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Kinetic Sorption Studies of Heavy Metal Contamination on Indian Expansive Soil

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Abstract: Sorption of metallic cadmium from the pH adjusted aqueous solutions at varying initial concentrations onto an alluvial (clay) soil through batch sorption experiments was studied. The pH of the initial concentrations ranging between 50 mg/L to 250 mg/L was varied from 3.0 to 8.0. The sorption experiments were carried out for different durations and up to 16 hours. The cadmium continued to sorb till the last experimental pH=8. The experimental sorption data fitted very well with both Langmuir and Freundlich isotherm models and Freundlich model gave higher correlation coefficients. The pseudo-second order kinetics model was most agreeable with the experimental sorption data, whereas the pseudo-first order model was found to be insufficient.

Keywords: Heavy metals, Metals toxicity, Sorption, Isotherms, Kinetic models.

Introduction

Heavy metals are defined as metals and metalloids generally considered being of sufficient distribution and abundance as to be in some way environmentally or biologically significant as a toxic substance¹. The toxicity of a metal, as of any other substance, depends on a number of factors, such as (a) physical state (b) nature of its compound (c) mode of its entry into the human body and (d) susceptibility of the exposure. It is very difficult to demarcate toxic metals from essential ones. In fact, any metal could become toxic if ingested in sufficiently large amounts. However, it is possible to sort out those metals, which are not beneficial and at the same time show severe toxicity even at a very low concentration, *e.g.*, cadmium, lead, chromium, metabolic nickel etc. Hence a toxic metal is the one which is neither essential nor beneficial but exhibits a positive catastrophic effect on normal function

even when present even in small amounts, and may, at times, be responsible for permanent disorders or malfunctioning of organ system leading finally to death.

The fate and transport of a metal in soil and groundwater depends significantly on the chemical form and specification of the metal². The mobility of the metals in ground water system is hindered by reactions that cause metals to adsorb or precipitate or chemistry that tends to keep metals associated with the solid phase and prevents them from dissolving. This mechanism can retard the movement of metals and also provide a long term source of metal contaminants³. While the various metals undergo similar reactions in a number of aspects, the extent and nature of these reactions vary under particular conditions. The solubility of the metal in soil is influenced by the chemistry of the soil and groundwater⁴. Factors such as pH, Eh, ion exchange capacity, and complexation /chelation with organic matter directly affect metal solubility.

Cadmium is a rare soft metal that occurs in the natural environment typically in association with zinc ores and, to a lesser extent, with lead and copper ores. Cadmium pollution in soils⁵ includes phosphatic fertilizers; the mining of cadmium and smelting; atmospheric pollution from metallurgic industries; the disposal of waste containing cadmium; and urban/industrial pollution⁶. Cadmium can be bound in soil by simple electrostatic forces or intimately associated with metal oxides, carbonates, and organic matter. It is also found that the Cd solubility increases as pH decreases^{7,8}. A number of investigations have shown Cd solubility to be dependent also on the cation-exchange capacity (CEC), clay content, organic matter, and other metal ions present⁷⁻¹⁰. The environmental fate and health effects of cadmium and its compounds have been reviewed extensively in literature^{11,12}. For nonsmokers, ingestion of food is the largest source of cadmium exposure (about 94%) with the rest coming from air. Acute high level exposure to cadmium by inhalation or oral routes can be fatal, including gastrointestinal, liver, and other organ damage; tracheobronchitis, pneumonitis, pulmonary edema, and long term impairment of lung functions. Renal accumulation of cadmium may result in irreversible impairment in the reabsorption capacity of renal tubules. Cadmium can alter genetic materials particularly chromosomes in mammalian cells, can inhibit repair of DNA and thereby enhancing their genotoxicity. Inorganic cadmium compounds have been classified as carcinogenic by the inhalation route¹⁵.

