



# Journal of Environmental Science, Computer Science and Engineering & Technology

An International Peer Review E-3 Journal of Sciences and Technology

Available online at [www.jecet.org](http://www.jecet.org)

Environmental Science

Research Article

## A Study on Utilization of Groundnut Shell as Biosorbant for Heavymetals Removal

Kiran B.M, Srikantaswamy. S\*, Pallavi H.V, Manoj .V and Tahera Tasneem

Department of Environmental Engineering, AIT, Chikmagalur, India

\*Department of Studies in Environmental Science, Manasagangothri, Mysore, India

**Received:** 19 January 2013; **Revised:** 15 February 2013; **Accepted:** 18 February 2013

**Abstract:** This work includes the utilization of groundnut shell, which is a low cost biosorbent for the removal of heavy metals from aqueous solutions. Biosorption is a process that utilizes low-cost biosorbents to sequester toxic heavy metals. Biosorption has distinct advantages over the conventional methods, which include reusability of biomaterial, low operating cost, selectivity for specific metal, short operation time and no chemical sludge. The mechanism of biosorption is complex, mainly ion exchange, chelations, adsorption by physical forces, entrapment in inter and intrafibrillar capillaries and spaces of the structural polysaccharide network because of the concentration gradient and diffusion through cell walls and membranes. Equilibrium studies and kinetic studies conducted by varying parameters like pH, dosage, concentration. , it was observed that for a contact period of 12 h, the removal efficiency and specific uptake of Cu (II) depends on type and quality of the biosorbent. The percentage removal of Cu (II) using groundnut shell powder as a biosorbent of varied amount from 5 to 50 g/L was 30.4% to 68.2%. This shows that with the increase in concentration of biosorbent, the removal efficiency also increased. Further increase for dosage beyond 50 g/L, there was a negligible increase in percentage removal

**Keywords:** biosorbent, heavy metals, groundnut shell, equilibrium studies, kinetic studies

---

## INTRODUCTION

Heavy metals contamination exists in aqueous waste stream from many industries such as metal plating, mining, tanneries, paints, car radiator manufacturing, as well as agricultural sources where fertilizers and fungicidal spray are intensively used. The presence of heavy metal ions from the transition series, viz, Cu, Fe, Ni, Pb, etc. in the environment is of major concern due to their toxicity to many life forms. Unlike organic pollutants, the majority of which are susceptible to biological degradation, metal ions do not degrade into harmless products. Recently<sup>1-3</sup>, adsorption technology has become one of the alternative treatments, especially for the widespread industrial use. Activated carbon is the most abundantly used adsorbent. In spite of its prolific use, carbon remains an expensive material since higher the quality of activated carbon, the greater its cost. Activated carbon also requires complexing agents to improve its removal performance for inorganic matters. Therefore, this situation makes it no longer attractive to be widely used in small-scale industries because of cost inefficiency. Nowadays, biological adsorbents are being used effectively and efficiently<sup>1-3</sup>.

## BIOSORPTION

Biosorption is a physio-chemical process that occurs naturally in certain biomass, which allows it to passively concentrate and bind contaminants onto its cellular structure. Biosorption is a process that utilizes low-cost biosorbents to sequester toxic heavy metals. Biosorption has distinct advantages over the conventional methods, which include reusability of biomaterial, low operating cost, selectivity for specific metal, short operation time and no chemical sludge. This work includes the utilization of groundnut shell, which is a low cost biosorbent for the removal of heavy metals from aqueous solutions. Equilibrium studies and kinetic studies conducted by varying parameters like pH, dosage, concentration.

## BIOSORBENT MATERIAL

Strong biosorbent behaviour of certain microorganisms towards metallic ions is a function of the chemical make-up of the microbial cells. Some types of biosorbents would be broad range, binding and collecting the majority of heavy metals with no specific activity, while others are specific metals. Recent biosorption experiments have focused attention on waste materials, which are by-products or the waste materials from large-scale industrial operations. For example, the waste mycelia available from fermentation processes, olive mill solid residues. Another inexpensive source of biomass where it is available in copious quantities is in the oceans as seaweeds, representing many different types of marine macro algae. However most of the contributions studying the uptake of toxic metals by live marine and to a lesser extent fresh water algae focused on the toxicological aspects, metal accumulation and indicators by live, metabolically active biomass<sup>4</sup>.

