



Letter to the Editor

Selective adsorption of trivalent actinides from lanthanides onto activated carbons in acidic aqueous solution

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ABSTRACT

Adsorption of trivalent actinides (An(III)) and lanthanides (Ln(III)) in acidic aqueous solution using activated carbons was investigated. Activated carbons exhibited significantly selective adsorption to An(III) over Ln(III) in acidic aqueous solution from about pH 1–4, independently of the starting materials, activation methods and specific surface areas.

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The separation of long-lived trivalent actinides (An(III)) from lanthanides (Ln(III)) and transmutation of An(III) via neutron irradiation enables the reduction of radio-toxicity of high-level radioactive waste produced by the reprocessing of spent nuclear fuel. The selective separation of An(III) from Ln(III) is, however, a significant challenge because of the similarity of their chemical properties such as ionic radii and ionic binding nature. A variety of ligands that can distinguish An(III) from Ln(III) have been developed for solvent extraction in the past decades, but only a few of them could successfully separate An(III) from Ln(III), and those have problems such as poor solubility in organic solvent or instability in acidic conditions [1]. We have been focusing on the application of chromatographic separation of An(III) from Ln(III), in which a selective ligand for An(III) is incorporated into the design of ligands and materials [2].

Recently, we have discovered that activated carbon (AC) can separate An(III) from Ln(III) by adsorption. Despite the removal methods for palladium, and technetium by means of AC were established [3,4] and some studies on the adsorption behavior of Ln(III) onto AC have been reported heretofore [5–8], most studies have attempted to utilize AC for the removal of these metal cations from aqueous solution but not for the separation of metal cations. In general, in order to employ AC for the recovery of metal cations, oxidized functional groups, such as carboxylates, phenolates or lactones are attached to the surface of AC by pre-treatment with concentrated acids to enhance the adsorption ability of metal cations from aqueous solution [9,10]. In this study, the adsorption behavior of An(III) and Ln(III) was investigated using five types of ACs made from different starting materials and activation methods without pre-treatment.

Adsorption of Am(III) and Eu(III) in the static state was investigated by a batch method to determine their distribution coefficients

(K_d) to AC. Varied with starting materials and activation methods; five types of AC were used as obtained. AC-1, AC-2 and AC-5 were purchased from Wako Chemical Co. (Code Nos. 035-18081, 034-02125 and 031-02135, respectively). AC-3 (Code: M010) and AC-4 (Shirasagi C) were offered by Calgon Mitsubishi Chemicals Co. and Japan EnviroChemicals Ltd., respectively. Carbon material (50 mg) was put in a 6 ml glass vial and contacted with 2 ml of nitric media containing ^{241}Am and ^{152}Eu for 3 h. The radioactivities of ^{241}Am and ^{152}Eu in the aqueous phase before and after the adsorption were measured using γ -ray spectrometer. The K_d was calculated by the equation, $K_d = (C_0 - C)V_s/CM_R$, where C_0 and C indicate the radioactivities of M(III) in the aqueous phase before and after adsorption, respectively. V_s indicates the volume of the aqueous phase (ml) and M_R the weight of the dry AC (g). The pH values of aqueous phase were measured using a digital pH meter (PerPHect LogR meter model 350; Thermo Orion) after adsorption. Table 1 summarizes some properties of ACs, the K_d of Am(III) and Eu(III) at the equilibrated pH of around 2 and the separation factor, which is defined by the ratio between the K_d of Am(III) and Eu(III). It is notable that significantly higher K_d values of Am(III) than those of Eu(III) were observed, independently of the starting materials, the activation method of AC, the kind of inorganic acid, and the specific surface area of the AC. The separation factors ranged from 1.30 to 2.15, indicating the significant difference between K_d of Am(III) and of Eu(III) for chromatography according to its advantage of theoretical plate number.

