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ORIGINAL CONTRIBUTION

# Assessment of heavy metal adsorption potential of lateritic soil used as landfill liner material in waste containment structures

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**ABSTRACT**

Increasing soil and groundwater pollution by heavy metals through anthropogenic reason is a major concern of present environment. The objective of the present study was to assess the potential of lateritic soil to be used as liner material in landfill, effluent drain and effluent pond particularly with respect to subsurface transport of Zn & Cu. In the present study, the adsorption and migration of the two metals (Zn & Cu) through lateritic soil were studied using batch adsorption tests. The laboratory scale batch adsorption experiments were performed to determine adsorption capacity of the soil by carrying out adsorption isotherms and kinetic studies at different initial concentrations (0.5, 1, 5, 10 mg/l) of adsorbate at a fixed pH of 8 and with different adsorbent doses (5, 10, 20, 30 g/L) and an equilibrium contact time of 120 minutes. The soil used as adsorbent in batch adsorption experiments was found to have low hydraulic conductivity of $3.17x10^{-8}$ cm/s, and thus suitable to be used as a liner material in waste containment structures. The linear, Langmuir and Freundlich isotherm models were examined for fitting with the laboratory batch adsorption experimental results. The Langmuir isotherm provided best fit for Zn adsorption test data with $R^2$ (co-efficient of determination)=0.922 and RMSE(root mean square error) =0.000962 at a soil dose of 5.0 g/L. Similar trend was observed with Cu adsorption test results with $R^2$= 0.989, RMSE =0.000588 at a soil dose of 5 g/L. The higher values of adsorption capacity ($q_{Zn}$ =1845 mg/kg, $q_{Cu}$ = 1796.8 mg/Kg) of the soil for both the metals indicate good attenuative potential of the soil with respect to Cu & Zn. It was concluded from the present study that the lateritic soil can be used as an effective adsorbent and a barrier material and can be used as a primary liner material in a waste containment structure for retarding the migration of contaminants and thereby protecting the precious groundwater.

**Key words**: Heavy metals; Soil and groundwater pollution; lateritic soil; adsorption capacity; Hydraulic conductivity; Landfill liner.

## 1. INTRODUCTION

Anthropogenic activities, particularly untreated oil treated industrial effluents when released to the lithosphere the problems of soil pollution and possibility of ground water pollution crops up.It is directly discharged from metal industry, galvanized industry, Dyeing industries, Zinc processing units etc (Ref Annual report of west Bengal pollution control board,2014-2015). According to the USEPA list, the priority pollutants are antimony, arsenic, beryllium, Cd, $Cr^{+}$ ,$Cu^{+2}$ , $Zn^{+2}$ ,$Pb^{+2}$ , mercury, Selenium, silver, Thallium, these are top of the list. This study is focussed on mainly Zn & Cu for their high toxicity and mobility.Significant worldwide studies in different parts of the world show us that heavy metals from aqueous solution can be removed or adsorbed by various adsorbents, considering the economics of the adsorption process locally available lateritic soil has been taken as adsorbent.Copper is more toxic for plants than animals. It is studied that Cu is preferable absorbed and less affected by the other heavy metals, Zn also has its high mobility and it is highly associated with oxide and carbon bound fraction. Consideration on using of lateritic soil for heavy metal removal process is

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discussed in this present study. The adsorbent lateritic soil was collected from a stone quarry located in Durgapur, West Bengal . The physic-chemical properties of the soil are tested in the soil mechanics laboratory according to IS 2720. The initial concentration of the heavy metals were considered according to the present effluent discharge concentration of the industries. The stock solution the heavy metals $Zn^{+2}$ and $Cu^{+2}$ were prepared by $ZnSO_4$ and $CuSO_4$ respectively based on Lambert- Bears Law($V_1S_1=V_2S_2$). The adsorption study of the heavy metals were done by the lateritic soil under equilibrium conditions using batch adsorption studies. For the optimum pH and optimum contact time with the equilibrium soil dose , we have to done different batch test for the best result, in addition the point of Zero charge ($pH_{zpc}$) of the soil also determined to validate the batch result of the pH.(Al-Hamdan and Reddy 2005). By conducting different batch test, we have determinedthe optimum pH , contact time and maximum adsorbent dose for the isotherm study. The batch experiment result says that in the pH 8 the heavy metal removal is maximum about 90% with adsorption dose 1gm and for the contact period of 2hrs. In this present observation we have seen that the lateritic soil can remove heavy metals up to 90% when we consider the above condition. A number of mathematical models are studied for this adsorption process namely Linear, Langmuir and Freundlich Isotherm. The higher $R^2$ and lower RMSE value indicates better fit model with the experimental date. In present study the Langmuir and Freundlich Isotherm both are very closer but we have taken Langmuir Isotherm for it's better value. The b value is less than 1 in most of the cases in the adsorption process of Zn and Cu in the aqueous solution.(Vazquez et al 2007).

