

Comparative Study of Transport and Diffusion Coefficient of Copper and Cadmium in Saturated Clay and Fined Grained Soil

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Abstract— Heavy metal pollution is a major problem for soil and water because of their toxicity and hazardous nature. The main sources of heavy metals are activities such as mining, smelting, use of chemical fertilizers, discharging of untreated heavy metal industrial waste or effluent etc. To find out, how much their potential hazard, it is very important to understand their mobility in the soil. The objective of this study is to quantify heavy metals (Cu and Cd) transport and diffusion in two different simulated soils (Soil X and Soil Y) having different properties. Two separate tests, column test and diffusion test, have been conducted to meet this objective. Column study tries to investigate the BTC's of Cu and Cd, and relationship between depth and time in fined grained soil (Soil Y). While diffusion test carried out to find the effective diffusion coefficient (D^*) of Cu and Cd in clay soil (Soil X). In this study, batch equilibrium sorption experiments are carried out for different range of concentrations of Cu and Cd. The results shows the sorption of Cu and Cd in simulated fine grained soil and clay is nonlinear and follows Freundlich sorption isotherm. Cd exhibits higher K_f value and Cu exhibits lower N value for both types of soils. Moreover both metals have higher affinity in clayey soil, which has also higher cation exchange capacity than fine grained soil. In column test, vertical transport of Cu and Cd in saturated fined grained soil was also evaluated. Known concentration of simulated leachate of CuSO_4 and CdI_2 were introduced in the soil column. Samples of leachate flowing down the column were taken from different sampling ports at different height for Cu and Cd concentration. BTC's of Cu and Cd at different depth of soil column were drawn. Concentration ratio (C/C_0) versus depth curves were also drawn. Then $t_{1/2}$ ($C/C_0 = 0.5$) and t_1 ($C/C_0 = 1$) for different depths were calculated from the BTC's and investigated for their linear and polynomial relationship with depth. Results indicated that BTC's of Cu and Cd are "S" patterned. Concentration ratio (C/C_0) decreases sharply for initial number of days for smaller depths. At same depths, t_1 for Cd is significantly less than Cu. Cd was the more mobile with the higher recovery in the effluent solution. Time t_1 follows second order polynomial relationship with depth for both Cu and Cd, while $t_{1/2}$ and depth gives approximate same values of R^2 for linear and second order polynomial equations. In diffusion study, effective diffusion coefficient (D^*) of Cu and Cd in saturated clay soil were calculated using solution of transient diffusion equation. Different unknown parameters of equation were measured from laboratory experiments. Cu and Cd ions were contained in simulated leachate. The calculated D^* range for Cu and Cd is 2.02×10^{-10} to 2.25×10^{-10} and 2.109×10^{-10} to 2.28×10^{-10} respectively. The effective diffusion coefficient ranges are in good agreement with previous studies. In this study a very small range of D^* is given for Cu and Cd instead of a particular value. Since D^* value measurement is very sensitive and requires computer programs to solve equation, it is suitable to give a range of D^* to compensate the requirement of any numerical method.

Keywords— Diffusion, Transport, Simulated leachate, Simulated soil samples, Batch equilibrium Sorption test, Column study, Diffusion test, Freundlich sorption isotherm, BTC's, Effective diffusion coefficient

I. INTRODUCTION

Heavy metals found in the soils are the most toxic and hazardous inorganic pollutants. The main sources of the heavy metal that enter the soil are atmospheric deposition and soil amendments including sludge, fertilizer, compost manures, liming minerals and pesticides (Raven and Leoppert, 1996). Copper and Cadmium falls in the category of serious hazardous heavy metals and they are considered as a serious threat to health of human and also ecosystems because of their potentially high toxicity nature. Copper toxicity effect is more to plants than animals, whereas Cadmium is especially toxic to higher animals (McBride, 1994). So there is a need to understand the mobility and retention of these heavy metal in the soil. Several studies and research works have been followed up to find the effect of different parameters on heavy metal sorption/desorption (Lee et al., 2001; Liu et al., 2006; Sipos et al., 2008).

The mobility of heavy metal in soils may be described by different chemical mechanisms such as advection, dispersion or diffusion and sorption. Heavy metal's solubility and bioavailability may depend or be controlled by different soil characteristics such as pH, organic matter in soil, clay content, redox potential, Fe and Mn oxides present in soil, and calcium carbonate (Patil, 2014).

There are various mathematical models which are used to predict the transport of heavy metal. Traditionally the earthen barriers design for the buried waste contamination based on the assumption that the hydraulic conductivity i.e. permeability controls rate of leachate migration. Earlier experimental and field studies have predicted diffusion as the dominating and controlling mechanism of solute transport in many fine grained soils (Shackelford and Daniel, 1991). In this process dispersion coefficient and retardation factor of metals or nonmetals were determined by linear adsorption including convection-dispersion equations. But with time different mechanisms of transport came into existence. Transport of heavy metal is deeply affected or influenced by degree of sorption by soil grains (Naidu et al, 1994). The prediction of the fate of contaminants in surficial soil requires an understanding of chemical transport in unsaturated or saturated soil. The process that governs transport of contaminants in saturated soils are also applicable for unsaturated soil (Barbour et al., 1996).

This study focuses on the quantification of the transport and diffusion of Cu and Cd in saturated fine grained soil and clay. This can fill the gap of knowing BTC's of Cd vertical transport through soil column also the relationship between time and depth can be found out. This will help in comparing the transport and fate of Cu and Cd in simulated fine grained soil.

A. Aim and Objectives

1. To discuss the equations governing diffusion of contaminants through soil. (Analytical Solution)
2. Quantify competitive batch equilibrium sorption of Cu and Cd for simulated soil samples.
3. Compare the various curves of Cu and Cd for different depths in soil Y.
 - i. Breakthrough curves
 - ii. Depth vs time ($t_{1/2}$)
 - iii. Depth vs time (t_1)
4. To find the effective diffusion coefficients of Cu and Cd.

II. LITERATURE REVIEW

A. Major Sources of Heavy Metals in Soils

Heavy metals are considered as toxic pollutants that contaminate the soil. Major sources of heavy metals as contaminants are atmospheric pollution which causes from motor vehicles, combustion of fossil fuels, agricultural pesticides and fertilizers, city and industrial wastes, metallurgical industries, mining and smelting of non-ferrous metals. Most of the metals found in soil are because of the contamination of industrial emissions (Sharma et al., 2009).

