



Research article

Sorption of radioactive cesium and barium ions onto solid humic acid

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ABSTRACT

In this study, the sorption behavior of two important fission product radionuclides (¹³⁷Cs and ¹⁴⁰Ba) onto sodium form of insolubilized humic acid (INaA) were investigated as a function of time, cation concentration and temperature, utilizing the radiotracer method. The sorption processes are well described by both Freundlich and Dubinin–Radushkevich type isotherms. Thermodynamic constants such as; free energy (ΔG_{ads}), enthalpy (ΔH_{ads}), entropy (ΔS_{ads}) of adsorption were determined. It was found that Ba²⁺ was adsorbed five times more than Cs⁺ onto structurally modified humic acid and kinetic studies indicated that adsorption behavior of both ions obey the pseudo second order rate law. The effect of pH change on sorption was also examined. FTIR and solid-state carbon NMR (¹³CNMR) spectroscopic techniques were used to understand the structural changes during insolubilization process. Quantitative determination of adsorption sites was carried out using potentiometric titration.

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1. Introduction

There is an increasing effort for removing highly soluble radio-contaminants from aqueous waste solutions by fixing them onto solid waste forms that can be disposed of in a repository. The radionuclide ¹³⁷Cs is produced in high yield during the fission process and due to its long half-life ($T_{1/2} = 30.17$ yr) and its high solubility in aqueous media, it is a principal radiocontaminant in radioactive wastes [1,2].

Barium is an alkaline earth element ($Z = 56$), its radioactive isotope ¹⁴⁰Ba ($T_{1/2} = 12.79$ days) is a fission product with a high yield (6.21%). This radionuclide is a serious radiocontaminant, furthermore being a homologue of Ra, Ba²⁺ is a suitable cation for the radiochemical study of Ra²⁺, which has several radioisotopes that are important in radioactive waste considerations. ¹³³Ba²⁺ was chosen as a radiotracer in our studies because of its long half-life ($T_{1/2} = 10.7$ yr) and a γ -ray at 356 keV energy [3].

Humic substances (HSs) are an abundant reservoir of carbon on earth. Humic acids (HAs) are operationally defined as the fraction of HS that is insoluble in water at low pH (<2). HA perform various roles in soil chemistry. They act as soil stabilizers, nutrients and water reservoirs for plants, sorbents for toxic metal ions, radionuclides and organic pollutants. When leached into surface waters, they also play a pivotal role in the aquatic environment.

For example, they bind and transport metal ions. Early concepts, based on the developing field of polymer science assumed that humic substances comprised of randomly coiled macromolecules that had elongated shapes in basic or low-ionic strength solutions, but became coils in acidic or high-ionic strength solutions. However, recent information gathered using spectroscopic, microscopic, pyrolysis, and soft ionization techniques is not consistent with the polymer model of humic substances. A new concept of humic substances has thus emerged, that of the supramolecular association, in which many relatively small and chemically diverse organic molecules form clusters linked by hydrogen bonds and hydrophobic interactions. A corollary to this model is the concept of micellar structure, i.e., an arrangement of organic molecules in aqueous solution to form hydrophilic exterior regions shielding hydrophobic interiors from contact with vicinal water molecules [4].

Generally, humic acid is soluble above pH 2.0 in aqueous media and this makes humic acid inappropriate for traditional operations such as adsorption and recovery of metal ions. The solubility of humic acid depends on the number of –COOH and –OH groups present. These groups also give humic acid the ability to interact with metal ions through adsorption, ion-exchange, and complexation mechanisms. However, the high solubility of humic acid is a limiting problem. Accordingly, an appropriate treatment of humic acid is required [5]. The process developed by Seki and Suzuki [6] is called “insolubilization of humic acid” and with this method humic acid can be converted to a form which is insoluble up to pH 10 in aqueous media.

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A number of articles have been published in the field of adsorption of cations onto insolubilized humic acid (IHA) [7]. Gezici et al. [5] reported the sorption behavior of a nickel-insolubilized humic acid system in a column arrangement. In another study Baker and Khalili [8] examined the analysis of the removal of lead(II) from aqueous solutions by adsorption onto insolubilized humic acid. El-Eswed and Khalili [9] reported the adsorption of Cu(II) and Ni(II) on solid humic acid.

In this study, the adsorption behavior of the fission product radionuclides ^{137}Cs and ^{140}Ba onto insolubilized humic acid were investigated both kinetically and thermodynamically. The resulting data was analyzed using Freundlich and Dubinin–Radushkevich (D–R) isotherms. The structural changes during insolubilization process were determined by spectroscopic techniques and also quantitative determination of adsorption sites was carried out.

2. Experimental

2.1. Chemicals

All chemicals used were of analytical grade. Humic acid sample was taken from Nigde (Bor) region. Metal ion solutions were prepared by using only distilled water. No further ionic strength or pH control was attempted. The pH of the solutions in contact with insolubilized humic acid was 3.5.

2.2. Isolation and insolubilization of humic acid

Humic acid was isolated from soil sample by the following procedure; crude humic acid was stirred in 1% NaOH solution for 1 h and subsequently centrifuged at 5000 rpm. The dissolved fraction was adjusted to pH 2 with HCl, stirred for 4 h and centrifuged at 5000 rpm. The resulting precipitate was taken and this procedure was repeated two more times. The precipitate was then rinsed with deionized water many times to remove chloride ions. After dechlorination, HA was dried at 95 °C for 4 h.

Humic acid was insolubilized by heating in a temperature controlled oven at 330 °C for 1.5 h and solid, IHA, was converted to its sodium form (INaA) by stirring in a 1 M NaNO_3 solution for 2 days. The resulting solid phase was dried at 80 °C. The solid phase was ground to powder and the particle size was $\leq 30 \mu\text{m}$ in all experiments.

2.3. Quantitative determination of adsorption sites on HA

Adsorption sites (carboxylic and phenolic groups) were determined quantitatively by using potentiometric titration method. Model 5669-20 pH meter, Cole Parmer Instrument Company, was used for pH measurements. Titration was carried out from pH 3.5 to 10.58 using 0.1 M NaOH as titrant. Analyte was containing 50 ml suspension of humic acid (576 mg l^{-1}). This concentration was also used by other studies [10]. Nitrogen gas was passed through the solution during titration in order to prevent CO_2 interference. Resulting data was linearized by using the appropriate Gran functions [11]. The total acidity value was taken to be the sum of carboxylic and phenolic acidities.