Experimental

The soil sample for the experimental work was collected from non-vegetation depth through an open excavation and index properties were determined as per the relevant parts of IS 2720. The soil on the basis of index properties and relevant BIS code (IS 1498: 1970) was classified as CH. Standard stock solutions of cadmium metal (analytical reagent-grade) in deionized water were separately prepared from which 50 mg/L, 100 mg/L, 150 mg/L, 200 mg/L and 250 mg/L concentrations were used for sorption experiments. The sorption experiments were performed in a rotary shaker at 15-20 rpm for different time intervals ranging from 15 minutes to 16 hours using 300 mL stop corked bottles containing 250 mL of cadmium solution and 10 g/L of soil. The initial pH of the sorbate (metal solution) was adjusted for each set of experiment by adding 0.1 M HCl or 0.1 M NaOH. The partly desorbed sorbate corresponding to each time interval was centrifuged for at least 5 minutes at 500 rpm and then vacuum-filtered to separate out the soil particles. The filtrate was used to determine the residual metal using an atomic absorption spectrophotometer (Model: Perkin Elmer 3100). 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 equation¹³:

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

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 (10 g/L).

Results and Discussion

Composition and the relevant soil properties are presented in Table 1. Langmuir and Freundlich constants at different sorbate-pH have been given in the Table 2, whereas in Table 3 kinetic parameters for different initial sorbate concentrations have been presented.

Table 1. Composition and relevant properties of soil used.

Property	Value
Specific gravity	2.64
Particle size analysis	
Sand, %	3.3
Silt, %	70.0
Clay, %	26.7
Atterberg's Limits	
Liquid limit, %	60.5
Plastic limit, %	27.4
Plasticity index	33.1
Shrinkage limit, %	11.8
IS classification	CH
Chemical properties	
pH	7.80
Organic matter, %	2.25
Cation exchange capacity, meq/100 g	17.38

Table 2. Langmuir and Freundlich constants at different sorbate pH

pH	Langmuir Parameters			Freundlich Parameters		
	X _m (mg/g)	K (L/mg)	R ²	1/n	K _f	R ²
3.0	19.72	0.00536	0.99940	0.73	0.23	0.99802
4.0	23.27	0.00645	0.95021	0.72	0.32	0.98917
5.0	26.94	0.00843	0.96485	0.70	0.53	0.99923
6.0	28.51	0.01354	0.99652	0.64	0.93	0.98945
7.0	31.35	0.02811	0.99048	0.65	1.51	0.98937
8.0	33.61	0.04169	0.98099	0.66	2.04	0.97687

Table 3. Kinetic Parameters for the effect of initial sorbate concentration.

Initial conc, mg/L	First order kinetics			Second order kinetics		
	Q _e mg/g	k ₁	R ²	Q _e	k ₂	R ²
50	1.36	0.00640	0.71924	4.64	0.02799	0.99982
100	2.95	0.00697	0.75058	9.11	0.01352	0.99986
150	4.45	0.00583	0.073644	13.45	0.00935	0.99988
200	7.15	0.00672	0.83315	17.86	0.00487	0.999700
250	8.81	0.00691	0.86778	21.04	0.00386	0.99968

Effect of pH

The initial pH of the solution is a very important factor for metal sorption on soils. The pH, either directly or indirectly, affects several mechanisms of metal retention by soils. An important aspect of the effect of pH on metal mobility is the buffering capacity of soils for acidity. Many researchers have acknowledged that the adsorption of metals is directly proportional to the soil pH. Table 4 presents sorption of cadmium between various pH ranges at different initial concentrations of the metal. The effect of pH on the sorption of cadmium on soil is illustrated in Figure 1 through a relationship between C_e (sorbate remaining in solution at equilibrium conditions) and Q_e (sorption of sorbate at equilibrium conditions).

