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## Experimental and modelling investigation of caesium adsorption on soil samples around DAE facility, India

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### ABSTRACT

The kinetics and thermodynamics behind the sorption process of Cs (Caesium) on the soil are important to understand as these studies give information about the mobility of Cs in the environment. In the present study, sorption kinetics and the parameters influencing sorption (viz. time of contact, competing ions, temperature, solution pH and Cs concentration) were studied on the soil samples collected from Tarapur area. Site-specific distribution coefficient ( $K_d$ ) of Cs was also estimated in soil samples collected from different locations across Tarapur, India using laboratory batch method. The effect of soil parameters (viz. pH, cation exchange capacity, organic matter and  $\text{CaCO}_3$ ) on  $K_d$  values of Cs was also investigated. The data of Cs adsorption on the soil is well fitted with the pseudo-second-order kinetic equation with the correlation coefficient ( $R^2$ ) value of 0.99. The rate constant ( $k_2$ ) of Cs adsorption (at 25 °C) on collected soil samples was found to be  $3.33 \times 10^5 \text{ g } \mu\text{g}^{-1} \text{ min}^{-1}$ . In the present study, Cs adsorption data were well fitted with Freundlich and Dubinin–Radushkevich (D–R) isotherm models. The change of enthalpy ( $\Delta H$ ), entropy ( $\Delta S$ ) and Gibbs free energy ( $\Delta G$ ) were estimated for the Cs adsorption on soil samples. Results showed that the adsorption process was exothermic ( $\Delta H = -3.69 \text{ J mol}^{-1}$ ) and favoured at a lower temperature. The calculated  $\Delta G$  value ( $< 0$ ) indicates that the Cs sorption on the soil is a spontaneous process. The  $K_d$  values were found to the range of  $58 \pm 2$  to  $275 \pm 10 \text{ kg}^{-1}$ . The parametric study indicated CEC to have a stronger influence as compared to pH, OM and  $\text{CaCO}_3$  in the soil samples.

**Keywords:** Laboratory batch method, caesium, CEC, distribution coefficient ( $K_d$ ), chemical parameters, equilibration time, isotherm, rate constant

## 1. INTRODUCTION

$^{137}\text{Cs}$  which is one of the important radioisotopes of caesium (Cs) generated during nuclear testing, nuclear accidents, and operation of nuclear facilities.  $^{137}\text{Cs}$  is also generated as a fission product of  $^{235}\text{U}$ .  $^{137}\text{Cs}$  if released into the environment can pose considerable radioecological problems because it is a long-lived radioactive element ( $t_{1/2} = 30$  years) with high mobility resulting in easy assimilation in plants and other terrestrial and aquatic organisms. Cs adsorption on the soil is a strong determining factor for the entry of Cs into the human food chain [1, 2].

Cs can reach groundwater by different environmental processes and can also migrate from one location to another depending upon the groundwater flow direction. Migration of Cs in the environment is strongly dependent on the factors such as the permeability of the impoundment and liner (if present), the amount of precipitation, the nature of the underlying soils, and the proximity to both surface and groundwater. Estimation of migration of a given radionuclide is important in assessing the environmental effects and the process requires the availability of several important generic parameter values.

Solid-liquid distribution coefficient ( $K_d$ ) is one of the important parameters in environmental assessment, which predicts radionuclide–soil interactions and the transport of radionuclide in soil [3]. Realistic Cs migration assessment at any given location is very much dependent on soil parameters, such as pH,  $\text{CaCO}_3$ , organic matter content and cation exchange capacity [4].

The prediction of sorption kinetics and the thermodynamic parameters of sorption are important to explain how fast the rate of sorption occurs, which further gives information on the mobility of released contaminant [5, 6]. Information on the kinetics of soil sorption can also be used to investigate the reaction mechanisms.

Therefore, the estimation of site-specific distribution coefficient ( $K_d$ ) of Cs and understanding of sorption kinetics is necessary. The current study is carried out to investigate the thermodynamics and kinetics of Cs adsorption on soil samples of Tarapur, Maharashtra, India. The present study also investigates the effect of physicochemical properties of soil on  $K_d$  values of Cs.

## 2. EXPERIMENTAL

### 2.1. Study area

Tarapur is situated in Palghar district in the Maharashtra State of India. The study area is located at about 45 km north of Virar, on the western railway line of Mumbai suburban division.

Soil and groundwater sampling locations across Tarapur is represented in Figure 1.



**Figure 1.** Sampling Locations

## 2. 2. Sample collection and processing

Fifteen sampling locations were selected across Tarapur, India. All the soil samples were collected at a depth of 10 cm from the earth surface by grab sampling process using a wooden spatula. Collected soil samples were stored in polythene bags which were pre-cleaned with 1 (M) solution of HCl and rinsed with double distilled water. The soil samples were oven-dried at 95 °C and then sieved through electromagnetic sieve shaker to collect soil particles of size < 2 mm. Pre-cleaned polypropylene plastics containers were used to collect the groundwater samples from the same sampling locations and filtered through 0.45-micron filter paper to remove suspended solids. Chemicals used for the experiment were Merck, Analar and suprapur grade. Cs concentration was analyzed using Atomic Absorption Spectrometry (AAS) (model GBC Avanta). AAS parameters selected for Cs analysis is given in Table 1.

**Table 1.** AAS parameters for Cs analysis

Element	Wave length (nm)	Slit width (nm)	Sensitivity (µg/ml)	Lamp current (mA)	Flame type
Cs	852.1	1.0	0.1	15.0	Air-acetylene (oxidizing)

### 2. 3. Determination of equilibration time

Adsorption equilibrium time is an important parameter in determining  $K_d$ , was estimated experimentally by carrying out adsorption experiments for different time intervals (from 1 – 43 h). The laboratory batch method was adopted to carry out the sorption experiments (at 25 °C) using 16 mg/l concentration of Cs in 1:30 soil water ratio. The details on rotating shaker and how the sorption experiments were carried out are discussed in our previous study [7]. The solutions after predetermined shaking time were centrifuged and the filtered solution was analyzed for Cs.

### 2. 4. Cs adsorption kinetics

Different mechanisms are involved in sorption kinetics like diffusion control, mass transfer and chemical reactions. All steps of sorption are included both in pseudo-first-order and pseudo-second-order rate models. To determine the sorption characteristics of Cs on soil samples, an appropriate kinetic model is required. Pseudo-first-order and second-order kinetic rate models were used in this study.

#### 2. 4. 1. Pseudo-first-order kinetic model

The sorption rate is described by the pseudo-first-order kinetic model. The model assumes that the sorption rate is only time-dependent. The Lagergren first-order rate expression [8] is written as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} \times t \dots\dots\dots(2.1)$$

The parameters,  $q_e$  and  $q_t$  represent the sorbed Cs concentration on the soil at equilibrium and at the time “t”. Whereas, term  $k_1$  ( $\text{min}^{-1}$ ) is the pseudo-first-order rate constant.

#### 2. 4. 2. Pseudo-second-order kinetic model

The sorption equilibrium data is fitted to the pseudo-second-order rate model and is expressed as below:

$$\frac{t}{q_t} = \frac{1}{k_2 \times q_e^2} + \frac{1}{q_e} \times t \dots\dots\dots(2.2)$$

The term  $k_2$  is pseudo-second-order rate constant ( $\text{g } \mu\text{g}^{-1} \text{ min}^{-1}$ ) and  $q_e$  is the sorption capacity.

### 2. 5. Effect on pH

The pH of a solution is an important parameter that controls the surface charge of the soil particle and hence the adsorption capacity. A change in the pH of a solution affects in various ways like the degree of protonation, metal chemistry and the surface properties of the sorbents [9]. Cs adsorption studies were carried out at different solution pH (ranging from 2 to 9) keeping other parameters constant (initial Cs concentration  $16 \text{ mg}\cdot\text{l}^{-1}$ , soil to solution ratio = 1:30,

equilibration time = 16 hours and temperature = 25 °C) to investigate the effect of pH on Cs adsorption.