The mechanism of bio sorption is complex, mainly ion exchange, chelations, adsorption by physical forces, entrapment in inter and intrafibrillar capillaries and spaces of the structural polysaccharide network because of the concentration gradient and diffusion through cell walls and membranes.

## GROUNDNUT SHELL: AS BIOSORBENT

Groundnut shell is an agricultural based waste material and these materials as discussed previously have the potential to sequester metals from solutions. Groundnut, an important cash crop, is an annual legume. Its

seeds are a rich source of edible oil (43-55%) and protein (25-28%). About two thirds of world production is crushed for oil and the remaining one third is consumed as food. Its cake is used as feed or for making other food products and haulms provide quality fodder. The activated carbon prepared from groundnut shell has been utilized for the sorption of dyes methylene blue. No report on the utilization of groundnut shell, for biosorption of lead (II) and copper (II) has been found in literature. The present research was conducted to utilize groundnut hull for the biosorption of lead (II) and copper (II) from wastewater<sup>5</sup>.

**Table-1: Scientific classification of groundnut (Arachishypogaea)**

<b>Kingdom</b>	<b>Plantae</b>	Plants
<b>Subkingdom</b>	<b>Tracheobionta</b>	Vascular plants
<b>Superdivision</b>	<b>Spermatophyta</b>	Seed plants
<b>Division</b>	<b>Magnoliophyta</b>	Flowering plants
<b>Class</b>	<b>Magnoliopsida</b>	Dicotyledons
<b>Subclass</b>	<b>Rosidae</b>	-
<b>Order</b>	<b>Fabales</b>	-
<b>Family</b>	<b>Fabaceae</b>	Pea family
<b>Genus</b>	<b>Arachis</b>	-
<b>Species</b>	<b>Arachishypogaea</b>	Peanut

**Table- 2: Chemical composition of groundnut shell (in %)**

Chemical composition of groundnut shell (in%)				
Characteristics	Cellulose	Carbohydrates	Proteins	Minerals
Shell	65.7	21.2	7.3	4.5

Source: Reddy, P.S., 1988

## MATERIALS AND METHODOLOGY

**Biosorbent Preparation:** Groundnut shells collected from local market were extensively washed in running tap water for 1–2 h to remove colour and dirt, and then washed with distilled water several times. The washed sorbent was transferred to an oven maintained at at 150 °C for 24 h to reduce the moisture content. The dried sorbent was micronized using a kitchen grinder. The powder was sieved and a size fraction in the range of 200-300 µm was used in all the experiments. This powdered biosorbent was soaked (20g/l) in 0.1 M nitric acid for 24hrs and the mixture was filtered and the filtrate was washed with distilled water several times to remove any acid content. This filtered biomass was first dried, at room temperature and then in an oven at 105°C for 6-8 hrs. The dried biomass was stored in air tight glass bottles to protect it from moisture.

**Table- 3: Elemental analysis of Groundnut shell**

Elemental analysis of Groundnut shell										
Element	C	H	N	O	Ca	Fe	Mg	Mn	Na	K
% age	45.5	6.7	0.9	33.9	0.28	0.001	0.009	0.002	0.024	0.019

**Stock Solution Preparation:** Solutions of Pb (II) and Cu (II) ions were prepared by dissolving 1.6 g and 12.48 g of lead nitrate and copper sulphate, respectively, in distilled water, so as to achieve concentrations of 1000 mg/L in each flask. Different initial concentrations of metal ions were prepared by diluting the stock solution. The pH of the solution was adjusted using 0.1N HCl and 0.1N NaOH solutions to achieve the desired values.

