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Effect of fulvic acid and ionic strength on the sorption of radiostrontium on Chinese calcareous soil and its solid components

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The sorption and desorption of radionuclide $^{90}Sr^{2+}$ were investigated on untreated calcareous soil and two treated soils to remove organic matter and calcium carbonate using batch technique. The experiments were carried out at ambient condition, pH 7.8±0.1 and in the presence of 0.001M NaCl. Effects of fulvic acid and ionic strength on the sorption of $^{90}Sr^{2+}$ on calcareous soil were also studied. It was found that the sorption isotherms are linear in the strontium concentration range used herein, and the sorption of $^{90}Sr^{2+}$ on the calcareous soil can be described as a reversible sorption process and the sorption mechanism is mainly ion-exchange. The sorption is dependent on ionic strength, and fulvic acid enhances the sorption of $^{90}Sr^{2+}$ on calcareous soil. Organic matter present in the calcareous soil is a significant trap of $^{90}Sr^{2+}$ and is responsible for the sorption.

Introduction

This paper is an extension of our previous papers,[1–5] where we studied the sorption of radionuclides $^{134}Cs^{+}$, $^{75}SeO_3^{2-}$, $^{125}I^{-}$ on Chinese soils by batch and column techniques. Sorption and desorption hysteresis of cesium on calcareous soil was obvious, and organic matter has a positive, calcium carbonate has a negative contribution to the sorption of cesium.[1] The sorption of radioselenium is dependent on the interlaminary space of the calcareous soil and the retention of selenium is attributed to clays and oxides.[4] The sorption of radionuclides on soil is dependent on the property of nuclides, the property of soil and experimental conditions such as ionic strength and pH values.[2–5] The objectives of this present study were: (1) to determine the values of distribution coefficient (K_d) of radiostrontium on calcareous soil; (2) to explore the effects of ionic strength and fulvic acid on the sorption of radiostrontium on calcareous soil; (3) to investigate the sorption mechanism of radiostrontium on calcareous soil; and (4) to study the contribution of soil components on the sorption of radiostrontium on calcareous soil.

Radiostrontium is the characteristic radionuclide present in the fallout of nuclear reactor accident, nuclear weapons test and in leakage of cooling water from nuclear power plant. Therefore, it is of great importance to understand the sorption behavior of radiostrontium in the environment, because the sorption is an important tool to control the mobility of radionuclide in the environment. It has been demonstrated that radiostrontium is a very mobile nuclide in the environment and the diffusion and migration of radiostrontium in the environment is faster than that of radiocesium and lanthanides.[6–8] The radionuclides with high K_d values generally move slower than those with low K_d values in the environment.

Sorption mechanisms of metal ions on soils, oxides and minerals in the presence or absence of humic substances have been studied and discussed extensively, which includes: surface complexation, ion-exchange, physical/chemical sorption, ligand exchange, hydrolysis at the surface, surface precipitation and polynuclear species/colloids formed at the surface, etc.[9–13] Humic substances may influence the sorption of metal ions on mineral surface by their ability to complex metal cations. Whether humic substances exert a mobilizing or retarding effect depends on the complex behavior of metal ion with humic substances and minerals. In general, the sorption is enhanced at low pH and reduced at high pH as compared to the system without humic substances.[11,14–17] The increase can be explained by the sorption of HS onto the mineral surface followed by the complexation of metal ion with surface sorbed HA, whereas the decrease is explained by the formation of HS–metal ion complexes which stabilize the metal ion in aqueous solution.

Most of the papers mentioned above were mainly focused on the sorption of metal ions on oxides and minerals in the presence or absence of humic substances.[9–11,13–17] Sorption and desorption of radionuclides on calcareous soil and its solid components were also investigated extensively by using batch or column experiments.[1,2,4,5,18] However, the study of the effects of ionic strength and humic substances on the sorption of radionuclides on calcareous soil and its solid components is still scarce, especially the contribution of the solid components.