B. Mobility of Heavy Metal in Soil

- 1) *Advection*: Advection is the movement of dissolved solute or contaminants along with flowing groundwater at the seepage velocity in porous media. Advection is governed by Darcy's Law. Darcy's law states that the rate of flow of water in soil from point A to point B is directly proportional to the head loss and inversely proportional to the length of path of flow.

$$Q = -K \times A \times (h_2 - h_1) / L \dots\dots\dots (1)$$

Where, Q = Flow discharge in m^3/s , A = area of cross section of flow, $h_2 - h_1$ = head loss between point A and point B, L = distance between point A and point B, K = coefficient of permeability or hydraulic conductivity.

- 2) *Dispersion*: Dispersion is because of mechanical mixing and molecular diffusion. When water containing pollutants mixes with non-polluted water resulting in a dilution of the pollutants is mechanical mixing and when ionic or molecular pollutants move in the direction of their concentration gradients is called molecular diffusion. Molecular diffusion is governed by Fick's law.

- 3) *Retardation*: Retardation is a processes that tries to slow down the transport of contaminants by eliminating or immobilizing them from a free state. Ionic exchange is the sorption of ions present in the solution to the oppositely charged individual sites on the surface of a particle of soil. There is a relationship between the sorbed quantity to the soil (S) and the concentration remained in soil solution which is described by various equations. These equations help us to predict the contaminant retention onto soil. They are termed as sorption isotherms. The equation that is used, when there is a direct linear relationship between S and C, is as follow:

$$S = K_d C \dots\dots\dots (2)$$

Another equation that is extensively used to relate the nonlinear sorption behavior is Freundlich equation which is as follow:-

$$S = K_f C^b \dots\dots\dots (3)$$

Where, K_f = distribution coefficient, b is a reaction order (dimensionless quantity) which indicates the shape of isotherm: for $b < 1$, shape is concave, for $b = 1$, shape is linear and for $b > 1$, shape is convex.

- C. *Transient State Diffusion Equation (Fick's Second Law)*: For time dependent (transient) transport of nonreactive solutes in soil, Fick's second law is assumed to apply, or

$$\frac{\partial c}{\partial t} = D^* \frac{\partial^2 c}{\partial t^2} \dots\dots\dots (4)$$

Where D^* is the effective diffusion coefficient

D. *Review of Research Work in the Field*:

- 1) *Ogata and Banks (1961)*: presented a solution for the differential equation governing the diffusion process. They provide a solution without using coordinate transformation (x-ut), thus obtaining asymmetrical concentration distribution, assuming that the dispersion coefficient D is small and the region near the source is not considered.
- 2) *Charles D. Shackelford, et al. (1991)*: presented steady-state and transient equations describing the diffusive transport of inorganic chemicals. Definition of diffusion coefficient was shown to vary widely and volumetric water content was also included differently. A method for measuring diffusion coefficient for compacted clay was presented and the results could show variation as definition changes.
- 3) *Charles D. Shackelford, et al. (1991)*: second paper calculated the effective diffusion coefficient for cations (Cd^{2+} , K^+ and Zn^{2+}) and anions (Cl^- , Br^- and I^-) for compacted kaolinite and Lufkin clay. The calculated diffusion coefficient values varied between $4 \times 10^{10} \text{ m}^2/\text{s}$ and $2 \times 10^9 \text{ m}^2/\text{s}$. The measured diffusion coefficient values for Cl^- and Br^- in kaolinite agrees with previous studies whereas D^* values for the cations are relatively high because of nonlinear adsorption behavior. D^* values calculated from reservoir concentrations are higher than D^* values determined from soil concentration profiles.
- 4) *Rosqvist and Destouni (2000)*: took an undisturbed solid waste sample and saw the lithium transport through it using probabilistic Lagrangian approach. The waste sample was 3.5 m^3 of old, well-degraded waste, and the experimental landfill 545 m^3 of fresh municipal waste. Four tracer tests were done for the test sample under constant head or sprinkling input boundary condition. Breakthrough curves (BTCs) were then drawn that can be explained by a local dispersion mechanism. Diffusive mass transfer also included in this mechanism. Two-domain conceptual model was assuming for transport model. The waste sample has 55–70% of the total infiltrated water moves through only 5–16% of the total water content. In the landfill, it is 90% of the vertically flowing water that moves preferentially through 47% of the total water content.
- 5) *S K Sharma et al. (2009)*: described the mechanisms of transport and fate of copper in terrestrial environment using column studies. Square column of dimension $15 \times 15 \text{ cm}$ and 1.35 m long was filled with poorly graded sandy loam soil from Mohali (India). BTCs for various depths of the column were plotted. The results showed that the copper has high tendency to flow in the soils. The $t_{1/2}$ time for copper was estimated and can be used to design copper laden wastewater disposal systems.
- 6) *Sharma et al. (2014)*: conducted a study on solute transport through saturated multi-layer soils with the help of soil column experiment. Reactive and conservative chemical used were sodium chloride and sodium fluoride. A finite difference numerical analysis was used to get solution of advection-dispersion equation. The results were expressed in terms of breakthrough curves (BTCs) and concluded that the order of stratification of soil layers had no effect on effluent solute concentration distribution. Other factors influence the BTCs were retardation factor, first order degradation coefficient and pecelet number.

III. MATERIAL AND METHOD

A. Simulated Soil Sample Preparation for Diffusion test and Column Study

First simulated soil sample (say Soil X) consist of the particles having size less the 75-micron IS Sieve size. The liquid and plastic limit was determined according to IS: 2720-5 (1985). The soil came out to be plastic in wide range of water content. Thus the first simulated soil sample can be classified as Clay.

In other simulated soil sample (say Soil Y) more than half of the material by weight was smaller than 75-micron IS Sieve size. As per IS: 1498 (1970) the soil sample can be classified as Fined Grained Soil.

