

DETERMINATION OF RETARDATION FACTORS FOR ADSORPTION OF CESIUM, COBALT AND STRONTIUM ON THE SOIL OF PINSTECH WASTE DISPOSAL AREA

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The adsorption of cobalt, cesium and strontium on the soil of PINSTECH radioactive waste disposal area was studied to find the adsorption parameters and retardation factors. Standard batch adsorption experiments were performed for three known concentrations of nitrate solutions of stable nuclides by equilibrating them with soil samples. The treated/equilibrated solution concentrations were measured on adsorption spectrophotometer (Hitachi Model Z8000) equipped with Zeeman background corrector using flame atomization mode. Masses adsorbed were calculated by the difference of initial and equilibrated solution concentrations. The adsorption isotherms were obtained by plotting the values of masses of nuclides adsorbed per unit mass of soil versus equilibrium solution concentrations that resulted into straight lines. The Freundlich adsorption parameters were calculated from the slope and intercept of straight lines. The calculated parameters were then used to find the retardation factors at different equilibrium solution concentrations.

Keywords: Adsorption isotherms, Adsorption coefficients, Retardation factors

1. Introduction

Study of adsorption behaviour of radionuclides on the geological medium of a radioactive waste disposal site is important as adsorption retards the transport of radionuclides in the medium. During the transport of dissolved radionuclides in the pore water of a porous medium, a certain radionuclide mass is adsorbed to the medium particles reducing the porewater concentrations. Therefore, the net rate of transport of radionuclides is controlled by the process of adsorption.

During the adsorption of a solute from solution to the adsorbent, a chemical equilibrium is established between the amount of solute adsorbed and solute amount in solution. Different amounts of solute adsorb to the adsorbent when solutions of different initial concentrations are brought in contact with adsorbent. Relationships have been found to exist between the adsorbed mass per unit mass of adsorbent and concentration of solute in solution at equilibrium. These relationships are established by adsorption isotherms which can also be represented in mathematical form. The plots of adsorbed mass per unit mass of adsorbent versus equilibrium solution concentration result into the linear,

Freundlich and Langmuir isotherms [1].

In the linear adsorption isotherm, the adsorbed mass per unit mass of porous medium directly relates to the equilibrium solution concentration as:

$$S = K_d C_e \quad (1)$$

Where S (M/M) is the mass of solute adsorbed per unit mass of porous medium, C_e (M/L³) is the equilibrium solution concentration and K_d (L³/M) is the distribution coefficient. The plot of S versus C_e gives a straight line the slope of which is the distribution coefficient.

In the Freundlich isotherm, the solute mass adsorbed per unit mass of porous medium relates to the exponent of the equilibrium solution concentration as:

$$S = K_f C_e^{1/n} \quad (2)$$

Where K_f (L³/M)ⁿ is Freundlich constant and n is an exponent. By taking the log on both sides the equation becomes:

$$\log S = \log K_f + 1/n \log C_e \quad (3)$$

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The values of $1/n$ and K_f can be found by plotting $\log S$ versus $\log C_e$ that give a straight line with slope equal to $1/n$ and intercept equal to $\log K_f$.

The third isotherm, Langmuir isotherm, takes into account the maximum adsorption capacity of the medium and is represented as:

$$S = \frac{C_e K V_m}{1 + C_e K} \quad (4)$$

Where K (L^3/M) is a constant and V_m is the maximum amount of solute that can be adsorbed per unit mass of porous medium. The isotherm can also be written as:

$$\frac{C_e}{S} = \frac{1}{K V_m} + \frac{C_e}{V_m} \quad (5)$$

The plot of $\frac{C_e}{S}$ vs C_e gives straight line with slope equal to $\frac{1}{V_m}$ and intercept equal to $\frac{1}{K V_m}$.

