of Sciences (CAS), whereas $^{152\text{-}154}$Eu(III) was purchased from the China Atomic Energy Agency (CAEA). The nuclide purity of ^{241}Am and $^{152+154}$Eu were above 99%. FA extracted from weathered coal (Gongxian, Henan Provence) have been used and characterized in our previous paper [23]. All other chemicals used in this study were of analytical reagent grade.

Experimental procedures of adsorption were essentially identical to those employed in previous papers.[24-28] Batch experiments were performed in 10 mL polyethylene test tubes (14×100 mm), which had an inner surface (geometrical) of 33±1 cm^2. It was found that the adsorption of $^{152+154}$Eu(III) and ^{241}Am(III) on the wall of polyethylene tubes could be negligible under the experimental conditions conducted. The γ-activities of ^{241}Am solution aliquots were measured using a counter with a well type NaI(Tl) detector, and the radioactivity of $^{152+154}$Eu was determined by liquid scintillation counting using a Packard 3200 TR/AB Liquid Scintillation analyzer (PerkinElmer). The scintillation cocktail was ULTIMA GOLD AB (Packard). Finally, the concentration of Eu and Am were calculated from the count difference in the aqueous phase before and after adsorption. All the experimental data were the averages of duplicate experiment, and the average relatively error is less than 5%.

Results and discussion

Kinetic study on Eu(III) and Am(III) adsorption

Adsorption of Eu(III) and Am(III) on TPD as a function of contacted time are shown in Figs.1 and 2, respectively. The adsorption of Eu(III) quickly increased from 0 to 80% within 10 hours, and the adsorption equilibrium of Am(III) on TPD can achieve within 16 hours (Fig. 2). Moreover, the adsorption of Am(III) on TPD maintains around 70%, which is a little bit lower than that of Eu(III). It might be due to that the adsorption experiment of Am(III) is conducted at pH 4.1 a little bit higher than that of Eu(III) (pH~3.8), where the adsorption of Am(III) and Eu(III) was very sensitive to pH. The kinetic results suggested that the main chemisorption was dominant for Am(III) and Eu(III) on TPD.[24, 27] In addition, both Eu(III) and Am(III) adsorption on TPD were following the pseudo-second-order model (data not shown), which suggested that the sorption mechanisms of Eu(III) and Am(III) might be similar to each other.

Effect of solid-to-liquid (*S/L*)

The effect of *S/L* on the adsorption of Eu(III) and Am(III) has been shown in Fig. 3. Am(III) adsorption increased from 47.7% to 95.8% as the ratio of *S/L* increased from 1.67 to 20 g/L, and Eu(III) adsorption increased from 34.8% to 96.3%. The increasing adsorption of Eu(III) and Am(III) was attributed to the increasing dose of TPD that can supply more adsorption sites to adsorb Eu(III) and Am(III).[28, 29]

K_d of Eu(III) and Am(III) as a function of *S/L* were also plotted in Fig. 4. K_d can be calculated from the concentration of adsorbate in suspension (C_0) and that of adsorbate in supernatant (C_{eq}) according to the following equation:

$$K_d = \frac{C_0 - C_{eq}}{C_{eq}} \times \frac{V}{m} \qquad (1)$$

where V is the volume of the solution and m is the mass of TPD. Although the adsorption percent of Am(III) is seemly higher than Eu(III) on TPD at different *S/L*, no obvious difference could be observed in K_d value between Eu(III) and Am(III) (Fig. 4). Moreover, it should be noted that K_d value is strongly increased with the increasing of S/*L*, by contrast, the physicochemical property of K_d, in principle, is independent of the ratio of *S/L*. It might be related to the properties of TPD colloids in the studied system changing with the increasing of *S/L,* whereas more information and evidences are needed especially at micro-scale in future.

Effect of pH

As it is well known, pH is the most important factor controlling radionuclides behaviors in environment. The adsorption edges of Eu(III) and Am(III) on TPD were shown in Fig. 5. With the increasing of pH, it was found that the adsorption of Eu(III) and Am(III) on TPD quickly increased and then maintained a level, almost 100%, above pH~5.0. The strongly pH-dependent adsorption of Am(III) and Eu(III) possibly suggested that a complicated adsorption mechanism, for example, ion exchange and surface complexation, contributed to their adsorption, which is really similar to the adsorption of Eu(III) and Am(III) on attapulgite.[1] Where the initial concentrations of Eu(III) and Am(III) were too small to form precipitation or surface precipitation, it can infer no contribution from precipitation to Eu(III) and Am(III) adsorption on TPD. The adsorption mechanism of Eu(III) and Am(III) on TPD will be discussed in the following section using SCM.

The point of zero charge (pH_{pzc}) of TPD is about 6.8.[9] TPD owns a positive charged surface at pH less than 6.8, whereas negative charges above pH 6.8. Moulin et al.[30] have reported that when ionic strength of 0.1mol/L $NaClO_4$, $pCO_2=10^{-3.5}$atm, Am^{3+} was almost the sole species at pH less than 5.0; above pH 6.0, the hydrolysis species of Am(III) started to forming present as $Am(OH)^{2+}$, $Am(OH)^{2+}$, $Am(OH)_2^{+}$, and $Am(OH)_3$. Meanwhile at pH<6, Eu^{3+} in the aqueous solution is the predominant species[1]. As shown in Fig. 5A, the adsorption of Eu(III) and Am(III) occurred at low pH and a sharp increase in pH range of 2.0-6.0. It was in terms of the electrostatic repulsion between the positive charged surface of TPD and the positive charged species Eu^{3+} and Am^{3+} at low pH, and then such repulsion will be gradually decreased as pH increased.

As shown in Fig. 5A, a higher adsorption of Am(III) on TPD in comparison with Eu(III) was observed in pH range of 2.0-5.0. The trends of K_d for Am(III) and Eu(III) estimated in the whole pH range were shown in Fig. 5B, one can see that the adsorption of Am(III) were indeed higher than that of Eu(III) below pH 6.0, which is basically similar to the adsorption edges of Eu(III) and Am(III) on TPD in the Fig. 5A. The higher K_d of Am(III) might be raised by one magnitude order lower concentration of Am(III) added in the adsorption experiment in comparison with Eu(III), although K_d is normally independent of adsorbate concentration especially at low concentration as well as adsorbent dose.

