

The adsorption of Strontium on soils developed in arid region as influenced by clay content and soluble cations

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Abstract

The retention of strontium from solutions (concentration range 2 to 30 mg/l) by soils developed under arid conditions of Iran was investigated using a batch technique. Sr sorption characteristics a clayey and a silty clay loam soil were examined at room temperature and with 0.01M CaCl₂ as a background electrolyte. Sorption processes are found to show a Freundlich-type behavior. Results indicated the clay content and ionic strength play predominant role on sorption of Sr. At soil with high soluble cations (saline-sodic soil) less strontium was adsorbed at lower concentrations of strontium due to greater competition with other cations especially with soluble Ca and Mg. Electrical conductivity and ratio of soluble Ca and Mg to total soluble cations is important especially in soils with high EC and SAR.

Key Words

Strontium adsorption, Freundlich isotherm, Soils of arid region.

Introduction

The investigation of sorption-desorption phenomena of contaminants by soils is of great importance from the viewpoint of environment and agriculture. The knowledge of sorption-desorption characteristics of contaminants by soils is useful in simulation and prediction of contaminant transport and diffusion in soil-water systems and uptake by plants (Smolders *et al.* 1997; Cox *et al.* 1995). One of the important contaminants is radionuclides. The interest in the behavior of Sr in soils has mainly brought about by the fact that long-lived radionuclide of ⁹⁰Sr ($T_{1/2} = 28.8$ y), which is produced by nuclear fission and one of the radionuclides most frequently released from low-level radioactive waste to the environment. The sorption characteristics of radiostrontium on various soils, sediments and minerals have been the subject of many recent investigations (Shenber and Eriksson 1993). Therefore, it is of great importance to understand the sorption behavior of radiostrontium in the environment in order to control the mobility of this element in the environment. Many studies have demonstrated that the transport of radiostrontium in soil is faster than that of other elements such as cesium, cobalt and plutonium. In this sense, radiostrontium has a greater threat to our environment than other radionuclides (Bachhuber *et al.* 1982; Price 1991). The sorption and migration of strontium in soil could be influenced by many factors and the nature of radionuclides in the solution as well as chemical and mineralogical nature and physical environment of the soil (Yasuda and Uchida 1993; Lieser *et al.* 1986). CaCO₃ has a negative contribution to the sorption due to its interaction with the other solid components in the soil to suppress Sr sorption on the other solid components (Jin Zhou *et al.* 1996). The Sr adsorption mechanism in soil is mainly an ion exchange reaction, and adsorbed Sr could not exist in the fixation fraction (Krouglov *et al.* 1998). In addition, adsorption of Mg⁺² and Ca⁺² are in competition with Sr⁺². Indeed, the amount of sorbed Sr in soil was observed to decrease with increasing Mg and Ca concentrations in soil solution (Bunde *et al.* 1997).

Bascetin and Atun (2006) studied the adsorption behavior of Kaolinite and Montmorillonite minerals and their mixtures with Sr ion were studied by a batch method. The Freundlich parameters were used to characterize a site distribution function for binary exchange between Sr and Na. The adsorption capacity of clay mixtures decreased as kaolinite fractions increased.

The sorption and desorption of radionuclide ⁹⁰Sr⁺² were investigated by Zhang *et al.* (2006) on calcareous soil using batch technique. It was found that the sorption is dependent on ionic strength, and fulvic acid enhances the sorption of ⁹⁰Sr⁺² on calcareous soil.

The present work was performed in order to investigate behavior of Sr adsorption in a saline-sodic soil and a normal soil developed in arid environment in Central Iran.