## 2. MATERIALS AND METHODS

### SOIL SAMPLING AND CHARACTERISATION:

The Lateritic soil sample were collected fromKamalpur, a stone quarry near Durgapur, West Bengal,India The sample was collected from 2m below the ground surface by auger boring and brought to the Soil mechanics and Foundation Engineering laboratory of NIT Durgapur, West Bengal for determination of it'sphysico-chemical properties according to IS 2720. The dried sample was then perished by means of a wooden mallet for preparing it for different types of laboratory tests. The results were plotted in Table 1.

### BATCH ADSORPTION STUDIES:

The heavy metal adsorption capacity of the collected lateritic soil was done at room temperature of 32±2°C by means of batch adsorption studies. The synthetic stock solutions of 100mg/L of Cu & Zn were prepared in the laboratory and diluted to different initial concentrations for the batch studies. The 50ml of solutions were then taken in a 100ml capacity conical flask and mixed with predefined dosage of lateritic soil and shacked in a BOD shaker at a speed of 150rpm.

### BATCH ISOTHERM STUDIES:

Adsorption Isotherm studies were performed at different initial concentration of 0.5, 1.0, 5.0, 10.0mg/l and pH was adjusted to 8 by NaOH buffer solution at adsorption doses of 5, 10, 20, 30 g/L in a 100ml conical flask at constant room temperature. After each test the mixture was then filtered using 0.22µandmilipore filter paper and analysed by Atomic Adsorption Spectrophotometer(Perkin- Elmer). The maximum heavy metal adsorption capacity of lateritic soil was determined by using the eqution no 1

$$Qe = \frac{(C0 - Ce)V}{M}$$

Where V = Volume of the solution in ml and M = mass of the soil taken.

The Isotherm Study was calculated by Linear model, Langmuir and Freundlich isotherm model and the distribution coefficients were determined.

Linear Isotherm Model:$Qe = K_dC_e$

Langmuir Isotherm Model::$Q_e = K_f C_e^n$

Freundlich Isotherm Model: $Qe = \frac{QmaxbCe}{1+bCe}$

Where$K_d$ is in litres per kilogram, $K_f$ is adsorption capacity(litres per kilogram), n=adsorption intensity, $Q_{max}$ is maximumadsorption capacity at monolayer (milligrams per kilogram),and b is a measure of affinity of binding sites (litres permilligram).

## 3. RESULT AND DISCUSSION

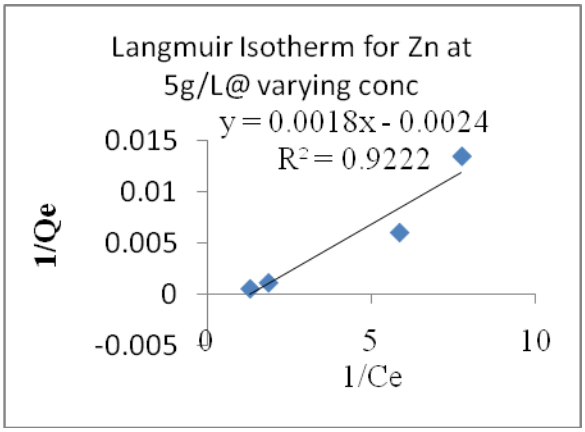
**Test results of lateritic soil:**

**Table 1:Physico- Chemical properties of Lateritic soil**

| Physical Properties | Lateritic soil | Physical Properties | Lateritic soil |
|---|---|---|---|
| Specific Gravity | 2.69 | Total Porosity(%) | 53.53 |
| Natural Moisture Content(%) | 12.61 | Organic Carbon(%) | 0.55 |
| Bulk Density(g/cc) | 1.25 | Sand(%) | 49 |
| Liquid Limit(%) | 26 | Silt(%) | 39 |
| Plastic Limit(%) | 13.12 | Clay(%) | 12 |
| pH | 6.51 | Max dry density(g/cc) | 1.93 |
| Hydraulic Conductivity(cm/sec) | $3.71x10^{-8}$ | | |

