



# INTERNATIONAL JOURNAL OF ADVANCE RESEARCH, IDEAS AND INNOVATIONS IN TECHNOLOGY

ISSN: 2454-132X

Impact factor: 6.078

(Volume 6, Issue 1)

Available online at: [www.ijariit.com](http://www.ijariit.com)

## A study on competitive sorption of combined heavy metals in low permeable soil

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### ABSTRACT

*A widespread and pervasive global problem now existing in the environment is the subsurface contamination. The contaminants found may include wide range of toxic pollutants such as heavy metals, radionuclides, and organic compounds. Thus, there is an urgent need for the remediation of these sites. The knowledge of sorption characteristics of the contaminants in the soil helps in the selection of appropriate method of remediation in order to achieve the maximum eddicacy. Only if appropriate method is chosen, the remediation can be done effectively. In general, sorption refers to the transfer of mobile contaminant ions from the pore fluid to soil particle surfaces, rendering them immobile. For the study, the soil sample was collected from Tamil Nagar, Tirunelveli and a combination of heavy metals like zinc and copper was selected as this combination of contaminants is been reported as most prevalent in major of the industrial effluents. The particularity of these contaminants is that these are the most widely found elements in most of the industrial effluents. The influence of the initial concentration of the heavy metals on the sorption capability of soil was studied. It was found that increased initial concentration of heavy metal in the pore fluid, results in increase amount of heavy metal uptake per unit weight of the sorbent of heavy metal. Data analyzed plotted using Langmuir isotherm [18] concludes that copper is preferably more absorbable on soil than zinc.*

**Keywords**— Heavy metal, Remediation, Sorption, Sorbent, Langmuir Isotherm

### 1. INTRODUCTION

Due to improper past waste disposal practices and accidental spills numerous sites worldwide are found to be contaminated. Contamination of soils and groundwater is well known, but the ever - growing problem of large quantities of contaminated dredged sediments has only received attention recently [1-2]. For the remediation of the contaminated sites, several technologies have been developed from past so as to protect the public as well as environment. But the degree of success greatly depends on the nature of soil, nature of contaminant, concentration of contaminant and so on[15]. Contaminants found include a wide range of toxic pollutants such as heavy

metals, radionuclides, and organic compounds. The public and the environment are being exposed to these pollutants through different exposure pathways to unacceptable dosages, leading to intolerable adverse effects on public health and the environment. The remediation of these sites has become an urgent priority to environmentalists and regulatory bodies. Several different technologies have been developed to remediate soils, sediments, and groundwater based on physicochemical, thermal, and biological principles [9-11].

Contamination of environment may occur due to compounds like petroleum hydrocarbons, poly nuclear aromatic hydrocarbons, solvents, pesticides and heavy metals. Soil is mostly contaminated by rapidly expanding industries, mine tailings, disposal of high metal wastes, leaded gasoline and paints, coal combustion residues and spillage of petrochemicals. Once metal contaminates the soil, it can have complex interactions with natural binders that can lead to both short (delaying the normal hydration reaction) and long (release of the heavy metals in groundwater) term problems. The heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations [5-6]. The heavy metals such as Arsenic (As), Cadmium (Cd), Copper(Cu), Chromium(Cr), Lead(Pb), Nickel(Ni), Zinc(Zn), Cobalt(Co) etc cannot be destroyed or degraded[3].

Before carrying out the various remediation technologies in the soil from the different contaminants, it is necessary to analyze the sorption characteristics of the selected combination of contaminants in the soil sample [13]. With the input of contaminants in various forms and from different directions, it is important to understand those processes that promote the accumulation of contaminants in unsaturated soil and those that reduce the soil contaminant load [22]. To gain this understanding, we need to know the forms and reactivities of the soil constituents, the nature and mode of action of mobilizing agents, the forms in which the mobilized material is transported whether colloidal or in true solution, in ionic or complex form, alone or in association with other soil constituents and the stability of the mobile and immobile forms toward oxidation, reduction, microbial action, pH, sorption, and coprecipitation[2]. Understanding these processes may

eventually provide us with methods to treat contaminated sites, such as flushing or leaching, addition of chelating agents, or application of electrochemical techniques [26].