B. Tests Done on Simulated Soil Samples (Soil X and Soil Y)

TABLE I

Property	Method of measurement
Grain Size Analysis (Wet sieve Analysis and Hydrometer Analysis)	IS 2720-4 (1985): Methods of test for soils, Part 4: Grain size analysis.
Liquid and plastic limit	IS 2720-5 (1985): Methods of test for soils, Part 5: Determination of liquid and plastic limit.
Permeability	IS 2720-17 (1986): Methods of test for soils, Part 17: Laboratory determination of permeability.
Cu and Cd Concentrations	Ion Chromatograph
Cu and Cd sorption	Batch Kinetics

C. Simulated Leachate Preparation for Diffusion Test and Column Study

The standard simulated leachate solutions of copper and cadmium were prepared from their soluble salts. For Copper, copper sulphate salt was used and for Cadmium, Cadmium Iodide was used. The concentration of each metals and nonmetals (ligands) attached to it in the simulated leached are shown in Table II

TABLE II

Heavy Metal	Metal	Concentration mg/L	Nonmetals (ligands)	Concentration mg/L
Column Test				
Copper Sulphate (CuSO ₄)	Cu ²⁺	100	SO ₄ ²⁻	151.6
Cadmium Iodide (CdI ₂)	Cd ²⁺	30	2I ⁻	67.7
Diffusion Test				
Copper Sulphate (CuSO ₄)	Cu ²⁺	600	SO ₄ ²⁻	907
Cadmium Iodide (CdI ₂)	Cd ²⁺	500	2I ⁻	1129

D. Batch Equilibrium Sorption Test of Binary Solutions of Cu and Cd on Soil X and Soil Y

- 1) *Experimental Setup:* A water-bath temperature controlled shaker was used for the batch equilibrium study. The temperature range of 293 K to 323 K was used. The batch experiments were performed at the constant shaking speed. For each experimental run, 20 ml aqueous solution of the known concentration of binary solutions of Cu and Cd was taken in a 150 ml conical flask containing 5 g of the soil (adsorbent).the ratio of soil to solution was taken as 1:4. These flasks were agitated at a constant shaking rate of 150 rpm in a temperature controlled orbital shaker maintained at a constant temperature. The equilibrium Cu and Cd concentrations in the supernatant were measured by Ion Chromatograph. The difference between the concentrations of the supernatant and the initial solutions concentrations were used to measure the amount of sorbed metal. The results were plotted as adsorption isotherms, or sorbed concentration (q) versus equilibrium concentration (c). All paragraphs must be indented.

E. Column Study

- 1) *Experimental setup:* A column of square cross-section (15 cm*15 cm) was taken to model the transport of simulated leachate in soil in vertical direction. The column was made of Perspex glass of length 180 cm to have a clear visual of the leachate flowing in the soil. The column setup is shown in Figure 1. A water storage tank was also fitted near the input of column to facilitate the constant flow of input liquid. Eight sampling ports of different spacing were provided along the depth of the column. The upper part of the column was kept empty to have a constant head of 10 cm above the soil.

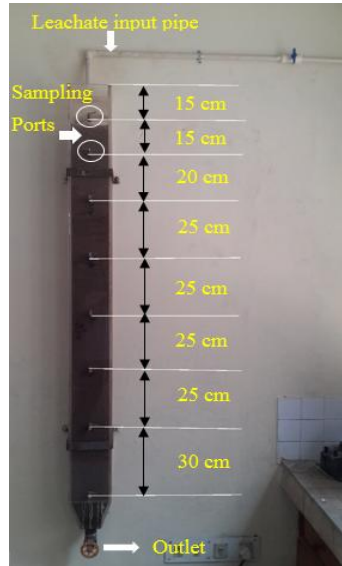


Fig. 1 Perspex Glass Column with Additional Setup

- 2) *Soil preparation and filling:* The soil sample for column test was prepared by mixing oven dried Soil Y with distilled water. Soil was filled in the column in four layers of different length. Each layer had different water content and bulk density as specified in Table III. This ensured the actual condition of increase of water content and bulk density of soil with depth.

TABLE III

Layers of soil	Volume of column section (cm ³)	Soil Y mass in kg	Water Content	Bulk Density g/cm ³
0-15 cm	3375	-	-	-
15-30 cm	3375 cm ³	4.657	0.15	1.38
30-50 cm	4500 cm ³	6.372	0.18	1.416
50-75 cm	5625 cm ³	8.032	0.19	1.428
75-100 cm	5625 cm ³	8.032	0.19	1.428
100-180 cm	18000 cm ³	25.702	0.19	1.428

- 3) *Saturation stage:* The distilled water was introduced in the column. The distilled water start saturating the soil. The valve was open at the bottom. The saturation stage was continued till the decrease in water level at the top became nearly constant. The saturation stage lasted for 8 days.
- 4) *Column test:* The column was fed with simulated leachate containing both Cu and Cd concentrations as shown in Table II. A constant head of 10 cm was maintained above soil surface. Samples were collected from the sample ports at regular interval of time. Breakthrough curves were then drawn for ports at different depths.

F. Diffusion Test

- 1) *Experimental setup:* A cylindrical cell of internal diameter of 100 mm and effective height of 120 mm was used as diffusion cell. The cell had removable countertop extension. Diffusion cell is shown in Figure 2. It had two porous discs of 12 mm thick fitted at top and bottom for inlet and drainage. A burette was attached to the hole at top cap of diffusion cell for fluid insertion.



Fig. 2 Diffusion Cell

- 2) *Sample preparation:* The soil sample for diffusion test was prepared by mixing oven dried Soil X with distilled water to desired water content of 25%. The 632 g of prepared soil was compacted in diffusion cell up to a height of 5.75 cm. Bulk density of soil became 1.4 g/cm^3 . Height of 6 cm from base in which soil was filled was termed as soil column. Height of 6 cm above soil column in which leachate was filled in the diffusion cell was termed as leachate column.
- 3) *Saturation stage:* The leachate column was filled with distilled water. The distilled water started saturating soil column. This was done before diffusion stage to minimize the effect of soil suction to the simulated leachate. The exit valve was opened to let the water to flow out. The saturation stage was continued till the rate of decrease of water level in the burette became constant. At that time the equilibrium had been established between soil column and leachate column containing distilled water. The remaining distilled water in water column was discharged out. The soil column had swelled to 6 cm length. The time taken for reaching the equilibrium was 17 days.
- 4) *Diffusion stage:* The simulated leachate was introduced in the leachate column and remaining half of 6 cm was filled with it. pH of the simulated leachate was adjusted to 3.7 to 6.7 to minimize the effect of adsorption characteristics of soil. The leachate samples were taken from the sample port at a regular interval of time. Samples were analyzed for the copper and cadmium concentration using IC. Variation of concentration of Cu^{2+} and Cd^{2+} in the leachate column with respect to time was plotted. The diffusion stage last for 32 days.
- 5) *Soil test after diffusion stage:* After diffusion stage the soil column of 6 cm length was subjected to different types of soil test.

