

Transport and Fate of Copper in Soils

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Abstract—The presence of toxic heavy metals in industrial effluents is one of the serious threats to the environment. Heavy metals such as Cadmium, Chromium, Lead, Nickel, Zinc, Mercury, Copper, Arsenic are found in the effluents of industries such as foundries, electroplating, petrochemical, battery manufacturing, tanneries, fertilizer, dyeing, textiles, metallurgical and metal finishing. Tremendous increase of industrial copper usage and its presence in industrial effluents has led to a growing concern about the fate and effects of Copper in the environment. Percolation of industrial effluents through soils leads to contamination of ground water and soils. The transport of heavy metals and their diffusion into the soils has therefore, drawn the attention of the researchers.

In this study, an attempt has been made to delineate the mechanisms of transport and fate of copper in terrestrial environment. Column studies were conducted using perplex glass square column of dimension side 15 cm and 1.35 m long. The soil samples were collected from a natural drain near Mohali (India). The soil was characterized to be poorly graded sandy loam. The soil was compacted to the field dry density level of about 1.6 g/cm³. Break through curves for different depths of the column were plotted. The results of the column study indicated that the copper has high tendency to flow in the soils and fewer tendencies to get adsorbed on the soil particles. The $t_{1/2}$ estimates obtained from the studies can be used for design copper laden wastewater disposal systems.

Keywords—Column study, copper, soil, transport.

I. INTRODUCTION

RAPID industrialization coupled with geochemical alterations pose a major threat to environment. Pollution of air, soil and water with both organics and inorganics is a matter of great concern. However, the non-degradable persistent trace metals are the most pressing problem of the present decade. They are the most insidious pollutants because of their non-biodegradable nature and property to affect all forms of ecological systems. The contaminants present in Industrial effluents get adsorbed in soils and are transported to the ground water table and pollute the ground water besides polluting the soils.

Heavy metal pollution is therefore, of major concern to environment. It is caused by various industries such as foundries, electroplating, petrochemicals, battery manufacturing, tanneries, fertilizers, dyeing, textile, metallurgical and metal finishing and many more. These industries discharge effluents containing toxic heavy metals such as copper, nickel, zinc, lead, arsenic, cadmium and chromium. Owing to the toxicity and ill effects of heavy metals on living being, the present day scientists and

researchers have developed interest in the origin and fate of these elements in the environment. Among these heavy metal ions, copper is one of the major toxic metals which is present in many industrial effluents.

Copper, a highly reactive metal, which is commonly used in a wide variety of process industries, results in large quantities of this element in their discharge. The various potential sources of copper pollution are metallurgical and metal finishing, corrosion inhibitors in cooling and boiler systems, drilling mud's catalysts, primer paints, fungicides, copper plating and pickling, corrosion of copper piping, copper releases from vehicle brake pads, architectural copper, Vehicle fluid leaks and dumping, domestic water discharged to storm drains etc.

A. Need to Analyze the Heavy Metals in Soils and their Transport

The determination of heavy metals in soils includes the measurement of total elementary content of metals and their transport. Importance of study of transport of heavy metals arises due to the fact that contaminants are absorbed in soils and also reach the groundwater table, thus polluting both soil and ground water. It is often more important to be able to estimate the mobile fraction, the readily soluble fraction, the exchangeable fraction, or the plant available fraction of the heavy metal content of a soil as a more direct indication of the likelihood of deleterious or toxic effects on soils and groundwater.

B. Aim and Objective

The objective of this study is to determine the transport of copper through soil layer and establishing its breakthrough curve for different depths in the soil profile. The studies are hence carried out in two phases:

- (i) Percolation of copper solution through soil column; and
- (ii) Copper diffusion at different depths of soil.

This information would be useful in designing and managing effluent disposals of industries processing heavy metals and land disposal system where sewage sludge and city refuse containing metals is to be disposed off. It will also provide valuable data for predicting heavy metal movement in soils and contamination of ground water.

II. LITERATURE REVIEW

A. Sources of Heavy Metals in Soils

Major sources of heavy metals pollutants in soils include atmospheric pollution from motor vehicles, the combustion of fossil fuels, agricultural fertilizers and pesticides organic manures, urban and industrial wastes, metallurgical industries, mining and smelting of non-ferrous metals. Most of the metals in soil are mainly the result of contamination by industrial emissions. Some contamination arises from the use of sewage

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sludge added to land. With the increase in industrial activities, usage of heavy metals in industries has increased tremendously. Which in turn pollute the land or water, depending upon the source of disposal. Metals are utilized in many ways in industries, agriculture, food processing and households in many forms.