Effect of ion strength

Effects of ionic strength on the adsorption isotherms of Eu(III) and Am(III) are shown in Fig. 6 A and B, respectively. It was found that the K_d of Am(III) and Eu(III) was strongly dependent on ion strength at the observed condition, which suggested that the increasing concentration of K^+ can reduce the adsorption of Am(III) and Eu(III) as an efficient competitive cation.

The adsorption isotherms of Am(III) and Eu(III) on TPD basically exhibited a linear relationship and the correlation coefficients (R^2) were over than 0.9000 with an exception of Eu(III) adsorption at 0.1 mol/L KNO_3 solution (R^2 = 0.7632). Furthermore, the correlation coefficients of Eu(III) and Am(III) were decreasing with the increase of ion strength as shown in the Fig. 6 A and B, which might indicate the changes in adsorption species or mechanism of Eu(III) and Am(III) at different ion strength. Outer-sphere complexes (OSCs) and ion exchange might be responsible for the ion strength-dependence rather than the inner-sphere complexes (ISCs), because the OSC and ion exchange are very sensitive to ion strength, whereas ISCs is mainly affected by pH.[1, 15, 27]

As discussed above, it can be deduced that the adsorption of Am(III) and Eu(III) was following empirical distribution model, i.e., K_d model, therefore K_d can be easily obtained from the slope of their linear relationships. In order to compare both adsorption behaviors of Am(III) and Eu(III), the effect ion strength on K_d was plotted in Fig. 7. One can be seen that the K_d of Am(III) adsorption on TPD was decreased so quickly from 4335 to 245 mL/g as ion strength increased from 0.01 to 0.1 mol/L

KNO_3 solution. Similar decreasing trend of Eu(III) adsorption on TPD was observed as like the case of Am(III), however the K_d for Eu(III) was only decreased so slowly from 2681 to 1169 mL/g, which indicated that there were some difference in the adsorption affinity for Eu(III) and Am(III).

Similar ion strength-dependent phenomena were often observed in the other cases.[31, 32] Guo et al.[31] reported that the adsorption of Th(IV) on TiO_2 was decreased with the increasing ionic strength from 0.01 to 0.05 mol/L KNO_3. In contrast, the positive and independent effects of ionic strength were found in the previous researches.[7, 33] Tao et al.[7] found Am(III) adsorption on alumina gradually increased with the increase in ionic strength from 0.01 to 2.0 mol/L $NaNO_3$, whilst the Am(III) adsorption on silica increased in the range of ion strength from 0.001 to 0.1mol/L $NaNO_3$ and remained practically constant from 0.1 to 2.0 mol/L $NaNO_3$. Moreover, the adsorption of Eu^{3+} onto alumina is practically independent of ionic strength in range of 0.5 to 4.0 mol/L $NaNO_3$ solution.[33]

Effect of FA

Due to the carboxylic and phenolic moieties distributed through the entire macromolecule, FA is generally negatively charged in the natural environment. The widely distributed FA is important for the fate of heavy metal ions and radionuclides in environment because of its strong complex capability that can change metal ions and radionuclides' mobility and bioavailability to a large extent.[2, 15] Effects of FA on the adsorption of Eu(III) and Am(III) onto TPD were shown in Fig. 8. The results showed that adsorption isotherm of Eu(III) and Am(III) on TPD in the presence of FA was much higher than that in the binary system with FA-free, suggesting the presence of organic matters can enhance the adsorption of Eu(III) and Am(III) to a large extent and can reduce their mobility in environment. Two possible reasons could explain the enhancement of FA on Eu(III) and Am(III) adsorption. One possibility is that FA covered TPD surface could reduce the surface charge density that is very important factor to control Eu(III) and Am(III) adsorption at acidic condition. The other possible reason might be that FA bounded TPD can supply high amounts of function groups from FA molecules to form a very stable complexes with Eu(III) and Am(III). In this case, one kind of ternary surface complexes as TPD-FA-Eu^{3+} and/or TPD-FA-Am^{3+} can form on the TPD/FA hybrids. Moreover, it must be noted that in the ternary system FA can provoke the K_d of Am(III) (4149 mL/g) as ten times high as the binary system (without FA, K_d ~435 mL/g), however, for the case of Eu(III) only two times higher K_d was found in the presence of FA. It might indicate that the complex ability of FA-Am^{3+} is much larger than that of FA-Eu^{3+}. On the other hand, so large different enhancement between Am(III) and Eu(III) suggested that the ternary surface complexes are the main reason to the increasing adsorption of Eu(III) and Am(III) on TPD in the presence of FA.

Comparative adsorption mechanism of Eu(III) and Am(III)

As yet, there is still scarce to discuss whether it is completely reliable that the adsorption-desorption behaviors of Eu(III) and Am(III) are similar, because adsorption/desorption behaviors of lanthanides and actinides are quite complicated processes. Fig. 9 A and B show the adsorption species of Am(III) and Eu(III) on TPD using CCM and MINTEQ 3.0 code. Drot et al.[8, 9] had conducted the potentiometric titration and X-ray photon spectrum to confirm the possible adsorption sites on TPD surface. The result showed that protonation and deprotonation reactions of strong adsorption site (≡XOH, presenting for PO_4 group) and weak adsorption site (≡YOH, representing for P_2O_7 group) can describe the titration curve in the constant capacitance model (CCM), and the relative parameters during the fit have been list in the Table 1. However, in this work, one exchange site was included in our modeling because of the possible occurrence of exchange reactions between Th^{4+} and K^+ or other cations.