**BATCH ISOTHERM STUDIES:**

Adsorption results of the heavy metals(Zn & Cu) in Lateritic soil were described by Linear,Langmuir andFreundlich Isotherm models were plotted in the graph. The isotherm parameters ($K_d$,$K_f$,1/n,$Q_{max}$,b)and coefficient of determination(R2) and RMSE are summarized.



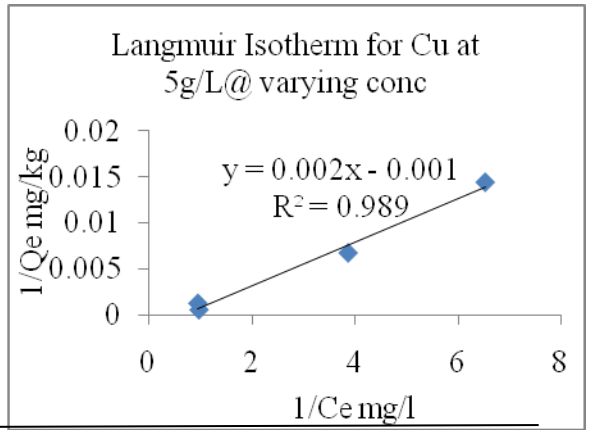




Figure 1: 1/Qevs 1/Ce graph Langmuir isothermcurve for 5 gm/l of soil dose,PH 8.0, at RPM

Fig2: $1/Q_e$vs $1/C_e$ graph Langmuir isotherm curve for 5g/l of soil dose,PH 8.0, atRPM 150

150 at varying concentration of Zn. at varying concentration of Cu.

Table 2: Linear, Langmuir, Freundlich isotherm constant,$R^2$ and RMSE for Zn and Cu adsorption of 5g/L of soil.

| Model Used for Zn | Isotherm Constant | $R^2$ | RMSE | Model Used for Cu | Isotherm Constant | $R^2$ | RMSE |
|---|---|---|---|---|---|---|---|
| Linear | $K_d$=2078 l/kg | 0.91 | 213 | Linear | $K_d$= 1224 l/kg | 0.69 | 380.55 |
| Langmuir | Qmax=416.67mg/kg<br>b=1.33 l/mg | 0.92 | 0.0009 | Langmuir | $Q_{max}$=625mg/kg<br>b= 0.666 | 0.989 | 0.0006 |
| Freundlich | 1/n=1.6945 mg/l<br>$K_f$=31.14mg/kg | 0.99 | 0.054 | Freundlich | $K_f$=21.25 mg/kg<br>1/n=1.4936 | 0.94 | 0.1312 |

It can be observed from the fig. and table that Langmuir and Freundlich isotherm models reasonably fitted to the test data with higher coefficient of determinations and lower error values. However the Langmuirisotherm model fits best for both Zn & Cu with higher $R^2$value and lower RMSE value. The shape of the Langmuir isotherm model was estimated by dimensionless separation factor ($R_L$) using the equation no 2.

$$RL = \frac{1}{1 + bC0}$$

Where $C_0$is the initial concentration is the initial heavy metal concentration in mg/L and b is the constant related to the free energy of adsorption and the calculated $R_L$is 0.069 and 0.13 fr Zn & Cu respectively which is within the range ($0 < R_L < 1$) and indicates the heavy metal adsorption capacity of lateritic soil is favourable.

## 4. BATCH ADSORPTION STUDIES

Batch Agitation Studies were performed to evaluate the metal mobilization from soil. To study the kinetics of heavy metal adsorption on soil, first we have selected the suitable PH, suitable time and suitable adsorption dose to meet the optimum and effective adsorption.