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Experimental

Sample of calcareous soil, an irrigated warped soil, was derived from the surface horizon (0–20 cm) of cultivated land of Jiuquan county (Northwest area of China), which is near to the location of nuclear weapon tests. The soil was air-dried and ground to pass a 1 mm sieve, and then conditioned with 0.1M NaCl and washed 5 times with distilled water. The soil sample in Na-form was air-dried prior to use. Two portions of the sample were treated with HAc-NH_4Ac (0.5M) at pH 5 to remove calcium carbonate and with 30% H_2O_2 to remove organic matter.[19] The organic matter was determined to be 1.7% by dichromate oxidation method,[20] and calcium carbonate was evaluated to be 13.5% by modified manometric method.[21]

Fulvic acid was extracted from weathered coal from the area of Gongxian (Henan Province, China) and has been used in many investigations.[11,17,22] The concentration of FA was determined by UV vis spectrosphotometry at wavelength of 294 nm. The concentration of radiostrontium was analyzed by liquid scintillation using a Packard 3100 TR/AB scintillation analyzer (PerkinElmer). The scintillation cocktail was Ultima Gold AB™ (Packard).

The sorption of Sr on calcareous soil sample was studied by batch technique. The experiments were carried out at pH 7.8±0.2 and in 0.001M NaCl. Sodium chloride, soil sample, Sr, fulvic acid, HCl or NaOH were added to achieve the desired background electrolyte concentration, FA concentration and pH of aqueous solutions.

Polyethylene tubes were used in the batch experiments. The test tubes were shaken for 2 days so as to obtain the equilibration states. From the kinetic study, the time was sufficient to get into equilibration. The solid phase was separated from the aqueous one by centrifugation for 25 minutes at 7000 rpm. It was necessary to note that the sorption of Sr on the tube wall was negligible according to the test of Sr sorption in the absence of soil sample.

For the desorption measurements, after centrifugation at the end of sorption experiments, half of the supernatant was pipetted and an equal volume of background electrolyte solution was added. The pH was adjusted with 0.01M HCl or NaOH to obtain the same pH values as in the sorption experiments. Then the mixture was shaken and centrifugation at the same conditions as in the sorption experiments.

Results and discussion

Effect of the ionic strength

The sorption isotherms of $^{90}Sr^{2+}$ on the untreated soil at 0.01M and 0.001M NaCl solutions are shown in Fig. 1. As can be seen from the figure, the sorption isotherm at ionic strength of 0.001M NaCl is higher than that at 0.01M NaCl. The sorption of Sr on calcareous soil is dependent on the ionic strength, which indicates that the sorption is mainly dominated by cation-exchange.[23] The sorption mechanism of cation-exchange is generally influenced by the ionic strength, whereas the sorption mechanism of surface complexation is significantly affected by the pH. The distribution coefficient, K_d, is calculated by:

$$K_d = \frac{C_0 - C_{eq}}{C_{eq}} \cdot \frac{V}{m} \tag{1}$$

where C_0 is the initial concentration (mol/l), C_{eq} is the concentration of Sr in the supernatant after equilibration (mol/l), m is the mass of soil in the solution (g), and V is the volume of the solution (ml). The K_d values are 33±4 ml/g ($I = 0.01$M NaCl) and 43±4 ml/g ($I = 0.001$M NaCl), respectively.

Effect of fulvic acid

The sorption isotherms of $^{90}Sr^{2+}$ on the untreated calcareous soil in the presence and absence of fulvic acid are shown in Fig. 2. The initial concentration of FA is 12 mg/l and about 94–97% of FA is adsorbed on the soil after equilibration by measuring the concentration of FA in the supernatant. FA enhances the sorption of $^{90}Sr^{2+}$ on calcareous soil, which indicates that the complexation of Sr with FA sorbed on the calcareous soil is stronger than the ion-exchange between Sr and cations (such as Na^+ herein mainly) at the soil surface.

Comparing to the sorption of Sr on bentonite[7,17,24] and hydrous alumina,[25] the sorption mechanism of Sr on calcareous soil is very similar to that on clay and minerals. The sorption of Sr is mainly dominated by the free cations at the solid surface, which could provide the exchange sites to adsorb strontium. TRIVEDI and AXE[25] studied the sorption of Sr on hydrous alumina and manganese oxides and found that the sorption is a physical reaction and it is also a rapid and reversible adsorption reaction to the external surface. WANG and LIU[7] studied the sorption of Sr on bentonite by using capillary method and found that Sr sorption is very weakly dependent on pH, independent on Sr concentration, which indicates a linear sorption.

