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Removal of Heavy Metals from Industrial Sludge Using Soil Washing Technique

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Abstract: In the present study, column leaching tests were conducted with two leaching solutions, i.e., distilled water and 0.1N HCl + 0.1N EDTA to know their removal efficiencies of heavy metal ions of Cu, Zn, Ni, Cd, Pb, Fe and Cr present in the industrial sludge. It was observed that distilled water was able to remove only a few metal ions Cu, Zn, and Ni in lesser quantities. Using 0.1N HCl + 0.1N EDTA, all the heavy metals were leached out with removal efficiencies in the range of 71-98%. Using the results of column leaching tests, the migration rates of different metal ions were determined which can be used to design the soil washing programme at the site to treat the similar sludge.

Key words: HCl, EDTA, elution curves, dispersion coefficient, retardation factor.

Introduction

Rapid industrialization has led to economic development, but at the same time has adversely impacted the environment leading to its severe degradation. The different types of industries release various types of effluents with different characteristics. As the sludge production from industries is an unavoidable problem, the sludge should be handled and disposed off properly. Different pathways exist for its disposal, but their indiscriminate disposal contaminates the soil and water bodies. The sludge contains considerable amounts of various contaminants and if it is not properly handled and disposed off, it may produce extensive environmental and health hazards. The treated sludge has benefits for plants and soils. Land application of treated sludge has received much attention over the traditional incineration and indiscriminate dumping.

The highly contaminated sites are generally found in industrial areas which often contain toxic metals such as lead, chromium, cadmium, nickel, and zinc (Gusiatin and Klimiuk, 2012). Unlike organic contaminants, most of the heavy metals do not undergo microbial or chemical degradation. The heavy metal contaminated sites cause threats and hazards to humans and the ecosystem by direct contact with contaminated soil through the food chain (soil-plant-human) by contaminating the ground and surface water resources (Wuana and Okieimen, 2011). Due to its seriousness, the industrial sludge is listed as hazardous waste in India by Ministry of Environment and Forests (MoEF, 2008).

The costs associated with the transport of the large volumes of sludge and construction of landfills are very high, recycling of this waste as a substitute for building materials (like bricks and low-cost concrete) is a better option (Balasubramanian et al., 2006; Baskar et al.,

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2006). Kakati et al. (2013) studied the use of textile sludge as a fertilizer at low concentration to enhance the plant growth. They found that 10% sludge plus 90% farmyard manure enhances the plant growth and further proposed that the accumulation of toxic materials in the plant system after the treatment should be studied in detail. Hence, we may use the industrial sludge as fertilizer if the pollutants are removed from it to the required level by using washing technique.

Washing may be in-situ or ex-situ, which involves the addition of chemicals to water to remove the metals. The commonly used flushing solutions are plain water, surfactants and/or co-solvents, acids, bases, chelates, and solvents. Gebreyesus (2015) discussed in detail about the research on remediation techniques and concluded that chemical extractants are the most cost-effective and less damaging, including organic acids and chelating agents. Mulligan et al. (2001) indicated that biosurfactants and biologically produced surfactants enhance the removal of metals from contaminated soils and sediments.

The commonly used chelating agents for soil washing include Ethylenediaminetetraacetic acid (EDTA), Nitrilotriacetic acid (NTA), Diethylenetriaminepentaacetic acid (DTPA), Ethylenediaminedisuccinic acid (EDDS) and citric acid (CA) which form stable complexes with most heavy metals over a broad pH range (Bilgin and Tulun, 2016). EDTA has the ability to chelate with almost all heavy metals (Zou et al., 2009). Khalkhaliani et al. (2006) used various concentrations of EDTA for evaluating the soil washing technique on an artificially contaminated sandy loam soil.

Generally, the leachability of metals depends on the type of metal, its form, and pH of the system. This research article discusses the effects of washing the sludge with two leaching solutions, i.e. distilled water and 0.1N HCl + 0.1N EDTA and to find the appropriate leaching solution to remove the metal ions. The migration rates of selected heavy metals were also determined from the results of column leaching tests which can be used to design a soil washing programme at the site to treat the similar type of sludges.