As an preliminary example, a column chromatogram of Am(III) and Eu(III) by using AC-5, which indicated the highest separation factor, is shown in Fig. 1. A stock solution of the mixture of ^{241}Am , ^{152}Eu was dissolved into nitric acid (i.e. 0.1 mol/L- HNO_3). A 0.1-ml portion of the stock solution was loaded into a column, in which 5 mm \varnothing \times 400 mm of the sawdust AC was packed. Subsequently, 0.1 mol/L of the nitric acid solution was introduced into the column as an eluent. The effluent from the bottom of the column was collected in fractions. The ^{241}Am and ^{152}Eu in

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Table 1

Distribution coefficient of Am(III) and Eu(III), and their separation factor (SF) using five types of ACs.

Acid	HNO ₃					HCl
	AC-1	AC-2	AC-3	AC-4	AC-5	AC-5
pH _{eq}	2.142	2.081	3.212	2.141	1.93	2.11
K _d (Am)	689.6	42.5	28.2	22.5	32.1	57.9
K _d (Eu)	444.3	29.3	21.8	15.0	14.9	32.5
SF ^a	1.55	1.45	1.30	1.50	2.15	1.78
S _{BET} ^b (m ² /g)	780	1060	1100	890	1480	1480
Materials ^c	Beet	Palm shell	Coal	Ligneous	Sawdust	Sawdust
Activation ^d	Steam	Steam	Steam	Steam	ZnCl ₂	ZnCl ₂

^a SF = separation factor.

^b S_{BET} = BET specific surface area.

^c Materials = starting materials.

^d Activation = activation method.

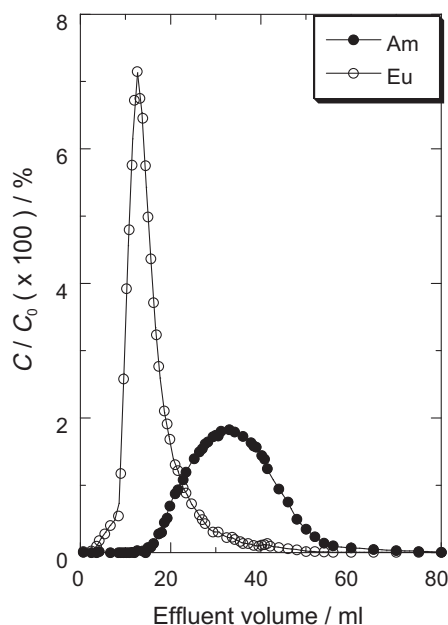


Fig. 1. Chromatogram of Am(III) and Eu(III) in AC-5/HNO₃ system: column size, 5 mm \varnothing \times 400 mm; flow rate, 0.1 ml/min; effluent, HNO₃ (pH 1).

the fractions were measured by gamma-ray spectrometry. The experiments were carried out at ambient temperature. The flow rate was adjusted to 0.1 ml/min. Am(III) and Eu(III) were sufficiently separated using HNO₃ (pH 1) as an eluent, and were recovered at yields of more than 99%. The theoretical plate number, N , was calculated by the equation $N = 5.54(t_R/W_{1/2})^2$, where t_R refer to retention time and $W_{1/2}$ denoted elution half band width of elution peak. The theoretical plate number of Eu(III) and Am(III) were rather low, 358 and 352, respectively, due to broad dispersion of particle size of AC-5 from 63 μ m to several hundred microns in diameters. The resolution (R_s) between Am(III) and Eu(III) was also calculated by the equation, $R_s = 2\Delta t_R/(W_{Am} + W_{Eu})$, where W_{Am} and W_{Eu} denoted elution peak width of Am and Eu, respectively. The R_s was calculated as 1.2 which showed significance of activated carbon for analytical use for the separation of An(III) from Ln(III) in acidic aqueous solution without pre-treatment.