B. Sources of Copper

The various sources of copper in the environment are industrial copper use, copper pesticides, vehicle fluids leaks and dumping, vehicle brake pads and architectural and marine antifouling coatings of copper etc. Out of these industrial effluents are the largest.

C. Effect of copper on Health and Environment

Copper must be absorbed in small amounts on a daily basis to maintain good health. A daily dietary intake of 1–2 milligrams is required. However, high levels of copper can be harmful to health. Inhaling high levels can cause irritation to the nasal passages, mouth, eyes and throat, and ingesting high copper concentrations can lead to nausea, vomiting and diarrhoea. Exposure to very high levels can damage the liver and kidneys and may lead to death. Copper is classified as a hazardous substance.

D. Mobility of Heavy Metals Through Soil

1) Transport of Heavy Metals

Water is an excellent medium for the transport of contaminants in the environment. The varieties of aqueous waste streams with direct discharges to surface water are nearly endless. Examples include effluent from treatment works, cooling water scrubber blow down from incinerators, treated leachate from landfills, etc. Virtually every industrial and commercial activity generates a wastewater. The following are the ways in which heavy metals get transported through the soil:

a) Advection

Contaminants that are capable of dissolving in water and then moving along with it are said to undergo advection. Advection is the transport of solutes along stream lines at the average linear seepage flow velocity.

b) Dispersion

When flowing water encounters solid particles of the porous media, it alters its course by flowing around the solids. This process is repeated millions of times. The result is the mixing of flowing water by mechanical means termed dispersion.

c) Molecular Diffusion

Contaminants (particularly ionic and molecular constituents) will also move in response to their chemical kinetic activity. The movement is from areas of higher concentration to areas of lower concentration and is termed as molecular diffusion.

2) Fate of Heavy Metals

In addition to the three transport processes, a myriad of complex chemical and biological processes affects the fate of contaminants in the subsurface.

a) Retardation

It refers to processes that impede the transport of contaminants by removing or immobilizing them from a free state. The processes that result in retardation are sorption and precipitation.

b) Precipitation

It is the converse of dissolution: the concentration of a solute exceeds the solubility of that particular compound, and any excess solute changes to a solid and thus precipitates out of the solution.

c) Ion Exchange

It involves the sorption of ions in solution onto oppositely charged, discrete sites on the surface of a soil particle. It is driven by the attractive force of maintaining electrostatic neutrality.

E. Review of Research Work in the Field

Reference [1] studied adsorption characteristics of some heavy metals by some soil minerals. The objective of this study was to compare three different soil minerals (montmorillonite, kaolinite and calcite) for their ability to remove heavy metals (HM). The metals selected were Pb (II), Cd (II) and Zn (II). These minerals were applied in chloride form dissolved in aqueous solutions of these metals at two concentrations i.e. 2000 and 6000 ppm. The effect of contact time, initial metal concentration and type of natural soil minerals on the adsorption process at $20 \pm 2^\circ\text{C}$ was studied using kinetic approach. Data gathered from Electrical Stirred Flow Unit (ESFU) used for kinetic study indicated that almost steady state adsorption conditions were reached after 2–4 h of unit working for the adsorption of Pb (II), Cd (II) and Zn (II). At 2000 ppm metal concentration and 2h reaction time, for example, the maximum Pb metal removed from the solution was found in calcite by about 74.2%, followed by montmorillonite and kaolinite by about 66% and 58% respectively.

Reference [2] evaluated concept and testing method for heavy metal contaminant transport in the underground. The evaluation of the contaminant transport is dictated by the Federal Soil Protection Regulation for sites that are suspected to endanger the ground water. The concept considers the estimation of the emission of the contaminant, i.e. the amount and concentration of the leachate of the contamination source in correlation with the time. The amount of leachate for every hydrological year using hydrological parameters. The expected concentration can be obtained from illusion tests.