One can see in Fig. 9A that the adsorption species of Am(III) was controlled by one ion exchange ($\equiv S_3Am$) at pH < 3.0 and two ISCs ($\equiv(XO)_2AmNO_3$ and $\equiv(YO)_2AmNO_3$) above pH~3.0. As an expected that basic same adsorption species on TPD surface were got as well as the case of Am(III) (Fig. 9B). The result clearly showed that the ion exchange played important role to different extent in Eu(III) and Am(III) adsorption on TPD in the low pH range, which is coincided well with the discussion of ion strength-dependence above. However, Drot et al.[9] only found two ISCs, i.e. $\equiv(XO)_2EuNO_3$ and $\equiv(YO)_2EuNO_3$ for Eu(III) adsorption on TPD. Ion exchange not taken into account might be due to the narrow adsorption edge estimated from pH~3.5 to pH~7.0. Therefore, the ion exchange can not be negligible for Eu(III) and Am(III) adsorption especially in the low pH range. Moreover, it is worth to note that the adsorption reaction constants (K^{int}) of Am(III) seems much larger than that of

Eu(III), which suggested that Am(III) has much higher adsorption affinity to TPD than Eu(III) (Table 1). Therefore, the reason of higher adsorption of Am(III) observed in Figs. 4 and 5 becomes more clear that it is controlled by the chemical properties of Am(III) rather than the different concentration used in the both systems.

Conclusion

In this study, the adsorption behaviors of Eu(III) and Am(III) were studied and compared at various conditions such as pH, ion strength, and contact time to confirm the adsorption mechanisms of Eu(III) and Am(III). The adsorption of Eu(III) and Am(III) on TPD was strong pH-dependence suggesting that ISCs might be responsible for the adsorption of Eu(III) and Am(III). Moreover, Eu(III) and Am(III) adsorption on TPD was decrease to a large extent with the increase in ion strength, which can at least confirm the ion exchange and/or OSCs contributing to Eu(III) and Am(III) adsorption to a certain extent. It is a very important finding which was neglected in previous literatures. The presence of FA can enhance Eu(III) and Am(III) adsorption on TPD mainly due to the ternary surface complexes (TPD-FA-Eu^{3+} and TPD-FA-Am^{3+}), however the enhancement extent of Am(III) is much larger than that of Eu(III). One ion exchange ($\equiv S_3Am/Eu$) and two ISCs ($\equiv(XO)_2Am/EuNO_3$ and $\equiv(YO)_2Am/EuNO_3$) were the main adsorption species of Eu(III) and Am(III) on TPD in the whole observed pH range. As discussed above, the adsorption behaviors of Eu(III) were basically similar to Am(III), which indicated that Eu(III) could be a good candidate to model actinides' behaviors in environment. However, basing on our findings it must be careful that there are still some large differences between Eu(III) and Am(III), for example, their complex ability with organic matters and adsorption affinity to solid phase, when we try to extrapolate actinides' behaviors from that of Eu(III).

Acknowledgements: We thank the reviewers for their great contribution in improving the quality of this work. This work got supporting from the "100-Talent" Program from Chinese Academy of Sciences (CAS) in Lanzhou Center for Oil and Gas Resources, Institute of Geology and Geophysics and the National Natural Science Foundation of China (No. 41402129). The authors greatly acknowledge Dr. Li P. (Lanzhou University) for the efforts on the SCM.

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Table 1 Summary of modeling parameters of Eu(III) and Am(III) adsorption on TPD using CCM

1. Surface properties of TPD [9]	
Capacitance (F) = 3.08 F/m^2	
$T[\equiv XOH]^a = 6.1$ mmol/g, $T[\equiv YOH]^b = 1.9$ mmol/g, $T[\equiv SK] = 2.68$ mmol/g	
Reactions	logK^{int}
$\equiv XOH \leftrightarrow \equiv XO^- + \mathrm{H}^+$	-7.80
$\equiv XOH + \mathrm{H}^+ \leftrightarrow \equiv XOH_2^+$	6.50
$\equiv YOH \leftrightarrow \equiv YO^- + \mathrm{H}^+$	-6.30
$\equiv YOH + \mathrm{H}^+ \leftrightarrow \equiv YOH_2^+$	5.40
$\equiv SK + \mathrm{H}^+ \leftrightarrow \equiv SH + \mathrm{K}^+$	-0.85 (this work)
2. Description of Eu(III) adsorption species	
$2\equiv XOH + \mathrm{Eu}^{3+} + \mathrm{NO}_3^- \leftrightarrow \equiv(XO)_2EuNO_3 + 2\mathrm{H}^+$	-0.40 (this work)
$2\equiv YOH + \mathrm{Eu}^{3+} + \mathrm{NO}_3^- \leftrightarrow \equiv(YO)_2EuNO_3 + 2\mathrm{H}^+$	-0.15 (this work)
$3\equiv \mathrm{S}K + \mathrm{Eu}^{3+} \leftrightarrow \equiv \mathrm{S}_3Eu + 3\mathrm{K}^+$	-1.70 (this work)
3. Description of Am(III) adsorption species	
$2\equiv XOH + \mathrm{Am}^{3+} + \mathrm{NO}_3^- \leftrightarrow \equiv(XO)_2\mathrm{Am}NO_3 + 2\mathrm{H}^+$	0.75 (this work)
$2\equiv YOH + \mathrm{Am}^{3+} + \mathrm{NO}_3^- \leftrightarrow \equiv(YO)_2\mathrm{Am}NO_3 + 2\mathrm{H}^+$	0.82 (this work)
$3\equiv \mathrm{S}K + \mathrm{Am}^{3+} \leftrightarrow \equiv \mathrm{S}_3\mathrm{Am} + 3\mathrm{K}^+$	-0.99 (this work)
4. The reaction of Eu(III) and Am(III) in aqueous phase [c]	
$\mathrm{Eu}^{3+} + \mathrm{NO}_3^- \leftrightarrow \mathrm{EuNO}_3^{2+}$	-4.60
$\mathrm{Eu}^{3+} + \mathrm{H}_2\mathrm{O} \leftrightarrow \mathrm{Eu(OH)}^{2+} + \mathrm{H}^+$	-7.64
$\mathrm{Eu}^{3+} + 2\mathrm{H}_2\mathrm{O} \leftrightarrow \mathrm{Eu(OH)}_2^+ + 2\mathrm{H}^+$	-15.10
$\mathrm{Eu}^{3+} + 3\mathrm{H}_2\mathrm{O} \leftrightarrow \mathrm{Eu(OH)}_{3(aq)} + 3\mathrm{H}^+$	-23.70
$\mathrm{Am}^{3+} + \mathrm{NO}_3^- \leftrightarrow \mathrm{AmNO}_3^{2+}$	1.30
$\mathrm{Am}^{3+} + \mathrm{H}_2\mathrm{O} \leftrightarrow \mathrm{Am(OH)}^{2+} + \mathrm{H}^+$	-6.50
$\mathrm{Am}^{3+} + 2\mathrm{H}_2\mathrm{O} \leftrightarrow \mathrm{Am(OH)}_2^+ + 2\mathrm{H}^+$	-14.09
$\mathrm{Am}^{3+} + 3\mathrm{H}_2\mathrm{O} \leftrightarrow \mathrm{Am(OH)}_{3(aq)} + 3\mathrm{H}^+$	-25.69