Copper	500
	400
	300
	250
	200

## 2. MATERIALS AND METHODS

### 2.1 Collection of soil sample

The soil sample was collected from Tamil Nagar, Tirunelveli (8°40'41"N and 77°43'58"E). The sample was found to be sandy clayey soil. The sample was taken from 30cm depth. The sample collected was air dried for four days. After proper drying of the sample, it was tamped to particular size. The tamped soil was sieved through 425-micron sieve. The initial characteristics of the soil sample are listed in Table I.

Table 1: Initial characterization of soil sample

Parameter	Value
pH	7.90
Specific gravity	2.26
Atterberg limits(%)	
i. Liquid limit	66.538
ii. Plastic limit	9.40
iii. Plasticity index	49.6
Moisture content(%)	10.26
Hydraulic conductivity(cm/s)	0.0256
Organic content(%)	10.23

### 2.2 Spiking of heavy metals in soil

The collected sample was spiked with a combination of heavy metals with desired concentration. The spiked soil was dried at room temperature for about 48 hours. The dried spiked soil was rammed with hammer and then water was added up to the saturation limit. The spiked and saturated soil was used in the reactor.

### 2.3 Batch sorption studies of contaminants in soil sample at various concentrations

The air-dried spiked samples could attain equilibrium. The soil was added with different concentrations of contaminant. The samples were shaken continuously in a water bath shaker at 120 rpm for 96 hours. The clear supernatant was removed and diluted to the required concentration as per the AAS standard and was analyzed for the different contaminants added with atomic adsorption spectrophotometer (AAS). The total amount of metal adsorbed in the adsorption processes was calculated from the difference between the amount added initially and that remaining in solution after equilibrium [7-8].

The concentration variation was carried out by keeping both the pH and the liquid to solid ratio (L/S) constant, i.e, pH same as soil pH and L/S as 20:1. Five variations of concentration was carried out in combined form of copper and zinc.

**2.2.1 Collection of samples:** The samples were periodically withdrawn from the batch reactors in order to check the sorption rate of soil sample and to perform analyses [12]. The samples were collected at different intervals from the zeroth minute to 96<sup>th</sup> hour. Since in the initial hours the adsorption rate would be more, the sampling frequency was kept high during the initial period and was gradually reduced later [16-17].

Table 2: Concentration variations followed in the study

Heavy metal	Concentration(mg/L)
Zinc	1000
	800
	600
	500
	200

**2.2.2 Analysis of samples:** The collected samples were analyzed using Atomic Absorption Spectrometer (AAS), Agilent 3000 series. For analyzing in AAS, the samples were diluted according to the AAS standards depending upon the type of heavy metal. The obtained results were graphically represented in the form of “1/C<sub>s</sub> with 1/C<sub>i</sub>”, where C<sub>s</sub> is the amount of contaminant sorbed by the soil and C<sub>i</sub> is the initial metal concentration [24-25].

**2.2.3 Plotting of the adsorption isotherms:** The results of batch sorption studies were modeled using Langmuir isotherms. For modeling, the amount of contaminant absorbed by the sorbent, C<sub>s</sub>, and the equilibrium concentration of the solute, C<sub>e</sub>, were used as model parameters [18-20].