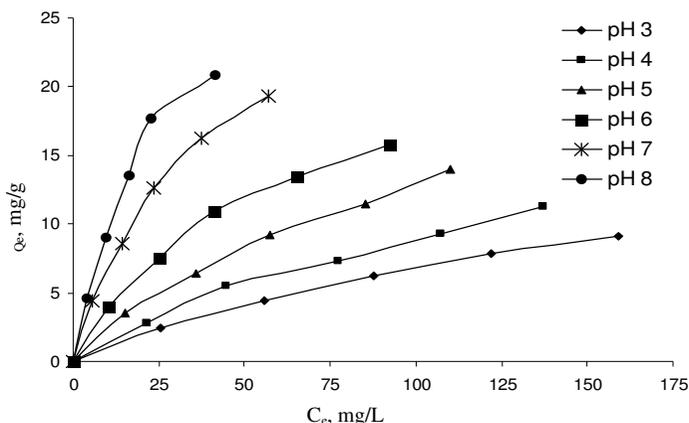


Figure 1. Effect of initial pH on Cd uptake by soil.

In the Table 4, effects of both the initial pH and initial solute concentration are seen on the sorption of Cd. An adsorption edge starts right at the first experimental pH of 3 and continues up to pH 5.

Table 4. Sorption (%) between pH Ranges at different initial concentrations.

Initial Concentration mg/L	Sorption, %				
	Initial pH range				
	3-4	4-5	5-6	6-7	7-8
50	16.4	22.9	13.7	11.8	4.0
100	24.6	15.8	16.9	14.4	6.0
150	16.5	27.0	17.7	16.0	7.5
200	18.9	23.2	17.6	20.6	9.0
250	23.8	24.0	12.6	22.3	8.1

The second sorption edge is seen between pH 6 and 7 for higher initial concentrations. Between pH 7 and pH 8 the sorption declines considerably, although the effect of initial concentration is quite visible. Figure 1 illustrates the comparison of sorption at different pH ranges shown in Table 4. Relatively small Cd sorption took place at the initial pH 3, increased little at pH 4 and then picked up momentum at pH 5 and 6. The sorption at initial pH 7 was quite strong and at pH 8 dropped substantially. The removal of Cd from the solution continued to increase for the maximum experimental initial pH of 8. Lesser metal uptake at low pH values indicates that the excess of protons compete for the same binding sites on the soil particle surfaces. Previous studies^{14,15} reveal that the pH dependence of

adsorption reactions of cationic metals is attributed partly to the preferential adsorption of hydrolysed metal species to the free metal ion. The result trends were similar to a large extent with the earlier findings reported¹⁶ that the sorption of Cd(II) on kaolinite clay increased with pH in both single and multi-element sorption systems. The study, for sorption of Cd(II) as a single element system, reports two adsorption stages involving adsorption edges, the first between pH 4 and 6, at which more than 50% of the Cd was absorbed and the second edge commencing at pH 6.5 and continuing up to pH 10, wherein 95% of the Cd is reported to have been sorbed. Sorption studies¹⁷ on Cd and Pb at varying pH on tropical coastal clay have reported that the sorption of Cd may be complete only at pH>8.

Langmuir and Freundlich models

The Langmuir sorption model was chosen for the estimation of maximum sorption by the sorbent. The Langmuir adsorption isotherm can be expressed¹⁸ as:

$$Q_e = \frac{X_m K C_e}{(1 + K C_e)} \quad (2)$$

Where, Q_e is amount of metal sorbed at equilibrium per unit weight of the sorbent (mg/g), X_m , is the maximum sorption or metal uptake from solution (mg/g) and K , is the Langmuir equilibrium constant (L/mg). For fitting the experimental data the Langmuir equation can be linearized as follows:

$$\frac{C_e}{Q_e} = \frac{1}{X_m K} + \frac{C_e}{X_m} \quad (3)$$

The Freundlich model is represented by the following equation¹⁸:

$$Q_e = K_f C_e^{1/n} \quad (4)$$

Where, K_f (L/g) and n , are Freundlich constants. For fitting the experimental data, the Freundlich model can be linearized as follows:

$$\ln Q_e = \ln K_f + 1/n \ln C_e \quad (5)$$

The Langmuir and Freundlich constants were found through linearization of experimental sorption data, and are presented in Table 2. The linearized plots of Langmuir and Freundlich models are shown in Figures 2 & 3. The results reveal that the model parameters are largely dependent on the initial sorbate concentration values. Langmuir sorption model served to estimate the maximum metal adsorption values where they could not be reached in batch equilibrium experiments. Both the maximum metal adsorption, X_m and the Langmuir equilibrium constant, K increased with increasing pH values.