Fig. 2 shows the dependence of the K_d s of Am(III) and Eu(III) on equilibrated pH in the AC-5/HNO₃ system. The K_d of Am(III) was higher than that of Eu(III) in the pH range between 1.25 and 3.42, indicating that An(III) is more selectively adsorbed onto activated carbons than Eu(III). The K_d of both Am(III) and Eu(III) increased with an increase of pH. Since the pH point of zero charge

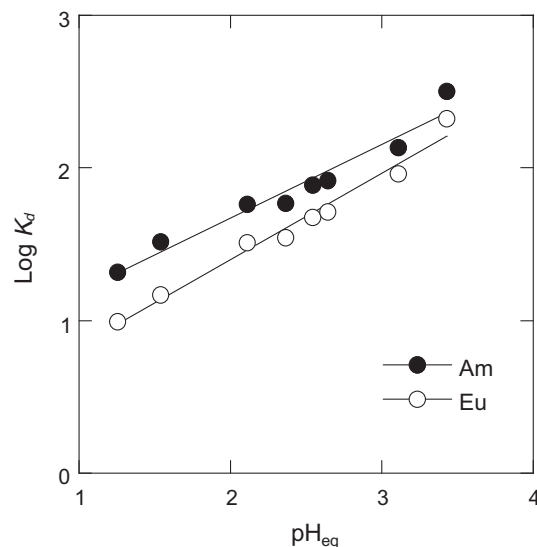


Fig. 2. Dependence of K_d of Am(III) and Eu(III) on aqueous phase pH value in the AC-5/HNO₃ system. [Am³⁺], [Eu³⁺]: 1.0×10^{-9} mol/L, AC-5: 50 mg, pH_{eq}: pH equilibrated from 1.25 to 3.42.

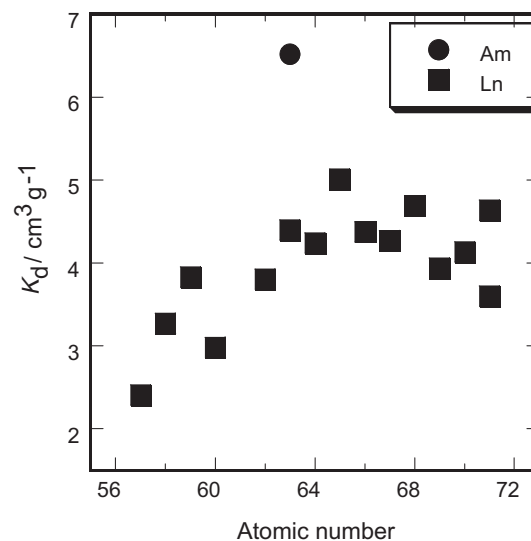


Fig. 3. K_d s of the series of lanthanides and Am(III) in the AC-5/HNO₃ system at pH_{eq} 3.2. [Am³⁺]: 1.0×10^{-9} mol/L, [Ln³⁺]: 1.0×10^{-3} mol/L, AC-5: 50 mg.

was 6.86 for AC-5, this appears to be partially due to the ion exchange reaction, but the fact that the slope was less than 1 would be indicative of an interaction such as an electrostatic interaction between the cation and the AC surface. The separation factor ranged from 1.37 to 2.15 with AC from pH 1.2 to 3.5.

The K_d s of Ln(III) and Am(III) were plotted against atomic number in Fig. 3. The K_d values of all Ln(III) were almost constant among the lanthanide series, while the K_d values of Am(III) were significantly higher than those of Ln(III). This result would suggest that the affinity of Am(III) would be due to electrostatic interaction on the surface of ACs, not the size effect on hydrated or ionic radii of cations.

Table 2 summarizes the composition of surface groups by Boehm titration [11] of AC-5. The main component of surface groups of AC was basic groups such as basal planes and carbon edges of aromatic moieties on AC. To elucidate the effective surface group on the adsorption of Ln(III) and An(III) onto the AC, the

Table 2
Composition of surface groups of AC-5.