**2. 6. Effect of the initial Cs concentration**

Cs concentration in the aqueous solution may affect the sorption on the soil. To understand the influence of the initial Cs concentration, sorption experiments were carried out with different Cs solution concentration (ranging from 1.66 to 33.33 mg·l<sup>-1</sup>) keeping other parameters (pH = 6.95, soil to solution ratio = 1:30, equilibration time = 16 hours and temperature = 25 °C) constant.

**2. 7. Adsorption isotherms**

The affinity of sorbent and surface properties at constant pH and temperature are expressed by the parameters involved in the isotherm equation. Adsorption isotherms describe how the adsorbate interacts with adsorbents. The data generated from sorption of Cs on soil using different initial Cs concentration were fitted with different isotherm models including Langmuir, Freundlich and Dubinin-Radushkevich (D-R) in their linearized expressions to get the adjusting parameters graphically [10].

**2. 7. 1. Langmuir isotherm model**

Langmuir sorption isotherm model assumes that sorption occurs only on the monolayer surfaces [11]. Negligible interaction between adsorbed molecules is also considered in Langmuir isotherm. The linear form of Langmuir adsorption isotherm is presented as follows:

$$\frac{C_e}{C_{ads}} = \left(\frac{1}{Q} \times b\right) + \left(\frac{C_e}{Q}\right) \dots \dots \dots (2.3)$$

The terms, C<sub>e</sub>, C<sub>ads</sub>, Q and b represents the Cs concentration in solution (µg mL<sup>-1</sup>) at equilibrium, amount of Cs sorbed onto the soil (µg g<sup>-1</sup>), and Langmuir constants related to sorption capacity and sorption energy, respectively.

**2. 7. 2. Freundlich isotherm model**

Sorption exhibiting complex interactions between surface-binding sites and bound sorbate is mainly described by Freundlich isotherm. The Freundlich sorption isotherm is commonly used over a wide range of concentrations [12]. The Cs sorption data were fitted to Freundlich sorption isotherm equation in its linearized form as below:

$$\log C_{ads} = \log C_m + \frac{1}{n} \times \log C_e \dots \dots \dots (2.4)$$

C<sub>ads</sub> and C<sub>e</sub> are the amount of Cs adsorbed on adsorbent (mg g<sup>-1</sup>) and concentration in supernatant solution (mg l<sup>-1</sup>) at equilibrium. Whereas, 1/n and log C<sub>m</sub> are constants related to the intensity of adsorption and adsorption capacity, respectively.

### 2. 7. 3. Dubinin-Radushkevich (D-R) isotherm model

D-R isotherm assumes a homogeneous surface and is more general than the Langmuir adsorption isotherm model. The sorption data of Cs were tested on the following linearized form of D–R sorption isotherm:

$$\ln C_{ads} = \ln X_m - \beta \times \varepsilon^2 \dots\dots\dots (2.5)$$

$C_{ads}$  is the amount of adsorbed Cs (mole  $g^{-1}$ ),  $X_m$  is the maximum sorption capacity.  $\beta$  and  $\varepsilon$  are the sorption energy and Polanyi potential which can be expressed as given below:

$$\varepsilon = R \times T \times \ln \left(1 + \frac{1}{C_m}\right) \dots\dots\dots (2.6)$$

where: the terms R and T are gas constant ( $J \text{ mol}^{-1} \text{ K}^{-1}$ ) and temperature (K).

The mean free sorption energy (E) is defined as the amount of energy released when one mole of ions are transferred from the solution to the surface of the adsorbent.

$$E = \frac{1}{(-2\beta)^{1/2}} \dots\dots\dots (2.7)$$

The mean free sorption energy (E) can be used to predict the type of sorption (physical, ion-exchange, chemical etc.) occurring at the adsorbent surface.

### 2. 8. Thermodynamic study

In the adsorption process temperature is one of the most important controlling parameters. The adsorbent capacity at equilibrium can be influenced by temperature for a given adsorbate [13]. To understand the spontaneity of Cs adsorption, energy and entropy considerations must be taken into account. The sorption of Cs onto soil was examined at different temperatures ranging from 5 to 55 °C. Thermodynamic parameters, i.e., change in enthalpy ( $\Delta H$ ) ( $J \text{ mol}^{-1}$ ) and change in entropy ( $\Delta S$ ) ( $J \text{ mol}^{-1} \text{ K}^{-1}$ ) for the sorption of Cs on soil was calculated for this system by the following equation:

$$\ln K_d = \left(\frac{\Delta S}{R}\right) - \left(\frac{\Delta H}{R \times T}\right) \dots\dots\dots (2.8)$$

The changes in Gibbs free energy values  $\Delta G$  ( $kJ \text{ mol}^{-1}$ ) were calculated from the following equation:

$$\Delta G = \Delta H - T \times \Delta S \dots\dots\dots (2.9)$$

### 2. 9. Characterization of soil

Soil chemical parameters such as pH, Cation Exchange Capacity (CEC), Calcium Carbonate ( $CaCO_3$ ), Organic Matter (OM) were determined in soil samples collected from fifteen different locations across Tarapur, India. The details of the procedure were discussed in our previous publication [14].

**2. 10. Determination of distribution coefficient of Cs in soil**

Laboratory batch method was used for determination of distribution coefficient of Cs in soil samples [15]. The distribution coefficient was calculated as per the following equation:

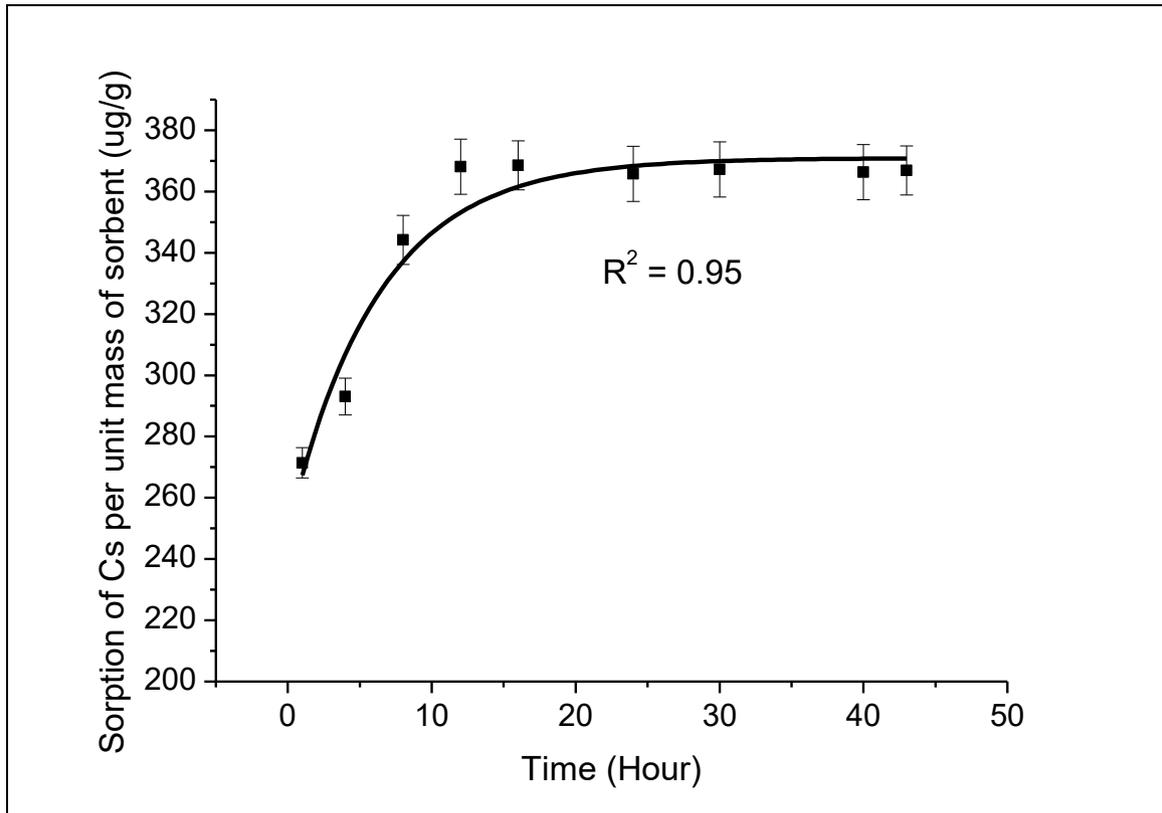
$$K_d = \left(\frac{C_0 - C_e}{C_e}\right) \times \frac{V}{m} \dots\dots\dots(2.10)$$

The parameters in Eq. 2.10 i.e.,  $C_0$ ,  $C_e$ ,  $V$  and  $m$  represents initial concentration ( $\text{mg}\cdot\text{l}^{-1}$ ) of the solution, concentration ( $\text{mg}\cdot\text{l}^{-1}$ ) of solution at equilibrium, the volume of solution (l), and mass of adsorbent (kg).