2.4. Adsorption experiments

2.4.1. Radiotracer method

Batch method was used throughout the study. The tracers used in sorption experiments were ^{137}Cs ($T_{1/2} = 30.17 \text{ yr}$) and ^{133}Ba ($T_{1/2} = 10.7 \text{ yr}$). 11 of stable isotope solutions were spiked with few microliters (400 μl) of the corresponding radionuclide solutions. The initial count rates were measured in 2.5 ml aliquots of cesium and barium solutions using the prominent γ -rays of 662

and 361 keV, respectively. Initial activities were adjusted not to be lower value than 10,000 (cps)/ml.

A NaI(Tl) detector was used during radioactivity measurements. All the experiments were performed in duplicate. Any loss in activity originating from adsorption on the tubes, was checked by blank experiments using solutions without adsorbent. Adsorption onto the tube walls was found to be negligible.

2.4.2. Kinetic studies

To each of a set of 5 g INaA samples placed in tubes, 7.5 ml of Cs^+ and Ba^{2+} solution (prepared from CsCl and BaCl_2 salts) containing an appropriate amount of ^{137}Cs and ^{133}Ba radiotracers was added. The initial Cs^+ and Ba^{2+} concentrations in solution was $1 \times 10^{-4} \text{ M}$. Samples were shaken at room temperature for periods ranging from 5 min to 48 h. They were centrifuged at 5000 rpm and 2.5 ml portions of the liquid phases were counted.

2.4.3. Effect of loading, temperature and pH

Loading experiments were carried out to investigate the effect of initial cation concentrations on sorption at four different temperatures; 15 °C, 25 °C, 35 °C, 45 °C. The initial concentrations were 5×10^{-4} , 1×10^{-4} , 1×10^{-5} , 5×10^{-6} (mmol/ml) for Cs^+ solutions. In the case of Ba^{2+} sorption the highest temperature was 55 °C and concentrations used were 1×10^{-4} , 1×10^{-5} , 5×10^{-6} , 1×10^{-6} (mmol/ml). No other electrolytes were added. The effect of pH upon sorption of Ba^{2+} onto INaA was investigated at a fixed concentration ($1 \times 10^{-5} \text{ mol/l}$) at room temperature. The pH range was from 1.5 to 10. The samples were shaken for 1 day, centrifuged and 2.5 ml of portions of the liquid phase were counted. For loading experiments shaking was done in a temperature controlled environment ($\pm 1 \text{ }^\circ\text{C}$) using a Nuve ST 402 water bath shaker equipped with microprocessor thermostat.

2.5. Spectroscopic characterization of humic acid and insolubilized humic acid

2.5.1. FTIR

FT-IR spectra were recorded using a Bruker Tensor 27 FTIR spectrometer with a standard high sensitivity DLATGS detector, with a resolution of 4 cm^{-1} and 64 scans. The KBr pellets were obtained by pressing a mixture of 1:100 ratio of humic samples and KBr, respectively.

2.5.2. ^{13}C NMR

Solid-state ^{13}C NMR spectra were obtained at the ^{13}C resonance frequency of 125.721 MHz on a Bruker Avance ASX 500 spectrometer, equipped with a double resonance HX probe. The samples were confined in a zirconium oxide rotor with an external diameter of 2.5 mm. The cross-polarization magic angle spinning CPMAS technique was applied with a contact time of 1 ms, a spinning speed of 15 kHz MAS and a pulse delay of 2 s.

3. Results and discussion

3.1. Potentiometric titration

To quantify the acidic functional (carboxylic and phenolic) groups, potentiometric titration method was used. It is usual to plot the differential curves, $\Delta\text{pH}/\Delta V$ or $\Delta E/\Delta V$ against volume of titrant added, but when the titration curve is not symmetrical close to the equivalence point, as in Fig. 1, then it is possible to obtain erroneous results. Therefore, Gran [11] developed a mathematical expressions to linearize titration curves. In our data treatment, we chose the following equation, assuming that humic acid is a polymeric acid and

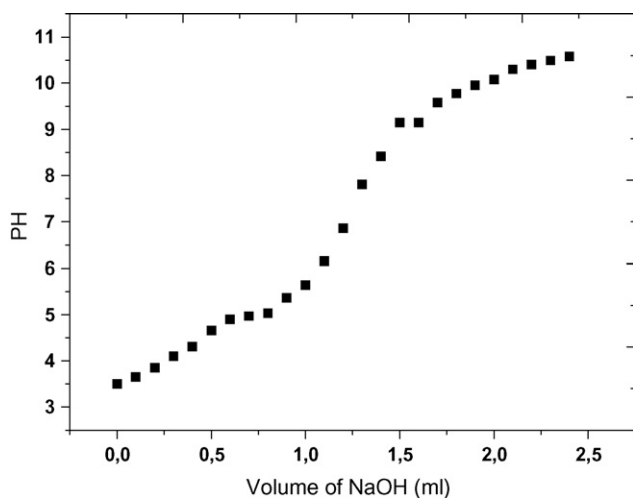


Fig. 1. Potentiometric titration curve of humic acid.

the titration type as weak acid-strong base titration.

$$G = V \times 10^{\text{pH}-k} \quad (1)$$

where V represents the amount of titrant used (ml) and k is an arbitrary constant with a value such that the antilogarithms will fall in a suitable range such as 0–100.

After conversion of the potentiometric titration data to linearized form using Gran functions, two associated lines were obtained as shown in Fig. 2. The intersection point of the first line gives the amount of base needed to neutralize carboxylic acid groups and the second intersection point is the amount of total base which is required to neutralize all acidic functional groups. The difference is the amount of base which is required to neutralize phenolic groups. The following quantitative acidic functional group and total acidity values are obtained; carboxylic acidity, 249 ± 25 mequiv./100 g phenolic acidity, 190 ± 19 mequiv./100 g and total acidity value is 439 ± 44 mequiv./100 g.