IV. RESULTS AND DISCUSSIONS

A. Grain Size Analysis

- 1) *Soil X:* Clay (particle size less than 0.002 mm) is 79%, silt (particle size between .002 to 0.075 mm) is 17% and sand (particle size between 0.075 to .475 mm) is 4%.
- 2) *Soil Y:* Clay (particle size less than 0.002 mm) is 47%, silt (particle size between .002 to 0.075 mm) is 12%, fine sand (particle size between 0.075 to 0.4.75 mm) is 11%, medium sand (particle size between 0.425 to 2 mm) is 28% and course sand (particle size between 2 to 4.75 mm) is 2%

B. Liquid and Plastic Limit

- 1) *Soil X:* Plastic limit (w_p) is 26.444, water Content at 25 number of blows (w_L) is 43.309 and plasticity index (I_p) is 16.865. According to the plasticity chart of IS 1498 (1970): Classification and identification of soils for general engineering purposes, the soil X fall on the category of clay with medium compressibility.
- 2) *Soil Y:* Plastic limit (w_p) is 20.697, water content at 25 number of blows (w_L) is 27.2615 and plasticity index (I_p) is 6.564. According to the plasticity chart of IS 1498 (1970): Classification and identification of soils for general engineering purposes, the soil Y fall on the category of CL-ML, clay mixed with silt of low compressibility

C. Permeability

- 1) Soil X: The permeability (K_X) of soil X is 5.688×10^{-6} cm/s at 28°C.
- 2) Soil Y: The permeability (K_Y) of soil Y is 7.759×10^{-5} cm/s at 26°C.

D. Batch Equilibrium Sorption Isotherm of Cu and Cd for Soil X

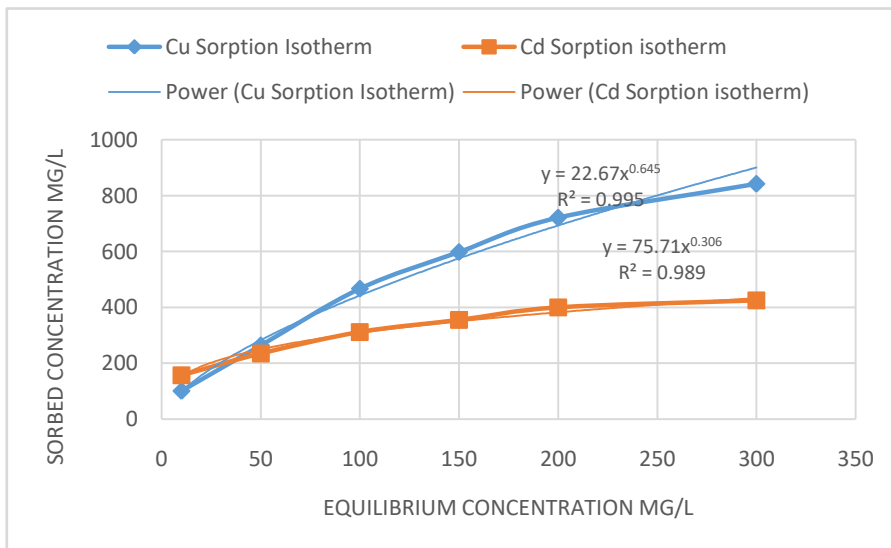


Fig. 3 Cu and Cd Sorption Isotherm for Soil X

Comparing the Figure 3 with Freundlich isotherm, the Freundlich isotherm parameters (K_f and N) are as follow:

$K_f = 22.67$ and $N = 0.6455$ ($R^2 = 0.9951$) (Cu Sorption in Soil X)

$K_f = 75.71$ and $N = 0.3061$ ($R^2 = 0.9899$) (Cd Sorption in Soil X)

E. Batch Equilibrium Sorption Isotherm of Cu and Cd for Soil Y

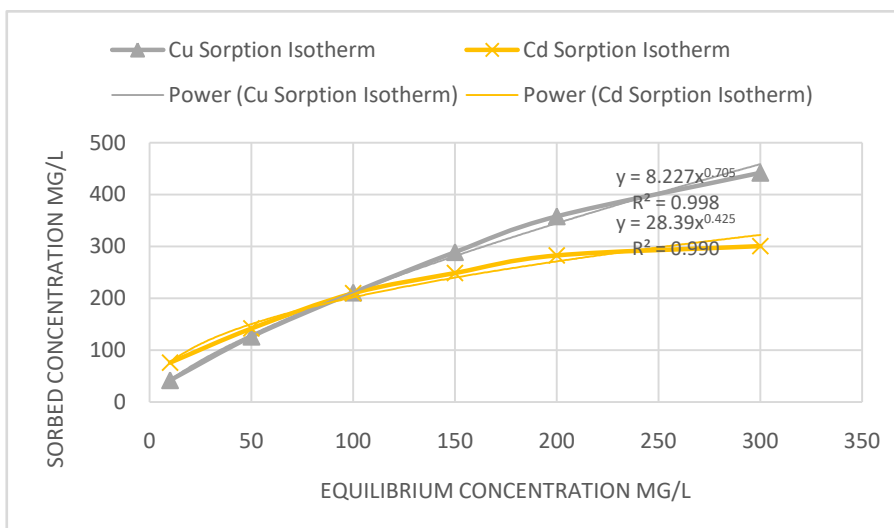


Fig. 4 Cu and Cd Sorption Isotherm for Soil Y

Comparing the Figure 4 graphs with Freundlich isotherm, the Freundlich isotherm parameters (K_f and N) are as follow:

$K_f = 8.2278$ and $N = 0.7051$ ($R^2 = 0.9988$) (Cu Sorption in Soil Y)