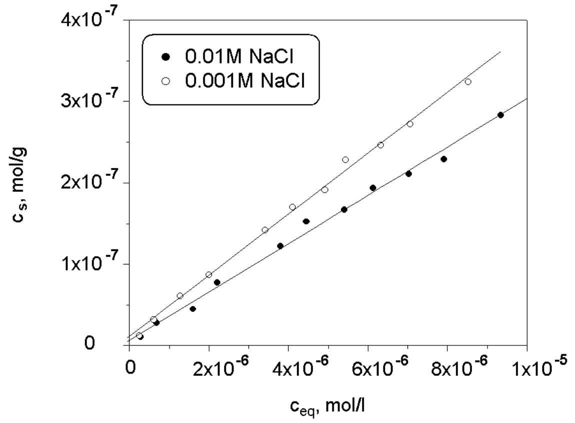

Fig. 1. Effect of ionic strength on the sorption of $^{90}Sr^{2+}$ on untreated soil; pH 7.8±0.2, $V/m = 50$ ml/g, $T = 25±2$ °C

Sorption isotherms on calcareous soil and its solid components

The sorption isotherms of Sr on the untreated calcareous soil and two treated soil samples to remove organic matter and calcium carbonate, respectively, are shown in Fig. 3. The K_d values and the relative contribution of organic matter and calcium carbonate of the soil are listed in Table 1. The sorption isotherm of Sr on the soil to remove calcium carbonate is higher than that of Sr on the untreated soil, whereas the sorption isotherm on the soil to remove organic matter is lower than that of Sr on the untreated soil. Calcium carbonate has a relative negative contribution to Sr sorption, while organic matter has a relative positive contribution to Sr sorption on calcareous soil. As can be seen from Table 1, the organic matter represents 1.7% of the mass and contributes 21% to the sorption of Sr on the whole soil. The results indicate that the organic matter in the calcareous soil has a very great affinity for Sr. The calcium carbonate represents 13.5% of the mass and contributes –21% to Sr sorption on the whole soil.

Table 1. Distribution coefficients and relative contributions of organic matter and $CaCO_3$

	K_d, ml/g	Relative contribution, %
Untreated soil	43±4	
Treated soil to remove organic matter	34±3	
Treated soil to remove $CaCO_3$	52±8	
Organic matter		$\frac{43-34}{43}\times 100 = 21$
$CaCO_3$		$\frac{43-52}{43}\times 100 = 21$

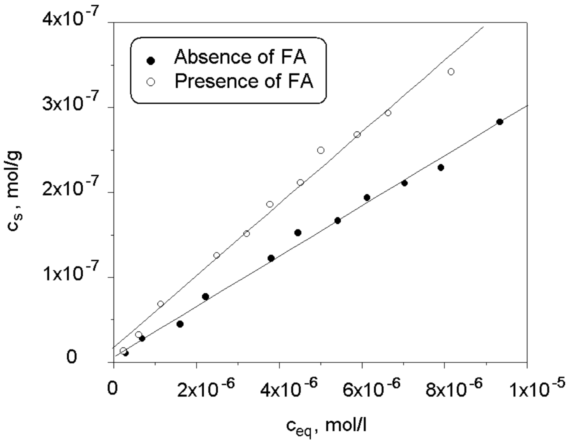

Fig. 2. Effect of fulvic acid on the sorption of $^{90}Sr^{2+}$ on the untreated soil; pH 7.8±0.2, $V/m = 50$ ml/g, 0.01M NaCl, $T = 25±2$ °C