Reference [3] investigated the EDTA-enhanced remediation of copper contaminated sandy-loam soil of volcanic origin. The soil, from an orchard, was contaminated with about 250 mg/kg of copper due to the excessive use of copper sprays. Copper-contaminated soil packed into 100-mm-long columns, and solutions of $\text{Na}_2\text{H}_2\text{EDTA}$ with CaCl_2 , raised to a pH of 6.2, were applied at a flow rate of 24 mm/h. application of an excess of 0.01 M EDTA leached about half the acid-extractable copper from the soil; most of it coming out in the first 3 liquid-filled pore volumes (P/V). Also a 0.5 PV pulse of 0.001 M EDTA was applied to similar soil columns and then either leached immediately with 0.005 M CaCl_2 , or left for

periods of up to 1 month before leaching. With immediate leaching, 70% of the EDTA applied was complexed with copper in the leachate, but after a month's delay only 24% was complexed with copper in the leachate, the rest being complexed with iron. There was no evidence of EDTA retardation or adsorption.

Reference [4] studied leaching of copper, chromium and arsenic through some free-draining New Zealand soils. Authors found that concentrated toxic solutions of copper, chromium and arsenic (CCA) were used extensively in the New Zealand timber preservation industry. A 2% w/v solution containing cupric, dichromate and arsenate ions was leached through undisturbed soil monolith lysimeters containing the surface and subsurface horizons of 2 free-draining New Zealand soils. The resulting breakthrough curves were successfully modeled using the Gompertz equation for biomass growth. Differences between soil horizons in the fitted Gompertz parameter values were related to differences in soil physical and chemical properties affecting leaching.

Reference [5] initiated a research to study metal movement within soil and metal availability to plants following long term, massive additions of sludge. Sewage sludges were incorporated annually into the surface 20 cm of Dublin loam over a period of 8 years. Metals extracted from the soil generally increased yearly with each addition of sludge. The acidity of soil also increased.

Reference [6] studied short-term natural attenuation of copper in soils. They considered Effects of time, temperature and soil characteristics. Natural attenuation of metals added to soils refers to the processes by which the mobility and bioavailability / toxicity of the added metals decline with time. Authors used isotopic dilution techniques to investigate the short-term (30 d) natural attenuation of Cu added to 19 European soils at two effective concentrations shown to inhibit plant (tomato) growth by 10 and 90%. The results showed that the bioavailability of Cu added to soils rapidly decreased after addition, especially in the soils with $\text{pH} > 6.0$, followed by a slow decreased in Cu bioavailability. The bioavailability of Cu added to soils also decreased with increasing incubation temperature. The activation energies and the apparent diffusion rate coefficients for the attenuation processes were 33 to 36 kJ/mol and 0.66 to 20.9×10^{-10} s at 20°C, respectively, and were consistent with Cu diffusion in meso- and micro-pores. The attenuation of Cu bioavailability was modelled on the basis of three processes: precipitation/nucleation of Cu on soil surface, Cu occlusion within organic matter, and diffusion of Cu into micro-pores. The soil and environmental factors governing attenuation rates were soil pH, organic matter content, incubation time and temperatures. Soil pH is the key factor for natural attenuation of Cu added to soils. The model can be used to scale ecotoxicological data generated from different soils and under different incubation times and temperatures.

Reference [7] studied kinetics of copper retention in Soil. Retention and release kinetics of Cu on four acid type haplumbrepts developed on two different types of parent rock material (granite and amphibolite) were studied with a stirred-flow chamber (SFC) method. The process of retention and release of Cu was found to be hysteretic, which suggest that the de-sorption mechanism or path is not an exact opposite of

the adsorption mechanism or path.

III. MATERIAL AND METHODS

A. Soil Sample

Soil sample were taken from the local nallah in Mohali (India), upstream of the industrial area to obtain the virgin soil. This soil was characterized in the laboratory using the standard procedure as per the provision of relevant BIS codes. The soil was classified as sandy loam.

B. Experimental Set-up

A column of square cross section (15×15 cm) at 135 cm depth made of Perspex glass, to facilitate visual observations, was used in column studies (Fig. 1). Sampling ports at the rate of 15 cm centre-to-centre were provided along the depth of the column. Soil was filled in the column to simulate the field conditions by compacting it to a dry density of about 1.6 gm/cm³.