Material and Methods

The soil samples used in this study, which are representatives of the calcareous soils in Iran, were collected from the surface horizons (0-25cm) in Karaj and Eshtehard regions from dominant soil series. The soils were classified in the order Aridisols. After being air-dried at room temperature and passed through a 2 mm sieve, the selected properties of the soil samples were analyzed. Particle size analyses were performed by hydrometer method for determination of clay fraction. Sand fraction (0.05-2mm) was determined by 0.05 mm sieve. The EC values were measured in saturation extract. Organic carbon was determined by the dichromate oxidation method. The CaCO₃ was determined by titration method and the cation exchange capacity (CEC) was measured according to the ammonium acetate (pH=7.0) method. The soil samples were treated in triplicate. Clay minerals were identified using X-Ray Diffraction (XRD) analysis on the sub-2 μm fraction.

The two soils studied showed a wide range of physical and chemical properties. One soil was barren with very high EC and SAR values (Haplosalids), and the other was normal productive soil under wheat cultivation with low EC and SAR (Haplocambids).

The adsorption of Sr was measured using a batch technique at room temperature (22.5±0.5). Adsorption experiment was performed in 50 ml screw cap centrifuges tubes. The Sr adsorption isotherms were obtained using eight concentration of SrNO₃ in the range 2 to 30 mg/l, in the presence of 0.01 M CaCl₂. The time selected for full equilibrium was 3 hours.

A 25 ml of each concentration was mixed with 0.5 g of soil (1:50), and the samples was shaken for 3 hours, using a reciprocating shaker. The soil suspensions were centrifuged at 4500 rpm for 15 minutes and the supernatant was filtered through Whatman No.42 filter paper. Sr concentrations of the supernatants were determined by Atomic Absorption Spectrometer. The amounts of Sr sorbed were deduced from the difference between the solution concentration added and Sr concentration remaining in the supernatant (Bohn *et al.* 1985; Sparks *et al.* 1996; Jinzhou *et al.* 1996).

Results and Discussion

The values for particle size distributions, concentrations of soluble cations, CEC and organic carbon content for each soil type are given in Table 1. The particle size distribution shows higher amount of clay content of the saline-sodic soil compared to normal soil. The particle size and clay mineralogical analyses indicated that the Soil 1 had higher amounts of clay content (%58.85) and vermiculite and illites type clay minerals and Soil 2 contained lower amount clay content (% 28.75). These differences were also reflected by the higher value of CEC in the saline-sodic soil.

The Freundlich isotherm equation has been used to describe the adsorption characteristics of soils at the end of 3-hour. It was found that the data are not consistent with Langmuir isotherm.

Freundlich isotherms are illustrated in Figure 1 from the experimental data obtained. Table 2 shows the Freundlich adsorption parameters, correlation coefficients (R²) and standard error (SE) of fitting. In saline-sodic soil the slope (1/n) of the best fitted line was higher than 1, whereas in normal soil 1/n was less than 1. As it is observed from Figure 2, comparison of Freundlich isotherms in both soils shows that higher amount of Sr adsorption occurs in Soil 1 than Soil 2. But in lower concentrations of Sr, less than about 10 mg/l strontium, Soil 2 adsorbed more Sr than the Soil 1.

Table 1. Selected chemical and physical properties the studied soils

	Clay (%)	Silt (%)	Sand (%)	Texture	dg	δg	Na ⁺ (mg/L)	K ⁺ (mg/L)	Ca ⁺⁺ (mg/L)	Mg ⁺⁺ (mg/L)
Soil 1	58.85	38.19	2.19	Clay	0.0043	6.27	17627.9	70.05	1372.67	436.27
Soil 2	28.75	51.87	19.37	Silty Clay Loam	0.0208	10.69	79.3	19.92	90.18	37.67
	CEC (meq/100g)	CaCO ₃ (%)	OC (%)	EC (dS/m)	SAR (mmol/L) ^{0.5}	Soil type				
Soil 1	17.65	21.15	0.51	60.1	106.13	Saline-Sodic				
Soil 2	11.69	22.03	0.97	1.003	1.77	Nonsaline				

Notwithstanding higher clay content specially fine clay (higher adsorbent) in saline-sodic soil, lower sorption of Sr at initial concentration of Sr added likely can be attributed to higher ionic strength (ionic strength have direct relationship with EC (Griffin and Jurinak 1973)) in saline-sodic soil and Sr competition with other cations specially Ca, Mg and Na. But at higher Sr concentrations competition for occupy of exchange sites have decreased. Therefore with rising amounts of Sr added in Soil 1 sorption of strontium increase.

