KINETIC AND EQUILIBRIUM STUDIES OF CESIUM AND STRONTIUM ADSORPTION ON A NATURAL SAND SOIL

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Abstract

Modeling radionuclide migration is important to understand both environmental effects and develop remediation strategies. The key factors for modeling are the physical and chemical interactions of radionuclides with soil components, which depend on soil types and geochemical conditions. Although radionuclide adsorption on many soils has been studied, their migration behaviour is still not well understood due to the complexity of the environment.

Radioactive cesium and strontium are present as fission products ^{137}Cs and ^{90}Sr in nuclear wastes and spent fuels, and pose a major concern to pollution control because of their biological activity and long decay half-lives. This paper will present bench top test results and discussions on the kinetics and equilibrium of the adsorption of inactive Cs^+ and Sr^{2+} ions on a natural sand soil under a pH range of 3 to 10, temperatures (25 to 50 °C) and concentrations (10^{-8} to 10^{-3} mol/kg). It was found that the adsorption of Cs^+ and Sr^{2+} followed second order reaction kinetics and generally required more than a week to reach equilibrium. The adsorption equilibria of Cs^+ followed a Freundlich isotherm, while those of Sr^{2+} followed a Langmuir isotherm, suggesting different adsorption mechanisms. Adsorption increased with increasing pH for both ions at all temperatures studied, which is likely due to an increasingly negative surface charge on the sand soil. The desorption tests suggest that Cs^+ is more tightly bound than Sr^{2+} to the surface of the adsorbent under the same chemistry conditions and that Cs^+ is less mobile than Sr^{2+} in natural sand soil.

1. Introduction

Radionulides can be released to the environment not only through large scale nuclear accidents such as Fukushima Daiichi and Chernobyl, but also on a small scale through leakage of nuclear waste storage facilities. When radionuclides are released into the environment, they can be transported as aerosols, dissolved species and adsorbed materials. As adsorption and desorption of radionuclides onto adsorbents in the environment are a major mechanism for radionuclide migration in the ground, fundamental data on sorption of radionuclides are required to understand the physical and chemical interactions with soil components in order to model activity transport and remediate the contaminated environment during post nuclear accidents.

Radioactive cesium and strontium are present as fission products ^{137}Cs (γ emitter with a half-life of approximately 30 years) and ^{90}Sr (β emitter with a half-life of approximately 29 years) in

nuclear wastes and spent fuels as well as in nuclear reactors. The release of these radionuclides into the environment poses a major concern to pollution control due to their biological activity and long decay half lives. Although adsorption of radioactive cesium and strontium on many sand soil samples has been studied because sand soil are commonly found at or near nuclear waste storage sites, their migration behaviour is still not well understood due to the complexity of the environment including soil types and geochemical conditions. One example is the organic matter effect on radionuclide migration in the environment and different results can be obtained even for similar adsorbents [1][2]. Moreover, adsorption data are typically obtained for a single radionuclide at room temperature. Very limited studies are carried out for the temperature effect on radionuclide adsoption and even less data are available for muti-radionuclide adsorption on the same adsorbent under the same conditions. This paper will present bench top test results and discussions on the kinetics and equilibrium of the adsorption and desorption of inactive Cs^+ and Sr^{2+} ions on a natural sand soil under various pH conditions ranging from 3 to 10, temperatures ranging from 25 to 50 °C and concentrations ranging from10^{-8} to 10^{-3} mol/kg. The measured data are analysed using adsorption isotherm models.

2. Experimental

Non-radioactive natural sand soil samples were cored from a depth of approximately 25 cm from the ground surface in Deep River, Ontario at coordinates of 46°6'49"N and 77°30'4"W, about seven kilometres from Canadian Nuclear Laboratories (CNL). Samples were kept in 9” x 12” Poly Zip-Lock Nalgene LDPE sample bags and were further processed at CNL. In order to remove biological impurities, sand samples were rinsed with deionized water, followed by three repetitions of five minute sonicated rinses with 10% hydrogen peroxide. The sterilized sand was rinsed with deionized water and dried for 24 hours at 100°C overnight in an oven.