$K_f = 28.393$ and $N = 0.4259$ ($R^2 = 0.9908$) (Cd Sorption in Soil Y)

F. Summary and Discussion

Soil X and Soil Y is characterized as clay with medium compressibility and clay mixed with silt of low compressibility respectively. Soil X has very low percentage of silt and sand in it as compared to soil Y. Higher the clay content, higher will be cation exchange capacity and higher will be the retention capacity. The permeability of soil Y is higher than soil X. Soil X has more tortuous path than soil Y because of its smaller size particle percentage. That is why permeability of soil X is smaller than soil Y. Since the permeability of both simulated soil samples are of order 10^{-5} and 10^{-6} , the other transport mechanisms are dominant and fully responsible for mobility of heavy metal in the soils. Cu and Cd sorption behavior in soil X and soil Y is nonlinear, the affinity for retention of Cu and Cd is higher in soil X, it may be due to the higher percentage of clay. Freundlich modeling for Cu and Cd data for soil X and soil Y is applicable as R^2 are significantly high and N values are less than 1. K_f values illustrates the extent of metal affinity and N parameter illustrates the extent of heterogeneity of sorption sites, which means sorption sites have different affinities for heavy metal retention, where sorption by the highest energy sites takes place preferentially at the lowest solution concentration before those sites of lower energy. K_f value of Cu for soil X is greater than soil Y, this means soil X has more affinity for Cu sorption than soil Y. Similar for K_f value of Cd. But N value of Cu and Cd is greater in soil Y.