[a] $T[\equiv XOH] = [\equiv XOH_2^+] + [\equiv XOH] + [\equiv XO^-]$; [b] $T[\equiv YOH] = [\equiv YOH_2^+] + [\equiv YOH] + [\equiv YO^-]$; [c] The thermodynamic data were cited directly from the MINTEQ 3.2 code.

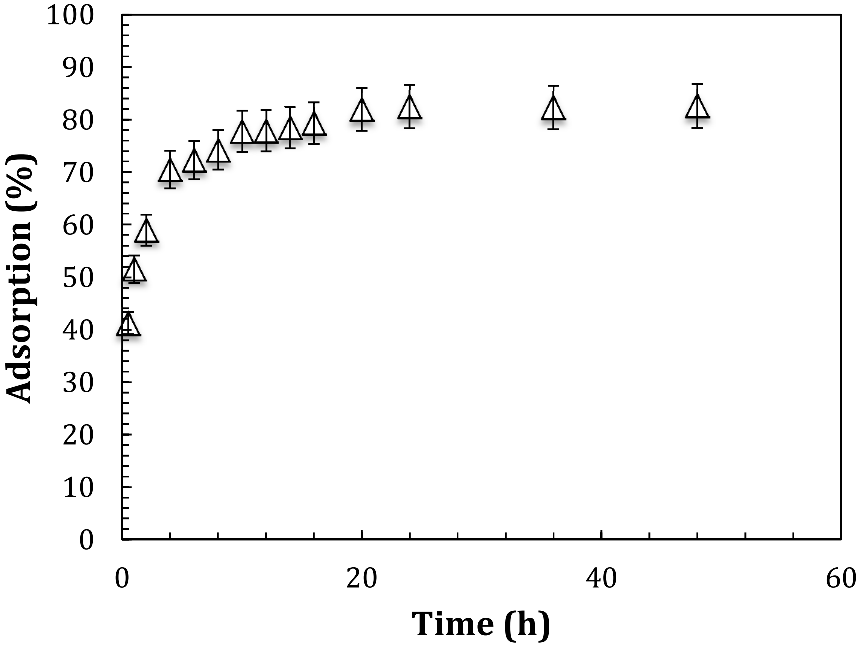


Fig.1 Variation in adsorption percentage of Eu(III) on TPD as a function of contact time. *S/L* = 10g /L, C $_{Eu}{}^{o}$ = 4.8×10^{-8}mol/L, I = 0.1 mol/L KNO_3, pH=4.1, T = 25 °C.

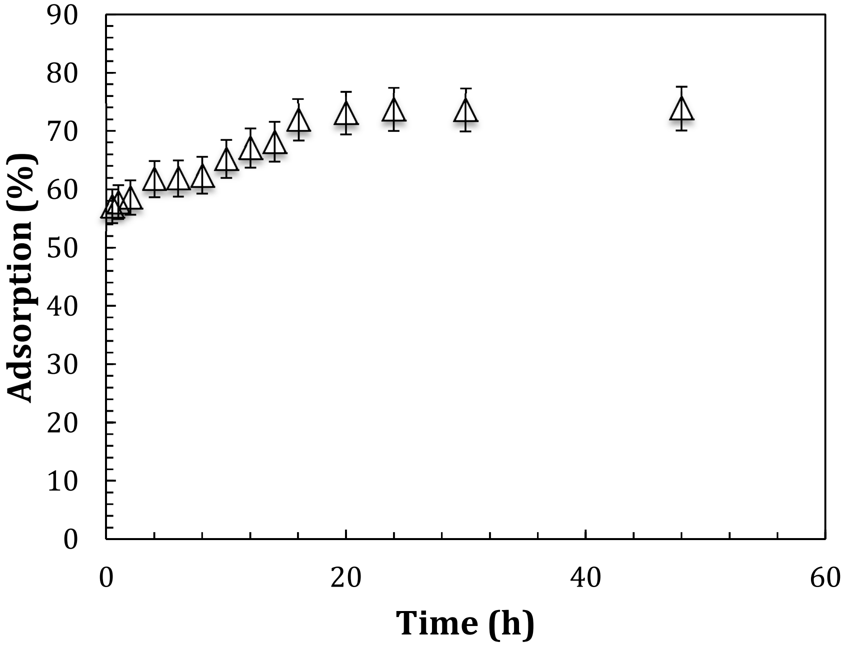


Fig. 2 Variation in adsorption percentage of Am(III) on TPD as a function of contact time. *S/L* = 10 g/L, $C_{Am}{}^{o}$ = 2.3×10^{-9}mol/L, I = 0.1 mol/L KNO_3, pH=3.8, T = 25 °C.