3.2. FTIR and ^{13}C NMR spectra of humic acid and sodium form of insolubilized humic acid

FTIR spectroscopy was used to examine the structural changes after insolubilization process. The peaks and corresponding functional groups in FTIR spectrum shown in Fig. 3 are as follows; a broad band at 3387 cm^{-1} primarily corresponds to O–H stretching

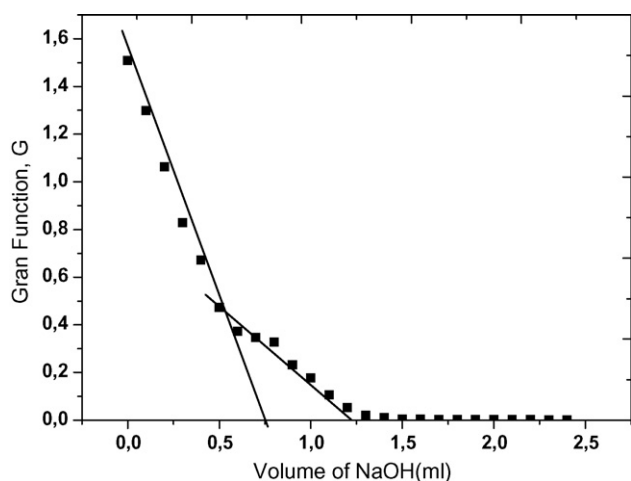


Fig. 2. Linearized plot potentiometric titration curve of humic acid.

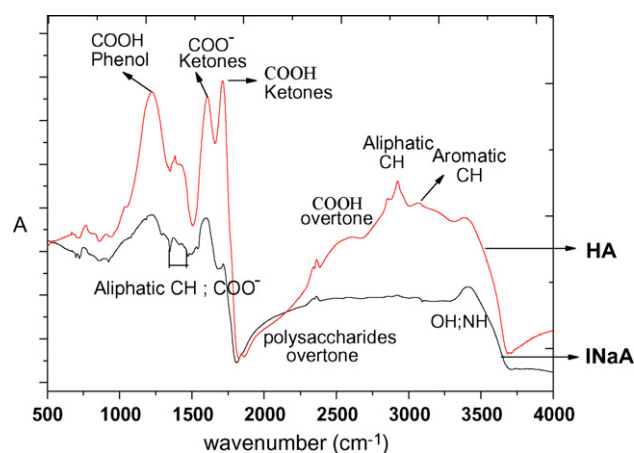


Fig. 3. FTIR spectra of humic acid and sodium form of insolubilized humic acid.

and secondarily to N–H stretching, the peak at 3071 cm^{-1} represents stretching of aromatic C–H, absorption bands at 2928 and 2857 cm^{-1} are attributed to aliphatic C–H stretching in CH_2 and CH_3 , respectively.

Broad bands at 2500 cm^{-1} is overtone from carboxylic groups stretching ($2 \times 1246\text{ cm}^{-1}$) and at 2000 cm^{-1} is overtone from C–O polysaccharides stretching mode ($2 \times 1060\text{ cm}^{-1}$), strong absorption band at 1704 cm^{-1} is due to C=O stretching of carboxylic acid and ketone and absorption bands at 1602 cm^{-1} and 1372 cm^{-1} are ascribed to stretching of carboxylate ion and the peak at 1602 cm^{-1} can also be attributed to structural vibrations of aromatic C=C bonds, the peak at 1222 cm^{-1} represents C–O stretching in phenols and O–H deformation of COOH. The absorptions from deformation of aliphatic C–H and, H-bonded C=O of conjugated ketones and water deformation occurs at 1448 cm^{-1} , the band at 1033 cm^{-1} represents C–O stretching of polysaccharides [12–14].

The ^{13}C spectra in Fig. 4 of HA and sodium form of insolubilized humic acid (INaA) include the following peaks: (a) alkyl carbons and O-alkyl carbons (aminoacids/carbons adjacent to ester/ether/hydroxyl) (0–60 ppm). Because that peak was not well resolved we observe those two groups in a broad band; (110–145) ppm is assigned to aromatic carbon, that at (150–190) ppm include phenolic and carboxylic carbons [15–17].

When we examine FTIR and ^{13}C NMR spectra of HA and INaA, we observe that there is a decrease at the intensities of aliphatic alkyl groups, –COOH group and phenolic groups. The effect caus-

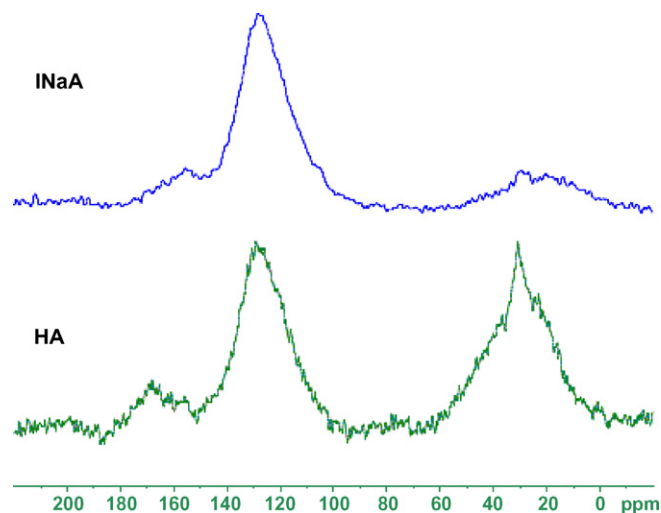


Fig. 4. ^{13}C NMR spectra of humic acid and sodium form of insolubilized humic acid.

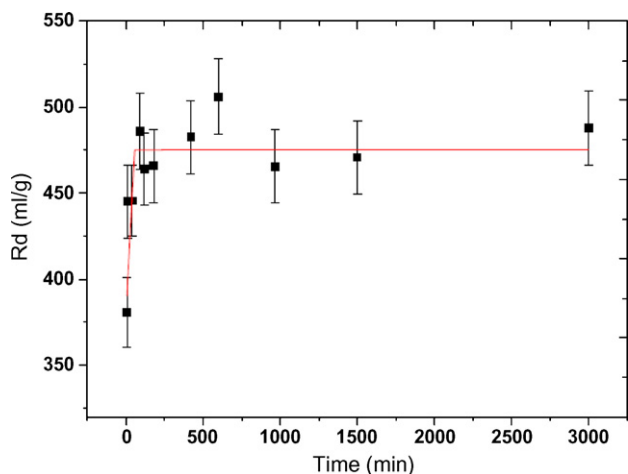


Fig. 5. Variation of R_d values with shaking time for Cs^+ sorption onto sodium form of insolubilized humic acid at an initial concentration of 1×10^{-4} M at 25°C .

ing insolubilization is mainly due to loss in carboxyl groups, but as we see on spectrum, not all of the adsorption sites are lost during insolubilization. By this way, the ability of HA to make hydrogen bonding decreased and that caused the insolubilization of HA in water at high pH values. It is also clear from the ^{13}C NMR that aromatic part of HA is not affected after insolubilization, because there is no intensity change.