**3. RESULTS AND DISCUSSION**

**3. 1. Cs adsorption kinetics**

Figure 2 shows the amount of Cs adsorbed on the soil at different time intervals at constant initial Cs concentration. From Figure 2, it is observed that initially there is a rapid Cs adsorption (up to 10 h.), after that the adsorption increased gradually reaching the plateau after 16 h, which is considered as an equilibrium time. This equilibrium time was used in further experiments.

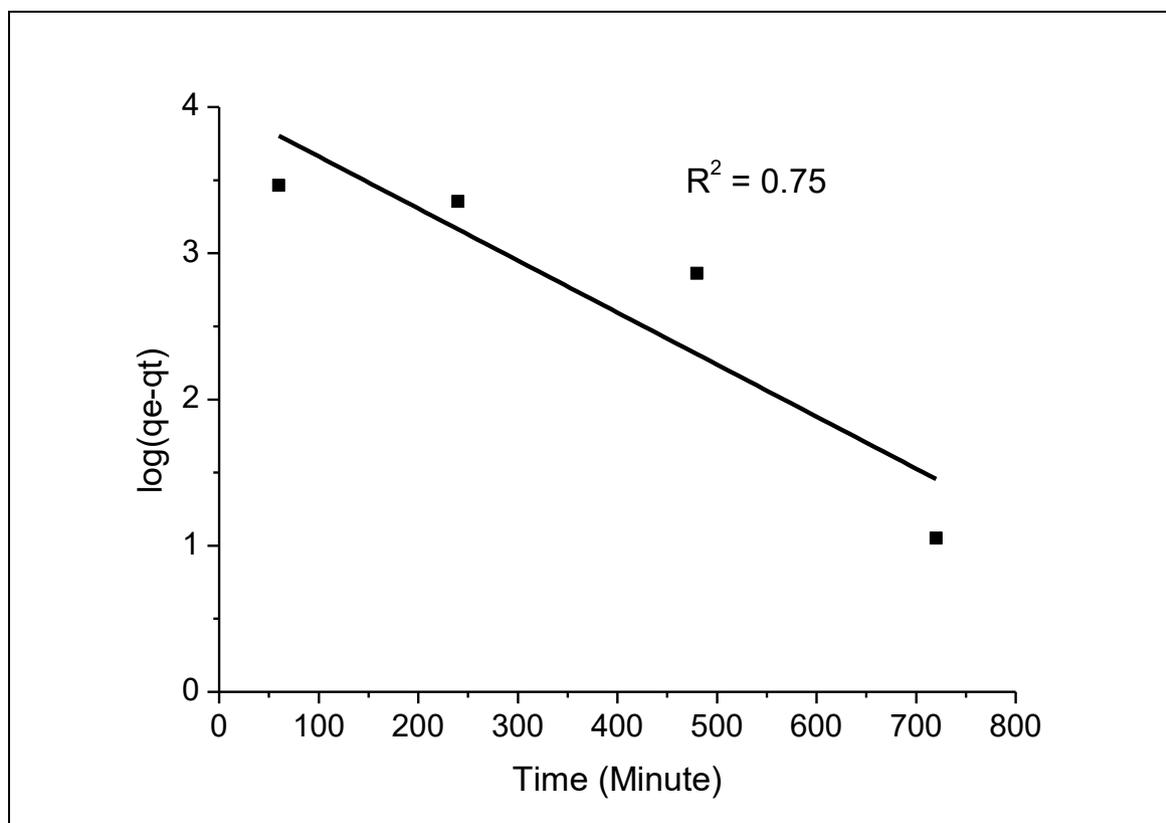


**Figure 2.** Variation of sorption for Cs on the soil at different contact time

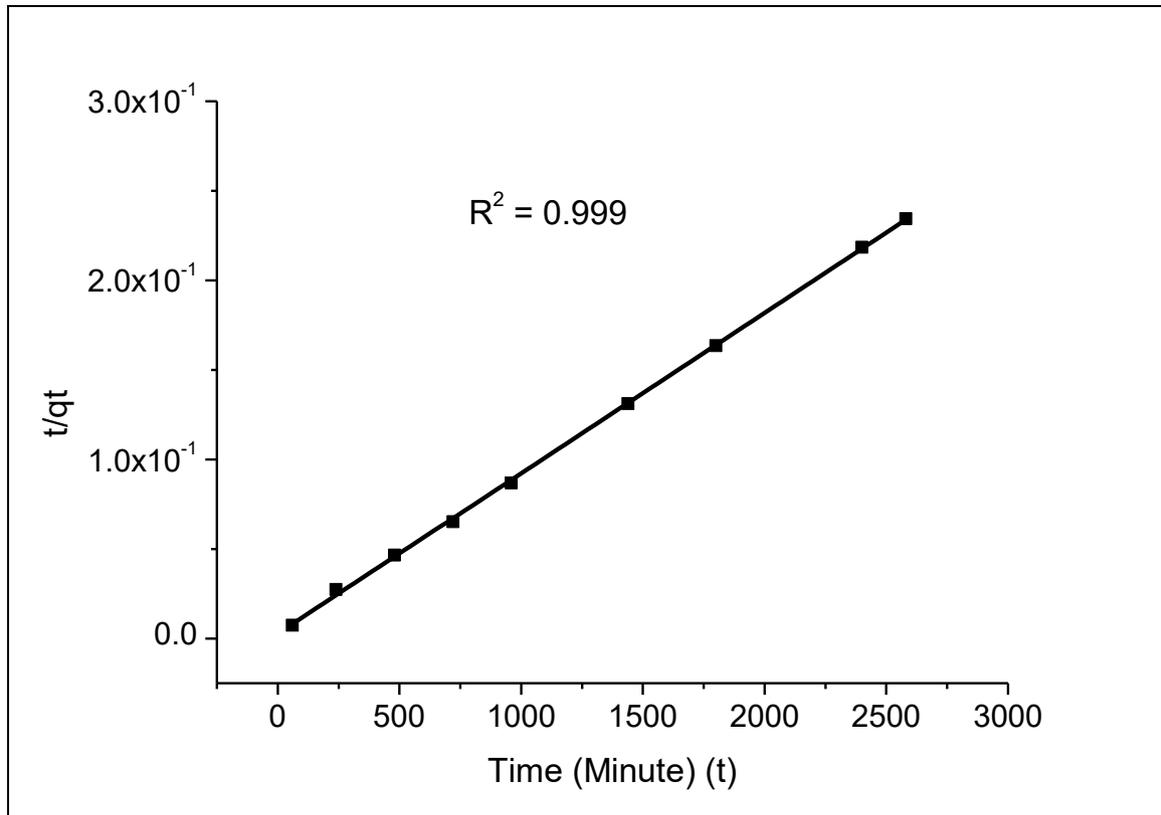
Log ( $q_e - q_t$ ) vs time of shaking was plotted (Figure 3) to get an idea about the pseudo-first-order rate constant ( $k_1$ ) of the adsorption study. The kinetic study results are elaborated in Table 2. A linear plot ( $R^2 = 0.75$ ) is obtained, from the slope and intercept of this plot, pseudo-first-order rate constant ( $k_1$ ) and the theoretical equilibrium sorption capacities ( $q_e$ ) is estimated. In the present study pseudo-first-order rate constant ( $k_1$ ) of Cs adsorption on the soil at 25 °C temperatures is observed as  $8.2 \times 10^{-3} \text{ min}^{-1}$ .