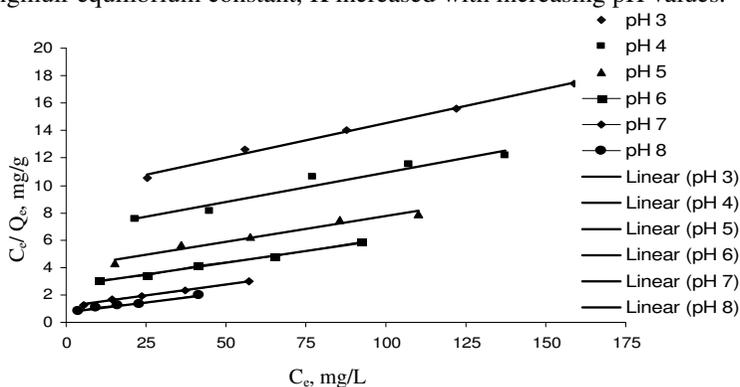


Figure 2. Linearized Langmuir isotherms at different solution pH values.

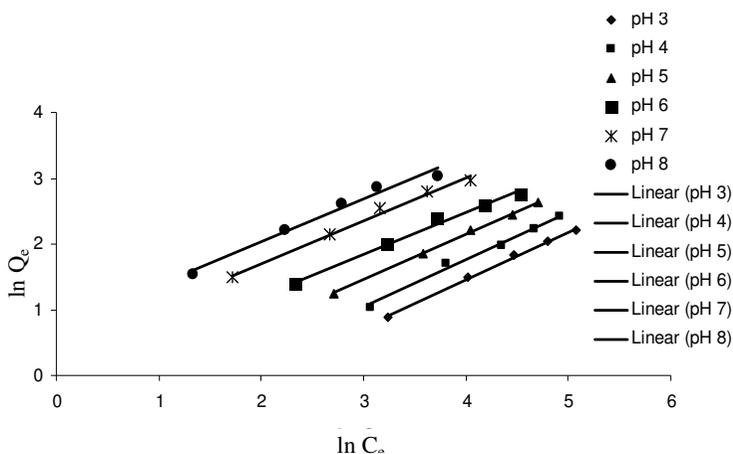


Figure 3. Linearized Freundlich isotherms at different solution pH values.

The Maximum sorption X_m increased by nearly 70% from initial pH=3 to the last experimental initial pH=8. The constant K , which represents the affinity between the sorbate and the sorbent was seen to increase continuously in the experimental pH range. There was a substantial increase in binding constant K between pH=6 and 8, denoting that this pH range was particularly favourable for sorption for Cd to the experimental soil. The Freundlich sorption intensity parameter $1/n$ continued to decrease right from experimental initial pH=3 up to the last pH=8, implying that the sorption intensity of the soil for Cd continued to increase up to the last experimental pH. It was also obvious that between pH 5 and 6 there was a sorption edge, which continued up to pH=8. The Freundlich constant K_f also continued to increase from the first initial pH up to the last, registering a eruption after pH=5, which suggested that the higher pH values were more amenable to Cd sorption for the soil. The correlation coefficients R^2 , which were very high and close to unity for both the Langmuir and Freundlich models (Freundlich model gave higher coefficients for all pH values) together with other parameters, confirmed that the sorption of Cd followed Langmuir and Freundlich adsorption models.

Kinetic models

The batch sorption data was analysed using pseudo-first and second kinetics models.

Pseudo-first-order model

The linearized form of pseudo-first-order equation is given by the following expression¹⁹:

$$\log(Q_e - Q_t) = \log Q_e - K_1 t / 2.303 \tag{6}$$

Where, Q_t is the amount of metal sorbed 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 $\log(Q_e - Q_t)$ against t , were made at different initial metal concentrations and are shown in Figure 4.