$CsNO_3$ and $Sr(NO_3)_2$ powder samples were purchased from Aldrich with purity greater than 99% reported by the manufacturer. A 500 ml of 10^{-3} mol/kg stock solutions of $CsNO_3$ or $Sr(NO_3)_2$ was used to prepare a series of diluted solutions. About 1.5 g of prepared natural sand soil and 40 ml of cesium or strontium solutions were loaded into 50 mL polypropylene centrifuge tubes with plug seal caps. The pH of the solutions was adjusted using 0.01 mol/kg HCl and NaOH solutions. These test solutions were then kept in a water bath shaker at the desired temperatures. The temperature controller of the water bath was calibrated and certified by Canadian Nuclear Laboratories Electronic Shop and the uncertainty of the measured temperature was within 0.03 °C. Typically adsorption equilibrium was reached within seven days. Two 10 ml samples from each test solution were taken at the test temperature and filtered using sterile 33 mm Millex 0.1μm syringe driven filter, one for pH measurement and one for Inductively Coupled Plasma Mass Spectrometry (ICP MS) measurement.

Cs^+ and Sr^{2+} adsorbed sand soils were dried in an oven at 55 °C over night and added in 40 ml of 10^{-3} mol/kg NaCl or $CaCl_2$ solutions for desorption testing at 25 °C for seven days. A 10 ml sample of each desorbed solution was obtained for ICP MS analysis to determine the desorbed Cs^+ and Sr^{2+} concentrations.

3. Results and discussions

3.1 Sand soil characterization

The sand soil sample was analysed by X-ray diffraction and the major component was determined to be quartz with a small amount of feldspar. Scanning Electronic Microscopy (SEM) showed that the particle size of the sand is generally between 0.25 and 0.50 mm. EDX elemental analysis showed that major components of the sand were oxygen and silicon (90%), followed by aluminum (1 to 8%), sodium and potassium (1 to 7%). Elemental analysis was carried out using ICP-MS from which each of the oxide contents are listed in Table 1. The trend of element content from ICP-MS agreed with those from the semi-quantitative method EDX.

Table 1 Sand soil sample analysis by ICP-MS

Oxide	Na_2O	MgO	Al_2O_3	K_2O	CaO	Fe_2O_3	SiO_2
Percentage	3.5	0.20	11.0	2.5	2.1	0.47	80

3.2 Adsorption kinetics

Adsorption of Cs^+ and Sr^{2+} with initial concentrations of 1.1×10^{-5} and 9.5×10^{-5} mol/kg, respectively, on sand increases with increasing elapsed time and follows second order reaction kinetics (Figure 1):

$$\frac{t}{q_t} = \frac{1}{k q_e^2} + \left(\frac{1}{q_e}\right) t \qquad (1)$$

where t is adsorption time, q_t is adsorbed quantity at time t, q_e is the adsorbed quantity at equilibrium and k is the reaction rate constant.