The adsorption coefficients are used to calculate the value of retardation factor which represents the ratio of the velocity of conservative solute to the velocity of solute under the effect of adsorption. It is represented by the relationship as:

$$R = 1 + \frac{\rho}{\theta} \frac{dS}{dC_e} \quad (6)$$

Where R (dimensionless) is the retardation factor, ρ is the density and θ is the porosity of the porous medium. The retardation factors for Linear, Freundlich and Langmuir isotherms then become as:

$$R = 1 + \frac{\rho}{\theta} K_d \quad (7a)$$

$$R = 1 + \frac{\rho}{\theta} \frac{1}{n} K_f C_e^{1/n-1} \quad (7b)$$

$$R = 1 + \frac{\rho}{\theta} \left[\frac{K V_m}{1 + K C_e} \right] \quad (7c)$$

Equation 7 shows that retardation factor for linear isotherm depends only on the value of

distribution coefficient while the retardation factors for other two isotherms involve the values of solute equilibrium concentration. This is the reason that the adsorption of solute is assumed to follow the linear adsorption isotherm in many solute transport studies due to simplicity. However, the actual adsorption behavior may or may not follow this isotherm. In order to precisely define the amount of solute adsorbed and the solute in solution during transport in a geological porous medium, the actual adsorption isotherm of that solute is needed to be determined to find out the adsorption parameters such as distribution coefficient or Freundlich constant etc.

The liquid and solid radioactive waste generated at PINSTECH laboratories is managed at Radioactive Waste Management Group of Health Physics Division [2,3]. The waste is immobilized in conditioned waste packages which are disposed off in a shallow ground engineering trench. In case of any accidental release into the ground, the soil of waste disposal area will adsorb radionuclides and retard their transport to the far field. The high adsorption capacity is a desirable characteristic responsible for the retardation of solute transport. Since the disposal site soil has a high ion-exchange capacity of the order of 5–7 meq/100 g soil [2], therefore, it seems of interest to measure the retardation capacity of waste disposal site soil in order to evaluate the transport rate of radionuclides in the soil. The lithology of the waste disposal site consists of seven to twenty meters thick alluvium overlying the bedrock. The alluvium is composed of brown to reddish calcareous clay having minor fractions of silt, fine sand and gravel. A shallow water bearing permeable zone exists at the contact of recent alluvium with bedrock at a depth between seven to twenty meters. Therefore, it is important that the retardation should be high enough to stop the released activity from reaching to the permeable zone before it decays to the harmless levels. In this perspective, a study is made on the adsorption of cesium, cobalt and strontium on the soil of PINSTECH waste disposal area to find out the adsorption parameters. From the adsorption parameters, the retardation factors are calculated that give the ratio of transport rate when no adsorption occurs to the transport rate under the effect of adsorption.

2. Experimental Procedure

Adsorption experiments were performed on the soil samples collected from two locations of waste disposal area. The samples were collected at a depth of one foot to get fresh soil free of surface environmental effects. Standard batch adsorption experiments were performed to find out the amount of nuclides adsorbed on the soil [4,5,6]. 15 ml of 0.5×10^{-3} , 1×10^{-3} and 5×10^{-3} molar nitrate solutions of stable cobalt, cesium and strontium were equilibrated with 1 g of soil samples and separated by a centrifuge after equilibrating for two

hours. All the experiments were performed at neutral pH. Concentrations of equilibrated solution samples were measured on an Atomic Adsorption Spectrophotometer (Hitachi Model Z8000) equipped with Zeeman background corrector using flame automation mode. Molar masses adsorbed were calculated by the difference of initial and equilibrated solution concentrations. The molar masses of nuclides adsorbed per unit mass of soil and equilibrium solution concentrations are given in Table 1.