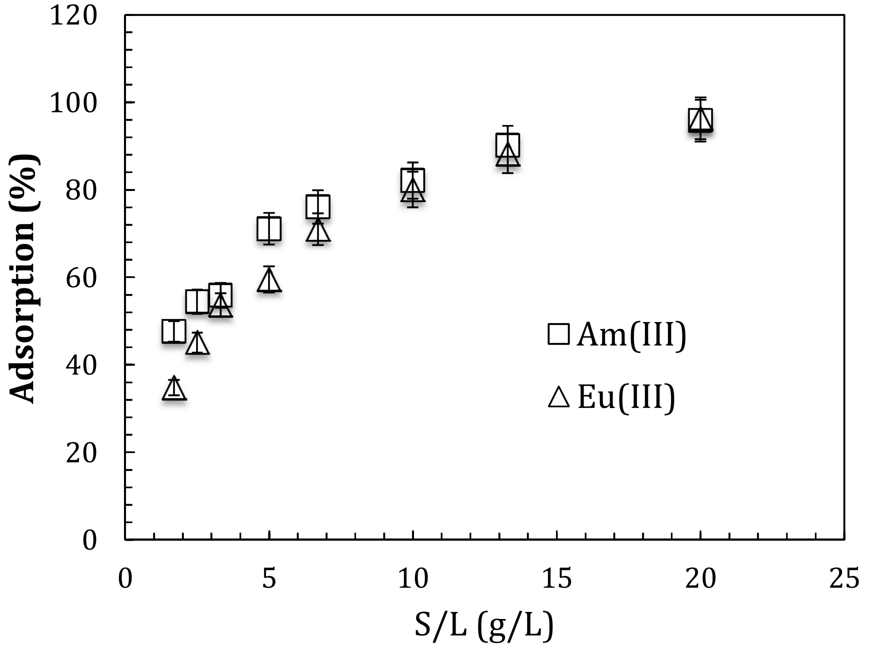


Fig. 3 Effect of solid-to-liquid ratio (*S/L*) on the adsorption of Eu(III) and Am(III). $C_{Eu}^{o} = 4.8\times10^{-8}$ mol/L, $C_{Am}^{o} = 2.3\times10^{-9}$ mol/L, $I = 0.1$ mol/L KNO_3, $pH = 3.9$, $T = 25$ °C.

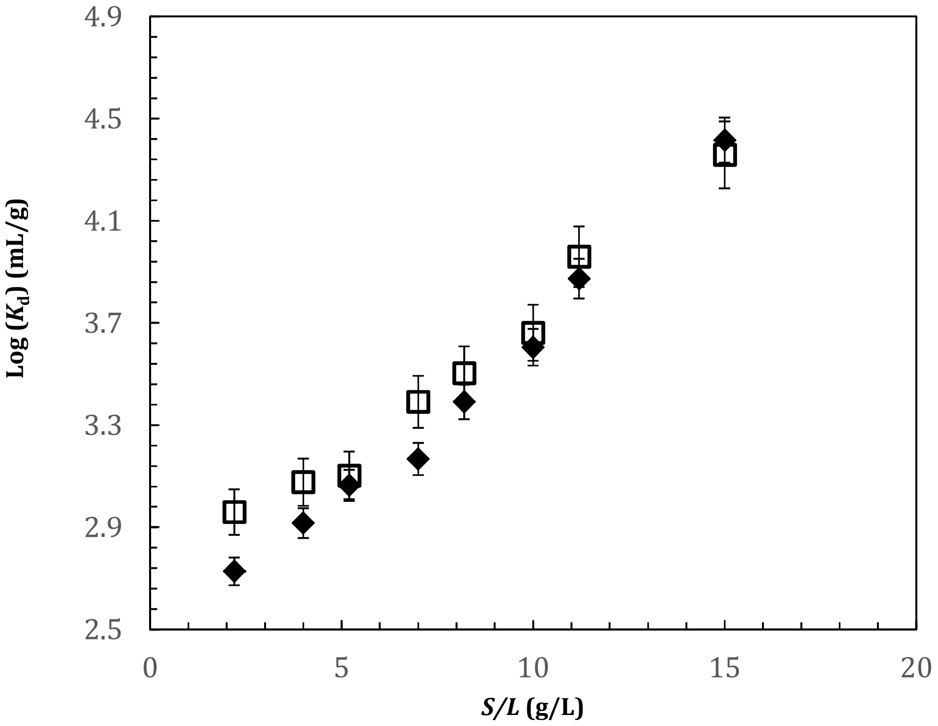


Fig. 4 Relationship between distribution coefficient and solid-to-liquid ratio (S/L). □: Eu(III), □: Am(III), I = 0.1 mol/L KNO_3, $pH = 3.9$, $T = 25$ °C.