The theoretical equilibrium sorption capacities ( $q_e$ ) and experimental equilibrium sorption capacities ( $q_{e, \text{exp}}$ ) are not very close to each other indicating sorption of Cs did not follow the Lagergren first-order rate expression. The plot between  $t/q_t$  vs  $t$  is shown in Figure 4. The sorption capacity ( $q_e$ ) and second-order rate constants are calculated from the slope ( $1/q_e$ ) and intercept ( $1/K_2q_e^2$ ) of the linear plot and represented in Table 2.

The products  $k_2q_e^2$  is the initial sorption rate which is presented as  $h = k_2q_e^2$ . Pseudo-second-order rate constant ( $k_2$ ) of Cs adsorption on the soil at 25 °C temperature is observed as  $3.33 \times 10^{-5} \text{ g } \mu\text{g}^{-1} \text{ min}^{-1}$ . The correlation coefficient ( $R^2 = 0.99$ ) of the second-order rate model plot is found to be better than the first order and the  $q_e$  (calculated) values for Cs agrees with  $q_e$  (experimental). From this, it can be inferred that sorption of Cs onto soil followed second-order rate equation.



**Figure 3.** Kinetic experimental data for adsorption of Cs on soil showing pseudo-first-order



**Figure 4.** Kinetic experimental data for adsorption of Cs on soil showing pseudo-second-order.

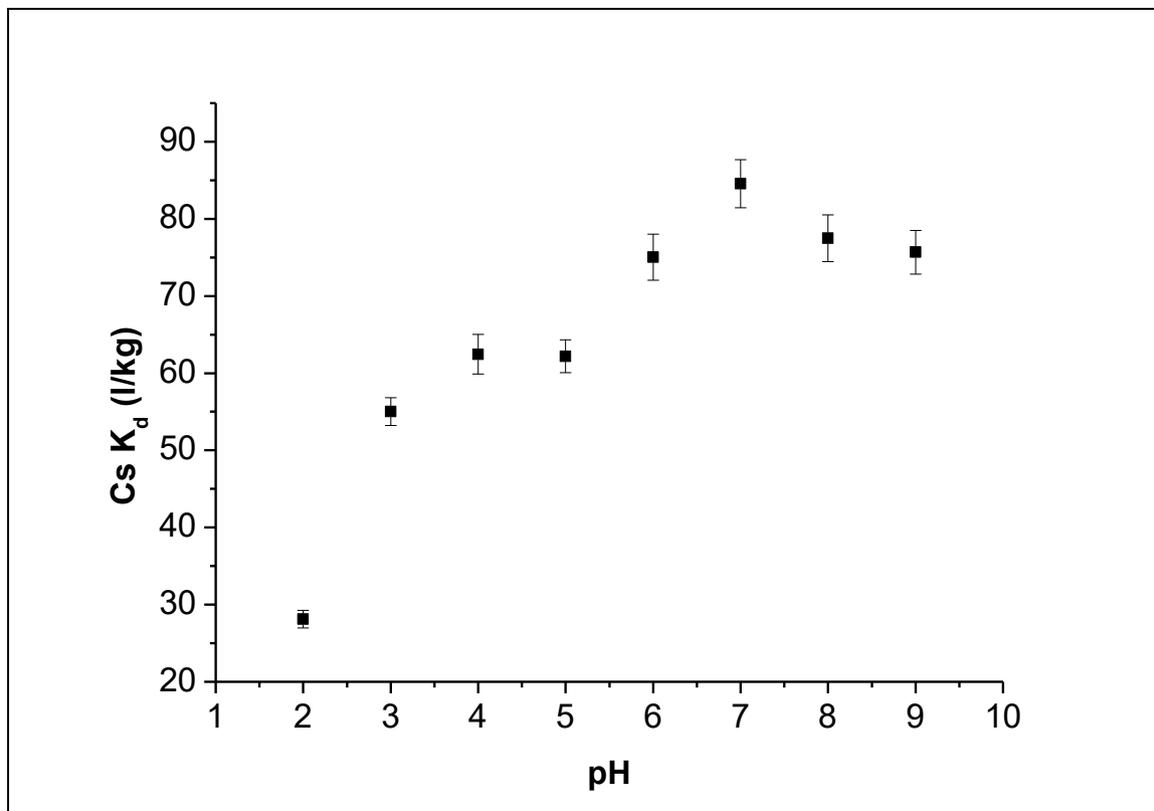
**Table 2.** Kinetic parameters of Cs adsorption on the soil

Metal	First-order kinetic parameters		Second-order kinetic parameters			q <sub>e,exp.</sub> (mg/g)
	k <sub>1</sub> (min <sup>-1</sup> )	q <sub>e,calc.</sub> (mg g <sup>-1</sup> )	k <sub>2</sub> , (g μg <sup>-1</sup> min <sup>-1</sup> )	q <sub>e,calc.</sub> (mg g <sup>-1</sup> )	h (μg. g <sup>-1</sup> .min <sup>-1</sup> )	
Cs	0.0082	10418	333323	11173	374.53	11055

### 3. 2. Effect of pH

Variation of Cs distribution coefficient with solution pH is shown in Figure 5. Figure 5 shows Cs K<sub>d</sub> values increase with increasing pH (up to 7), then decreases. Lesser sorption at lower pH observed might be due to competition between H<sup>+</sup> and Cs<sup>+</sup> ions for adsorption on the soil. In the present study, the highest K<sub>d</sub> value was observed at pH 7.

Ararem, Bouras and Arbaoui (2011) [16] also reported that Cs sorption increases with increase in pH (decrease of H<sup>+</sup> ions); the level of high values of K<sub>d</sub> begins at pH 4.0 and does not change significantly for higher pH values, a maximum of adsorption is observed at pH 7.0.



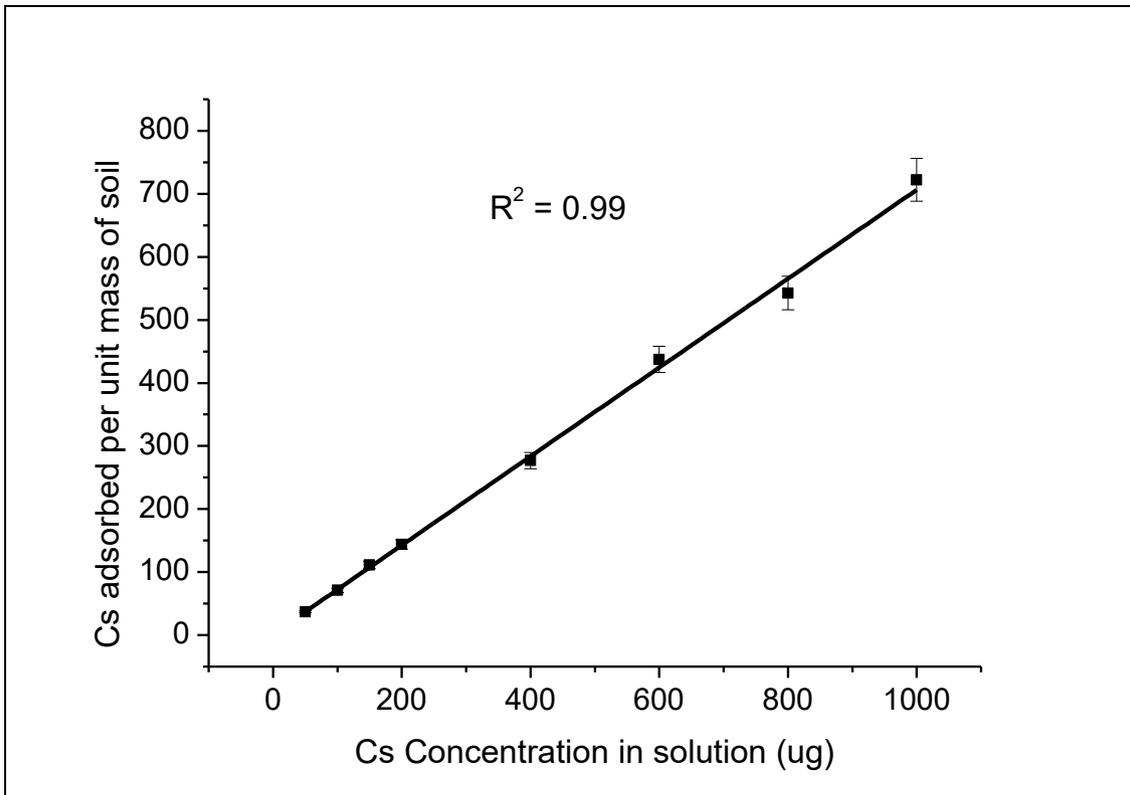
**Figure 5.** Change of Cs adsorption on soil with the change in solution pH