G. Column Test Results

1) Breakthrough curves of Cu for Soil Y

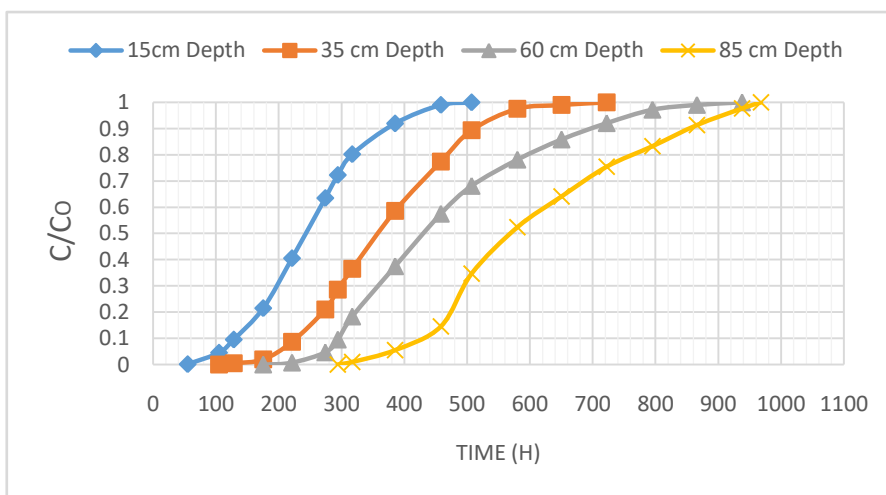


Fig. 5 Breakthrough curves of Cu at different depths for Soil Y

2) Concentration ratio versus depth curves of Cu for Soil Y

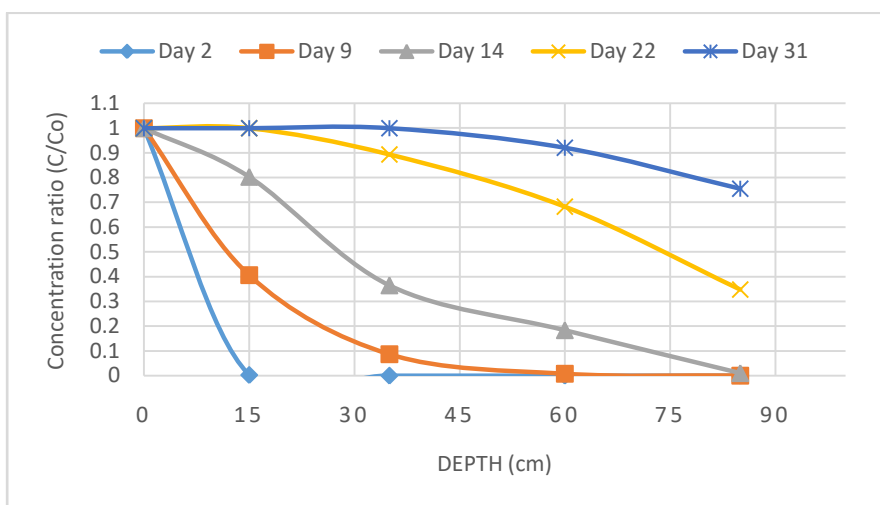


Fig. 6 Graph between Concentration Ratios versus Depth (cm) of Cu for Soil Y

3) Depth versus Time $t_{1/2}$, t_1 ($C/C_0 = 0.5, 1$) of Cu for Soil Y

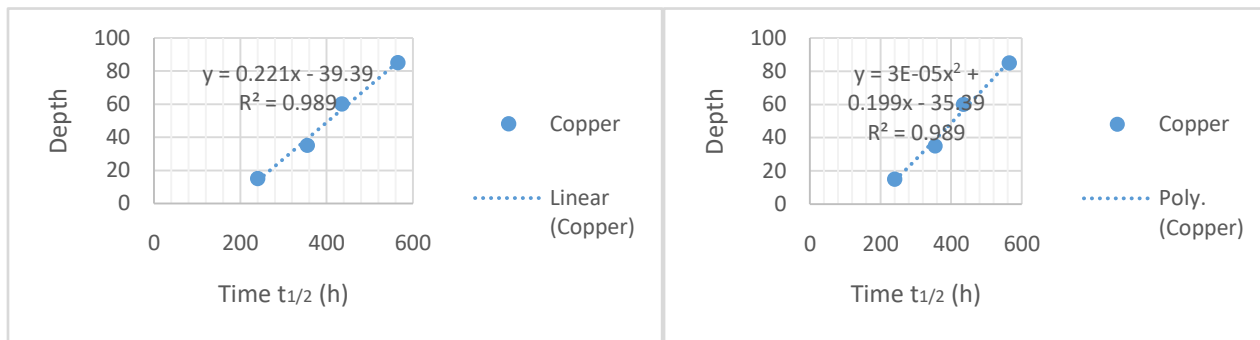


Fig. 7 Depth versus Time $t_{1/2}$

Fig. 8 Depth versus Time $t_{1/2}$

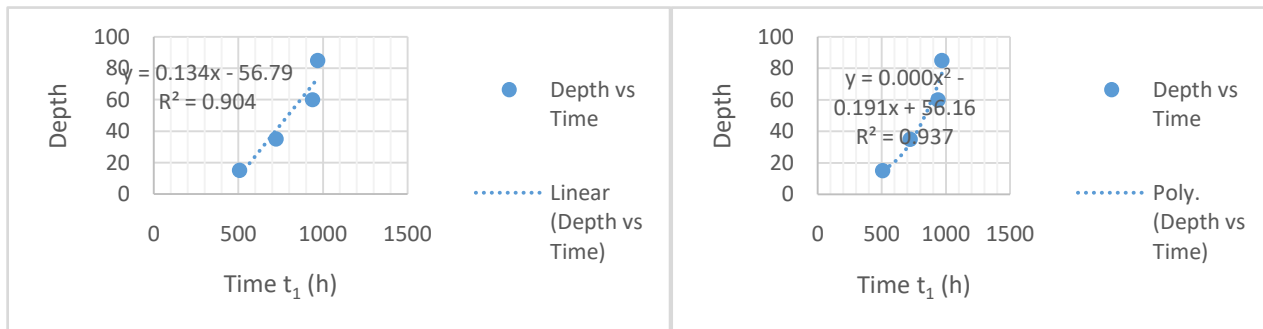


Fig. 9 Depth versus Time t_1

Fig. 10 Depth versus Time t_1

The mathematical relationships between depth (y) and time $t_{1/2}$ (x) obtained is as follow:

$y = 0.221x - 39.392$ (Linear equation) and $R^2 = 0.9895$

$y = 3 \times 10^{-5}x^2 + 0.1994x - 35.393$ (Polynomial second order equation) and $R^2 = 0.9896$

The mathematical relationships between depth (y) and time t_1 (x) obtained is as follow:

$y = 0.1347x - 56.796$ (Linear equation) and $R^2 = 0.9049$

$y = 0.0002x^2 - 0.1912x + 56.16$ (Polynomial second order equation) and $R^2 = 0.9374$

