



Single and Competitive Sorption of Heavy Metal Ions (Cd^{2+} & Cu^{2+}) on a Clayey Soil

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Abstract: The present paper focuses on the sorption behavior of Cd^{2+} ion on clayey soil at different initial concentration at natural soil pH and sorption of Cd^{2+} ion in the presence of Cu^{2+} ion (competitive-ion solution) on clayey soil at different initial concentrations at the same soil pH. Sorption experiments were carried out for the agitation period of 1 to 10 days. It was observed that in both the cases concentration of both the metals remaining in the solution with the agitation time was non linear. Maximum adsorption capacities of Cd^{2+} ion in both the solutions were calculated. It was observed that sorption of Cd^{2+} ion was decreased in the presence of Cu^{2+} ion. It was concluded that as a result of competition of ions, sorption of Cd^{2+} decreased.

Keywords: Batch sorption experiment, Cadmium, Copper, Contaminated soil, Soil remediation

Introduction

At many sites around the world, heavy metals have been mined, smelted or used in several industrial processes. The waste (tailings, smelter slag, *etc.*) some times is left behind resulting in pollution of surface and ground water. The heavy metals most frequently encountered in this waste include arsenic, cadmium, copper, lead, nickel and zinc all of which pose risk for human health and environment. Heavy metal contamination can be transported along with soil particles swept away from the initial area of pollution by wind and rain.

Soil contamination by cadmium has been occurring due to waste from Ni-Cd batteries, pigment coating and plating and plastic manufacturing industries. Cadmium may enter water and soil in waste from industries or waste disposal plant or due to leaching from landfill sites. Similarly Copper and its compounds are widely used by modern industries resulting in large quantities of this elements being discharged into the environment. The primary uses of copper compounds that historically have been source of environmental copper contamination are leather tanning and finishing metal finishing and corrosion control, drilling mud, textile dyes, pigments and primer paints, fungicides and wood treatment.

Copper and cadmium are toxic trace metals, which can be introduced into and accumulate in soil through agricultural application of sewage sludge and fertilizers and/or through land disposal of metal contaminated municipal and industrial wastes¹. They have been included on the US Environmental Protection Agency's (EPA) list of priority pollutants². Thus it is important to develop innovative technologies to clean and remediate the contaminated soils.

Tremendous efforts have been put and are being made to develop technologies that remediate contaminated soil on site. To develop an effective remediation technology for contaminated soil, it is crucial to understand the partition and mobility of contaminants in the soil solution. So it is important to have complete understanding of sorption phenomenon on soil *i.e.* how the contaminant is attached to soil and various other factors effecting sorption such as effect of pH of soil, effect of concentration of the contaminant, effect of contact or agitation time, effect of presence of other contaminants, *etc.* Therefore the present study was aimed to investigate sorption behavior of cadmium on soil. Cadmium and combination of Copper-Cadmium contamination of soil was done artificially. The study was conducted at natural pH (6.4) of the sample soil. The objectives of the study in the lab are (1) to explore the effect of metal concentration on sorption of the metal ions onto the soil, (2) to study the effect of agitation time, (3) to study the change in sorption behaviour of Cd^{2+} ion due to the presence of Cu^{2+} ion in the soil.

Experimental

Field soil was obtained from unpolluted agricultural field site near by Allahabad city (Uttar Pradesh, India) at a depth of 1-2 m. Soil sample was further washed through 0.425 mm sieve to obtain fine grained soil. Various physical and geochemical characterization tests were carried out. Table 1 shows the various physical and geochemical properties of the soil. Qualitative x-ray diffraction (XRD) (Figure 1) and scanning electron microscopy (SEM) (Figure 2) characterization tests were performed for thorough understanding of soil mineral structure.