## METHODOLOGY

For Single Metal System (SMS) solutions, a fixed volume (100 ml) of stock solution with varying concentrations in conical flasks were thoroughly mixed with 5 g of biosorbent dose at 30°C and 100 revolutions per minute (rpm) for 12h. A contact period of another 12h for sorption experiment will be used to ensure equilibrium. The pH range will be varied from 1 to 9 by using 0.1 M HNO<sub>3</sub> and 0.1 M HCl solutions. At the end of experiment the solution will be separated from the biomass by filtration using wattman filter paper. Filtrates of SMS will be diluted to 10 or 20 mg/L with deionized water and analysed for metal concentration using Atomic Absorption Spectrometer (AAS). Biosorption equilibrium isotherms were plotted for metal uptake capacity ( $q$ ) against residual metal concentrations ( $C_f$ ) in solution.

**Isotherm Experiment:** Experiments were carried out in a batch mode. 100 ml samples of aqueous solutions of metal ions at different initial concentrations (10-1000 mg/L) and at adjusted pH values were transferred into 250 ml Erlenmeyer flasks. Pre-defined amounts of the sorbent are added to these solutions. After 24h, solutions were filtered and heavy metal ion concentrations in the filtrate will be determined. Concentrations of metal ions in the samples were determined by Flame Atomic Adsorption Spectroscopy (FAS). Concentration of metal retained in the sorbent phase ( $q_e$ , mg/g) were calculated from the expression:

$$q_e = \frac{(C_o - C_e)V}{m}$$

Where,

$C_o$ = Initial concentrations of the metal ion in solution (mg/L),

$C_e$ = Final (equilibrium) concentrations of the metal ion in solution (mg/L),

$V$  = solution volume (L), and

$m$  = mass of the sorbent (g).

## ISOTHERM AND EQUILIBRIUM MODELING

**Isotherm Models:** Sorption equilibrium can be described by a number of models. In this work, two different models are considered:

- Freundlich
- Langmuir.

The Freundlich isotherm is an empirical expression that takes into account the heterogeneity of the surface and multilayer adsorption to the binding sites located on the surface of the sorbent. The Freundlich model is expressed as follows:

$$\frac{x}{m} = K_f \cdot C_e^{1/n}$$

Where,

$\frac{x}{m}$  = Amount of solute adsorbed per unit weight of adsorbent.

$K_f$  = Freundlich capacity factor.

$1/n$  = Freundlich intensity parameter.

$C_e$  = Equilibrium concentration of adsorbate (solute) in solution after adsorption.

The Langmuir model assumes a monolayer adsorption of solutes onto a surface comprised of a finite number of identical sites with homogeneous adsorption energy. This model is expressed as follows:

$$\frac{x}{m} = \frac{a b C_e}{(1 + b C_e)}$$

Where,

$\frac{x}{m}$  = amount of solute adsorbed per unit weight of adsorbent.

$a$  = empirical constant.

$C_e$  = equilibrium concentration of adsorbate (solute) in solution after adsorption.

$b$  = constant that represents the affinity between the biosorbent and the metal ion.

**Equilibrium Models:** Examination and preliminary testing of solid-liquid sorption system are based on two types of investigations:

- a. Equilibrium batch sorption test
- b. Dynamic continuous-flow sorption studies.

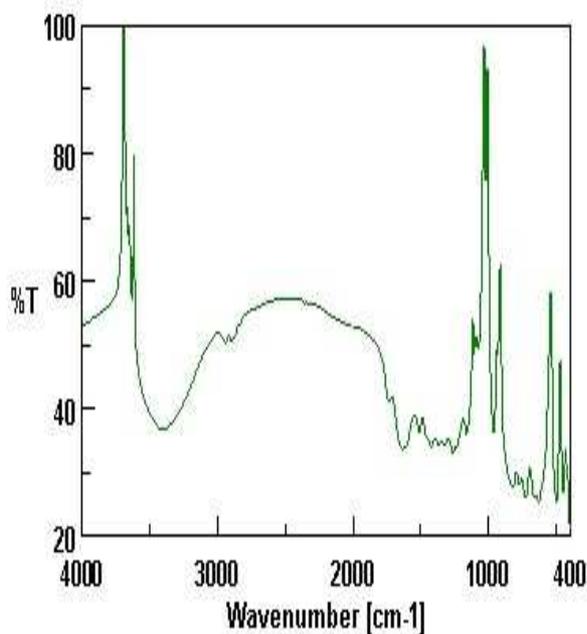
**Characterization Of Biosorbent:** The Fourier Transform Infrared (FTIR) spectroscopy was used to identify the functional groups present in the biomass. The biomass samples were examined, using JASCO FTIR spectrometer, within range of 400-4000  $\text{cm}^{-1}$ . All analysis were performed using, KBr as back ground material. In order to form pellets, 0.002 g of groundnut shell was mixed with 0.3 g KBr and pressed at 6-8 bar pressure. The surface structure and particle size distribution of biosorbent was examined using Hitachi Scanning Electron Microscope (SEM). The samples were covered, with a thin layer of gold and an electron acceleration voltage of 20 kV was applied. The surface area, pore volume and pore size measurements of biosorbent was carried out using, Quanta chrome NOVA 2200C USA, surface area and pore size analyzer. The gas mixture of 22.9 mole % nitrogen and 77.1 mole % helium was used for this purpose.