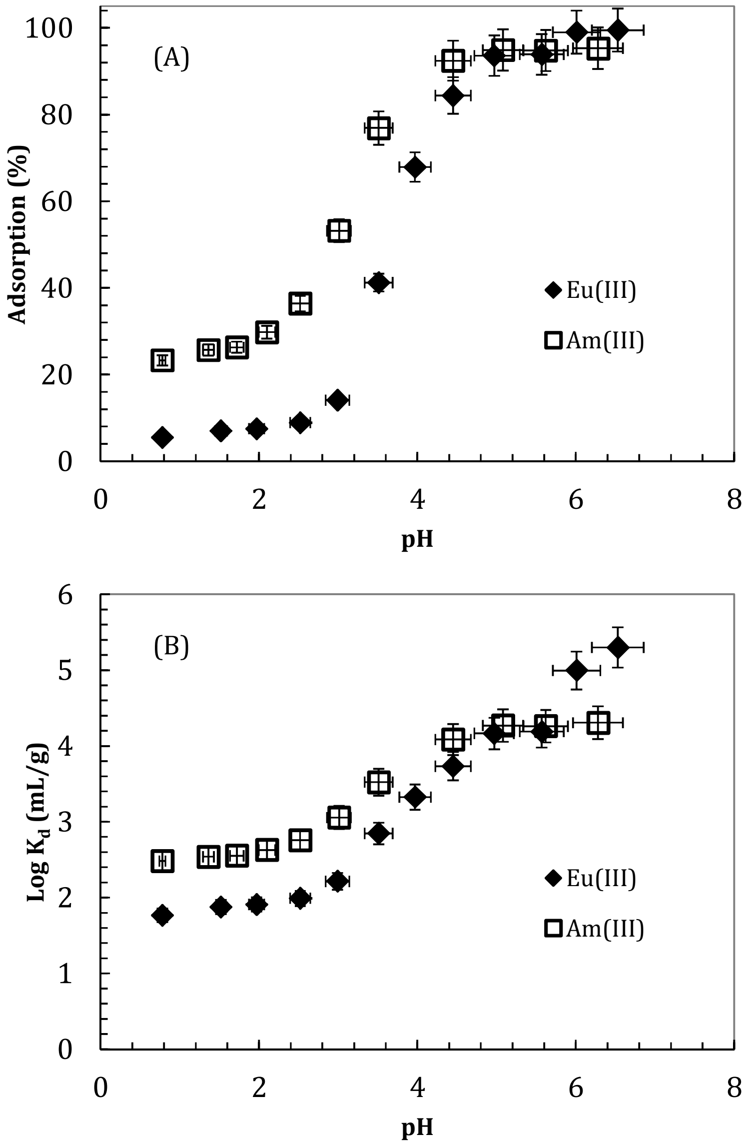


Fig. 5 (A) Adsorption edge of Eu(III) and Am(III) on TPD; (B) K_d patterns of Am(III) and Eu(III) adsorption on TPD as a function of pH. $C_{Eu}^{o} = 4.8\times10^{-8}$ mol/L, $C_{Am}^{o} = 2.3\times10^{-9}$ mol/L, $I = 0.1$ mol/L KNO_3, $S/L = 10$ g/L, $T = 25$ ^{o}C.

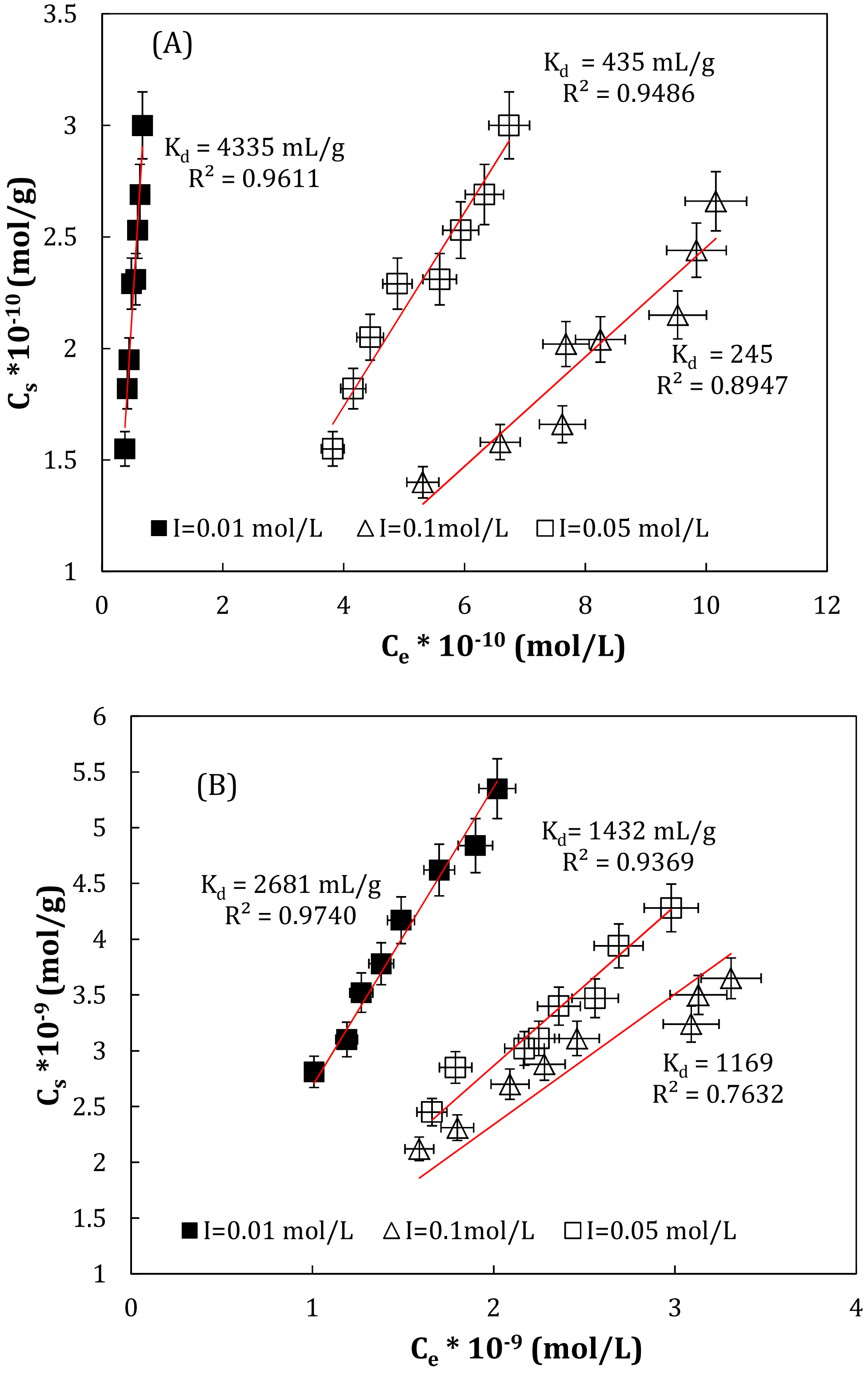


Fig. 6 Adsorption isotherms of Am(III) (A) and Eu(III) (B) on TPD surface at different ionic strength (KNO$_3$ solution with different concentration). *pH*=3.2, *T* = 25 °C; *S/L* = 10 g /L.