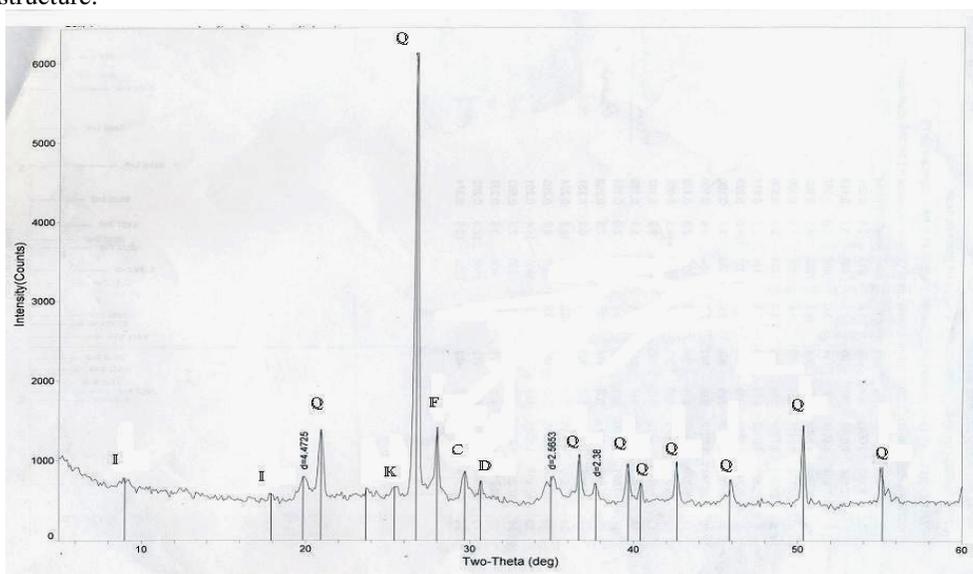


Figure1. XRD pattern of virgin soil Q-Quartz; F-Feldspar; C-Calcite; D-Dolomite; I-Illite; K-Kaolinite

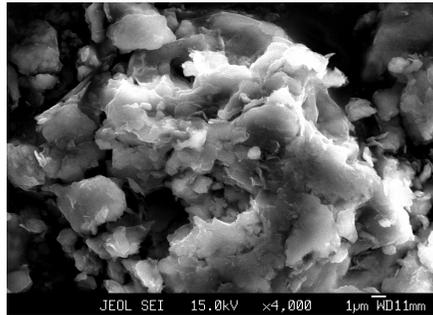


Figure 2. Scanning electron microscope picture of virgin soil

Table 1. Geotechnical and chemical properties of soil

S. No.	Property description	Property values
1.	Specific Gravity	2.62
2.	Particle Size Analysis:	
	Gravel, %	6.6
	Sand Content, %	18.4
	Silt Content, %	60.0
	Clay Content, %	15.0
3.	Atterberg's Limits:	
	Liquid Limit, w_L , %	45
	Plastic Limit, w_P , %	17
	Plasticity Index, I_P	28
	Shrinkage Limit, w_S , %	13
4.	Activity	1.87
5.	Compaction Characteristics:	
	Optimum Moisture Content, %	14.4
	Maximum Dry Density, kN/m^3	18.68
6.	Soil classification	Clay with intermediate plasticity (CI)
7.	Hydraulic Conductivity, m/sec	4×10^{-9}
8.	Specific surface area, m^2/g	0.18
9.	Chemical Parameters:	
	pH	6.4
	Organic Matter Content, %	6.25
	Loss on ignition (LOI), %	9.93
	$CaCO_3$, %	2.5
	Silica - sesquioxide ratio, SSR	5.74
	Cation Exchange Capacity, meq/100g	22

Cadmium nitrate ($Cd(NO_3)_2 \cdot 4H_2O$) and copper sulphate ($CuSO_4 \cdot 5H_2O$) were separately used to prepare stock solution of respective metal which were then diluted to different desired concentrations. To carry out sorption experiment the metal solution was added to the sample soil in 1:50 ratio in 10 different B.O.D bottles to be used one by one from day 1 to 10. In case of competitive-ion solution, competing metals (here Cu^{2+} & Cd^{2+}) were mixed in equal amount *i.e.* in 1:1 ratio. For cadmium and for copper - cadmium, the series of sorption experiments were conducted at five initial concentrations of 5 mg/L, 50 mg/L, 100 mg/L, 200 mg/L and 400 mg/L. The B.O.D. bottles containing the soil and the partly desorbed metal

(Cd^{2+} and $\text{Cu}^{2+} - \text{Cd}^{2+}$) solution corresponding to a particular concentration were stirred and shaken everyday after collecting sample for residual metal analysis at a particular time. The sample was then centrifuged and the filtrate was collected for residual metal analysis by Atomic Adsorption spectroscope (AAS). The amount of metal sorbed by the soil was calculated from the initial metal concentration of the solution and metal content of the supernatant after the specified period of shaking using the following equation (1).

$$Q = (C_o - C_e) * \frac{V}{M} \quad (1)$$

Where, Q is the metal uptake or sorption (mg/g) for the specified period, C_o and C_e are the initial and equilibrium metal concentrations in the solution (mg/L) respectively. V and M respectively are the volume of aqueous metal solution (250 mL) and mass of sorbent (10g/L).