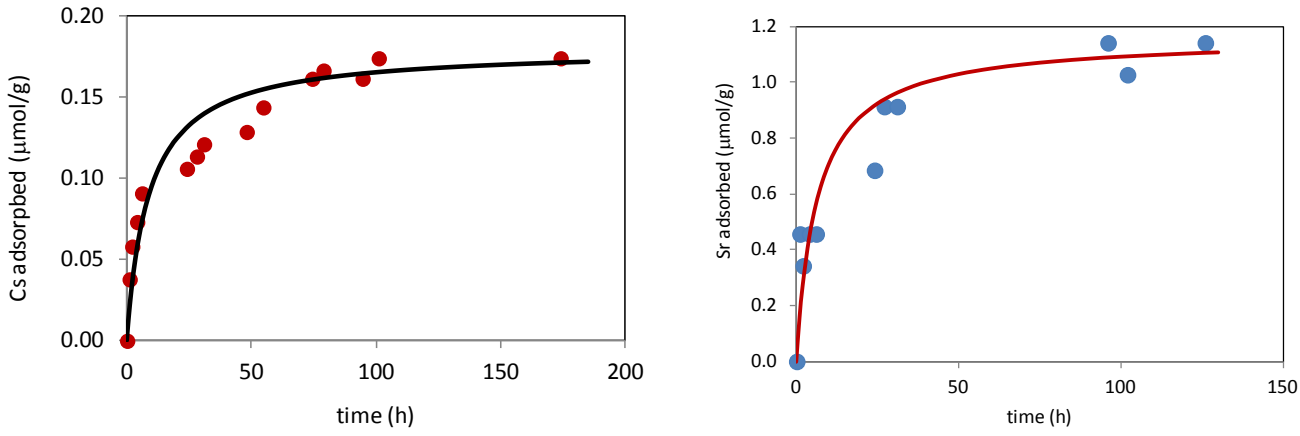

Figure 1 Reaction kinetics of Cs and Sr adsorption on natural sand soil at 25 °C; solid circle, experimental; solid curve, calculated using Equation (1).

It can be seen that most of Cs^+ and Sr^{2+} adsorption occurred in the first 50 hours and adsorption reached equilibrium in 7 days. Second order reaction kinetics was also observed for cesium and cobalt adsorption on other soil samples [3].

3.3 pH effect

Cs^+ and Sr^{2+} adsorptions on sand soil as a function of pH are shown in Figure 2 with initial concentrations of Cs^+ and Sr^{2+} around 1.0×10^{-5} mol/kg. Overall, adsorption percentages increased with the increasing pH of the solution due to the increasing negative surface charge of soil surface, which is favourable for cation binding. Adsorption reaches its maximum at a pH range between 7 and 10, beyond which increasing pH leads to decreasing adsorption, likely due to the dissolution of sand soil in alkaline solutions.

The mechanism of Cs^+ and Sr^{2+} adsorption can be expressed as

$$Cs^+ + \equiv S\text{-}OH = \equiv S\text{-}O\text{-}Cs + H^+ \quad (2)$$

$$Sr^{2+} + 2 \equiv S\text{-}OH = (\equiv S\text{-}O)_2\text{-}Sr + 2H^+ \quad (3)$$

where ≡S-OH is the hydrolysed surface of sand soil. Equation (3) suggested that the change of adsorption percentage as a function of pH is sharper for Sr^{2+} than Cs^+. This is due to additional proton release when Sr^{2+} is adsorbed on the soil surface as observed in Figure 2.

It was observed that Cs^+ and Sr^{2+} adsorbed on sand soil even under very acidic conditions (pH<4). This is likely due to low point of zero charge (pzc) of the soil surface as quartz is the major component of the sand soil and it has a pzc=2 [4].

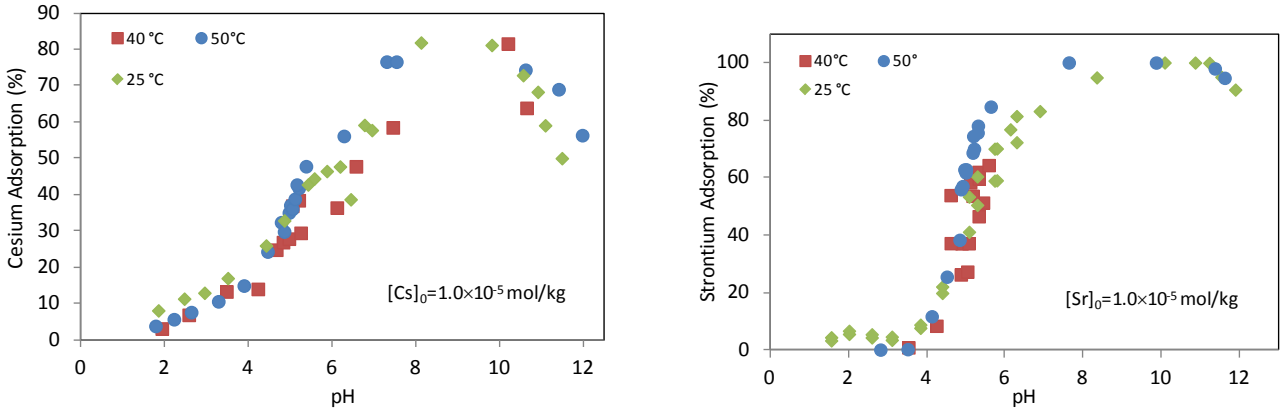

Figure 2 Cs and Sr adsorption on sand soil as a function of pH.