In clayey soil, $1/n$ value is equal to 1.2 ($1/n > 1$) and therefore adsorption is defined by S-type isotherm. With an S-type isotherm the slope initially increases with adsorptive concentration, but eventually decreases and becomes zero as vacant adsorbent sites are filled (Sparks 1995). In silty clay loam soil, $1/n$ value is equal to 0.74 ($1/n < 1$), adsorption isotherm is described by L-type isotherm. Such adsorption behavior could be explained by the high affinity of the adsorbent for the adsorptive at low concentrations, which then decreases as concentration increases (Sparks 1995). S-type isotherm is prevalent in soils with fine texture; therefore, Soil 1 with higher amounts of clay content and lower d_g is defined by S-type isotherm. In the 2 soils studied, the type of isotherms is different (Figure 2). Therefore comparison of K_d in these soils is impossible.

Consequently, to compare K_d , we need to assume the average slopes to be 1. The obtained isotherm is defined by C-type as in Figure 3. Therefore, the new equation is defined as follow (C-type):

$$q = K_p C$$

A partition coefficient, K_p , can be obtained from the slope of a linear adsorption isotherm using the above equation where q was defined earlier and C is the equilibrium concentration of the adsorptive. The K_p provides a measure of the ratio of the amount of a material adsorbed to the amount in solution (Sparks 1995). It was found that the value of K_p in Soil 1 is higher than that of Soil 2. Therefore, at similar Sr concentration with the exception of the lower concentration, adsorption of Sr by Soil 1 is higher than that by Soil 2. However, at the higher Sr concentrations; adsorption difference between the two soils will be enhanced.

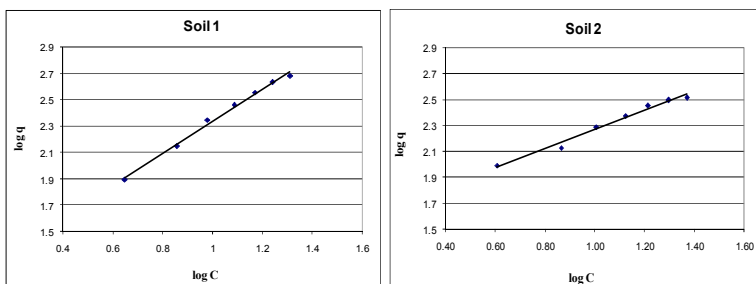


Figure 1. Freundlich isotherms (Linear form) of Strontium in the Soil 1 and Soil 2

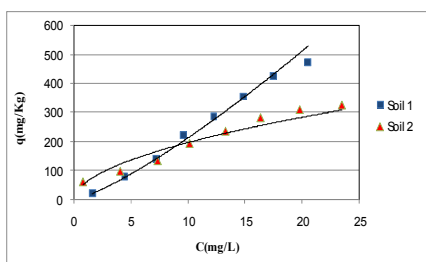


Figure 2. Comparison of Freundlich isotherms of strontium in two soils

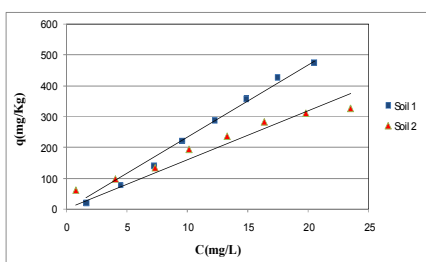


Figure 3. Comparison of K_d (k_p) in two soils (Average slopes of attained isotherms was assumed to be one ($1/n = 1$))

Table 2. Freundlich and C-type equation parameters for Sr adsorption on studied soils