Materials and Methods

Study Area

The industrial sludge was collected from KIADB Industrial Area, Doddaballapur, Bangalore, India. M/s Eco Green Solutions Systems (P) Ltd, which handled this sludge is located in the villages of Doddaballapur Taluk, Bangalore rural District. The area lies (northern latitude of 12°59’03”N and eastern longitude of 77°35′16.2″E) in the Doddaballapur and is about 40 km from Bangalore towards North on Bangalore-Hindupur state highway (SH-9).

Chemical Properties of Industrial Sludge

In order to observe the chemical properties of industrial sludge, samples were collected from Eco Green Solutions Systems plant in the month of November 2013 and the analysis was carried out immediately. The analysis was carried out according to the standard methods as stated in USEPA 3050B (USEPA, 1996). The heavy metals present in the sludge and their chemical properties are shown in Table 1.

Table 1: Chemical properties of industrial sludge

Pollutant	*Quantity of metals in industrial sludge (mg/kg)*
Copper (Cu)	92.3
Zinc (Zn)	152.7
Iron (Fe)	414.5
Chromium (Cr)	74.2
Cadmium (Cd)	4.7
Nickel (Ni)	52.3
Lead (Pb)	11.2

Physical Characteristics of Industrial Sludge

The wet sludge was air-dried and then sieved through 2mm sieve to determine the index properties which are given in Table 2.

Results and Discussion

EDTA is a strong organic polyacid and is present as a metal complex. It is usually applied in soil studies to

Table 2: Characteristics of industrial sludge

Specific gravity (G)	*Liquid limit (%)*	*Plastic limit (%)*	*Shrinkage limit (%)*	*Plasticity index (Ip)*	*Maximum dry density (MDD), (g/cc)*	*Optimum moisture content OMC, (%)*
1.7	38%	Non-plastic	9.8	-	0.98	33.5

extract metallic cations from different soil matrices by metal-metal-EDTA exchange reactions. The complexing ability of EDTA also enables it to extract the precipitated or co-precipitated cations in soil solid phase. It is one of the popular chelating agents for removing heavy metals from soils because of its high chelating ability (Manouchehri and Bermond, 2009). According to Elless and Blaylock (2000), the EDTA extractable lead corresponds mainly to the exchangeable and carbonate fractions of soil while lead associated with oxide, organic and residual fractions were less solubilized by EDTA. To increase the availability of lead, caprylic acid was used in combination with EDTA. Elliott and Shastri (1999) found that an extractant like oxalate (Ox) may be a superior reagent to powerful EDTA when contaminating metals are associated with soil oxides. Ox released more Zn than EDTA, in a polluted soil from a Pennsylvania smelter site, because 40% of total Zn was associated with the oxide fraction. In fact, the high cost of EDTA has hampered its wide use for remediation of metal polluted soils (Kim et al., 2003). Hence to dissolve the oxide form of metals, reduce the pH of the system and to reduce the cost of the treatment, HCl is used in combination with EDTA.

Column Leaching Test

The column leaching tests were conducted on the sludge samples as per method reported by Rowe et al. (1988) to know the removal efficiencies of two leaching solutions, i.e., distilled water and 0.1N HCl + 0.1N EDTA. The samples were compacted to a density of 0.98 g/cc (MDD) and a water content of 33.5% (OMC). The void ratio and porosity of the test samples were found to be 0.82 and 0.45, respectively. The pore volume of the samples was estimated to be 56.55 cm^3 and the average seepage velocities with a hydraulic gradient of 10 were estimated to be $1.3 \times 10^{-5}$and 1.4×10^{-4} with distilled water and 0.1N HCl + 0.1N EDTA respectively. During the column leaching test, the seepage velocity was increased with time due to the removal of contaminants and hence an average value of seepage velocity was taken for the analysis.

The solution was allowed to pass through the sample and effluent samples were collected periodically. The volume of effluent and the amount of metals leached out (Δm) in each time increment were found. The number of pore volumes of flow (T') was calculated for each time interval. The ratio of the increment of solute mass (Δm) to initial solute mass (M_0) is called Leaching Mass Ratio (LMR) and the sum of these ratios is called Cumulative Leaching Mass Ratio (LMRm). The LMRm values were calculated corresponding to each time increment and plotted against the corresponding leached pore volumes (T_1) to get the experimental elution curves (i.e. breakthrough curves for leaching).

The experimental elution curves (number of pore volumes vs. leachate pore volume) of the metal ions with leaching solutions are given in Figures 1 and 2.