The modeling can be done with Linear, Langmuir or Freundlich isotherms. However, Langmuir sorption isotherm was used since offers an advantage over Linear and Freundlich sorption isotherms by limiting the amount of contaminant sorbed by the sorbent (Giles 1960). The assumption based on which the Langmuir sorption isotherm was developed was that, solid surface have finite amount of active sorption sites for sorption phenomena to take place (Langmuir, 1918). This implies, if all the active sorption sites are occupied with the contaminant(s), the solid surface will be unable to exhibit the affinity towards the contaminants present in the solution. This further implies, when the mass of contaminant sorbed by the sorbent, C<sub>s</sub>, reaches its threshold limit, no significant change in its value may be observed, irrespective of the initial concentration of solution [23]. The mathematical form of Langmuir sorption isotherm is presented as follows.

$$C_s = \frac{K_1 C_e b}{1 + K_1 C_e} \tag{1}$$

$$\frac{C_e}{C_s} = \frac{1}{K_1 b} + \frac{C_e}{b} \tag{2}$$

Where K<sub>1</sub> is sorption constant related to the binding energy or the affinity parameter and b is the maximum amount of solute that can be sorbed by the sorbent (Veith and Sposito, 1977).

## 3. RESULTS AND DISCUSSIONS

### 3.1 Characteristics of soil

pH of the soil sample was determined as 7.90. This indicates that the soil is slightly alkaline in nature. The pH of the soil influences the behavior of heavy metals in the water phase. The specific gravity of the soil was obtained as 2.26 and it is a known fact that soil with large amounts of organic matter or porous particles (such as diatomaceous earth) have specific gravities below 2.60. From the obtained values of Atterberg limits, the sample could be classified as CH soil which is called ‘flat clay’. Also, the solubility of contaminants will primarily depends on the amount of moisture content in it. The contaminants present in 10.65% moisture content will be adsorbed on the soil sample. The permeability value was obtained as 0.0256cm/s which indicates that, the contaminants would be forced to interact the structure of soil which allows more extent of reaction. Similarly, the organic content of the soil was obtained as 12.23%. While comparing with the organic content of pure clay (i.e, zero), the soil sample is having a higher organic content. This indicates the presence of

unknown matter with different surface charges which increases the sorption capacity of soil sample.

### 3.2 Effect of initial concentration of heavy metal

It was observed that, increase in the initial concentration of heavy metal in the solution, resulted in the increase in the amount of heavy metal uptake per unit weight of the sorbent of heavy metal [14]. This may be due to the fact that, at high initial concentrations, the ratio of number of moles of heavy metal to the available sorption sites present in the soil-contaminant mixture is high as compared to that in low initial concentration (see Fig 1).

### 3.3 Sorption isotherm

Using the amount of contaminant sorbed by the sorbent,  $C_s$ , and the equilibrium concentration of the solute,  $C_e$ , as model parameters the isotherms were developed. From the slope and intercept values, the values of the constants  $K_1$  and  $b$  were derived (see Table 3).

### 3.4 Selectivity order of heavy metals

Based on the values of the Langmuir constants, the selectivity order of the heavy metals was obtained. Since the value of Langmuir constant  $b$  obtained for copper is higher than that of zinc, it can be concluded that the heavy metal copper is more sorbable than zinc.

This can be explained in different ways. The affinity of the cations for oxygen and their relative tendency to form covalent bonds with that oxygen can be related to the electronegativity of the cations. Also, several other factors which could be considered are valency, ionic radius, hydrolysis constant, valency and Misono softness parameter [19-20] (see Table 4). Thus, from the above results, it can be concluded that copper is more adsorbable than zinc in the considered soil sample.