3.4 Concentration effect

3.4.1 Cs^+ adsorption

Adsorption of Cs^+ and Sr^{2+} on sand soil not only depends on pH but also on their concentrations. Overall, the percentage of cesium adsorbed on sand soil decreases as concentration increases due to saturation of available adsorption sites (Figure 3). Cesium adsorption on sand soil in neutral water was found to follow Freundlich adsorption isotherm:

$$\log(q_e) = \log(K_f) + \frac{1}{n}\log(C_e) \quad (4)$$

where q_e (mol/g) is the adsorbed mass on the adsorbent, $q_e = \frac{V_l(C_0 - C_e)}{m}$; V_l is the volume of solution; C_0 is the initial concentration of Cs^+; C_e is the equilibrium concentration of Cs^+ in solution (mol/kg); m is the mass of adsorbent (g); n is an empirical constant; K_f is a constant related to the adsorption capacity. The values of n and K_f in Equation (4) was obtained from the slope and y-axis intercept of the straight line in Figure 4 and are equal to 1.54 and 258 at 25 °C, respectively.

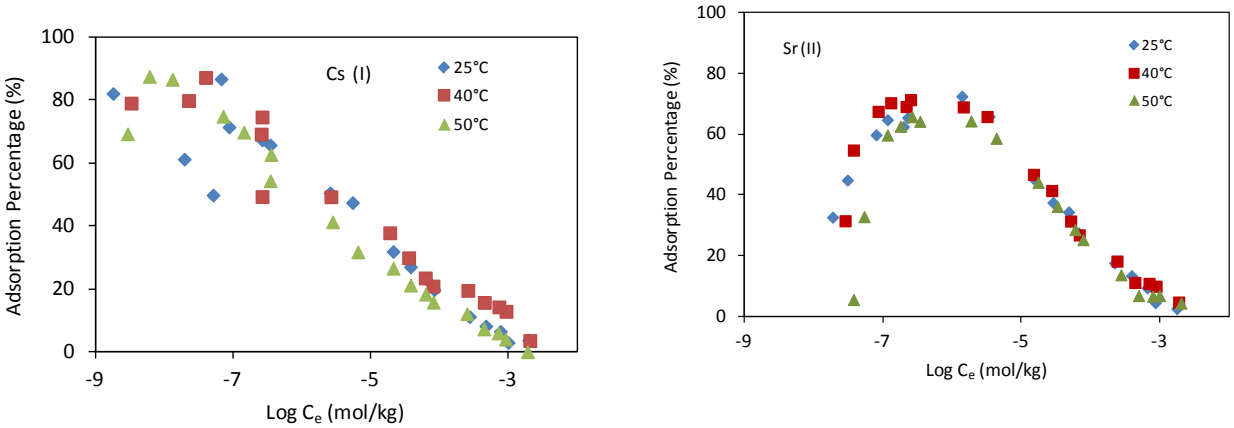

Figure 3 Cs (I) and Sr (II) adsorption on sand soil as a function of concentration.