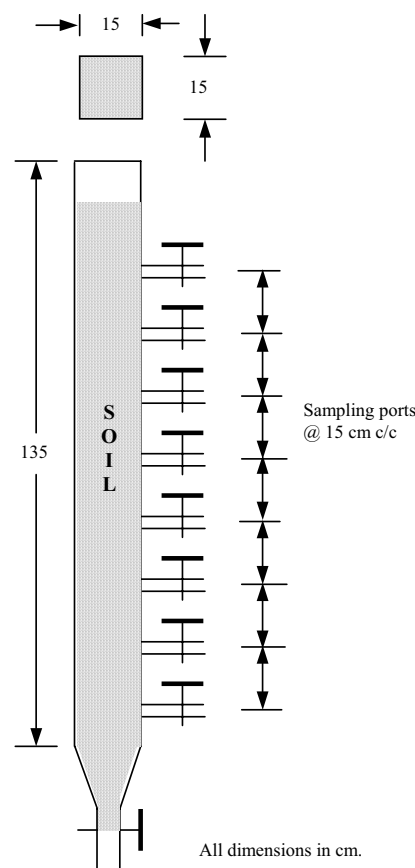


Fig. 1 Column apparatus

C. Copper Spiked Wastewater

Ordinary copper free tap water spiked with copper sulphate (CuSO_4) was used as the simulated waste effluent. The solution was prepared with the copper ion concentration of 50 mg/L.

D. Column Study

The column was fed with the waste water from a storage tank at a constant head of 10 cm above the surface of soil compacted to dry density of 1.6 g/cm³. The samples were collected from the sampling ports at regular intervals. The “Throughput” curves were drawn for the ports at the depths of 23cm, 38cm, 53cm and 68cm from the top of the soil. The carbon concentrations in the sample were determined using “spectroquant nova 60 photometer” apparatus with a sensitivity of 0.05 mg/L of copper concentration.

IV. RESULTS AND DISCUSSIONS

A. Column Soil Properties

1) Moisture Content and Dry Density

The Moisture content and dry density of the soil sample was found to be 10.27% & 1.6 g/cm³, respectively. The moisture content was high as the soil was collected from near the flow of the channel.

2) Grain Size Analysis

Results of grain size analysis (sieve analysis) are as given below:

- D₆₀ = 371.8 μm
- D₃₀ = 249.35 μm
- D₁₀ = 34.04 μm
- Cu = 10.922
- Cc = 4.91

So the soil sample of the channel’s bed is poorly graded as the Cc and Cu values are in range of poorly graded. The value of Cc should lie between 1 and 3 for well-graded gravels and sands.

3) Permeability

The permeability (K) was determined by constant head method. The permeability constant was found out to be 7.067x10⁻⁵ cm/sec. Hence the soil in column is classified as semi-pervious according to USBR recommendations.

B. Diffusion of Copper through Soil Column

1) Breakthrough Curves

The break through curves for initial copper concentration of 50 mg/L in the solution have been plotted for its residual concentration with time at four depths of 23 cm, 38 cm, 53 cm and 68 cm in column test and are shown in the Fig. 2. From these graphs the breakthrough times for the corresponding

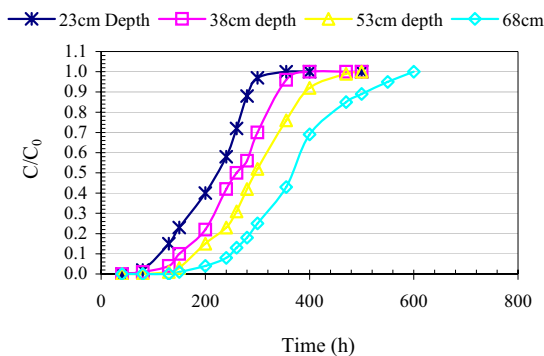


Fig. 2 Breakthrough curves at different depths of soil

depths are found as below:

- T_{1/2} for depth of 23 cm = 205 hrs.
- T_{1/2} for depth of 38 cm = 265 hrs.
- T_{1/2} for depth of 53 cm = 290 hrs.
- T_{1/2} for depth of 68 cm = 370 hrs.

T_{1/2} indicates the time when the concentration of copper in the flow at any depth becomes half of the applied concentration. This is 205 hrs (8.54 days) at 23 cm depth of soil as shown by blue curve in the graph. A further perusal of graph shows that the continuous flow occurs after 400 hours (16.67 days). This means that the soil column of 23 cm depth gets fully saturated with copper after 16.67 days.

Similarly the concentration of copper in the flow becomes half of the applied concentration in 265 hrs (11.04 days) at 38 cm depth of soil as shown by red curve in the graph and the continuous flow occurs after 450 hours (18.9) days meaning thereby that the soil column of 38 cm depth gets fully saturated with copper after 18.9 days.