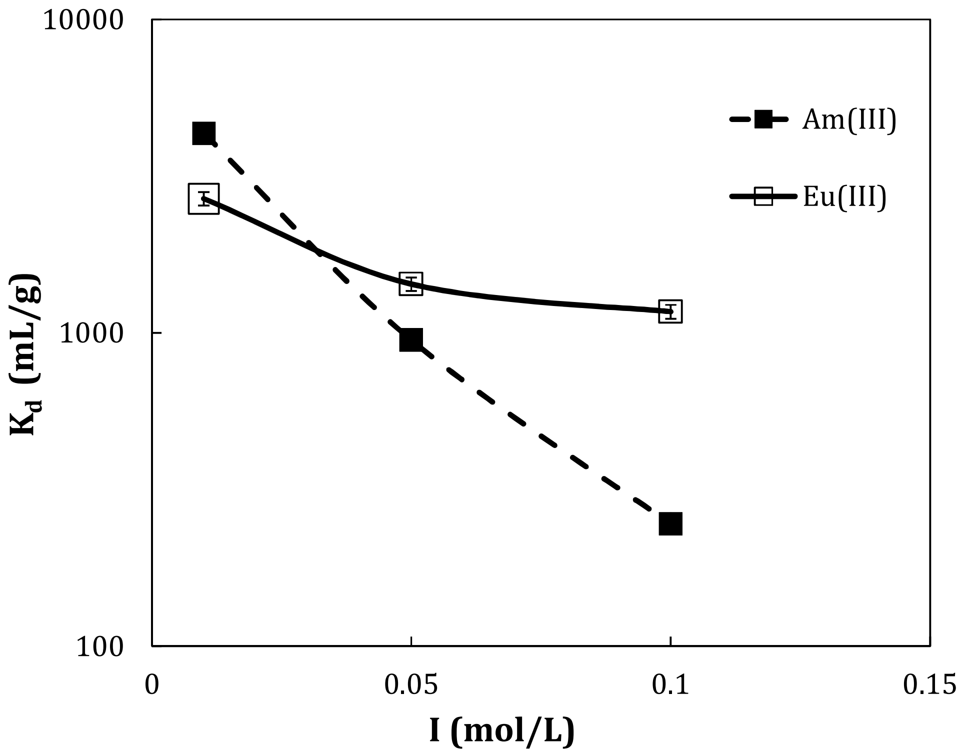
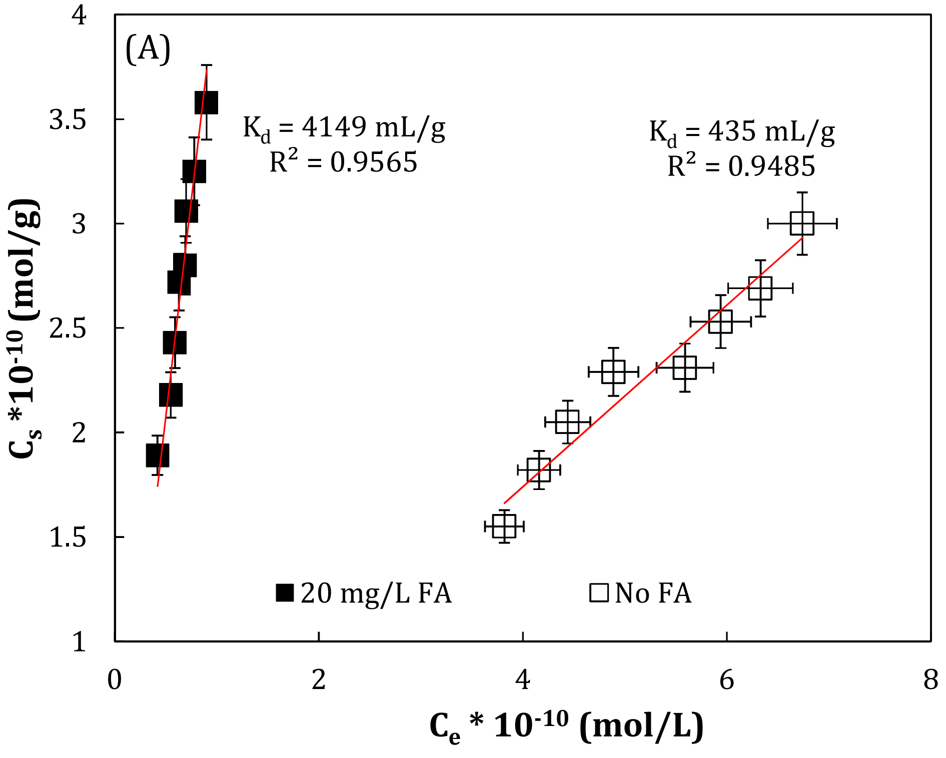


Fig. 7 Effect ion strength on the adsorption of Am(III) and Eu(III) on TPD surface. *pH*=3.22, *T* = 25 °C; *S/L* = 10 g /L.