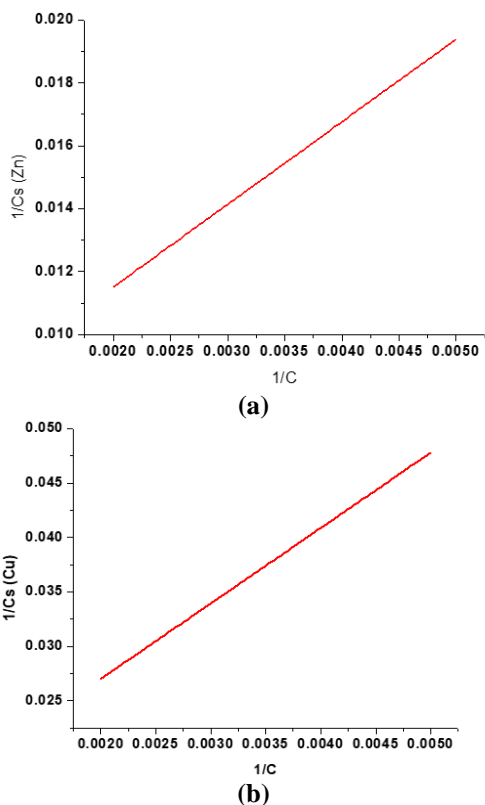


Fig. 1: Effect of initial concentration of heavy metal on the sorption capability of soil sample (a) Zinc (b) Copper,  $C_s$  – Amount of contaminant sorbed by the sorbent;  $C$  – Initial heavy metal concentration

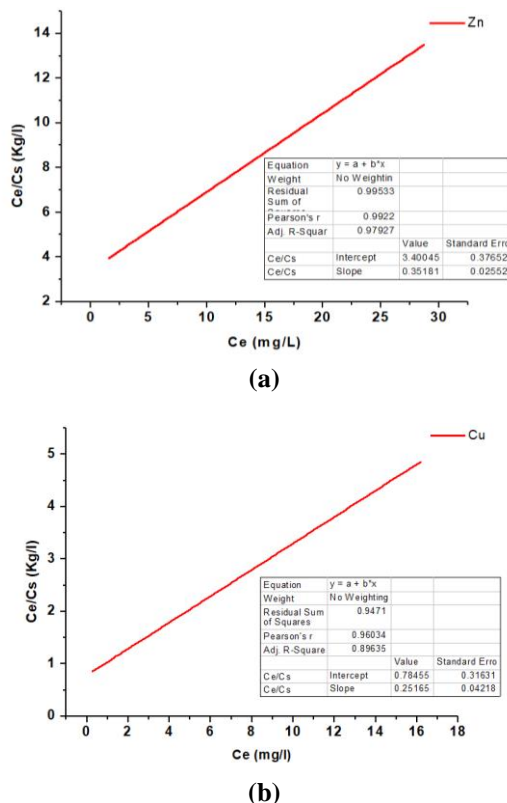


Fig. 2: Langmuir isotherms of soil sample (a) Zinc (b) Copper

Table 3: Langmuir Isotherm constants of copper and zinc

Heavy metal	$K_1$	$B$
Copper	0.32076	3.97377
Zinc	0.10346	2.8424

Table 4: Chemical characteristics of copper and zinc

Parameter	Copper	Zinc
Valence	38	5.000
Electronegativity	1.9	1.6
Ionic radius ( $\text{Å}^\circ$ )	0.71	0.74
Misono softness parameter (nm)	0.284	0.240
Hydrolysis constant	8.0	9.0

Sposito (1986)

## 4. CONCLUSION

For the study, soil sample was collected from Tamil Nagar, Tirunelveli. The soil characteristics were analyzed initially to study about the nature of soil. The soil was then spiked artificially with a combination of copper and zinc. Batch sorption study was conducted by varying concentration and keeping the  $L/S$  ratio and pH constant so as to study about the competitive sorption phenomenon. The following conclusions can be drawn out of the study:

- (a) The study quantifies the influence of initial heavy metal concentration on sorption phenomena which is really helpful in determining the long-term behavior of the soil.
- (b) Increase of heavy metal initial concentration, in the solution, results in increase amount of heavy metal uptake per unit weight of the sorbent of heavy metal. This is due to the availability of a greater number of moles of the heavy metal as compared to the low concentration.
- (c) The study illustrates the effect of competition of multiple heavy metals present in the real scenario on the sorption behavior of the soil sample considered.
- (d) Langmuir isotherm constants ( $K_1$  and  $b$ ) indicate that Copper is more preferably adsorbed in the soil sample than zinc.

## 5. ACKNOWLEDGMENT

It is impossible to conclude the paper without mentioning all the people whose contributions have affected one's thinking or implanted ideas which have later flourished. The support of all the researchers in Geotechnical and Environmental division of IIT Madras is gratefully acknowledged.

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