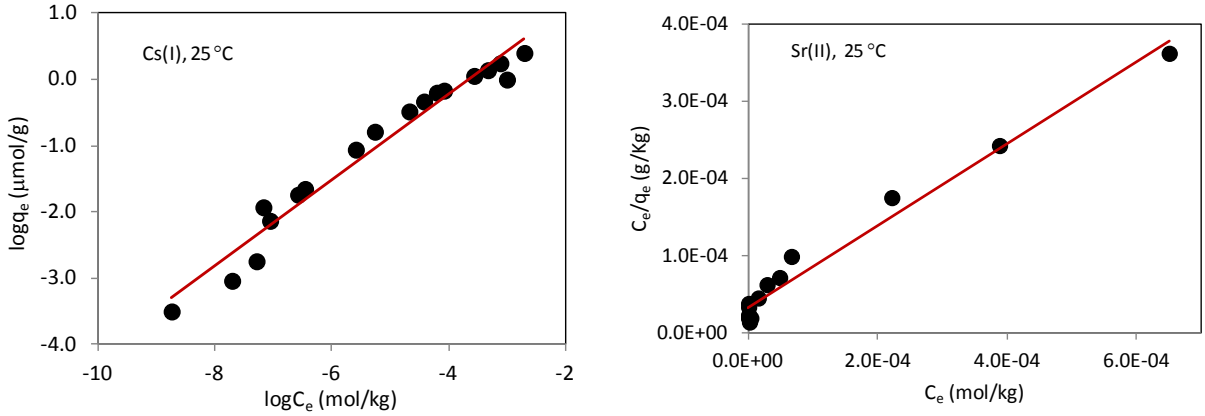

Figure 4 Freundlich isotherm model for Cs^+ adsorption (Equation 4) and Langmuir isotherm model for Sr^{2+} adsorption (Equation 5) on sand soil at 25 °C.

3.4.2 Sr^{2+} adsorption

Unlike Cs^+ adsorption, Sr^{2+} adsorption percentage increases rapidly with increasing concentration when Sr^{2+} concentration are lower than 2×10^{-7} mol/kg; at concentration above that point, the adsorption percentage decreases with increasing Sr^{2+} concentration. Such an adsorption is likely due to the transition of high bonding energy sites to low bonding energy sites [5]. Compared with Cs^+, the adsorption percentage of Sr^{2+} at concentrations below 2×10^{-7} mol/kg is lower than that of Cs^+ suggesting that Cs^+ is less mobile than Sr^{2+} under test conditions.

Adsorption of Sr^{2+} on sand soil can be represented by Langmuir isotherm, Equation 5:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}, \quad (5)$$

where q_e (mol/g) is the adsorbed mass on the adsorbent, $q_e = \frac{V_l(C_0 - C_e)}{m}$; V_l is the volume of solution; C_0 is the initial concentration of Sr^{2+} and C_e is the equilibrium concentration of Sr^{2+} in solution (mol/kg); K_L is the Langmuir adsorption constant related to the free energy of adsorption; q_m is the maximum capacity for mono-layer Sr^{2+} adsorption on soil. The values of K_L and q_m of Equation (5) can be obtained from the slope and y-axis intercept of the straight line in Figure 4 and have the values of 1.61×10^4 kg/mol and 1.9 μmol/g at 25 °C, respectively.

3.5 Temperature effect

Adsorption of Cs^+ and Sr^{2+} on sand soil under the conditions of different pH and cation concentrations was not significantly affected by temperature changes (Figures 2 and 3). This suggests that the enthalpy change of the adsorption was very small. It should be noted that the overall enthalpy change of adsorption (ΔH) depends on sum of the energy required for release of the hydration sphere from cations (ΔH_D) and the energy released from dehydrated cation adsorption on the sand soil surface (ΔH_A). A very small value of ΔH suggests that the value of ΔH_D is close to that of ΔH_A and the adsorption is not sensitive to temperature changes.

Since the overall enthalpy change of adsorption is very small, the driving force for Cs^+ and Sr^{2+} adsorption on sand soil is likely from an entropy effect (Δ*S*) based on the thermodynamic relationship, $\Delta G = \Delta H - T\Delta S$. Very small enthalpy changes for cation adsorption on attapulgite [6] and smectite [7] have been reported in literature.

3.6 Desorption of Cs^+ and Sr^{2+} from sand soil

Cs^+ and Sr^{2+} desorption percentage in 10^{-3} mol/kg NaCl or $CaCl_2$ solutions is shown in Tables 2 and 3 and they displayed different desorption behaviours discussed below.