Results and Discussion

The results of sorption experiments for Cd^{2+} and $\text{Cu}^{2+} - \text{Cd}^{2+}$ at different initial metal concentration and natural pH corresponding to various agitation (shaking) periods are shown in the Figure 3 & 4.

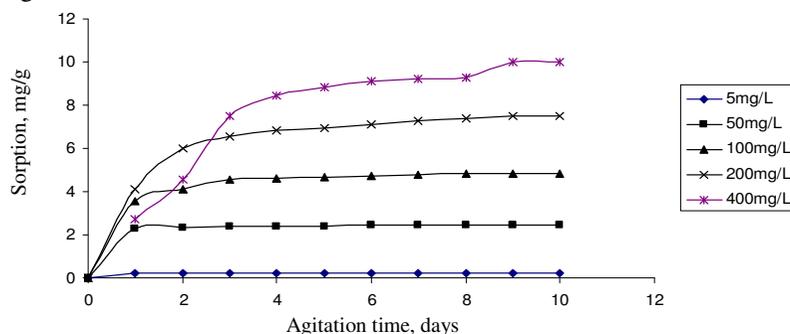


Figure 3. Sorption of Cd^{2+}

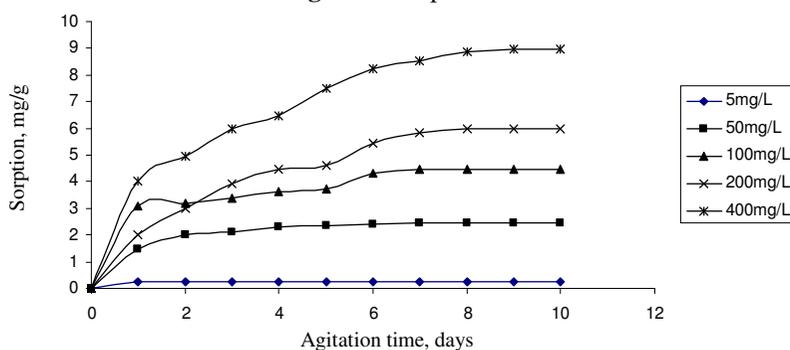


Figure 4. Sorption of Cd^{2+} in presence of Cu^{2+}

To study the adsorption behaviour of Cd^{2+} (in single-ion solution and in competitive-ion solution) adsorption isotherms were analysed using Langmuir and Freundlich equations. The results are shown in Table 2. The Cadmium sorption data were fitted satisfactorily by both equations, in both the cases, but slightly better by Langmuir equation than by Freundlich equation.

Table 2. Langmuir and Freundlich equations fitted to the Cd²⁺ adsorption data

	Isotherm equation	Linear regression	Coefficient (R ²)
Cd ²⁺ (Single-ion solution)	Langmuir	y=0.579x + 0.0737	0.9995
	Freundlich	y=0.4765x +0.2265	0.8322
Cd ²⁺ (Competitive-ion solution)	Langmuir	y=0.4364x +0.1192	0.9993
	Freundlich	y=0.3771x +0.1357	0.8807

In the present study, the first order and the second order kinetics have been used to analyse the sorption data for the Cadmium metal. The linearised form of pseudo-first-order equation is given by the following expression:

$$\log(Q_e - Q_t) = \log Q_e - K_1 t / 2.303 \quad (2)$$

Where Q_t is the amount of metal adsorbed at any time t (mg/g) and K_1 is the rate constant (1/ min). In order to obtain the rate constants, the plots of $\log(Q_e - Q_t)$ Vs. time were made at different initial metal concentrations. The kinetic constants and equilibrium adsorption Q_e values obtained from the linearised plots are given in Table 3. The calculated Q_e values from the intercept of the plots were much less than the experimental Q_e values, showing the insufficiency of first-order kinetics to fit the experimental data. Similarly, the expression for linearised form of pseudo-second- order kinetics is given equation (3).

$$t/Q_t = 1/K_2 Q_e^2 .t \quad (3)$$

In the equation (3) K_2 is the equilibrium rate constant (g/mg min⁻¹). The plots of second-order kinetics were drawn for t/Q_t Vs. time. The rate constants and the initial and equilibrium sorption values thus calculated are given in Table 3. Good fits were obtained for all the initial concentrations. The equilibrium adsorption Q_e values obtained from the plots were close to the experimental values. The correlation coefficients were very near to one, the highest value being equal to 1. All the facts suggested that the experimental sorption data approximated the second-order kinetic model very well.