The curve shown in green is the breakthrough curve at 53 cm of soil depth. The concentration of copper in the flow becomes half of the applied concentration in 290 hrs (11.25 days) at this depth of soil strata. The graph also indicates that the continuous flow occurs after 560 hours (23.33 days).

The concentration of copper in the flow becomes half of the applied concentration in 370 hrs (15.4 days) at 68 cm depth of soil strata and the continuous flow occurs after 640 hours (26.5 days), indicating that the soil at 68 cm depth get saturated in 26.5 days.

2) Concentration versus Depth Curves

The curves between concentration and depth after introduction of copper solution are shown in Fig. 3 for different time lags. The graphs show that the outflow concentrations of copper at different depth reduce with increased depth. This means that small depths are in contact of copper solution for a longer time and more adsorption of copper at these depths takes places. The deeper depths show lesser concentration in the outflow sample as higher material quantity is adsorbed in smaller depth in one day time. Similar curves plotted for 5, 10, 20 and 30 days time lags show the same trend of residual concentrations as they show for 1 day time lag.

From the perusal of these graphs (Fig. 3) it is clear that

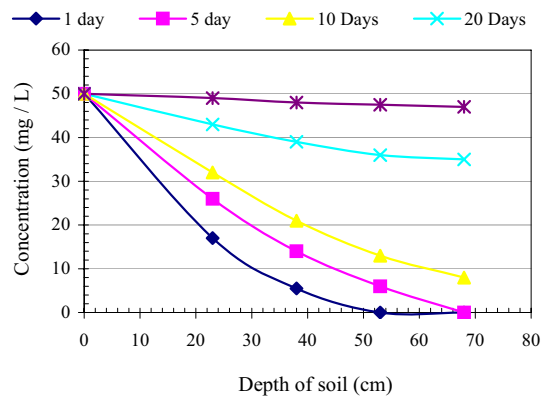


Fig. 3 Concentration v/s depth curve at different time

deeper depths of soil concentration adsorb more and more concentration of copper with respect to time lag.

3) Concentration Ratio versus Depth Curves

The curves between Concentration ratio i.e. C/C_0 against the

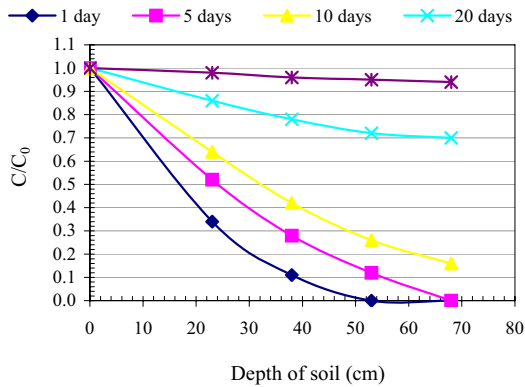


Fig. 4 Concentration ratio v/s depth curve at different time

depths after 1, 5, 10, 20 and 30 days after introduction of copper solution in the column are shown in Fig. 4. These curves also show the same trend as they show for concentration versus depths curves at various time gaps from the beginning. These curves help in predicting the residual copper concentration at different depth for different initial concentration of copper.

The following mathematical relationships between $C/C_0(y)$ and depth (x) at time gaps of 1 day to 30 days obtained are as given below:

$Y = 0.0003x^2 - 0.035x + 0.998$ (After 1 day with R^2 value of 0.998) (1)

$Y = 0.0002x^2 - 0.029x + 1$ (After 5 day with R^2 value of 0.989) (2)

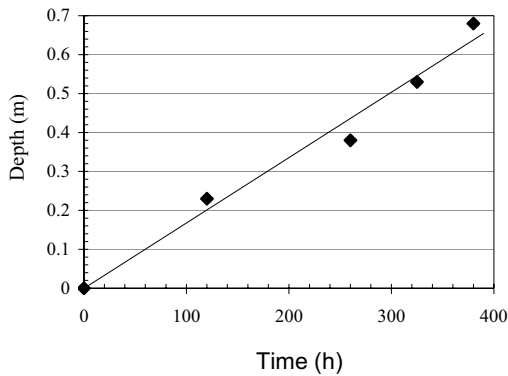
$Y = 0.000084x^2 - 0.018x + 1$ (After 10 days with R^2 value of 0.959) (3)

$Y = 0.00005x^2 - 0.001x + 1$ (After 20 day with R^2 value of 0.923) (4)