3.3. Kinetic studies

The experimental data in adsorption are expressed in terms of the distribution ratio, R_d , defined as the ratio of adsorbate concentration on solid phase to its concentration in liquid phase. The distribution ratio of adsorption is defined as

$$R_d = \frac{[C]_{\text{solid}}}{[C]_{\text{liquid}}} \quad (2)$$

where $[C]_{\text{solid}}$ (mmol/g) and $[C]_{\text{liquid}}$ (mmol/ml) are the concentrations of species C in the solid and liquid phases, respectively. At the beginning of the sorption step, V (ml) of solution with initial concentration $[C]^\circ$ (mmol/ml) is used and at the end of the sorption step V (ml) of solution with concentration $[C]_{\text{liquid}}$ are present, hence the concentration of C in the solid phase after sorption can be expressed as

$$[C]_{\text{solid}} = \frac{V([C]^\circ - [C]_{\text{liquid}})}{W_{\text{solid}}} \quad (3)$$

In terms of radioactivity, $[C]_{\text{liquid}}$ can be written as

$$[C]_{\text{liquid}} = \frac{A_{\text{liquid}}}{A^\circ} [C]^\circ \quad (4)$$

From (2) to (4), the following equation is obtained:

$$R_d = \frac{VA^\circ - VA_{\text{liquid}}}{A_{\text{liquid}}W_{\text{solid}}} \quad (5)$$

where A° is the initial count rate of solution added for sorption (cps)/ml, A_{liquid} is the count rate of solution after sorption (cps)/ml, W_{solid} is the weight of solid material (g) [23].

The sorption kinetics of Cs^+ and Ba^{2+} ions on INaA (sodium form of insolubilized humic acid) were examined by radioactive tracer method to determine the time required to reach equilibrium, rate constants and the nature of the kinetic model for each sorption process. The results of the variation of R_d as a function of time for Cs^+ and Ba^{2+} ions on INaA are given in Figs. 5 and 6 and in Tables 1 and 2.

The sorption studies of Cs^+ and Ba^{2+} ions on INaA as a function of time were performed for time intervals ranging from 5 min up to

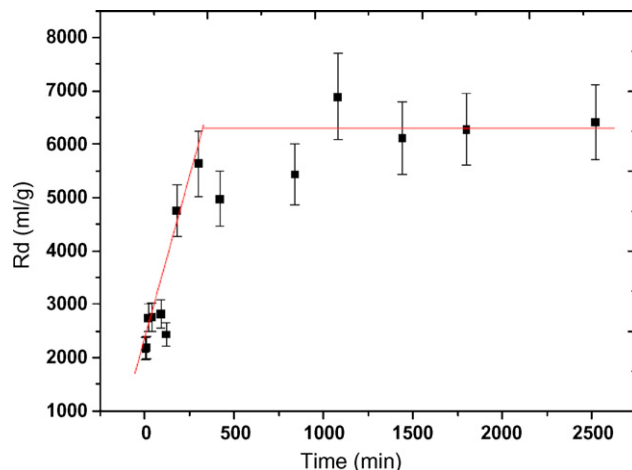


Fig. 6. Variation of R_d values with shaking time for Ba^{2+} sorption onto sodium form of insolubilized humic acid at an initial concentration of 1×10^{-4} M at 25°C .

Table 1

The sorption data for the kinetic behavior Cs^+ ion onto sodium form of insolubilized humic acid at an initial concentration of 1×10^{-4} M.

Time (min)	R_d (ml/g)	$[\text{Cs}]_{\text{liquid}}$ (mmol/ml)	$[\text{Cs}]_{\text{solid}}$ (mmol/g)	t/q
5	381	6.63×10^{-5}	0.0252	198
10	445	6.27×10^{-5}	0.0279	358
40	446	6.27×10^{-5}	0.0279	1431
90	486	6.07×10^{-5}	0.0295	3052
120	464	6.18×10^{-5}	0.0287	4186
180	466	6.17×10^{-5}	0.0287	6264
420	482	6.08×10^{-5}	0.0294	14,306
600	506	5.97×10^{-5}	0.0302	19,857
966	465	6.17×10^{-5}	0.0287	33,634
1500	471	6.14×10^{-5}	0.0289	51,869
3000	488	6.06×10^{-5}	0.0295	101,514

48 h. Equilibrium is reached after several hours of contact. Such a rapid process indicates that sorption is primarily a surface phenomena and the humic acid surface is readily accessible for ions from solution. On the basis of the obtained results an equilibrium period of 1 day was selected as a fixed parameter for further experiments, where the effects of loading and temperature, were examined.

Kinetic studies were also used to determine best fitting rate equations and rate constants of cation sorption. Azizian [7] has published kinetic models for the sorption behavior of solutes onto adsorbent and in his study, it has been shown that at low initial concentrations, the mechanism obeys pseudo second order model.

Table 2

The sorption data for the kinetic behavior Ba^{2+} ion on sodium form of insolubilized humic acid at an initial concentration of 1×10^{-4} M.

Time (min)	R_d (ml/g)	$[\text{Ba}]_{\text{liquid}}$ (mmol/ml)	$[\text{Ba}]_{\text{solid}}$ (mmol/g)	t/q
5	2177	4.53×10^{-5}	0.0985	51
10	2190	4.51×10^{-5}	0.0988	101
20	2749	3.96×10^{-5}	0.1088	184
40	2766	3.94×10^{-5}	0.1090	367
90	2825	3.89×10^{-5}	0.1099	818
120	2439	4.25×10^{-5}	0.1036	1159
180	4755	2.75×10^{-5}	0.1306	1378
300	5636	2.42×10^{-5}	0.1364	2199
420	4978	2.66×10^{-5}	0.1322	3177
840	5436	2.49×10^{-5}	0.1352	6212
1080	6890	2.07×10^{-5}	0.1427	7567
1440	6116	2.27×10^{-5}	0.1391	10,354
1800	6280	2.23×10^{-5}	0.1399	12,866
2520	6415	2.19×10^{-5}	0.1406	17,928

Table 3

Amount of sorbed cation per gram of sorbent at equilibrium, pseudo second order rate constants and correlation coefficient values for cesium and barium sorption.