3.6.1 Cs^+ desorption

Cs^+ has a low desorption percentage in 10^{-3} mol/kg NaCl which is below 40%. This suggests that Cs^+ has a higher affinity than sodium in solution, likely due to the smaller hydrated radius and stronger electrostatic attraction of Cs^+ compared to Na^+. The low desorption percentages in NaCl

solutions agree with the affinity order of alkali cation adsorption on clays: $Cs^+ > K^+ > Na^+ > Li^+$ [8].

The desorbed percentages of Cs^+ in $CaCl_2$ solution were mostly between 60 to 70% which is higher than in NaCl solution under same conditions likely because the affinity of Cs^+ ions to adsorption sites is less than that of Ca^{2+} ions [8].

3.6.2 Sr^{2+} desorption

Sr^{2+} had the same desorption percentage (40%) as Cs^+ in 10^{-3} mol/kg NaCl solution when initial adsorption quantities are low (around 0.7 μmol/g). However, when initial adsorption quantity (2.6 μmol/g) is large, Sr^{2+} showed a much higher desorption rate (71%) than that of Cs^+ (25%). The high adsorption quantity of Sr^{2+} significantly reduces the adsorption sites available for Na^+ and result in a strong competition between Na^+ and Sr^{2+} for adsorption sites on the surface of sand soil. Since Sr^{2+} has less affinity toward the surface of sand soil due to its higher hydration radius than Na^+ [9], most of Sr^{2+} adsorbed on the soil surface was replaced by Na^+ in NaCl solution.

In $CaCl_2$ solutions, Sr^{2+} desorption percentage is high and a majority (70 to 100%) of the adsorbed Sr^{2+}desorbed. The high desorption percentage of Sr^{2+} in $CaCl_2$ solution is likely related to the low dielectric constant of sand soil, which results in the adsorption of alkali-earth metal ions increasing in the sequence with increasing hydrated radii: $Ra^{2+} < Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+} < Be^{2+}$ [10].

Table 2 Cs^+ and Sr^{2+} desorption in 10^{-3} mol/kg NaCl solution at 25 °C.

Cs^+ desorption			Sr^{2+} desorption		
Before (μmol/g)	After (μmol/g)	Desorption %	Before (μmol/g)	After (μmol/g)	Desorption %
0.71	0.42	40	0.67	0.40	40
3.71	2.77	25	2.58	0.74	71

Table 3 Cs^+ and Sr^{2+} desorption in 10^{-3} mol/kg $CaCl_2$ solution at 25 °C.

Cs^+ desorption			Sr^{2+} desorption		
Before (μmol/g)	After (μmol/g)	Desorption %	Before (μmol/g)	After (μmol/g)	Desorption %
3.34	1.41	58	2.44	0.71	71
1.87	0.72	64	1.72	0.49	72
1.30	0.41	68	1.31	0.45	66
0.36	0.073	80	0.44	0.10	77
0.012	0.004	68	0.013	93.0	93
			0.0087	0.00	100

3.7 Competitive adsorption of Cs^+ and Sr^{2+}

Competitive adsorption of Cs^+ and Sr^{2+} on the same sand soil is shown in Figure 5. The results showed that there is no difference for Cs^+ adsorption with or without the presence of Sr^{2+} in the tested pH region. Adsorption of Sr^{2+} on sand soil is slightly higher without the presence of Cs^+ near neutral pH 7; however, overall Sr^{2+}adsorption was not significantly affected by the presence of Cs^+ under these test conditions. This result likely suggests that most of Cs^+ and Sr^{2+} occupy different adsorption sites on the surface of the sand soil and the interaction between adsorbed Cs^+ and Sr^{2+} is weak.