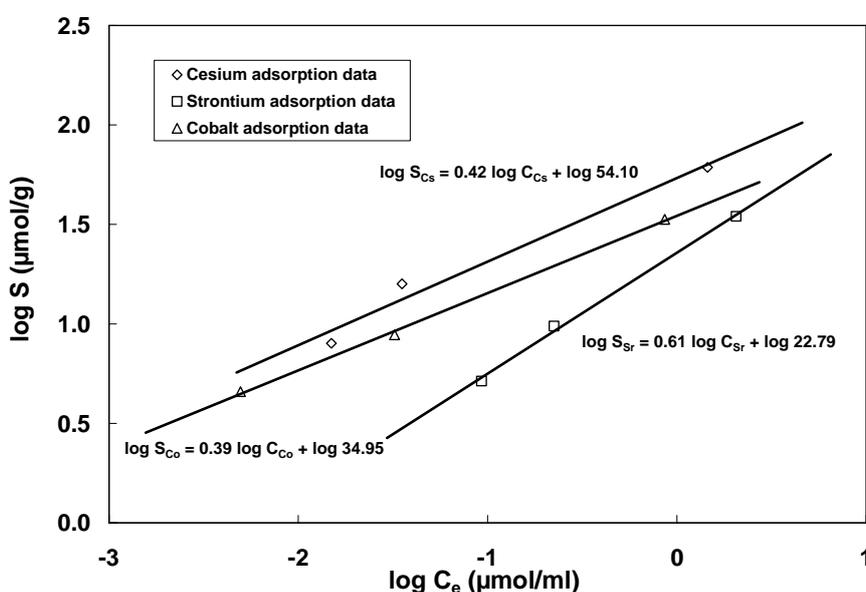


Figure 1. Adsorption isotherms of cesium strontium and cobalt.

Table 1. Equilibrium and adsorbed concentration values.

Sample Location	Cs		Sr		Co	
	C_e ($\mu\text{mol ml}^{-1}$)	S ($\mu\text{mol g}^{-1}$)	C_e ($\mu\text{mol ml}^{-1}$)	S ($\mu\text{mol g}^{-1}$)	C_e ($\mu\text{mol ml}^{-1}$)	S ($\mu\text{mol g}^{-1}$)
L1	1.580	59.311	2.064	34.598	0.892	33.065
	0.075	15.474	0.237	9.552	0.033	8.789
	0.035	7.770	0.093	5.153	0.005	4.559
L2	1.331	63.036	2.046	34.872	0.832	33.968
	0.016	16.354	0.212	9.929	0.031	8.825
	0.006	8.206	0.092	5.170	0.004	4.582

C_e = Equilibrium solution concentration

S = Adsorbed mass per gram of soil

Densities (ρ) of the soil samples were calculated by measuring the dry mass of soil in saturated soil column of known volume. Volumetric water contents (θ) or porosity of the soil samples were determined on the basis of weight differences between oven-dried and saturated samples by using column of known volume. The measured values of density and water content are given in Table 2.

Table 2. Input parameters for the calculation of D.

Sample Location	ℓ (gcm ⁻³)	θ (cm ³ cm ⁻³)	a_0 (cm)	t (days)
L1	1.36	0.47	11.2	35
L2	1.38	0.48	11.2	35

The average log values of molar masses adsorbed per unit gram of soil for the two locations were plotted versus average log values of equilibrium solution concentration that resulted into straight lines as shown in Figure 1. The straight lines indicated that the adsorption behaviour for the three nuclides follows Freundlich isotherm as given by the equations 2 & 3. The slopes of straight lines gave the values of exponent "1/n" equal to 0.42, 0.39 and 0.61 for cesium, cobalt and strontium respectively and intercepts gave values of Freundlich constant "K" equal to 54.1, 34.95 and 22.79 respectively. These values were put in equation 7b to find the retardation coefficients.

3. Discussion

The adsorption experiments were performed to find out the adsorption isotherms and retardation factors of cesium, cobalt and strontium for their adsorption on the soil samples obtained from two locations of PINSTECH waste disposal area. The adsorption data indicated that same molar masses of cobalt and strontium were adsorbed per unit mass of the soil obtained from two locations while more molar mass of cesium was adsorbed on the soil taken from location 2. In Figure 1, average log values of molar masses adsorbed per unit mass of soil were plotted against average log values of equilibrium solution concentration. The plots resulted into straight lines indicating that the data follows Freundlich isotherms. The values of exponent and Freundlich constant were found from

slopes and intercepts of the lines. The highest value of exponent equal to 0.61 was found for strontium, while the middle value of 0.42 was found for cesium and the lowest value equal to 0.39 was found for cobalt. The value of Freundlich constant came out to be highest equal to 54.10 for cesium, then for cobalt equal to 34.95 and for strontium equal to 22.79. The molar masses adsorbed on unit mass of soil were calculated for equilibrium concentrations ranging between 0.1 and 2.0 $\mu\text{mole/ml}$ for the three nuclides using equation 2. These adsorbed molar masses were plotted against equilibrium solution concentration in Figure 2. The plots show that at equilibrium, more cesium mass exists in adsorbed phase than strontium and