Functional groups	mmol/g
Carboxylic	0.225
Lactonic	0.375
Phenolic	0.150
Basic groups	0.600

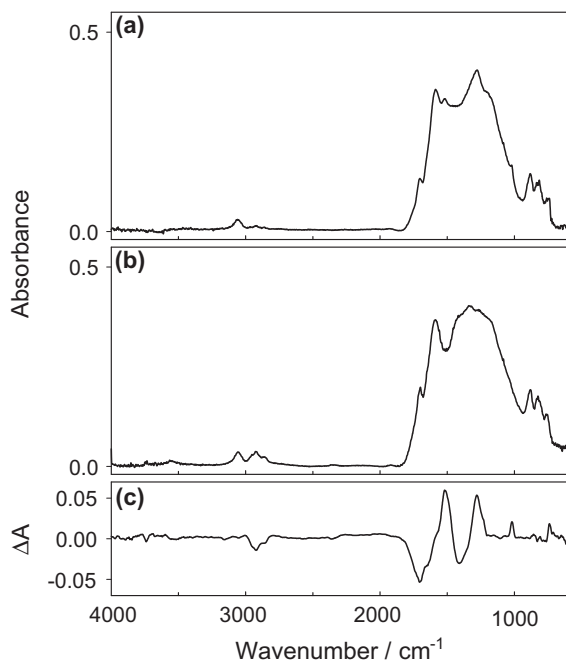


Fig. 4. Diffuse reflection FT-IR spectra of sawdust AC-5 soaked in pH 4 nitric acid solution: (a) ca 1% w/w of Eu(III) was adsorbed, (b) AC-5 alone, and (c) difference spectrum of (a) subtracted by (b), where ΔA indicates the difference of absorbance.

transformation of a surface group on the AC was characterized with the diffuse reflection of FT-IR spectra with and without adsorption of Eu(III) in Fig. 4a and b. Diffuse reflection of FT-IR spectra: 1.5 mg of each dried samples was measured by the diffuse reflection method in an FT-IR spectrometer (JASCO FT-630 with diffuse reflection sample manifold) *in vacuo*. Characteristic peaks were observed 2800–3100 cm^{-1} and from 1100 cm^{-1} to 1500 cm^{-1} at assigned C–H stretching and bending modes, respectively, and 1700 cm^{-1} at the assigned stretching vibration mode of the carbonyl group on the AC surface. As shown in Fig. 3c, the difference spectrum indicated that the bands at 2921 cm^{-1} (C–H stretching), 1704 cm^{-1} (C=O stretching) and 1405 cm^{-1} (C–H

bending) are decreased in intensity with the adsorption of Eu(III) cation, and also that the bands at 1520 cm^{-1} (N–O stretching) and 1280 cm^{-1} (N–O stretching) were increased with adsorption of the Eu(III) cation. Thus, it would be reasonable to consider that the oxygen donor group on the AC surface was subordinate to the mechanism of the adsorption of Ln(III) and An(III). This would suggest that the adsorption of Am(III) and Ln(III) would be mainly caused by the combined effect of the chelation of surface functional groups and electrostatic interaction. Since Béguin et al. has reported pi-electrons of benzenoids on carbon materials were categorized as a soft-donor, the electrostatic interaction could be due to an interaction between pi-electron and metal cations [12].

In summary, we have demonstrated that the intrinsic property of AC without pre-treatment is to selectively adsorb Am(III) rather than Ln(III). The K_{ds} of both Am(III) and Ln(III) depend on aqueous phase pH. Am(III) was sufficiently separated from Eu(III) using column chromatography. An(III) and Ln(III) were adsorbed to C=O functional groups on the AC surface by normal chelating as well as to C–H ends on the AC surface by electrostatic interaction identified by FT-IR. We consider this work to be merely a first step toward the separation of An(III) from Ln(III) by AC, and we expect this discovery of the selectivity to be generally valid and universally applicable.

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