### 3. 3. Adsorption isotherms

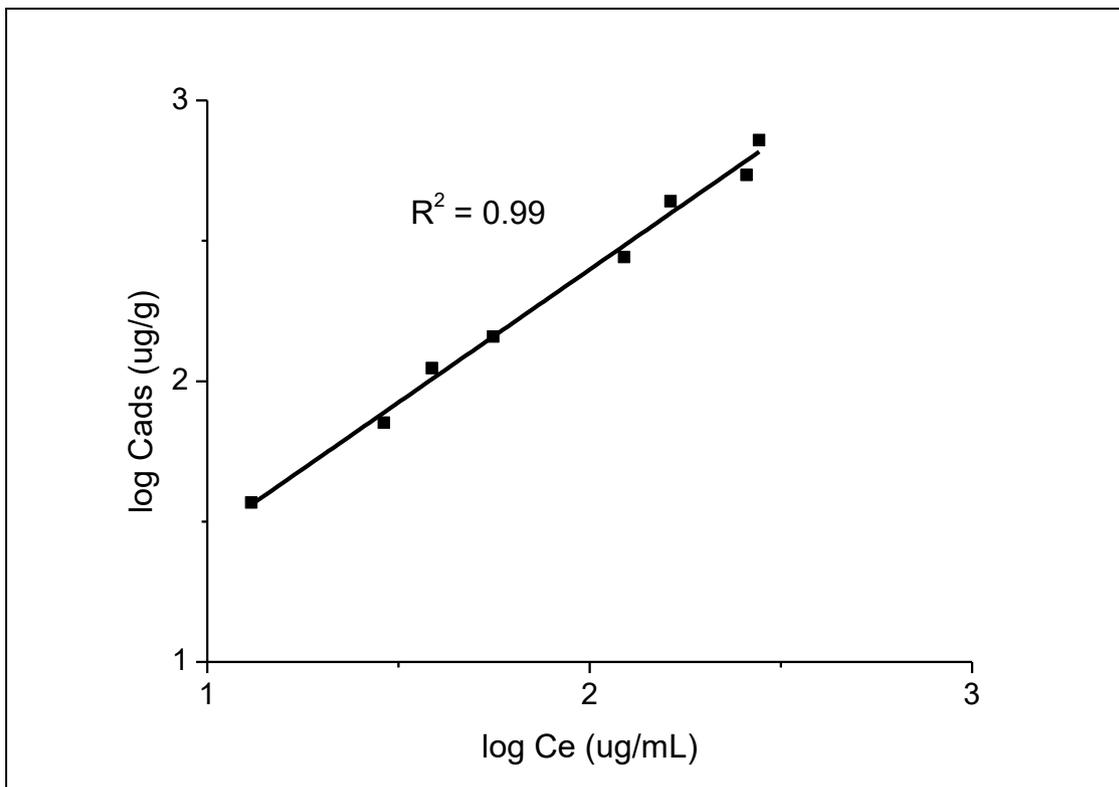
In the present study, a linear relationship is observed between Cs adsorption per unit mass of soil and Cs concentration in solution ( $R^2 = 0.99$ ) up to  $33.33 \text{ mg}\cdot\text{l}^{-1}$  of Cs concentration in solution (Figure 6). This indicates that the soil surface is not being saturated up to Cs solution concentration of  $33.33 \text{ mg}\cdot\text{l}^{-1}$ .

Data fits well with Freundlich and D-R isotherm expression but did not fit well with Langmuir expression. Values of Freundlich constants i.e.,  $C_m$  and  $1/n$  are estimated to be  $3.2 \times 10^{-3} \text{ mg g}^{-1}$  and 0.95 from the intercept and slope of the linear plot between  $\log C_{\text{ads}}$  and  $\log C_e$  (shown in Figure 7).

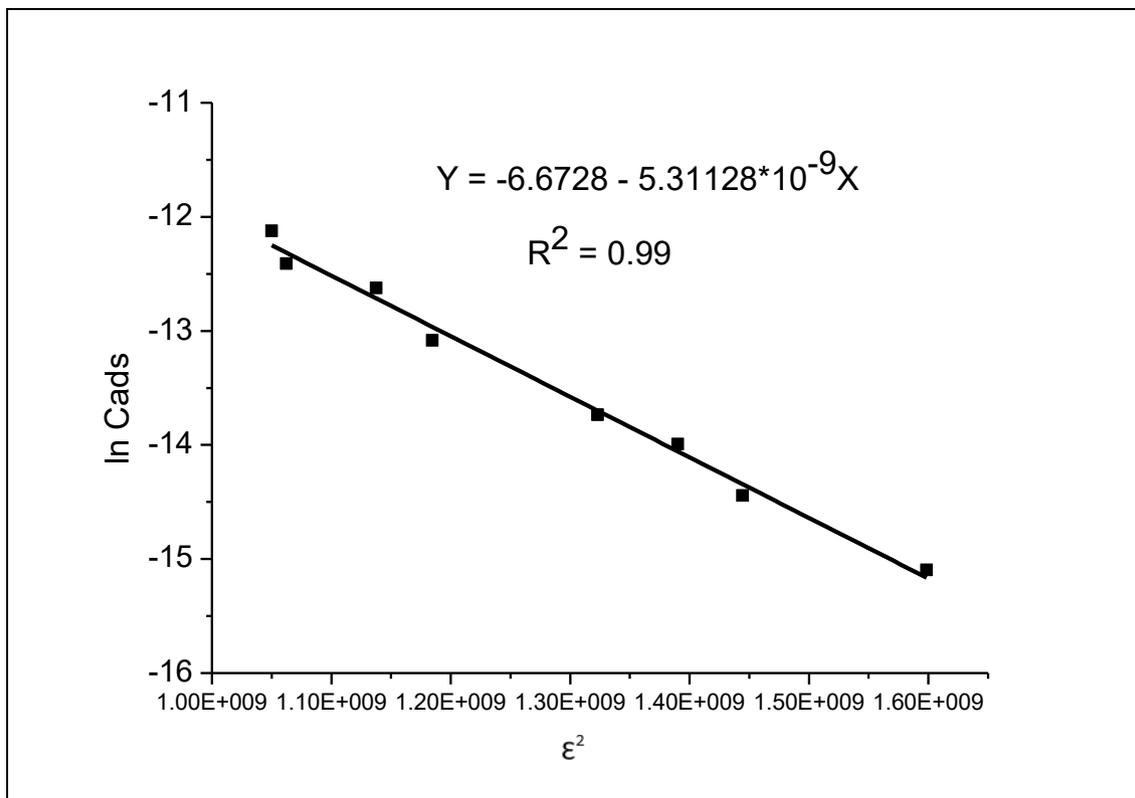
As shown in Figure 8, a plot of  $\ln C_{\text{ads}}$  versus  $\mathcal{E}^2$  gives the values of  $X_m$  and  $\beta$  from the intercept ( $X_m = 1.26 \times 10^{-3} \text{ mole g}^{-1}$ ) and slope ( $\beta = -5.31128 \times 10^{-9} \text{ mol}^2 \text{ J}^2$ ), respectively. In the present study,  $E$  is found to be  $9.7 \text{ kJ mol}^{-1}$ . This being greater than  $8 \text{ kJ mol}^{-1}$  indicates that Cs sorption on the soil is driven by ion-exchange as described by Kilislioglu and Bilgin, (2003) [17]. Physical forces dominate the sorption mechanism when  $E < 8.0 \text{ kJ/mol}$ .