4) Breakthrough curves of Cd for Soil Y

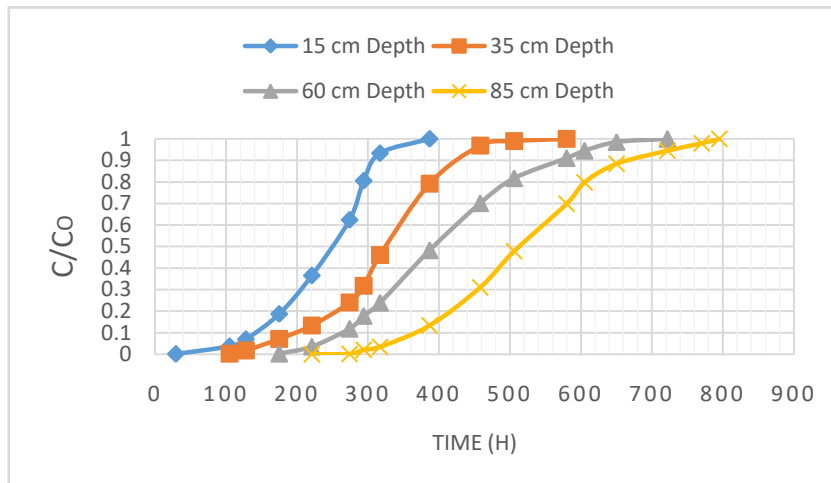


Fig. 11 Breakthrough curves of Cd at different depths for Soil Y

5) Concentration ratio versus depth curves of Cd for Soil Y

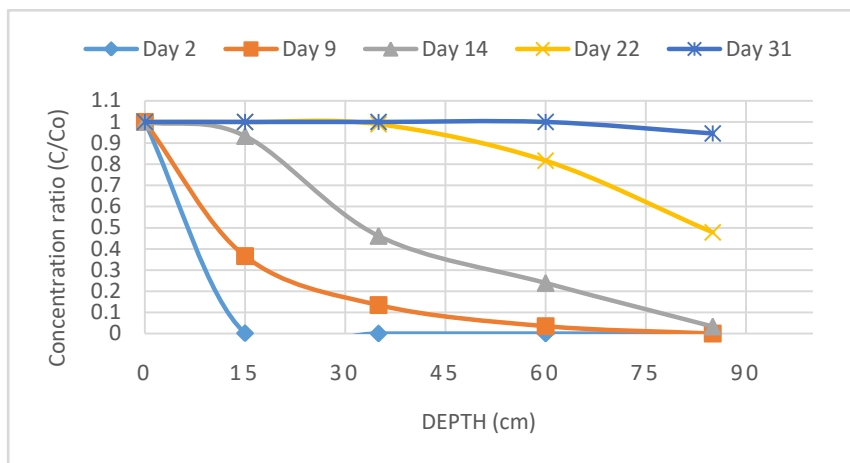


Fig. 12 Graph between Concentration Ratios versus Depth (cm) of Cd for Soil Y

6) Depth versus Time $t_{1/2}$, t_1 ($C/Co = 0.5, 1$) of Cd for Soil Y

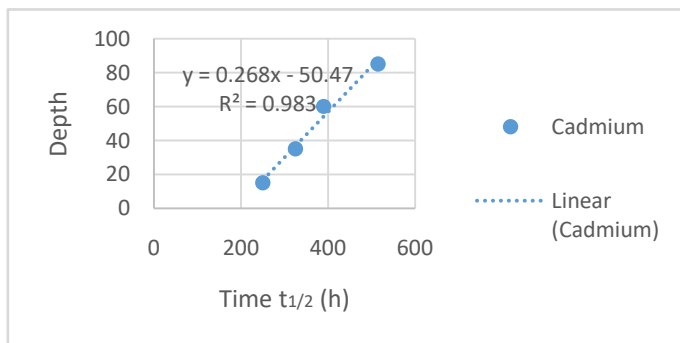


Fig. 13 Depth versus Time $t_{1/2}$

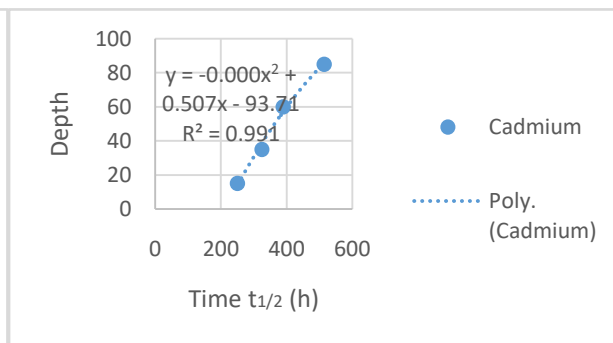


Fig. 14 Depth versus Time $t_{1/2}$

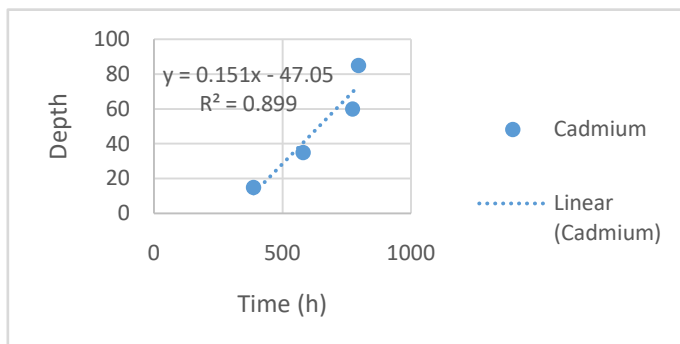


Fig. 15 Depth versus Time $t_{1/2}$

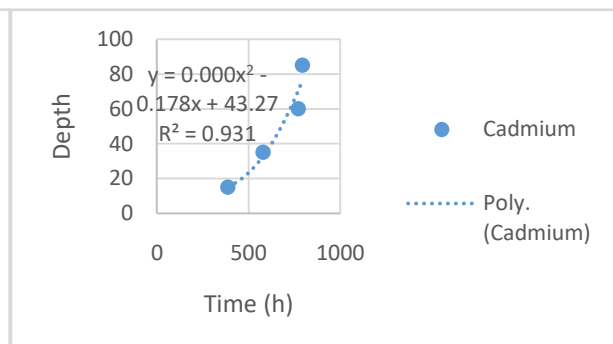


Fig. 16 Depth versus Time $t_{1/2}$

The mathematical relationships between depth (y) and time $t_{1/2}$ (x) obtained is as follow:

$y = 0.2682x - 50.471$ (Linear equation) and $R^2 = 0.9831$

$y = -0.0003x^2 + 0.5076x - 93.712$ (Polynomial second order equation) and $R^2 = 0.9919$

The mathematical relationships between depth (y) and time t_1 (x) obtained is as follow:

$y = 0.1512x - 47.055$ (Linear equation) and $R^2 = 0.8995$

$y = 0.0003x^2 - 0.1788x + 43.278$ (Polynomial second order equation) and $R^2 = 0.9316$

7) *Summary and Discussion*

For Cu and Cd BTCs are standard ‘S’ pattern. Similar results for Cu are shown by Sharma et al. (2009). These curves can be utilized for the calculation of $t_{1/2}$ and t_1 for the design of column used for removal of Cu and Cd impurities by retention. The quantity of Cu and Cd retained in the soil and the time taken to reach the ground water can be predicted.

The concentration ratio decreases very rapid for day 2 and day 9 at initial depths and became slower for higher days at higher depths. The time taken for the Cu and Cd leachate to reach saturation is more in 15 cm depth. The lower depths requires lesser time to attain saturation. At same depths, t_1 for Cd is significantly less than Cu, i.e Cd requires lesser time for full saturation. This is due to the lower sorption capacity of soil Y for Cd. The soil became readily saturated with Cd concentration as compared to Cu. Cd was the more mobile with the higher recovery in the effluent solution.

t_1 follows second order polynomial relationship with depth for both Cu and Cd, while $t_{1/2}$ and depth gives approximate same values of R^2 for linear and second order polynomial equations.

H. *Diffusion Study*

1) *Solution of transient diffusion equation*

After leachate was introduced in the diffusion cell at time zero ($t = 0$), the heavy metal transport through soil by molecular diffusion. This results in decrease concentration of the leachate w.r.t to time. The exit valve was closed so that no mass could get out. Based on these considerations the initial and final boundary conditions were

$$c = 0 \text{ at } 0 \leq x \leq L \quad (t = 0) \dots\dots\dots (5)$$

$$c = c_o \text{ at } L \leq x \leq H \quad (t = 0) \dots\dots\dots (6)$$

$$\partial c / \partial x = 0 \text{ at } x = 0 \quad (t > 0) \dots\dots\dots (7)$$

$$R_d y + H / \Theta \partial y / \partial x = H c_o \quad \text{at } x = L \quad (t > 0) \dots\dots\dots (8)$$

Where L = length of soil column, H = length of leachate column, Θ = volumetric water content (after diffusion process), y = amount of solute present between $x = 0$ to any distance x within soil column. C is the soluble concentration of the solutes and $c_o/c = R_d$ (Retardation factor)

Solution to the Fick’s second law for simultaneous diffusion and Sorption in soil with the above initial and boundary conditions is (Wilson 1948; Crank 1975)

$$\frac{c_t}{c_o} = \frac{\alpha}{1+\alpha} + \sum_{m=1}^{\infty} \frac{2\alpha}{1+\alpha+\alpha^2 q_m^2} e^{\left(\frac{-D^* q_m^2 t}{R_d L^2}\right)} \dots\dots\dots (9)$$

Where c_t is the concentration of solute in the leachate column at any time t , q_m is the non-zero positive roots of equation

$$\tan \alpha q_m \dots\dots\dots = \dots\dots\dots (10)$$

$$\text{and } \alpha = \frac{H}{\Theta R_d L} \dots\dots\dots (11)$$

The retardation factor (R_d) in Equation 18 is calculated by the following expression (Davidson et al. 1976):

$$R_d = 1 + \frac{\rho_d}{\Theta} \times K_f c_o^{N-1} \dots\dots\dots (12)$$

Where, ρ_d bulk density of soil, Θ is volumetric water content, c_o is initial concentration of cation in solution before diffusion and K_f, N are Freundlich isotherm parameters.