Table 3. Kinetic parameters for the effect of initial adsorbate concentration

Experimental Value Q_e , mg/g	Initial Concentration, mg/L	First Order Kinetics			Second Order Kinetics		
		Q_e , mg/g	K_1	R^2	Q_e , mg/g	K_2	R^2
0.242	5	2.072	0.5886	0.8172	0.2446	40	1
2.425	50	1.218	0.865	0.9556	2.451	4.63	1
4.826	100	3.11	0.64	0.9297	5.042	0.5	0.9996
7.50	200	5.277	0.471	0.9631	8.16	0.147	0.9992
10.50	400	1.555	0.553	0.9378	13.33	0.017	0.9565

Effect of contact time (agitation time)

It was observed that for the first 4-5 days of the batch sorption process, the rate of sorption was found to be initially very fast for all the initial concentrations. This was followed by a slow reaction rate and near equilibrium conditions reaching in about 9 days. The sorption process of cadmium was nearly complete up to 98% to 84% (minimum and maximum initial concentrations respectively) in the first 4-5 days. In competitive-ion solution, the sorption processes were nearly complete up to about 98% to 80% (minimum and maximum initial concentrations respectively). Many research workers have studied the effect of reaction time between metal ions and the soils and soil components for Ag⁺ sorption on goethite and other soil components³ and for Zn²⁺ and Pb²⁺ adsorption on volcanic ash⁴. The initial fast sorption rate, in the previous time course studies for adsorption of metals on soils and soil components,

has been attributed to the readily available external surface sites while the slow reaction rate corresponds to sorption onto less accessible sites and is controlled by diffusion of the metal into the adsorbing phase.

Effect of initial metal concentration

It is also seen that on increasing initial concentration, the amount of metal sorbed at the experimental equilibrium period increased. However the increase in metal uptake by the soil is not proportional to the increase in corresponding initial concentrations, instead a negative or decreasing trend is observed.

Comparison for Cd^{2+} for various initial concentrations shows that by increasing the initial concentration of the metal by 10 times, *i.e.*, from 5 mg/L to 50 mg/L, the uptake of metal by the soil increases by 10.02 times; by increasing the initial concentration by 20 times, the uptake becomes 19.94 times; by increasing it by 40 times, it is 31 times and by increasing the initial concentration of sorbate 80 folds, the corresponding uptake of metal by the soil registers an ascent of 41.32 times. Similarly in case of competitive-ion solution of copper - cadmium, comparison for Cd^{2+} for various initial concentrations shows that by increasing the initial concentration of the metal by 10 times, *i.e.*, from 5 mg/L to 50 mg/L, the uptake of metal by the soil increases by 10 times; by increasing the initial concentration by 20 times, the uptake becomes 18 times; by increasing it by 40 times, it is 24.5 times and by increasing the initial concentration of sorbate 80 folds, the corresponding uptake of metal by the soil registers an ascent of 37 times.

The reason to the above mentioned phenomenon may be ascribed to the fact that at lower concentrations the ratio of amount of sorbate available for the sorption process and that of number of sorption sites is low, hence comparatively a higher percent of adsorption results⁵. At subsequent higher initial concentrations, this ratio progressively increases due to number of sorption sites becoming fewer compared to the amount of adsorbate available and therefore a decreasing trend in percent sorption from a lower to a higher concentration is seen.

Effect of competition of cations

In the work presented here, adsorption competition is examined at natural pH and residual concentration and equilibrium concentration and hence sorption was calculated for both the competing cations *i.e.* Cd^{2+} and Cu^{2+} . Comparing the equilibrium adsorption for both the metals (Figure 5) shows that the copper is adsorbed preferentially to cadmium in the studied concentration range. Since Cu^{2+} has smaller ionic radius than Cd^{2+} (0.72 Å Vs 0.97 Å), so it may enter into the interlayer more easily, suggesting the greater exchangeable adsorption. Therefore, the soil adsorbed more copper than cadmium. It has also been reported^{6,7} that organic matters may adsorb more copper than cadmium.