**Figure 6.** The dependency of adsorption with changing initial Cs concentration on soil



**Figure 7.** Freundlich adsorption isotherm of Cs



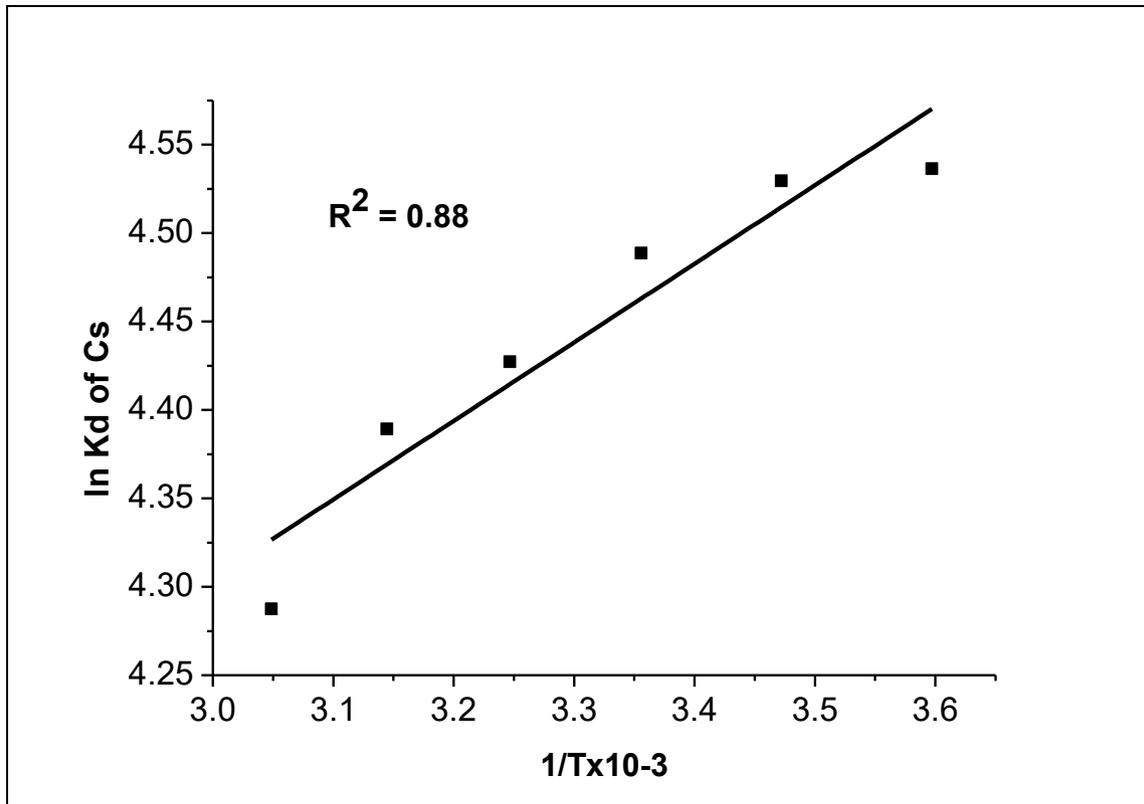
**Figure 8.** D-R adsorption isotherm of Cs

### 3. 4. Thermodynamic study

Figure 9 shows the linear relation between  $\ln K_d$  and  $1/T$ . Change in enthalpy and entropy values are calculated from the slope and intercept of the plot and are found to be  $-3.69 \text{ J mol}^{-1}$  and  $24.71 \text{ J K}^{-1} \text{ mol}^{-1}$ , respectively. The  $\Delta H$  value being negative indicates that the sorption of Cs on soil from Tarapur is exothermic.

With increasing temperature due to thermal destabilization, mobility of Cs ions increases on the surface of the soil and enhances the desorption. As temperature increases, there will be an increase in the diffusion rate of the adsorbate species across the external boundary layer and internal pores of adsorbent [18]. Temperature is having a significant role in the behaviour of the sorption process and the availability of active sorption sites [19]. The increase in solution temperature weakens the electrostatic interactions of the ions in solution hence the increase in the mobility of adsorbate.

$\Delta G$  at 298 K was found to be  $-7.37 \text{ kJ mol}^{-1}$ . The negative value of  $\Delta G$  indicates the spontaneous nature of Cs sorption on soil and the Cs sorption is more favourable at a lower temperature. The  $\Delta S$  values reflect the affinity between adsorbent and Cs. The observed positive entropy ( $\Delta S$ ) favours complexation and stability of sorption. The  $\Delta S$  and  $\Delta G$  values observed in the present study are a comparable range as reported in the literature [16].



**Figure 9.** Change of Cs adsorption on soil with a change in temperature

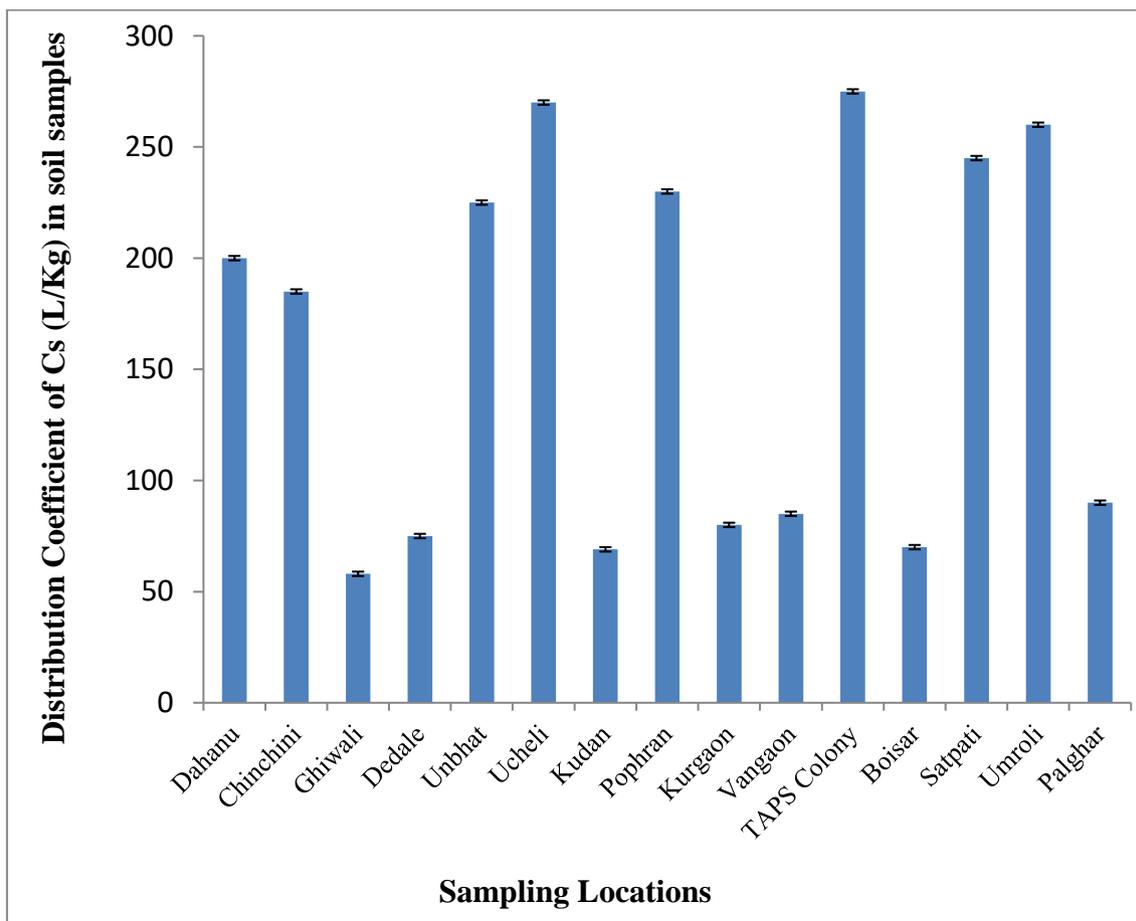
### 3. 5. Influence of different chemical parameters

Variation in chemical parameters (pH, calcium carbonate concentration, CEC and organic matter) in the soil samples studied are presented in Table 3 and compared with other literature reported values [7]. The maximum pH and CEC values were observed in TAPS colony samples whereas the minimum was found in Ghiwali. But in the case of % CaCO<sub>3</sub> content, the maximum and the minimum values were observed at Pophran and Ghiwali, respectively. % organic matter was observed to be highest at Vangaon and lowest at Pophran.