Leaching of Different Metal Ions with Distilled Water

From the elution curves of different metals with distilled water as leaching solution (Figure 1), it is observed that only few metal ions Cu, Zn and Ni leached out with distilled water but in lesser quantities. However, the metal ions Fe, Cd, Pb and Cr were not leached out even after washing with 60 pore volumes of distilled water. This may be due to the low solubility product of these metals in distilled water. Hence, it was noted that distilled water alone cannot be used to remove the heavy metals from this sludge. The order of removal efficiencies achieved with distilled water was found to be as: Cu (12.3%) > Zn (5.8%) > Ni (2.3%).

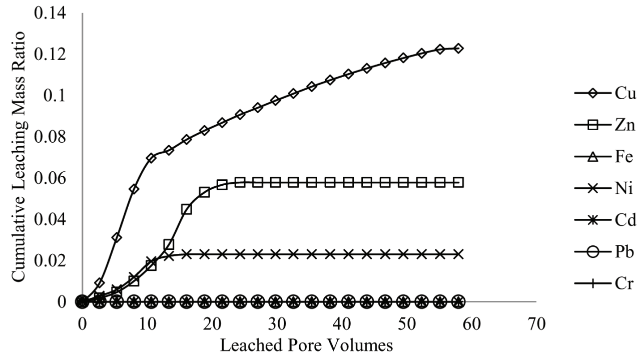


Figure 1: Experimental elution curves with distilled water.

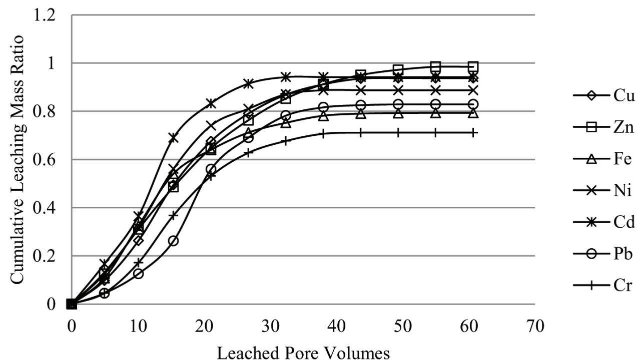


Figure 2: Experimental elution curves with 0.1N HCl + 0.1N EDTA.

Leaching of Different Metal Ions with 0.1N HCl + 0.1N EDTA

The sludge was also tested with 0.1N HCl + 0.1N EDTA to get the benefits of both acid and chelate. It can be observed that the elution curves of all the metals have followed the same trend indicating the effectiveness of this solution to remove the contaminants. The elution curves reached their equilibrium between 35-40 pore volumes of leaching with efficiencies are in the range of 70-95%. The removal efficiencies achieved by this solution were much higher compared to distilled water. The number of pore volumes required to achieve a particular efficiency were also less compared to those with distilled water. The order of removal efficiencies achieved with 0.1N HCl + 0.1N EDTA was estimated to be as: Zn (98.4%) > Cd (94.2%) > Cu (93.7%) > Pb (82.8%) > Ni (88.7%) > Fe (79.3%) > Cr (71.2%)

Estimation of Contaminant Transport Parameters

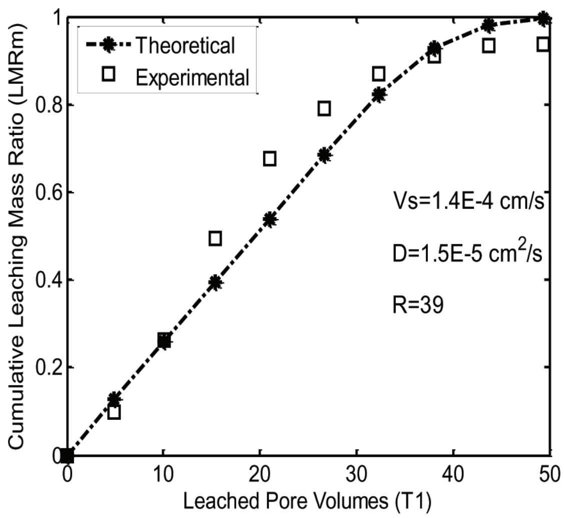
For a continuous point source of the contaminants leaching across the soil surface boundary for infinite duration, Ogata and Banks (1961) developed the analytical solution of Eq. (1) which gives the spatial and temporal distribution of concentration of contaminant. They used initial condition of $c\ (z, t = 0) = 0$ for $z \geq 0$; and the Diriclet boundary conditions of $c\ (z = 0, t) = C_0$ for $t \geq 0$ and $c\ (z = \infty, t) = 0$ for $t \geq 0$ and solution was obtained as:

$$C(z,t) = \frac{C_0}{2}\left\{\operatorname{erfc}\left(\frac{Rz - \bar{v}_z t}{2\sqrt{D_z R t}}\right) + \exp\left(\frac{\bar{v}_z z}{D_z}\right)\operatorname{erfc}\left(\frac{Rz + \bar{v}_z t}{2\sqrt{D_z R t}}\right)\right\} \quad (1)$$

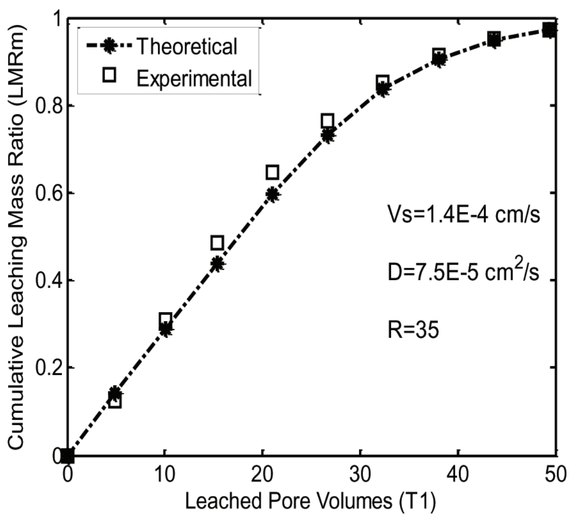
where C_0 is the concentration of the contaminant at the soil surface i.e., upstream boundary. The last boundary condition can only be appreciated mathematically. However, this is required to arrive at the analytical solution (Eq. 2). The erfc (u) is the complementary error function which is equal to 1 – erf (u). For estimation of contaminant transport parameters, the method as reported by Rowe et al. (1988) was used. A computer program was prepared for the above equation using MATLAB v7 software tool to perform the iterations. The experimental values of the seepage velocity ($\bar{v}_z$), thickness of the soil sample (z), time periods (t) and the effluent concentrations along with the trial values of dispersion coefficient D_z and Retardation factor (R) were incorporated into the computer program. By running this program the theoretical effluent concentrations were determined and the plot was generated with the theoretical breakthrough curves. The theoretical effluent concentrations were compared with experimental values and the iterations were continued till the theoretical curve match with the experimental values. The transport parameters were obtained by matching the theoretical elution curves (with a set of assumed diffusion coefficients and retardation factors) with the experimental elution curves (i.e. breakthrough curves for leaching).

Theoretical Elution Curves

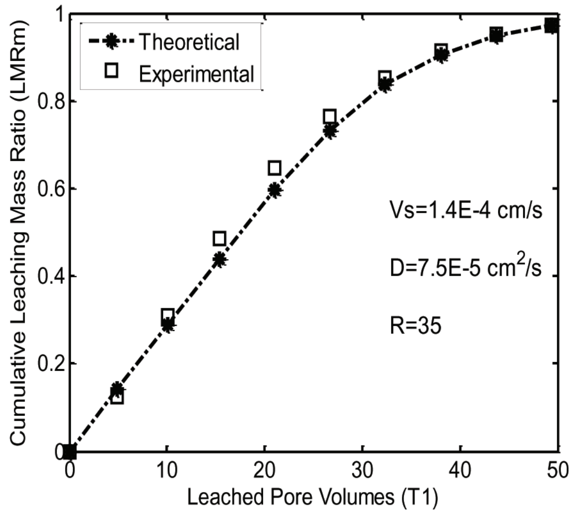
As the HCl + EDTA solution gave comparatively better results, the transport parameters were determined with respect to this solution. The theoretical elution curves obtained are shown in Figures 3(a-h) for this leaching solution. The estimated transport parameters are given in Table 3.