The kinetic constants and equilibrium adsorption Q_e values from the linearized 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. Moreover, the first-order equation did not fit well for the range of contact time used in the experimental work and was valid only over the initial 30 minutes to an hour of the sorption process. The correlation coefficients R^2 were also found to be rather smaller suggesting the inadequacy of the first-order kinetics. The expression¹⁹ for linearized form of pseudo-second- order kinetics is given as:

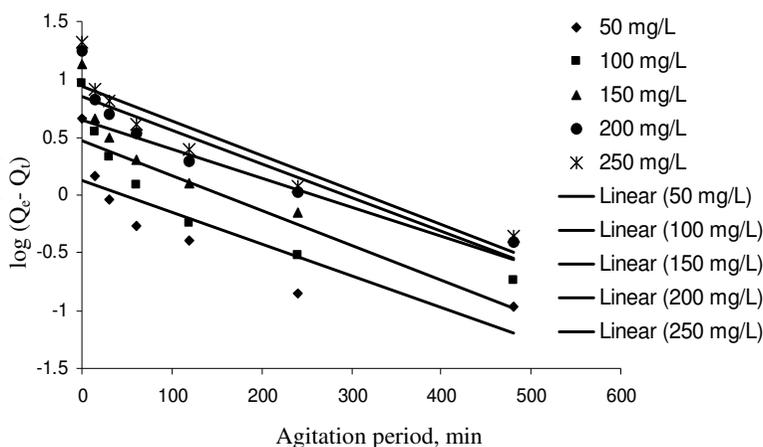


Figure 4. Pseudo-first order kinetics plot at different solute concentrations and for pH=8.

$$t/Q_t = 1/K_2 Q_e^2 . t \quad (7)$$

In the above equation K_2 is the equilibrium rate constant (g/mg min^{-1}). The plots of second-order kinetics drawn for t/Q_t against t are shown in Figure 5, whereas in the Table 3 the rate constants and the initial and equilibrium sorption values are given.

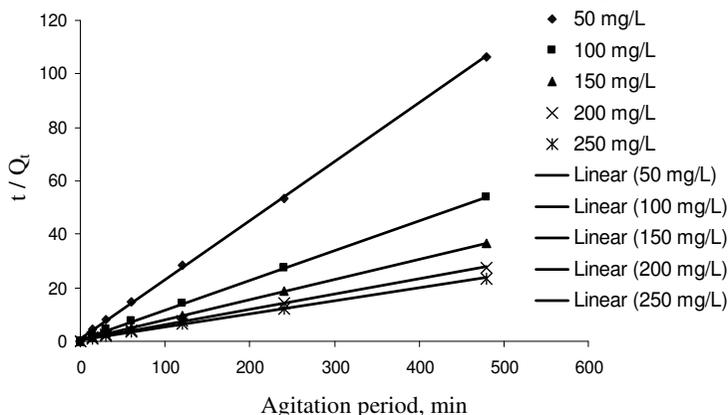


Figure 5. Pseudo-second order kinetics plot at different initial solute concentrations and for pH=8.

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 0.99990. All the facts suggested that the experimental sorption data approximated the second-order kinetic model very well.

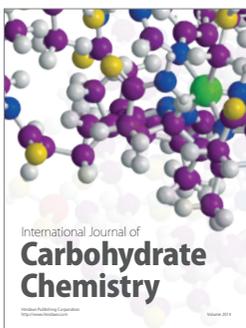
Conclusions

- Near equilibrium conditions were attained within 4 hours in all sorption experiments for all the initial concentrations of metal solution.
- Extraction of cadmium from the solution was found to be dependent both on the initial pH and the initial solute concentration.
- Both of the Langmuir and Freundlich models responded very well to the experimental sorption data, however, Freundlich model regression gave higher correlation coefficients.

- The Langmuir model gave the value of maximum sorption (X_m) of 33.61 mg/g, which is very close to the experimental value. Thus the use of Langmuir model is validated.
- 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.

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