Sorbed cations	q_e (mol/g)	k_2 ($\text{g mol}^{-1} \text{min}^{-1}$)	R^2
Cs^+	29.44×10^3	9.99	0.99
Ba^{2+}	141.30×10^3	0.43	0.99

The rate law for such a system is expressed as

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad (6)$$

where q and q_e are the amount of solute sorbed per gram of sorbent at any time and at equilibrium, respectively, and k_2 is the pseudo second order rate constant of sorption. After integration and rearrangement of the above equation, the following equation is obtained with a linear form

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

The plot of t/q versus t gives a straight line with slope of $1/q_e$ and intercept of $1/k_2 q_e^2$. So the amount of cation sorbed per gram of sorbent (INaA) at equilibrium q_e and sorption rate constant k_2 could be evaluated from the slope and intercept, respectively. The results obtained are shown in Table 3 and in Figs. 7 and 8.

It is apparent from q_e values that barium ions are sorbed five times more than cesium ions and rate constant values show that

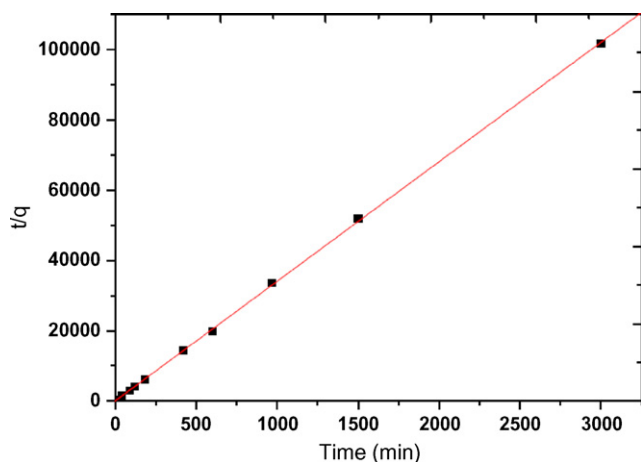


Fig. 7. Variation of t/q values with shaking time for Cs^+ sorption on sodium form of insolubilized humic acid at 25 °C.

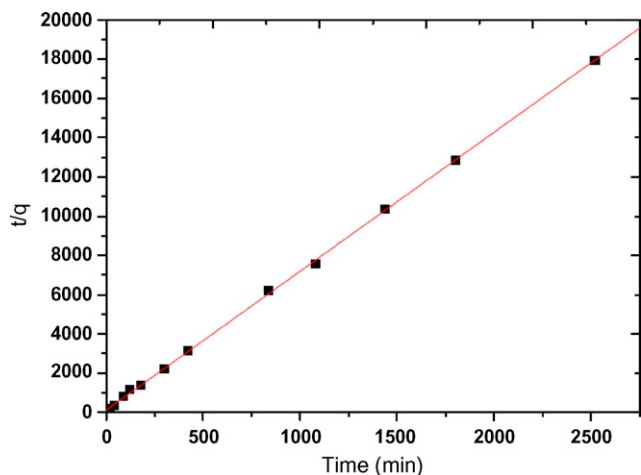


Fig. 8. Variation of t/q values with shaking time for Ba^{2+} sorption on sodium form of insolubilized humic acid at 25 °C.

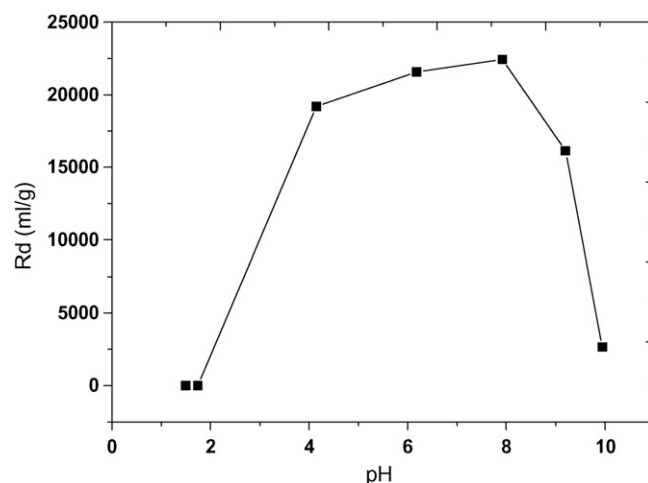


Fig. 9. Effect of pH upon sorption of Ba^{2+} onto sodium form of insolubilized humic acid at 25 °C.

cesium is much more rapidly adsorbed by INaA. Correlation coefficient values indicate that pseudo second order rate equation completely fits the sorption behavior of low concentrations of cesium and barium ions onto INaA.

The less sorption tendency of cesium ions onto INaA can be explained by its charge. An increase in the oxidation state favors the accumulation of these ions on the sorption surface leading to electrostatic neutrality.

3.4. Effect of pH upon cation sorption

The increase of pH value has a substantial effect upon sorption of Ba^{2+} onto INaA, as shown in Fig. 9. The experiment was carried out using 10 mg of INaA as sorbent, 9 ml of 1×10^{-5} M of Ba^{2+} solution with varying pH values. It is seen that there is almost no adsorption between pH (1–2) range. In the literature [5,8] it is also emphasized that in aqueous media there is a competition between H_3O^+ and metal ions toward the solid phase. At low pHs, the surface of the adsorbent is closely associated with the hydronium ions and repulsive forces limit the approach of the metal ions. As we increase the pH, we observe a dramatic increase of the uptake of Ba^{2+} by INaA, because the principal adsorption sites $-\text{COOH}$ and $-\text{COH}$ dissociate to their anionic forms $-\text{COO}^-$ and $-\text{CO}^-$. These dissociations cause negatively charged surfaces and cations could more easily adsorb onto the solid surface. At pH value beyond 8, we observe a sharp decrease at sorption capacity of sorbent. One possible explanation may be the formation of hydrolysed or barium carbonate complexes. In the case of Cs^+ sorption, we also expect an increased uptake of Cs^+ to the humic acid surface as the pH increases, but not as much as the uptake of barium ions, because of weaker interaction of Cs^+ ions with humic acid surface when compared to the interaction between Ba^{2+} ions and humic acid surface.