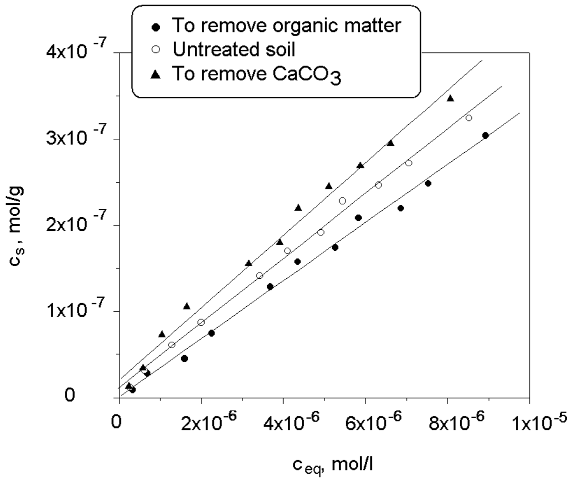

Fig. 3. Sorption isotherms of $^{90}Sr^{2+}$ on untreated and two treated soils; pH 7.8±0.2, $V/m = 50$ ml/g, 0.001M NaCl, $T = 25±2$ °C

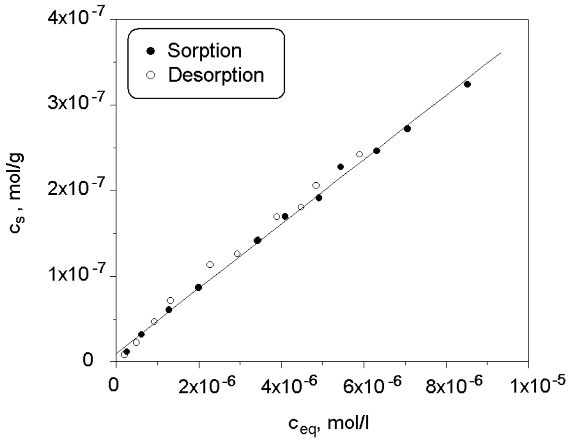

Fig. 4. Sorption and desorption isotherms of $^{90}Sr^{2+}$ on untreated soil; pH 7.8±0.2, $V/m = 50$ ml/g, 0.001M NaCl, $T = 25±2$ °C

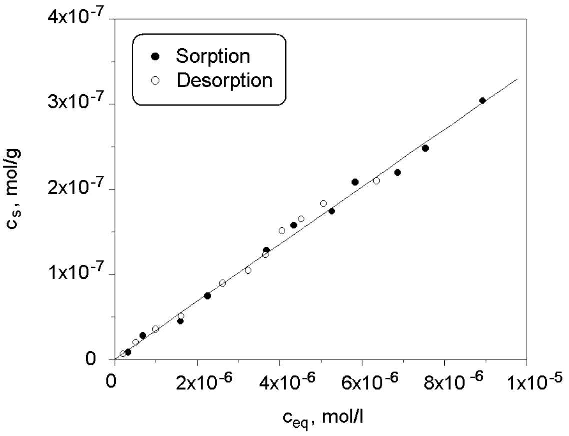

Fig. 5. Sorption and desorption isotherms of $^{90}Sr^{2+}$ on treated soil to remove organic matter; pH 7.8±0.2, $V/m = 50$ ml/g, 0.001M NaCl, $T = 25\pm2$ °C

This result can be possibly attributed to the fact that some sorption sites (such as clay minerals) were blocked by calcium carbonate to some extent. When calcium carbonate is removed from the whole soil, the sorption sites are freely provided to Sr sorption. Organic matter, calcium carbonate and other components play an important role in the sorption of Sr on the whole soil. However, the mechanisms of these interactions among the solid components are not very well understood.[3]

Sorption and desorption isotherms

The sorption and desorption isotherms of Sr on the untreated and treated soils to remove organic matter are shown in Figs 4 and 5, respectively. The K_d values of Sr sorption and desorption were 43±4 ml/g and 45±5 ml/g on the untreated soil; 34±3 ml/g and 35±3 ml/g on the treated soil to remove organic matter, respectively. According to the standard deviation, the sorption and desorption isotherms can be considered as a single straight line and, therefore, the sorption of Sr on calcareous soil is reversible. The result also indicates that the sorption is a physical reaction and reversible adsorption.[17,24,26]

Conclusions

The sorption and desorption of radiostrontium on calcareous soil and its solid components were studied. The results indicate that the sorption of strontium on calcareous soil is a physical adsorption, and the sorption is rapid and reversible. Organic matter is an important trap for strontium in the whole soil. Radiostrontium is a very mobile element in the environment and its reversible sorption property makes it dangerous to the environmental pollution.

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