**Table 3.** Different chemical parameters of soil samples across Tarapur, India

Parameters	Mean	Range	Reported value	Reference
pH	7.1	5.9 – 8.2	5.0 – 8.9	[7]
CaCO <sub>3</sub> (%)	2.51	1.05 – 4.84	0.2 – 1.49	[7]
CEC (meq/100g)	8.97	3.45 – 15.78	2.86 – 20.15	[7]
Organic Matter (%)	3.88	1.83 – 6.73	3.5– 7.47	[7]

The  $K_d$  values of Cs were observed to be in the range from  $58 \pm 2$  to  $275 \pm 10$  l kg<sup>-1</sup> across Tarapur with an average  $K_d$  value of  $161$  l kg<sup>-1</sup> as shown in Figure 10. The highest  $K_d$  value of Cs was observed at TAPS colony as compared to other locations in the study area. The lowest  $K_d$  value of Cs was observed at Ghiwali. The  $K_d$  values obtained from the present study are comparable with the published literature values (0.94 to 14591 l kg<sup>-1</sup>) by Vyacheslav and Nikulenkov, (2016) [20] and Hirose (2003), Kawamura (2011), Tsumune (2003) [32-34].



**Figure 10.** The distribution coefficient of Cs in soil

In the present study,  $K_d$  values of Cs were observed to be increasing linearly with increasing soil pH ( $R^2 = 0.84$ ) as shown in Figure 11. In section 3. 2. it was discussed that with increasing pH,  $K_d$  values of Cs increases until certain pH (pH = 7). In the case of section 3.2, the soil sample was the same and only solution pH was varied, i.e., other parameters were the same during the experiment. But in this plot in (Figure 11),  $K_d$  values versus pH of different soil samples are shown.

Herewith change in pH, other parameters are also changing. It has been observed that CEC values increases as soil pH increases in the studied soil samples (Figure 12). The observed linear relationship between  $K_d$  and pH of different soil samples is influenced more by CEC than the pH.

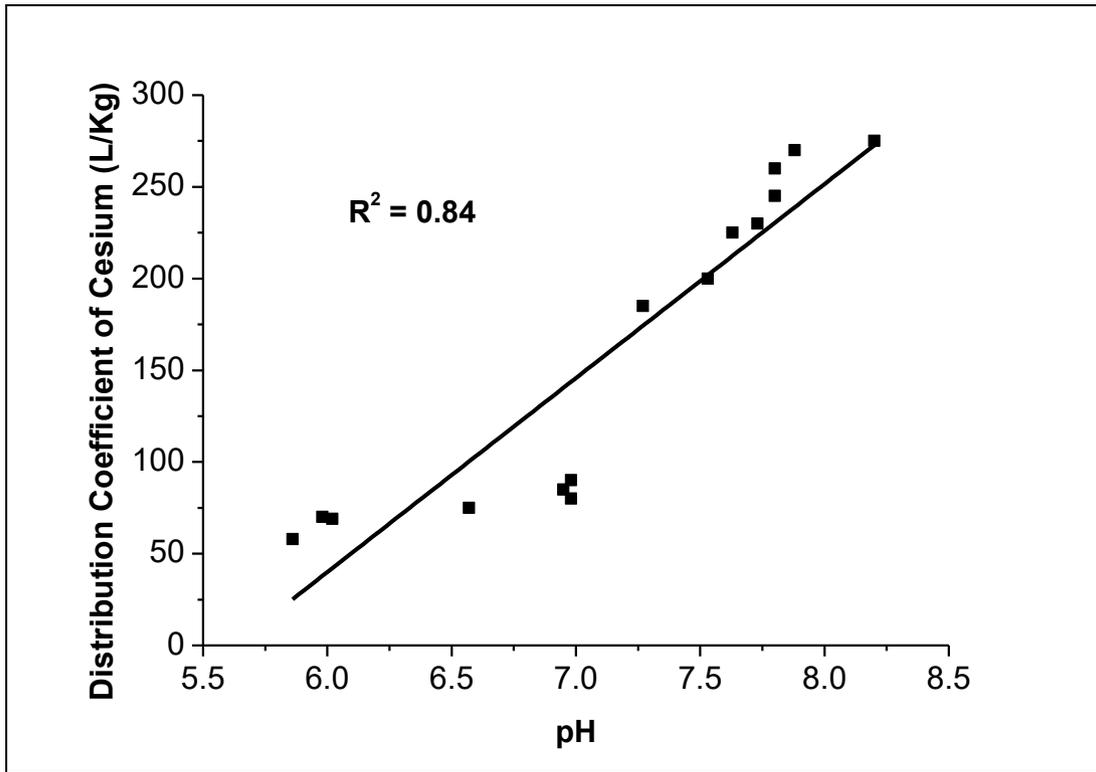


Figure 11. Variation of the distribution coefficient of Cs with pH in soil samples

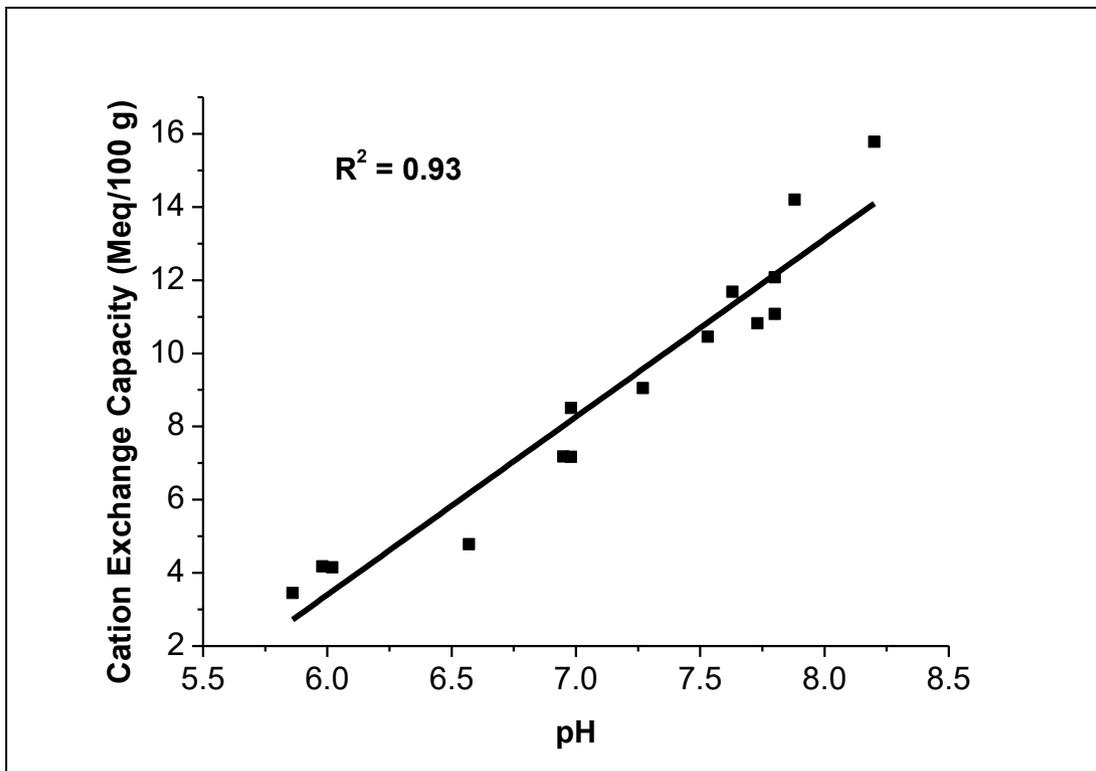
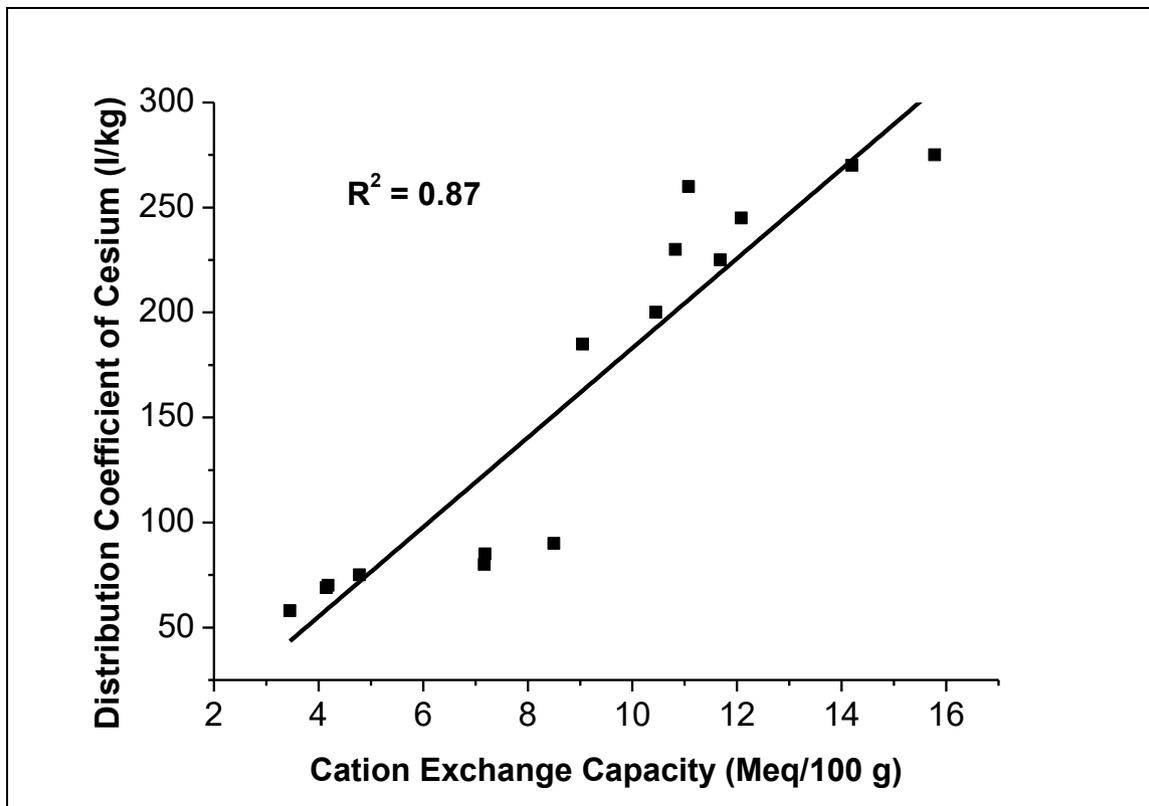