	K_d	$1/n$	SE	R^2	K_p $1/n=1$
Soil 1	13.33	1.210	0.025	0.993	23.43
Soil 2	33.81	0.738	0.028	0.983	15.98

Conclusion

The sorption of Sr in selected soils could be influenced by many factors specially clay content, predominant clay mineral, EC, SAR, dg. The Freundlich isotherm adequately describes the Sr adsorption for concentrations higher than 2_{mg/L} strontium. In addition to the effect of EC and ionic strength on Sr sorption, the ratio of water soluble Ca and Mg cations to total soluble cations are important factors especially in soils with high EC and SAR. In Soil 1 which contains higher amounts of clay content and higher amounts of vermiculite and illites, thus, Sr has been adsorbed more at the surface of the clay minerals.

References

- Bachhuber H, Bunzl K, Schimmack WG (1982) The migration of ¹³⁷Cs and ⁹⁰Sr in multilayered soils: results from batch, column, and fallout investigations. *Nuclear Technology* **59**, 291-301.
- Bascetin E, Atun G (2006) Adsorption behavior of strontium on binary mineral mixtures of Montmorillonite and Kaolinite. *Applied Radiation and Isotopes* 957- 964
- Bohn H, McNeal B, O'Connor G (1985) Soil Chemistry. Wiley, 341pp
- Bunde RL, Rosentreter JJ, Liszewski MJ, Hemming CH, Welhan J (1997) Effects of calcium and magnesium on strontium distribution coefficients. *Environmental Geology* **32**, 219–229.
- Cox, L., Hermosin, M. C., Cornejo, J. (1995) Adsorption and desorption of thiazafuron as a function of soil properties. *International Journal of Environmental Analytical Chemistry* **58**, 305-314
- Griffin Gp, Jurinak JJ (1973) Estimation of activity coefficients from the electrical conductivity of natural aquatic systems and soil extracts. *Soil Science* **116**, 26-30.
- Jinzhou D, Wenming D, Xiangke W, Zuyi T (1996) Sorption and desorption of radiostrontium on calcareous soil and its solid components. *Journal of Radioanalytical and Nuclear Chemistry* **203**, 31-36.
- Krouglov SV, Kurinov AD, Alexakhin RM (1998) Chemical fraction of ⁹⁰Sr, ¹⁰⁶Ru, ¹³⁷Cs and ¹⁴⁴Cs in Chernobyl-contaminated soils: an evolution in the course of time. *Journal of Environmental Radioactivity* **38**, 59–76.
- Lieser KH, Gleitsmann B, Peschke S, Steinkopff T (1986) Colloids formation and sorption of radionuclides in natural systems. *Radiocemica Acta*, **40**, 39-47
- Price KR, (1991) The Depth Distribution of ⁹⁰Sr, ¹³⁷Cs, and ^{239/240}Pu in Soil Profile Samples. *Radiochimica Acta* **54**, 145-147
- Shenber MA, Eriksson A (1993) Sorption behavior of cesium in various soils. *Journal of Environmental Radioactivity* **19**, 41–51.
- Smolders E, Brande KVD, Merckx R (1997) Concentration of ¹³⁷Cs and K in soils solution predict the plant availability of ¹³⁷Cs in soils. *Environmental Science & Technology* **31**, 3432-3438.
- Sparks DL, Page AL, Helmke PA, Leoppert RH, Soltanpour PN, Tabatabai MA, Johnston GT, Sumner ME (1996) Methods of soil analysis, Soil Science Society of American, Madison, Wisconsin, USA
- Sparks DL, (1995) Environmental soil chemistry. CRC Press, Boca Raton, F L.
- Yasuda H, Uchida S (1993) Statistical approach for the estimation of strontium distribution coefficient. *Environmental Science Technology* **27**, 2462–2465.
- Zhang ML, Ren A, Shao D, Wang X (2006) Effect of fulvic acid and ionic strength on the sorption of radiostrontium on Chinese calcareous soil and its solid components. *Journal of Radioanalytical and Nuclear Chemistry* **268** (1), 33-36.