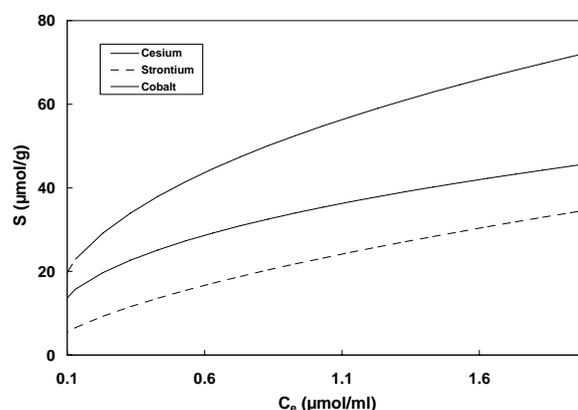


Figure 2. Adsorbed masses per unit mass of soil at different equilibrium solution concentrations.

cobalt at any solution concentration. Similarly, more cobalt exists in solid phase than strontium. In other words, if same molar concentrations of all the three nuclides are released into the soil of waste disposal area, more cesium atoms will adsorb leaving small porewater concentrations for transport further and hence the retardation will be the highest. Similarly, the retardation of cobalt will be higher than the strontium. Hence, in a particular time period, cesium will transport the least distance and strontium will transport the highest distance in the soil. In Figure 3, retardation factors calculated from equation 7b are plotted against equilibrium solution concentrations. The plots show that retardation factors rapidly decrease as concentrations are increased from 0.1 to 1.0 $\mu\text{mol/ml}$, after that the rate of decrease becomes almost constant upto equilibrium solution concentration of 2.0 $\mu\text{mol/ml}$. Also the rate of decrease is the highest for cesium and lowest for

strontium while the rate of decrease for cobalt remains in the middle of the two. The highest retardation factors at the equilibrium concentration of 0.1 $\mu\text{mol/ml}$ are 300, 200 and 100 for cesium, cobalt and strontium respectively that become 40, 24 and 30 at concentration of 2.0 $\mu\text{mol/ml}$. This indicates that at lower porewater concentrations, the rate of transport will be slow due to high retardation and at higher concentration, the rate of transport will be higher. Therefore, at high porewater concentrations the cesium, cobalt and strontium will transport 40, 24 and 30 times lower than the case if no adsorption occurs.

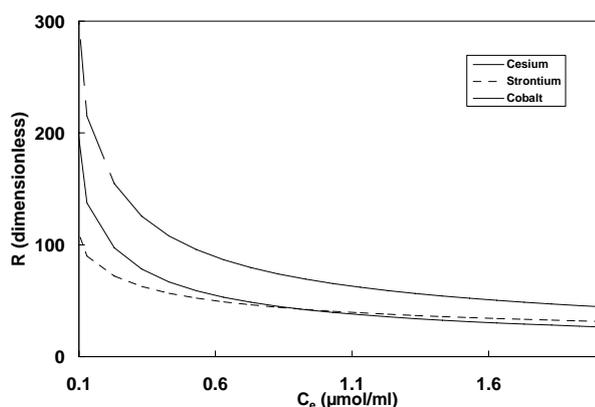


Figure 3. Retardation factors at different equilibrium solution concentrations.

4. Conclusion

The adsorption studies on the soil of PINSTECH radioactive waste disposal area indicated that the soil has high tendency to retard the transport of cesium, cobalt and strontium in the soil. The retardation capacity is in the order of cesium, strontium and cobalt i.e, the highest for cesium and lowest for cobalt. Also, the retardation of a single nuclide will not be constant at all equilibrium concentrations as in the case of linear adsorption isotherm but will be higher at higher porewater concentrations and vice versa.

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