**Effect of pH:**

For optimizing the suitable pH, the point of zero charge($PH_{zpc}$) was determined by conducting potentiometric batch tests(Al-Hamdan and Reddy 2005).It describe the condition where the charge on the surface is zero. The pH value at which the solid submerge in an electrolyte exhibits zero charge. So the surface whether acidic or basic no longer take part in activity the pH value of solution. Since pH is used for the system in which H+ or OH- ions are the potential determining ion. So when the pH is lower thanpHzpc, the system is said to be below $pH_{zpc}$ meaning at that range the H+ ions donate more proton on the surface and so the adsorbent surface is positively charged hence electrostatic force of attraction occur between positive charge on surface with the negative ion. So anions are adsorbed more. When pH is higher than pHzpc the oxygen in hydroxyl group make the surface negatively charge so electrostatic force of repulsion occur with the negative ion or anions. So here at higher value cations are adsorbed more (+ ve charged ions).

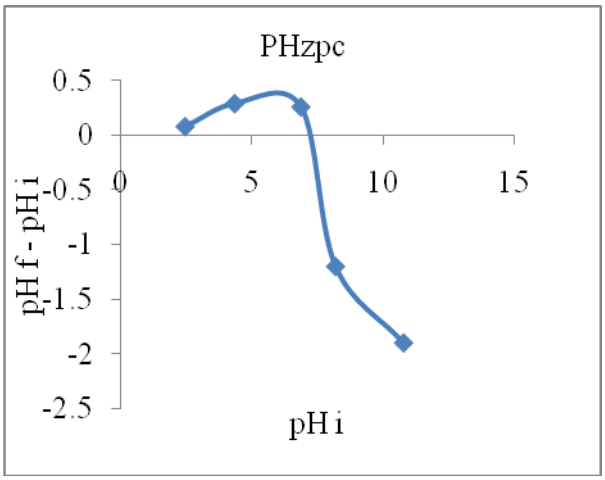



Figure 3: $pH_{zpc}$ of Lateritic soil

**Effect of adsorbent dosage:**

The amount of heavy metal removed from the synthetic solution is a function of adsorption dosage plotted in the fig.4. The adsorbent doses varies from 5, 10, 20, 30 g/L for the initial concentration of 0.5ppm, 1.0ppm, 5ppm, 10ppm. It is seen from the figure that heavy metal removal is best in the soil dose of 20g/l, it is increases from 5 g/L to 20 g/L and then it decreases in 30g/L. But we have chosen 5g/L for the isotherm study because the Qe value is best for 5g/L soil dose which is the maximum amount of heavy metal retained in the solid phase (mg/kg).

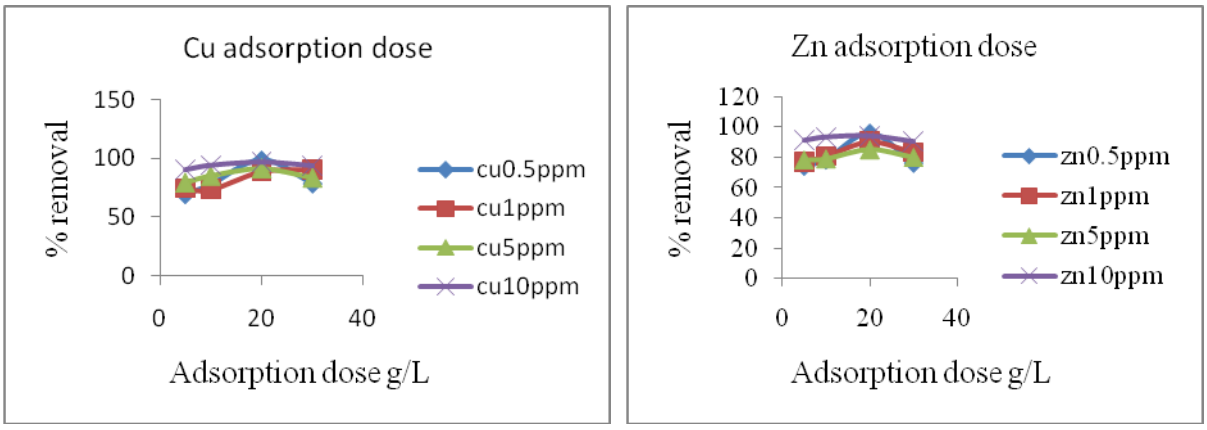



Figure 4: Effect of adsorbent dosage for heavy metal removal at pH 8 and contact time 2 hrs with varying initial concentrations.