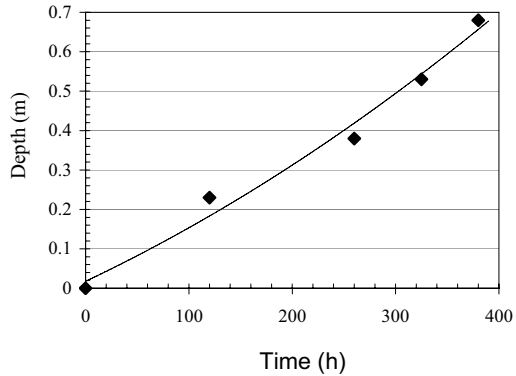
$Y = -0.00001x^2 + 1$ (After 30 day with R^2 value of 0.814) (5)

4) Time versus Depth Curves

The curve between time and depth for the concentration

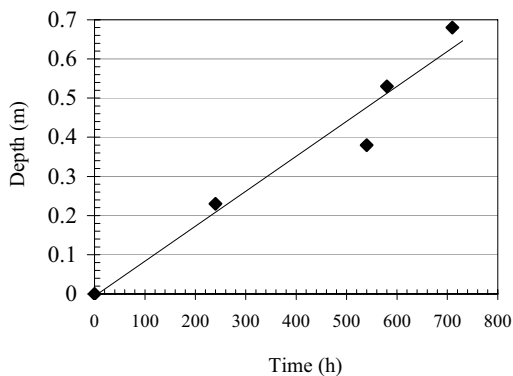


(a) Linear

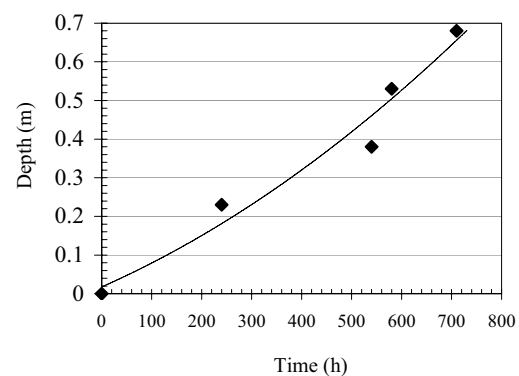


(b) Polynomial (second order)

Fig. 5 Depth v/s time curve for $C/C_0=0.5$



(a) Linear



(b) Polynomial (second order)

Fig. 6 Depth v/s time curve for $C/C_0=1.0$

ratio (C/C_0) of 0.5 and 1.0 have been plotted in Fig. 5 (a), (b) and Fig. 6 (a), (b). The trend lines in graphs (best fitted curves) are also shown.

C. Equations of Depth with Time Curve for C/C_0 Value of 0.5

Linear equation:

$$d=0.001t \quad (R^2 = 0.91) \quad (6)$$

Polynomial of second order:

$$d = 0.000002t^2 + 0.0009t \quad (R^2 = 0.941) \quad (7)$$

As the value of R^2 is more in second case so the polynomial of second order has more probability of depicting precise results. These equations can be used to depict the time required for transport of copper to any depth with concentration ratio of 0.5

D. Equations of Depth with Time Curve for C/C_0 Value of 1.0

Linear equation:

$$d = 0.00083t \quad (R^2 = 0.914) \quad (8)$$

Polynomial of second order:

$$d = 0.0000008t^2 + 0.0008t \quad (R^2 = 0.957) \quad (9)$$

Higher value of R^2 is in second case indicates that the polynomial of second order has more probability of depicting precise results.

V. CONCLUSIONS

From the overall studies the conclusions made are as below:

- The flow of copper follows the 'S' pattern to a great extent's' type pattern of the curve is a standard for the precise calculations of $t_{1/2}$ for the design of columns used for removal of metallic impurities by adsorption. $t_{1/2}$ values are equally important in metallic diffusion studies in soils.
- Even though the soil column was semi pervious the copper attained continuous flow only after 30 days even at a small depth of 0.7 meter of soil column after introduction of copper solution on the top of the soil. This implies that

copper has a high tendency to flow at a higher rate in soils and adsorption of copper is comparatively less in soils. Copper therefore is transported to lower depths or ground water table at a faster rate.

- The breakthrough curves show the same trend at all four depths of the soil column implying that adsorption rate is uniform over the entire depth of soil column.
- The relation between depth and time for any concentration ratio is best given by a second order polynomial.
- Depth time relationship at C/C_0 values of 0.5 and 1.0 can be useful in designing the proper disposal facility of copper laden waste effluents.

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