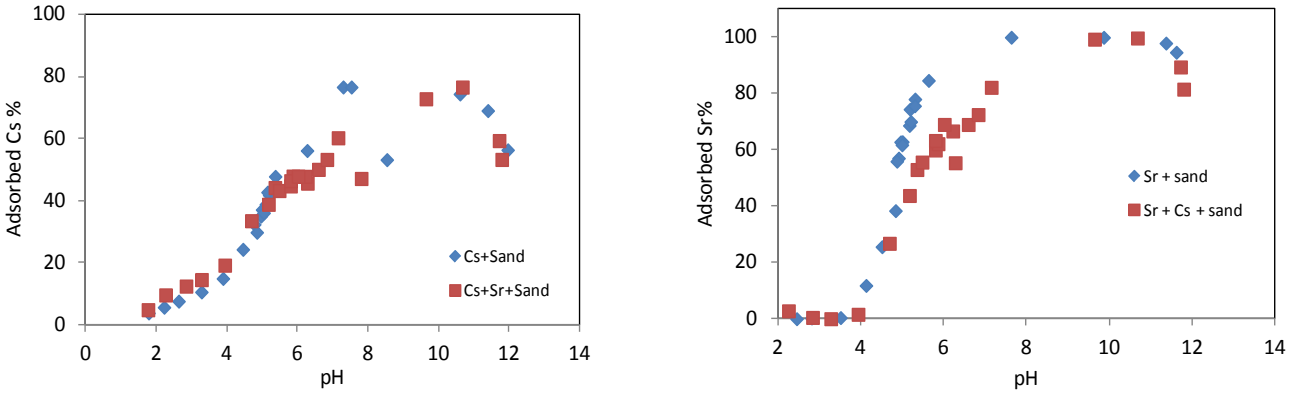

Figure 5 Comparison of Cs^+ and Sr^{2+} adsorption on sand soil with single or double cation adsorption

3.8 Organic matter effect

The effect of humic acid (5 ppm) on Cs^+ and Sr^{2+} adsorption on sand soil is shown in Figure 6. The results showed that humic acid has no effect on Cs^+ adsorption under the test conditions. Similar results were also reported for Cs^+ adsorption on natural silica [1] and on Al_2O_3 [11]. Adsorption of Sr^{2+} was not affected by the addition of humic acid below pH 8; however, adsorption of Sr^{2+} begins to decrease above pH 8, likely due to the formation of complexes between Sr^{2+} and humic acid [12][13]. Overall, the effect of the humic acid on Cs^+ and Sr^{2+} adsorption on sand soil was not significant.

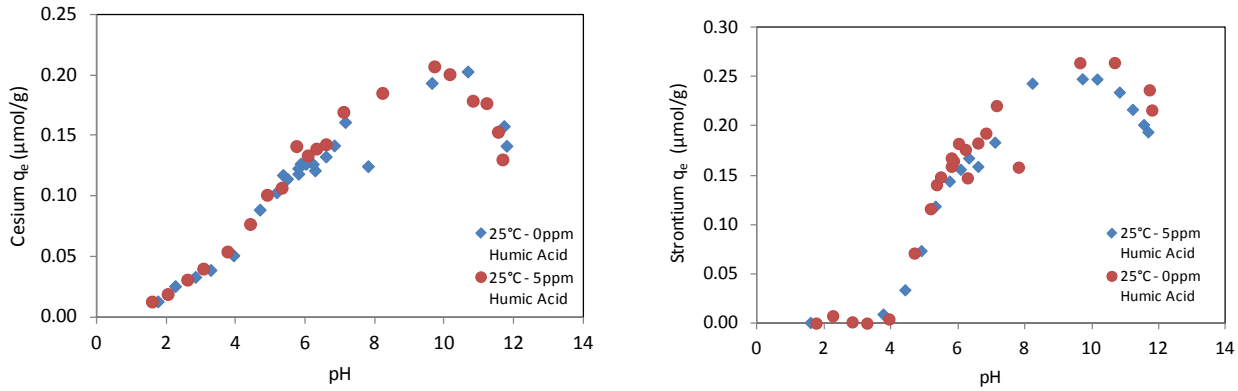

Figure 6 Comparison of Cs^+ and Sr^{2+} adsorption with or without humic acid.