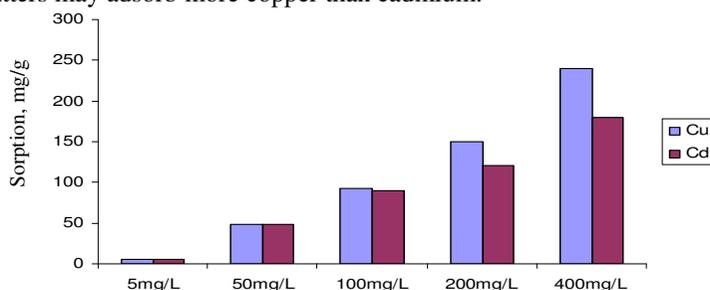


Figure 5. Comparison of maximum sorption of Cu^{2+} and Cd^{2+} at different initial concentration

It was also deduced that adsorption of Cd²⁺ ion in presence of Cu²⁺ ion (competitive-ion solution) participating in the adsorption phenomenon, has been significantly decreased. To study the adsorption competition, using Langmuir Isotherm, maximum adsorption capacity of the cadmium for the soil for single-ion solution and for competitive-ion solution was calculated and compared. The Langmuir adsorption model was chosen for the estimation of maximal sorption of Cd²⁺ by the soil as the model serves to estimate the maximum metal adsorption values where they can not be reached in batch equilibrium experiments. The plots of 1/Q_e, vs. 1/C_e (Figure 6 and 7), gave the linear isotherm parameters of Q_{max}, K_l and the coefficient of correlation R², where Q_e= adsorption at equilibrium, C_e=concentration at equilibrium, Q_{max}= maximum adsorption capacity, K_l= Langmuir constant.

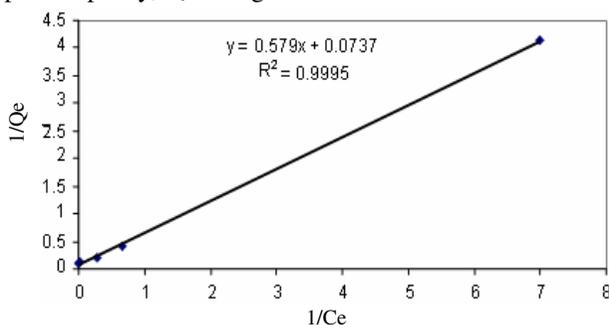


Figure 6. Linearised Langmuir Isotherm plot of cadmium

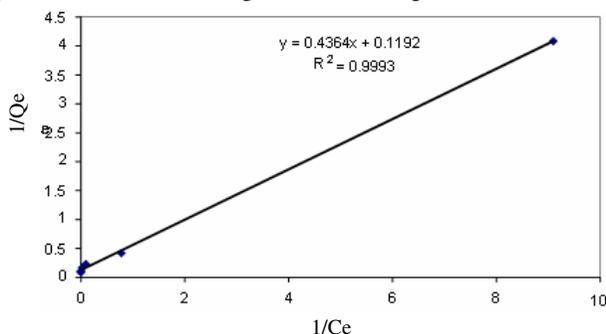


Figure 7. Linearised Langmuir isotherm plot of cadmium in presence of copper

Table 3 presents the Langmuir constants for Cd²⁺ as single ion solution and as competitive ion solution:

Table 3. Comparison of Langmuir constants for Cd²⁺ as single ion and as competitive ion solution

Adsorbate	Linear Regression	Q _{max} (mg/g)	K _l	R ²
Cd ²⁺ (as single ion)	y=0.579x + 0.0737	13.56	0.128	0.9995
Cd ²⁺ (as competitive ion)	y=0.4364x + 0.1192	9.1	0.2188	0.9993

On comparing the maximum adsorption capacity it is obvious that the adsorption of both the metals decreased due to competition of cations. The adsorption of Cd²⁺ is decreased by 33%. Thus as a result of competition of cations adsorption of Cd²⁺ is decreased. The reason behind this phenomenon may be attributed to the fact that when the specific sorption site become saturated, exchange reactions dominate and competition for these sites with cations becomes important.

Conclusion

The Cadmium adsorption data were fitted satisfactorily by both equations, in both the cases, but slightly better by Langmuir equation than by Freundlich equation. Also the first-order kinetics model was found to be inadequate in explaining the experimental sorption data, while the pseudo-second-order model was very much agreeable with the experimental sorption values.

In both the cases near equilibrium conditions were attained within 4 hours in all adsorption experiments for all the initial concentrations of metal solution.

On increasing initial concentration, the amount of metal adsorbed at the experimental equilibrium period increased. However in competitive-ion solution amount of cadmium adsorbed was slightly less than in single ion solution. As a result of competition of cations adsorption of Cd^{2+} is decreased by 33%.

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