3.5. Freundlich isotherm

Freundlich isotherm model [3] is one of the most used non-linear model for describing the dependence of sorption on sorbate concentration. This model allows for several kinds of sorption sites on solid and represents properly the sorption data at low and intermediate concentrations on heterogeneous surfaces. The general expression of Freundlich isotherm is given as

$$[C]_{\text{solid}} = k [C]_{\text{liquid}}^n \quad (8)$$

where $[C]_{\text{solid}}$ is the amount of ionic species adsorbed on the solid matrix at equilibrium (mmol/g), $[C]_{\text{liquid}}$ is the concentration of the

Table 4

The data of Cs⁺ sorption onto sodium form of insolubilized humic acid at different temperatures and initial concentrations.

Temp. (K)	[C] ⁰ (mmol/ml)	R _d (ml/g)	[Cs] _s (mmol/g)	[Cs] _{liq} (mmol/ml)
288	1 × 10⁻²	48	0.449	9.4 × 10⁻³
288	5 × 10 ⁻⁴	454	0.141	3.11 × 10 ⁻⁴
288	1 × 10 ⁻⁴	4548	0.0644	1.41 × 10 ⁻⁵
288	1 × 10 ⁻⁵	9849	0.00697	7.08 × 10 ⁻⁷
288	5 × 10 ⁻⁶	10,984	0.00351	3.20 × 10 ⁻⁷
298	1 × 10⁻²	119	1.028	8.63 × 10⁻³
298	5 × 10 ⁻⁴	507	0.151	2.98 × 10 ⁻⁴
298	1 × 10 ⁻⁴	3894	0.0629	1.61 × 10 ⁻⁵
298	1 × 10 ⁻³	10,554	0.00700	6.63 × 10 ⁻⁷
298	5 × 10 ⁻⁶	11,343	0.00352	3.10 × 10 ⁻⁷
308	1 × 10⁻²	52	0.491	9.35 × 10⁻³
308	5 × 10 ⁻⁴	405	0.131	3.25 × 10 ⁻⁴
308	1 × 10 ⁻⁴	2810	0.0592	2.11 × 10 ⁻⁵
308	1 × 10 ⁻⁵	10,693	0.00701	6.55 × 10 ⁻⁷
308	5 × 10 ⁻⁶	12,591	0.00354	2.81 × 10 ⁻⁷
318	1 × 10⁻²	42	0.398	9.47 × 10⁻³
318	5 × 10 ⁻⁴	332	0.115	3.46 × 10 ⁻⁴
318	1 × 10 ⁻⁴	2675	0.0586	2.19 × 10 ⁻⁵
318	1 × 10 ⁻¹¹	11,372	0.00704	6.19 × 10 ⁻⁷
318	5 × 10 ⁻⁶	12,416	0.00354	2.85 × 10 ⁻⁷

cation in solution at equilibrium (mmol/ml), k and n , are Freundlich constants.

This expression can be linearized as

$$\log [C]_{\text{solid}} = \log k + n \log [C]_{\text{liquid}} \quad (9)$$

Plotting $\log [C]_{\text{solid}}$ versus $\log [C]_{\text{liquid}}$ yields “ n ” as the slope and “ $\log k$ ” as the intercept.

The data of sorption of Cs⁺ and Ba²⁺ onto INaA at different temperatures and initial concentrations are given in Tables 4 and 5. The Freundlich isotherm plots for cesium and barium ions at different loadings and temperatures on INaA are shown in Figs. 10 and 11 and the Freundlich constants n and k obtained for different sorption cases are given in Table 6.

The values of ‘ n ’ being less than 1.0 in all cases indicate a non-linear sorption that takes place on a heterogeneous surface. The non-linearity indicates that the sorption energy barrier increases exponentially as the fraction of occupied sites on sorbent increases. Increase of temperature (40 °C) has no pronounced effect on “ n ” values for the sorption of these cations onto INaA.

The magnitude of “ k ” is related to sorption affinity. When we use INaA as a sorbent, we found that there is a significant difference between “ k ” values for the sorption behavior of cesium and barium ions. This clearly indicates that INaA has a much higher tendency to adsorb barium ions compared with cesium ions. This is in line with the observed lower R_d values of Cs⁺ sorption.

Table 5

The data of Ba²⁺ sorption onto sodium form of insolubilized humic acid at different temperatures and initial concentrations.

Temp. (K)	[C] ⁰ (mmol/ml)	R _d (ml/g)	[Ba] _s (mmol/g)	[Ba] _{liq} (mmol/ml)
298	1 × 10⁻⁴	7446	0.145	1.95 × 10⁻⁵
298	1 × 10 ⁻⁵	18,065	0.0164	9.06 × 10 ⁻⁷
298	5 × 10 ⁻⁶	26,153	0.00842	3.22 × 10 ⁻⁷
298	1 × 10 ⁻⁶	58,874	0.00175	2.97 × 10 ⁻⁸
308	1 × 10⁻⁴	8275	0.148	1.79 × 10⁻⁵
308	1 × 10 ⁻⁵	22,938	0.0167	7.28 × 10 ⁻⁷
308	5 × 10 ⁻⁶	32,368	0.00853	2.63 × 10 ⁻⁷
308	1 × 10 ⁻⁶	27,026	–	–
318	1 × 10⁻⁴	6439	0.141	2.18 × 10⁻⁵
318	1 × 10 ⁻⁵	23,292	0.0167	7.17 × 10 ⁻⁷
318	5 × 10 ⁻⁶	26,522	0.00843	3.18 × 10 ⁻⁷
318	1 × 10 ⁻⁶	37,487	0.00172	4.58 × 10 ⁻⁸
328	1 × 10⁻⁴	6896	0.143	2.07 × 10⁻⁵
328	5 × 10 ⁻⁶	38,156	0.00859	2.25 × 10 ⁻⁷
328	1 × 10 ⁻⁶	43,284	0.00173	3.99 × 10 ⁻⁸

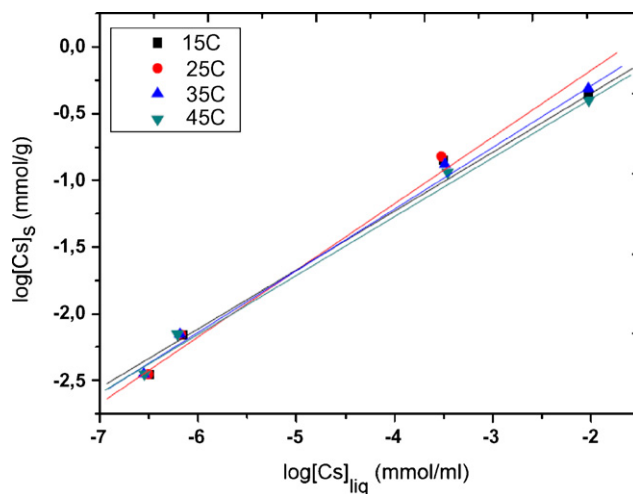


Fig. 10. Freundlich isotherm plots for the sorption of Cs⁺ onto sodium form of insolubilized humic acid at various temperatures using 10 mg sorbent.