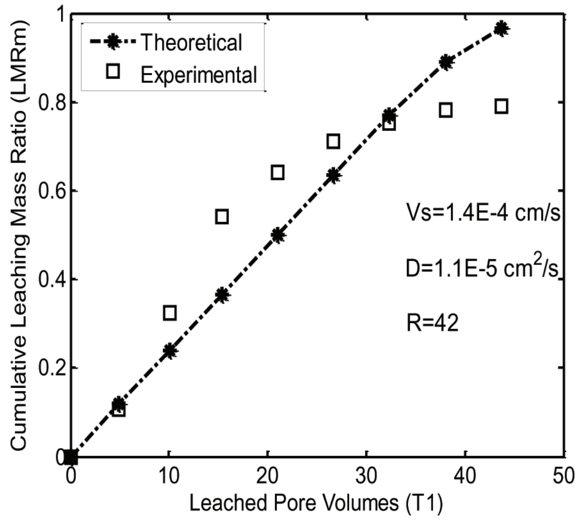
(a) Copper with 0.1N HCl + 0.1N EDTA



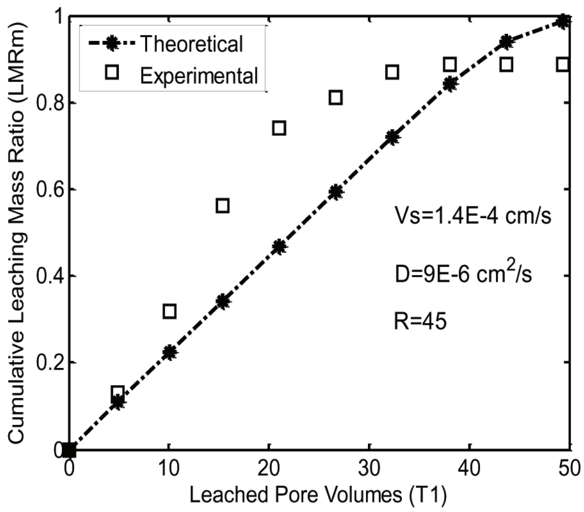
(b) Zinc with 0.1N HCl + 0.1N EDTA



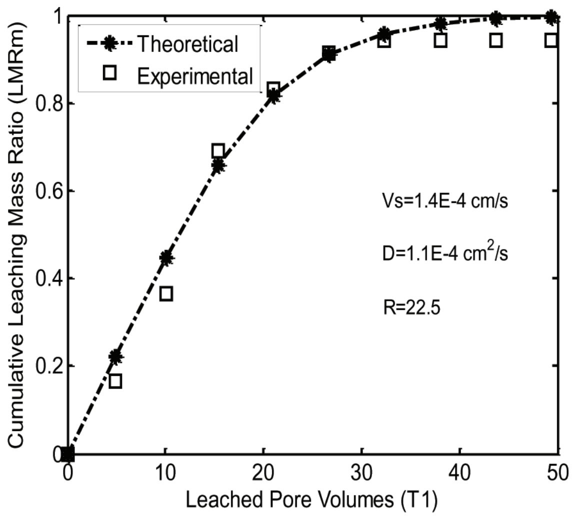
(c) Iron with 0.1N HCl + 0.1N EDTA



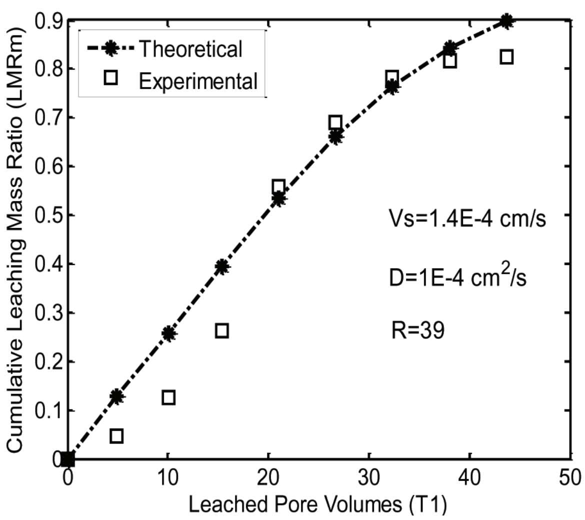
(d) Nickel with 0.1N HCl + 0.1N EDTA



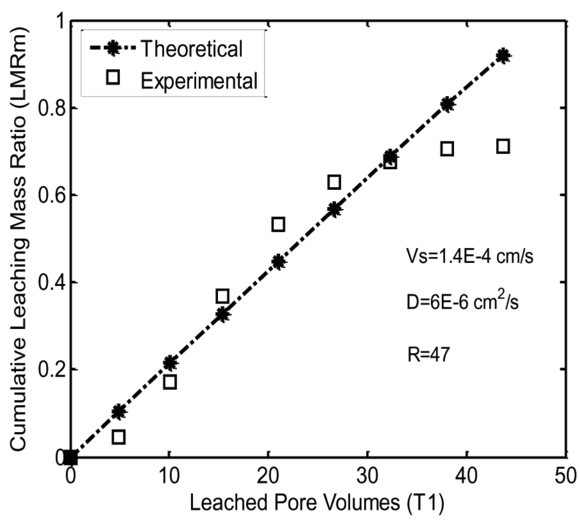
(e) Nickel with 0.1N HCl + 0.1N EDTA



(f) Cadmium with 0.1N HCl + 0.1N EDTA



(g) Lead with 0.1N HCl + 0.1N EDTA



(h) Chromium with 0.1N HCl + 0.1N EDTA

Figure 3: Theoretical elution curves.

Table 3: Contaminant transport parameters of different metal ions

Pollutant	With 0.1N HCl + 0.1N EDTA	
	Dispersion coefficient, D (cm²/s)	*Retardation Factor (R)*
Copper (Cu)	1.5×10^{-5}	39.0
Zinc (Zn)	7.5×10^{-5}	35.0
Iron (Fe)	1.1×10^{-5}	42.0
Chromium (Cr)	6.0×10^{-6}	47.0
Cadmium (Cd)	1.1×10^{-4}	22.5
Nickel (Ni)	9.0×10^{-6}	45.0
Lead (Pb)	1.0×10^{-4}	39.0

The dispersion coefficients (*D*) of different metals were observed to be in the range of 6.0×10^{-6}-1.1×10^{-4} cm²/s and retardation factor (*R*) were observed to be in the range of 22.5–47. The removal efficiencies of various metal ions were compared (Figure 4) and was observed that almost all metal ions have attained more than 85% removal efficiency except Fe, Pb and Cr. The highest removal efficiencies of Fe, Pb and Cr were observed to be 79.3, 82.8 and 71.2% respectively.