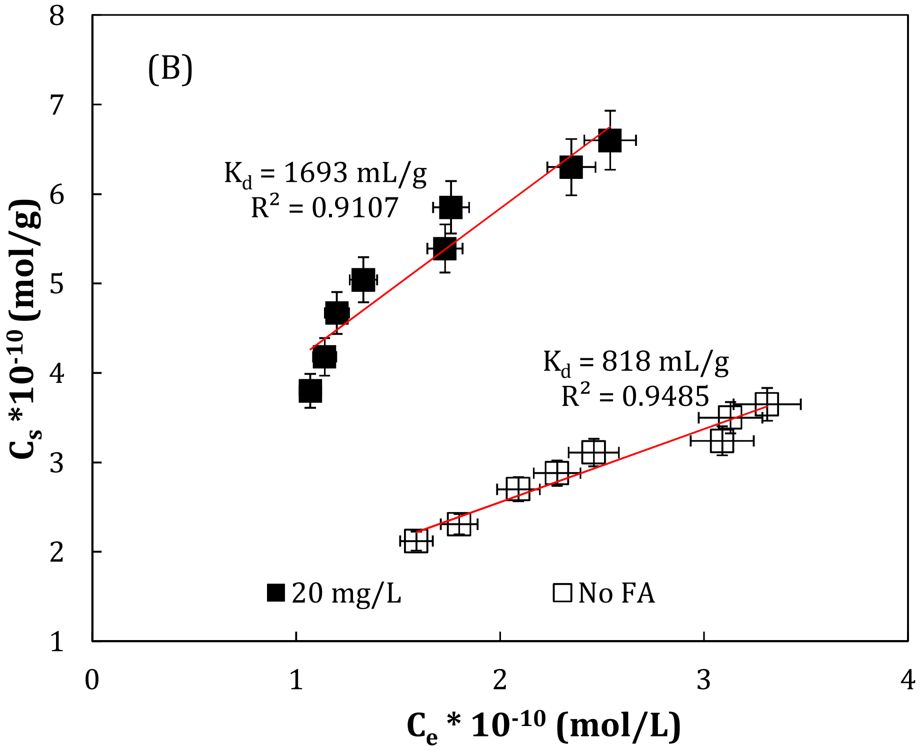
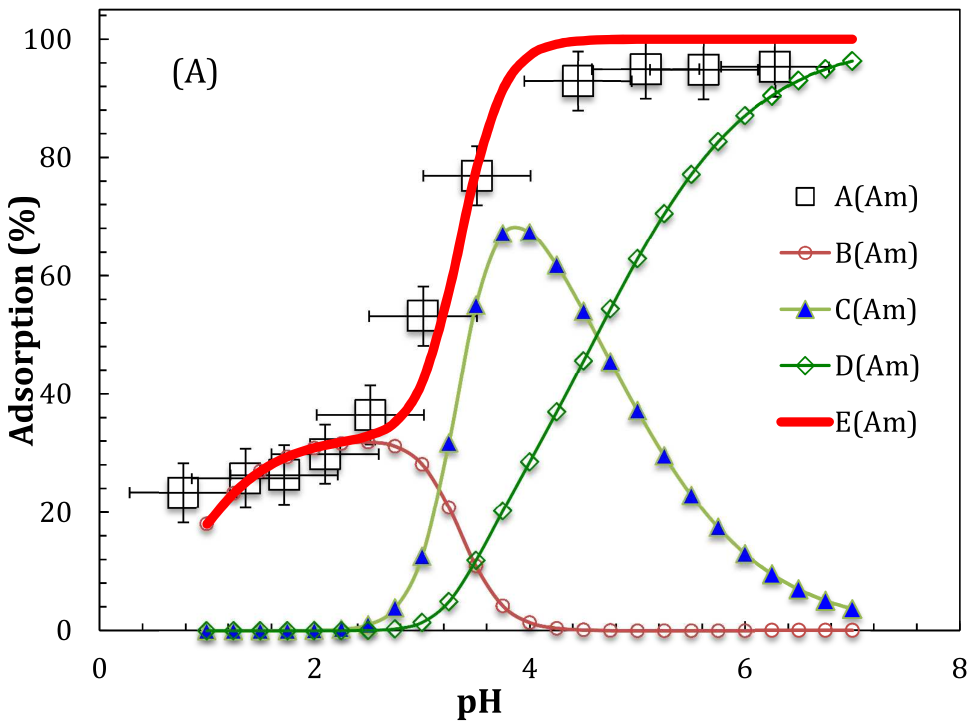


Fig. 8 Effect of FA on the adsorption isotherms of Am(III) (A) and Eu(III) (B). I = 0.1mol/L KNO$_3$, S/L = 10 g /L, pH = 3.0 ± 0.2, T = 25^{o}C.



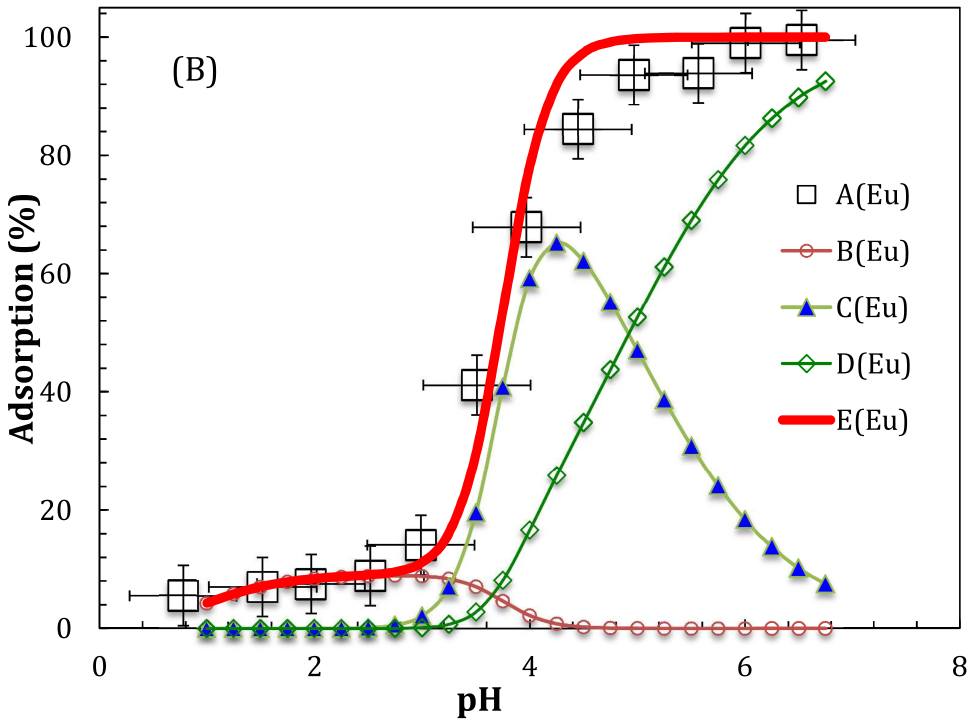


Fig. 9 The comparative adsorption species of Am(III) (A) and Eu(III) (B) on TPD surface as a function of pH. $C_{Eu}{}^{o} = 4.8\times10^{-8}$ mol/L, $C_{Am}{}^{o} = 2.3\times10^{-9}$ mol/L, $I = 0.1$ mol/L KNO_3, $S/L = 10$ g /L, $T = 25$ °C. A(Am): Experimental data, species B(Am): $\equiv S_3Am$, species C(Am): $\equiv(YO)_2AmNO_3$, species D(Am): $\equiv(XO)_2AmNO_3$, E(Am): Fitting data; A(Eu): Experimental data, species B(Eu): $\equiv S_3Eu$, species C(Eu): $\equiv(YO)_2EuNO_3$, species D(Eu): $\equiv(XO)_2EuNO_3$, E(Eu): Fitting data.