Figure 12. Variation of pH with Cation Exchange Capacity in soil samples

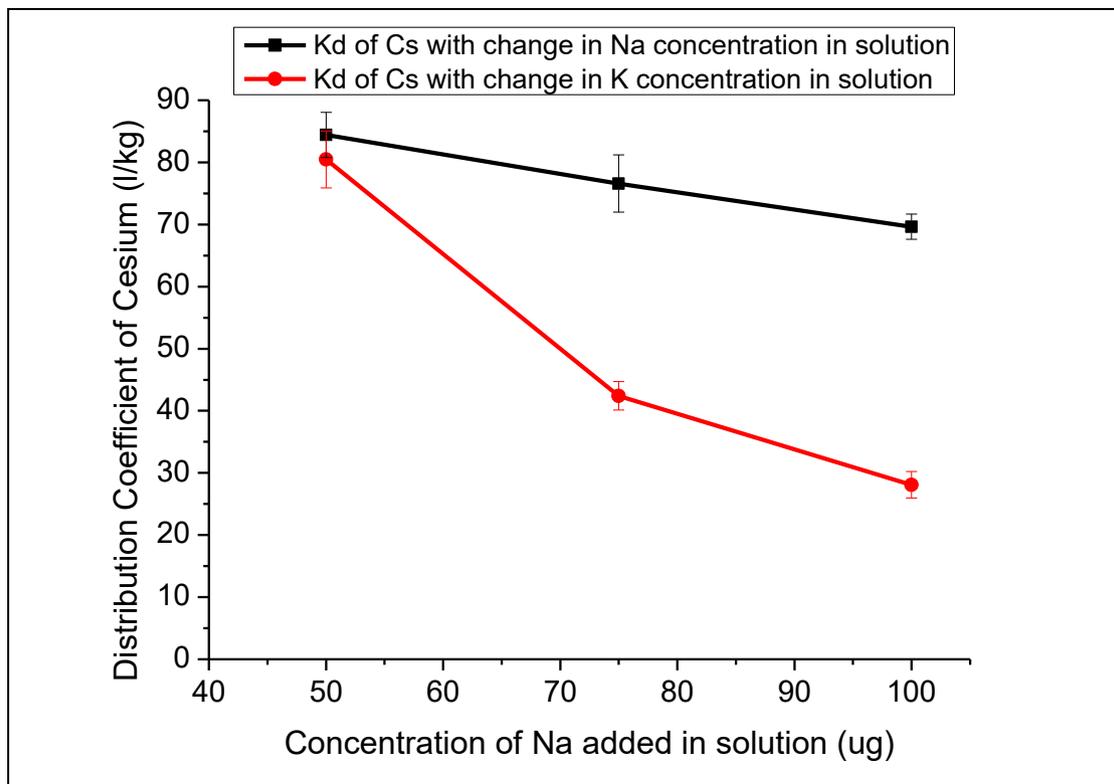
In the present study, it was found out that  $K_d$  values of Cs increase with increasing CEC values ( $R^2 = 0.85$ ) of soil samples and results are represented in Figure 13. In the published literature also it is discussed that Cs sorption decreases with decreasing cation exchange capacity and clay fraction content [21]. In the D-R isotherm model, it was observed that the Cs adsorption process is an ion exchange dominated process. Other soil parameters did not show a significant effect on  $K_d$  values of Cs. Sorption of Cs takes place via the ion-exchange process with surface hydroxyl groups and functional groups of organic matter. The concentration of other cations in the solution competes with Cs for sorption which restrains the sorption [22-26]. In the mineral soil, the most important factor was CEC for the sorption of Cs [27-30].



**Figure 13.** Variation of the distribution coefficient of Cs with cation exchange capacity in soil samples

### 3. 6. Role of competing ions in the adsorption of Cs

As Cs  $K_d$  is having a strong influence of cation exchange capacity, the effect of competing ions (exchangeable cations like  $Na^+$  and  $K^+$ ) on Cs adsorption was also studied. In the present study  $Na^+$  and  $K^+$  ion concentrations were increased in the solution gradually and in the same time distribution coefficient of Cs were determined and it was found that with increasing  $Na^+$  and  $K^+$  ions concentration in the solution  $K_d$  values of Cs decreases gradually (Figure 14) similar to that reported by Ding et al. (2014) [31]. Influence of  $K^+$  on adsorption of Cs was greater as compared to  $Na^+$ . This may be due to comparable ionic radius of  $Cs^+$  and  $K^+$  as compared to  $Na^+$ .



**Figure 14.** Role of competing ions in the adsorption of Cs on soil

#### 4. CONCLUSIONS

$K_d$  values of Cs were observed in the range of  $58 \pm 2$  to  $275 \pm 10$  l kg<sup>-1</sup> with an average value of 161 l kg<sup>-1</sup>. The adsorption process of Cs in soil samples of Tarapur followed pseudo-second-order rate equation with a rate constant  $3.33 \times 10^5$  g  $\mu\text{g}^{-1}$  min<sup>-1</sup> at 25 °C. Cs adsorption fits well with Freundlich and D-R isotherm models. From the D-R isotherm model, it is revealed that the Cs adsorption process is ion exchange in nature. Similarly,  $K_d$  values were observed to increase with soil CEC values. Cs adsorption on soil was found to be exothermic in nature and with the spontaneous process. With increasing temperature, mobility of Cs increases. Alkali metal ions (Na<sup>+</sup> and K<sup>+</sup>) have a strong influence on  $K_d$ .

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