2) Diffusion test results

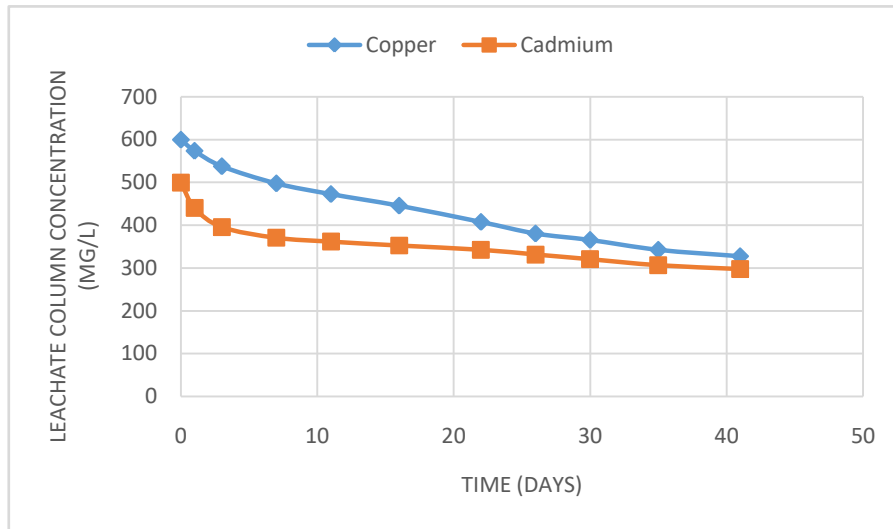


Fig. 17 Leachate Column Concentration versus time of Cu and Cd in Soil X

3) Soil properties after diffusion stage

TABLE IV

Soil Properties	Unit	Value
Water Content (w)	%	54.3
Bulk Density (ρ_d)	g/cm^3	1.728
Porosity (n)	%	62.8
Degree of saturation (S)	%	88.64
Volumetric water content (Θ)	%	55.55

4) Calculation of retardation factor of Cu and Cd in Soil X

The retardation factor (R_d) is calculated with the help of equation 24

$$\rho_d = 1.726 \text{ g/cm}^3 \text{ (Table IV)}$$

$$\Theta = 0.55 \text{ (Table IV)}$$

c_o of Cu and Cd are 600 and 500 mg/L (Table II)

$$K_f \text{ and } N \text{ (Copper)} = 22.67 \text{ and } 0.6455$$

$$K_f \text{ and } N \text{ (Cadmium)} = 75.71 \text{ and } 0.3061$$

Solution of the equation 8

Using Equation 12 we get

$$R_d = 8.366 \text{ (Copper)}$$

$$R_d = 4.184 \text{ (Cadmium)}$$

5) Calculation of Effective Diffusion Coefficient (D^*) of Cu

Effective diffusion coefficient (D^*) is calculated with the help of equation 9

$L = 6 \text{ cm}$, $H = 6 \text{ cm}$, $\Theta = 0.55$ (Table IV), $R_d = 8.366$, $c_o = 600 \text{ mg/L}$ and $c_t (t = 41 \text{ days}) = 327.9 \text{ mg/L}$ (Fig. 17)

$$D^* = 2.02 \times 10^{-10} \text{ to } 2.25 \times 10^{-10}$$

6) Calculation of Effective Diffusion Coefficient (D^*) of Cd

Effective diffusion coefficient (D^*) is calculated with the help of equation 9

$L = 6$ cm, $H = 6$ cm, $\Theta = 0.55$ (Table IV), $R_d = 4.184$, $c_0 = 500$ mg/L and $c_t (t = 41 \text{ days}) = 298$ mg/L (Fig. 17)

$$D^* = 2.109 \times 10^{-10} \text{ to } 2.28 \times 10^{-10}$$

7) Summary and Discussion

Cu and Cd diffusing in clay soil are subjected to reduced cross-sectional area and tortuous path as compared to free solution. Therefore effective diffusion coefficients (D^*) of Cu and Cd calculated in clay soil are less than the effective diffusion coefficients of Cu and Cd for infinite dilute solution. If we compare the effective diffusion coefficient of Cu and Cd, there is not much difference in their values. The effective diffusion coefficient values are in good agreement with previous studies. In addition to diffusion, Cu and Cd mobility also influenced by Sorption which is incorporated in the diffusion equation by using retardation factor. The value of the retardation factor (R_d) affects the determination of effective diffusion coefficients. If the values of D^* are higher, the possibility of nonlinear Sorption behaviour at higher concentrations or there may be Cu^{2+} and Cd^{2+} precipitation. D^* values depends on various sensitive parameter, therefore its measurement requires considerable precautions. In this study a very small range of D^* is given for Cu and Cd instead of a particular value. Since D^* value measurement is very sensitive and requires computer programs to solve equation, it is suitable to give a range of D^* to compensate the requirement of any numerical method.

V. CONCLUSIONS

The results shows the sorption of Cu and Cd in simulated fine grained soil and clay is nonlinear and follows Freundlich sorption isotherm. Cd exhibits higher K_f value and Cu exhibits lower N value for both types of soils. Moreover both metals have higher affinity in clayey soil, which has also higher cation exchange capacity than fine grained soil. Results indicated that BTC's of Cu and Cd are "S" patterned. Concentration ratio (C/C_0) decreases sharply for initial number of days for smaller depths. At same depths, t_1 for Cd is significantly less than Cu. Cd was the more mobile with the higher recovery in the effluent solution. Time t_1 follows second order polynomial relationship with depth for both Cu and Cd, while $t_{1/2}$ and depth gives approximate same values of R^2 for linear and second order polynomial equations. The calculated D^* range for Cu and Cd is 2.02×10^{-10} to 2.25×10^{-10} and 2.109×10^{-10} to 2.28×10^{-10} respectively. The effective diffusion coefficient ranges are in good agreement with previous studies. In this study a very small range of D^* is given for Cu and Cd instead of a particular value. Since D^* value measurement is very sensitive and requires computer programs to solve equation, it is suitable to give a range of D^* to compensate the requirement of any numerical method.

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