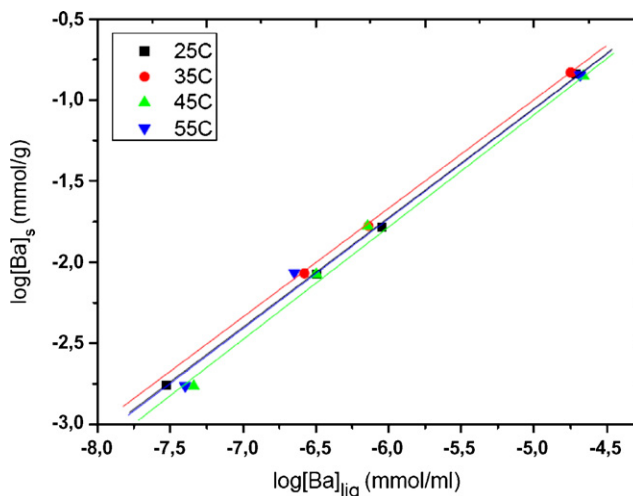


Fig. 11. Freundlich isotherm plots for the sorption of Ba²⁺ onto sodium form of insolubilized humic acid at various temperatures using 5 mg sorbent.

3.6. Dubinin–Radushkevich isotherms

The D–R isotherm model²⁰ is valid at low concentration ranges and can be used to describe sorption on both homogeneous and heterogeneous surfaces. It can be represented by the general expression:

$$[C]_{\text{solid}} = [C]_m \exp -(K\varepsilon^2) \quad (10)$$

Table 6

Freundlich constants, n and k , obtained from the least square fits of the sorption data of Cs⁺ and Ba²⁺ onto sodium form of insolubilized humic acid.

Sorbed cation	Freundlich constant	Temperature (K)			
		288	298	308	318
Cs ⁺	n	0.47	0.53	0.46	0.445
	k	4.86	11.40	4.89	3.51
Ba ²⁺	n	0.68	0.67	0.70	0.68
	k	226.93	243.61	307.26	257.57

The linear correlation coefficients were all greater than 0.99.

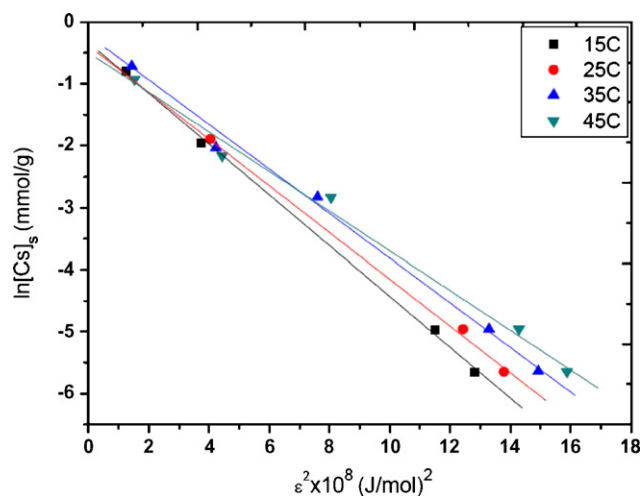


Fig. 12. Dubinin–Raduskevich isotherm plots for sorption of Cs⁺ onto sodium form of insolubilized humic acid at various temperatures using 10 mg sorbent.

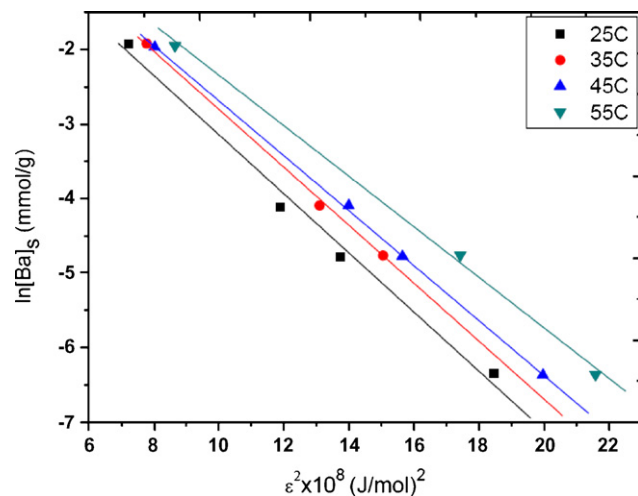


Fig. 13. Dubinin–Raduskevich isotherm plots for sorption of Ba²⁺ onto sodium form of insolubilized humic acid at various temperatures using 5 mg sorbent.

where ε Polanyi potential, $RT \ln(1 + 1/C_{\text{liquid}})$, C_{liquid} is the solute equilibrium constant in solution (mmol/ml), R is the ideal gas constant ($8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the absolute temperature (K), $[C]_m$ is the sorption capacity of sorbent per unit weight (mmol/g), K is the constant related to the energy of sorption, $[C]_{\text{solid}}$ is the amount of solute sorbed per unit weight (mmol/g).

The linear form of the equation above can be obtained by rearranging it to give

$$\ln C_{\text{solid}} = \ln C_m - K\varepsilon^2$$

If $\ln C_{\text{solid}}$ is plotted against ε^2 , K and $\ln C_m$ will be obtained from the slope and the intercept, respectively. The value of K (mol/kJ) [2] is related to the adsorption mean free energy, E (kJ/mol), defined as the free energy change required to transfer 1 mole of ions from infinity in solution to the solid surface. The adsorption mean free energy E is given as

$$E = (2K)^{-1/2} \tag{11}$$

Sorption of Cs⁺ and Ba²⁺ onto INaA fitted the D–R model well as shown in Figs. 12 and 13 and the corresponding values of C_m , K and E are given in Table 7. C_m values indicate that barium ions are sorbed 5 times more than Cs⁺ ions and decrease with increasing temperature, but changes are not significant. The affinity of a cation for ion-exchange sites is a function of the charge and size of the cation. Cesium ion sorption results showed lower sorption affinity onto INaA compared to barium ion, because of the higher charge density of barium leading to stronger sorption complexes.