4. Conclusions

Adsorption of Cs^+ and Sr^{2+} on a natural sand soil was studied under various chemistry conditions. Kinetic data showed that the adsorption of these cations on sand soil was slow and followed second order reaction kinetics. In general, increasing pH increases the adsorption of Cs^+ and Sr^{2+} while their adsorption slightly decreases above pH 10 likely due to the dissolution of sand soil. The overall temperature effect on adsorption of Cs^+ and Sr^{2+} was not significant suggesting that the entropy was the major driving force for the adsorption. Humic acid did not affect Cs^+ adsorption under these test conditions while the presence of humic acid slightly decreased Sr^{2+} adsorption above pH 8 probably due to the formation of complexes between Sr^{2+} and humic acid. Adsorption of Cs^+ can be described by Freundlich isotherm model while Sr^{2+} adsorption follows Langmuir isotherm model. The presence of both Cs^+ and Sr^{2+} in same solutions did not significantly affect each other suggesting most of these cations occupy different adsorption sites. Desorption tests showed that Cs^+ is less mobile than Sr^{2+} in NaCl and $CaCl_2$ solutions due to their different affinity to the surface of sand soil.

5. References

[1] N. Solovitch-Vella and J.M. Garnier, "Comparative kinetic desorption of ^{60}Co, ^{85}Sr and ^{134}Cs from a contaminated natural silica sand column: influence of varying physicochemical conditions and dissolved organic matter", Environmental Pollution, Vol. 141, No. 1, 2006, pp. 98-106.

[2] I.S. Shaban and F. Macášek, "Influence of humic substance on fixation of fission products in silicate media", Proceedings of Third Radiation Physics Conference, Al-Minia, Egypt, 1996 November 13-17.

[3] E.A. El-Sofany, A.A. Zaki. and H.S. Mekhamer, "Kinetics and thermodynamics studies for the removal of Co^{2+} and Cs^+ from aqueous solution by sand and clay soils", Radiochimica ACTA, Vol. 97, No. 1, 2009, pp. 23-32.

[4] M.C. Fuerstenau, G. Jameson and R.H. Yoon, "Froth Flotation: A Century of Innovation", Society for Mining, Metallurgy and Exploration, Inc. 2007.

[5] M.M. Benjamin and J.O. Leckie, "Multiple-Site Adsorption of Cd, Cu, Zn and Pb on Amorphous Iron Oxyhydroxide", Journal of Colloid and Interface Science, Vol. 79, No. 1, 1981, pp. 209-221.

[6] Q.H. Fan, X.L. Tan, J.X. Li, X.K. Wang, W.S. Wu and G. Montavon, [2009], "Sorption of Eu (III) on attapulgite studied by batch, XPS and EXAFS techniques", Environmental Science and Technology, Vol. 43, No. 15, 2009, pp. 5776-5782.

[7] A. Bauer, T. Rabung, F. Claret, T. Schäfer, G. Buckau and T. Fanghänel, "Influence of temperature on sorption of europium onto smectite: the role of organic contaminants", Applied Clay Science, Vol. 30, No. 1, 2005, pp. 1-10.

[8] W. Stumm and J.J. Morgan, "Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters", Wiley- Interscience, 1970.

[9] B.E. Conway, "Ionic Hydration in Chemistry and Biophysics", Studies in Physical and Theoretical Chemistry, Vol. 12, 1981.

[10] D. Sverjensky, "Prediction of the speciation of alkaline earths adsorbed on mineral surfaces in salt solutions", Geochimica et Cosmochimica Acta, Vol. 70, No. 10, 2006, pp. 2427-2453.

[11] X. Wang, T. Rabung and H. Geckeis, "Effect of pH and humic acid on the adsorption of cesium onto γ-Al_2O_3", Journal of Radioanalytical and Nuclear Chemistry, Vol. 260, No. 2, 2004, pp. 437-438.

[12] F. Macášek, I.S. Shaban and L. Mátel, "Cesium, strontium, europium and plutonium (IV) complexes with humic acid in solution and on montmorillonite surface", Journal of Radianalytical and Nuclear Chemistry, Vol. 241, No. 3, 1999, pp. 627-636.

[13] M. Samadfam, T. Jintoku, S. Sato and H. Ohashi, "Effect of pH on stability constants of Sr(II)-humate complexes", Journal of Nuclear Science and Technology, Vol. 35, No. 8, 1998, pp. 579-583.