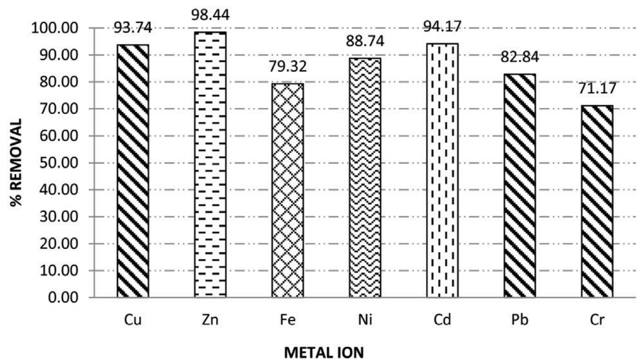


Figure 4: Removal efficiencies of 0.1N HCl + 0.1N EDTA for different metal ions.

Conclusions

- From the batch and column leaching tests conducted on the sludge, it was found that 0.1N HCl + 0.1N EDTA solution is the most efficient leaching fluid to remove the metal ions Cu, Zn, Fe, Ni, Cd, Pb and Cr present in the industrial sludge.
- The % removals obtained with the leaching solutions used are as follows.
  Distilled water:
  Cu (12.3%) > Zn (5.8%) > Ni (2.3%) > Cd (0%) > Pb (0%) > Fe (0%) > Cr (0%)
  0.1NHCl + 0.1N EDTA:
  Zn (98.4%) > Cd (94.2%) > Cu (93.7%) > Pb(82.8%) > Ni (88.7%) > Fe (79.3%) > Cr (71.2%).
- The transport parameters of different metal ions were found by comparing the theoretical elution curves with experimental elution curves. The Dispersion coefficients of different metals were in the range of 6.0×10^{-6}-1.1×10^{-4} cm²/s and Retardation factors were in the range of 22.5–47.
- The results of column leaching tests were used to estimate the contaminant transport parameters which are required to estimate the quantity of leaching fluid required in the field. Thus, this research work is useful in the design of the soil washing programme at the site to treat the contaminated sludges.

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