Table 7

The D–R isotherm constants, K (mol/kJ)², C_m (mmol/100 g), and E (kJ/mol) obtained from the least square fits for the sorption data of Cs⁺ and Ba²⁺ onto sodium form of insolubilized humic acid.

Sorbed ion	D–R constant	Temperature (K)			
		288	298	308	318
Cs ⁺	C_m	71.1	71.1	74.4	60.0
	K	4.09×10^{-3}	3.793×10^{-3}	3.542×10^{-3}	3.162×10^{-3}
	E	11.04	11.481	11.881	12.57
		Temperature (K)			
		298	308	318	328
Ba ²⁺	C_m	349.2	310.0	276.4	276.1
	K	4.439×10^{-3}	3.945×10^{-3}	3.690×10^{-3}	3.380×10^{-3}
	E	10.61	11.258	11.64	12.16

The linear correlation coefficients were all greater than 0.99.

In all cases, the mean free energy of sorption, E , is in 8–16 kJ/mol energy range corresponding to ion-exchange type of sorption [18].

3.7. Thermodynamic results

The values of ΔH° and ΔS° of Cs⁺ and Ba²⁺ sorption were obtained by fitting the experimental data to equation (12) which is deduced from Gibbs free energy change equation (13).

$$\ln R_d = \frac{\Delta S^\circ}{R} = \frac{\Delta H^\circ}{RT} \tag{12}$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \tag{13}$$

ΔH° and ΔS° values are dependent only on the temperature and pressure, therefore no concentration dependence is expected. Different R_d values are obtained at different loadings (initial concentrations of a particular cation). Therefore, distribution ratio, R_d , in Eq. (10) is an empirical equilibrium constant that is valid at a particular initial concentration and reaction conditions. This difficulty associated with the description of sorption data which is the lack of a thermodynamic equilibrium constant over a wide range of concentrations can be partially overcome by applying empirical distribution constants. In order to obtain values of these thermodynamic constants that are representative over the entire concentration ranges, averaged ΔH° and ΔS° values of different sorption cases were calculated. Consequently, an assumption is made in which the fluctuations in the ΔH° and ΔS° values are small enough to calculate the average of these values at different concentrations [21].

Table 8
The average values of the enthalpy change, ΔH_{av}° (kJ/mol), entropy change, ΔS_{av}° (J/mol K) and the calculated values of the Gibbs free energy change, ΔG° (kJ/mol), obtained at different temperatures for the sorption case of Cs^{+} and Ba^{2+} onto sodium form of insolubilized humic acid.

Sorbed ion	ΔH_{av}° (kJ/mol)	ΔS_{av}° (J/mol K)	ΔG° (kJ/mol) at different temperatures (K)			
			288	298	308	318
Cs^{+}	-3.67	48.85	-17.74	-18.23	-18.72	-19.21
			ΔG° (kJ/mol) at different temperatures (K)			
			298	308	318	328
Ba^{2+}	2.10	89.522	-24.57	-25.47	-26.36	-27.26

The results are given in Table 8. Average values for ΔH and ΔS at different temperatures were taken. The average ΔH° values for Cs^{+} and Ba^{2+} sorption onto INaA indicate that sorption of Cs^{+} onto INaA is exothermic, Ba^{2+} , endothermic. In liquid-solid systems, when temperature is increased, the behavior of ions in solution or on the solid will be subject to factors such as the interionic forces, the hydration energy, the availability of sorption sites and the relative stability of sorbed ions at these sites [19]. Exothermic behavior of Cs^{+} ion sorption onto INaA can be explained by the thermal destabilization leading to an increase in the mobility of cesium ions on the surface of the solid as the temperature is increased, thus enhancing desorption. Positive ΔH° value was obtained for Ba^{2+} sorption onto INaA. There is a large difference in hydration enthalpies, being -276 kJ/mol for Cs^{+} and -1305 kJ/mol for Ba^{2+} ions. In the literature [20], it is reported that metal ions with high hydration energies are well solvated in water and for cations that are solvated well in water, sorption requires that such ions should be stripped to a certain extent of their hydration shell which is a process that requires energy input. If this dehydration energy exceeds the exothermicity associated with the sorption of a metal ion on a solid, then the overall energy balance will lead to an endothermic behavior.

Generally, it is expected that the entropy change of the system would be negative at the end of the sorption reaction due to transferring the sorbate ions from a disordered state in solution to a more ordered state when fixed by sorbent. However, there are some other factors which should be considered. One of them is the dehydration step that increases the mobility of ions and that of the surrounding water molecules in solution. The release of bound sodium ions from solid phase to the liquid phase is another reason, especially in the case of Ba^{2+} sorption where two monovalent ions of Na^{+} is exchanged for each Ba^{2+} ions [21,22].

The calculated negative values of ΔG° for all cases indicate that the sorption process of each is spontaneous and preferentially driven toward the products. Temperature change has no significant effect on ΔG° values for both sorptions.

4. Conclusions

Insolubilized humic acid can be used as an effective adsorbent to remove radionuclides (Cs^{+} and Ba^{2+}) from aquatic environments. Equilibrium in cation sorption is achieved within hours of contact between the solution of adsorbed cations and insolubilized humic acid indicating that fast sorption mechanisms are involved and the sorption process is mainly a surface phenomena.

Structural changes were determined using FTIR and ^{13}C NMR techniques during modification of humic acid. The amount of adsorption sites (carboxylic and phenolic groups) decreased during insolubilization step.

Kinetic studies indicated that adsorption behaviors of cations (Cs^{+} and Ba^{2+}) obey pseudo second order rate law. Cation sorption data have been interpreted in terms of Freundlich and Dubinin–Radushkevich equations. There is an inverse relationship

between the rate of sorption and the sorption order for the cation sorptions studied.

The pH experiments showed that insolubilized humic acid has a higher sorption capacity towards cations at high pH values, because of the dissociation of all acidic hydrogens.

The sorption data obtained at different temperatures indicate that cation sorption onto insolubilized humic acid is not affected significantly by the temperature change, whereas cation sorption onto iron nanoparticles is an exothermic process. Positive entropy values were found in the case of cation sorption onto insolubilized humic acid. Negative ΔG° values in all cation sorption processes show that sorption process is spontaneous.

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