**Effect of contact time on adsorption:**

The contact time is also an important parameter to identify the removal efficiency of the adsorbent. Consideration of optimum time for the best removal efficiency is done by a time dependent batch test. The effect of contact time on the removal of heavy metals by lateritic soil is done in varying initial concentration. The fig shows that the removal efficiency increases gradually up to 120 minutes and then it becomes constant for both Zn & Cu. This is due to the fact that initially all the adsorbent sites were vacant and thus leading to increase in concentration

gradient between adsorbate in solution and the adsorbent surface. Thus the adsorbent is efficient to remove maximum at a contact time of 2hrs.

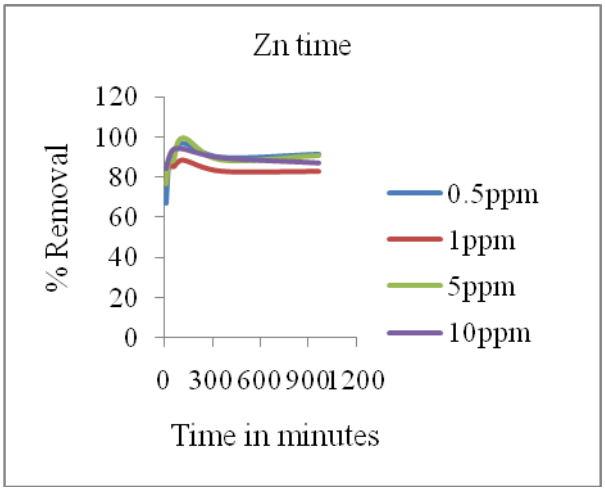



Fig5 : Effect of contact time for heavy metal removal with varying concentration of Zn at constant pH 8.

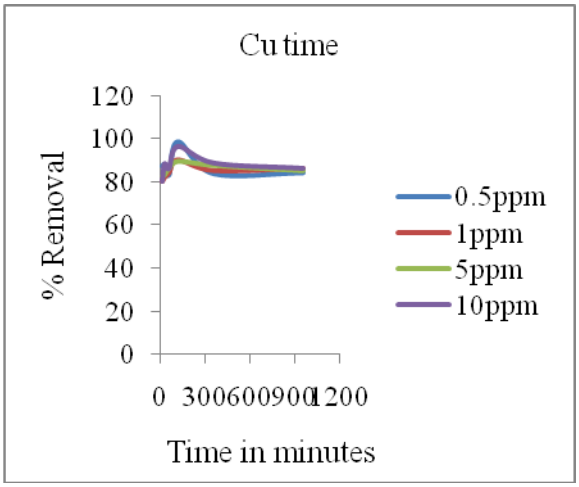



Fig6: Effect of contact time for heavy metal removal with varying concentration of Cu at constant pH 8.

## 5. C O N C L U S I O N S:

In the present study, the efficiency of lateritic soil for removal of two heavy metals ($Zn^{+2}$& $Cu^{+2}$) from aqueous solution was examined. The batch adsorption study shows that the maximum removal of heavy metals were found at pH of 8 and soil dose of 5g/L and contact time of 120 minutes. Under those optimum conditions the lateritic soil has potential to remove more than 90% of Zn and Cu. The relative adsorption of the two metals by using lateritic soil was found in the order of $Cu^{+2}$> $Zn^{+2}$. The adsorption isotherm studies revealed the reasonable agreement with both Langmuir and Freundlich isotherm models. However Langmuir isotherm provides best fit for Zn adsorption test data with $R^2$(co-efficient of determination)=0.922 and RMSE(Root mean square error)=0.000962, similarly for Cu, R2=0.989 and RMSE=0.000588.

As a result of this study, it may be concluded that the lateritic soil was feasible for removal of heavy metal contamination from ground water since it is a very low cost adsorbent and readily available. We can also conclude that the lateritic soil is very much potential for use as a liner material in landfill because it has a very low hydraulic conductivity.

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