Surface area and pore size analysis of Groundnut shell		
Langmuir surface	Pore volume	Pore diameter
area ( $\text{m}^2 \text{g}^{-1}$ )	( $\text{cm}^3 \text{g}^{-1}$ )	Å
24.75	0.07	120.61

INDIAN INSTITUTE OF HORTICULTURE RESEARCH

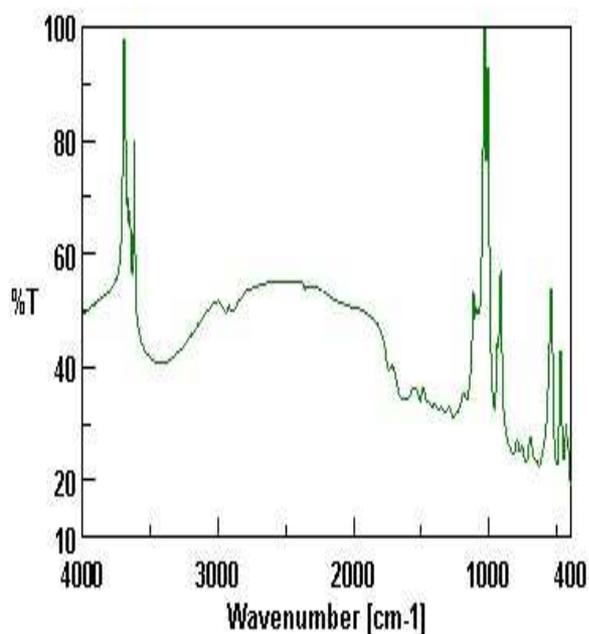
DATE: 25-04-2012 16:35 JASO

PRESENT  
 3400 cm-1 -OH, NH  
 1737 cm-1 ALDEHYDES  
 1633 cm-1 KETONES  
 1071 cm-1 C-H  
 1024 cm-1 C-O

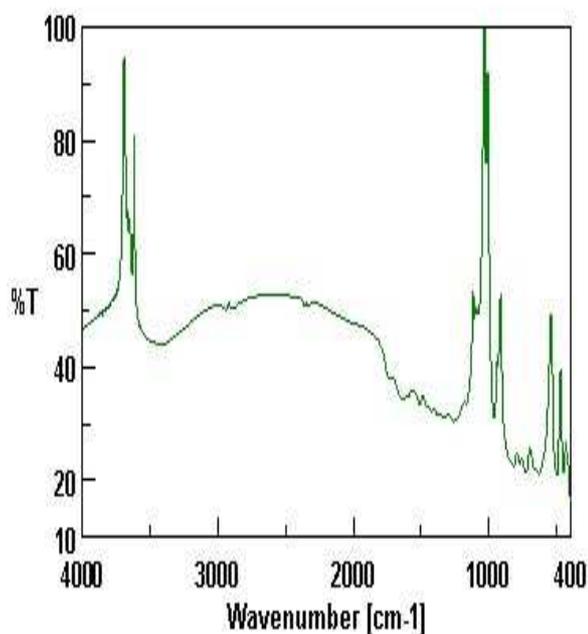


LATER  
 3400 cm-1 -OH  
 1633 cm-1 KETONES

FTIR spectra of groundnut shell



FTIR spectra of lead loaded groundnut shell



FTIR spectra of copper loaded groundnut shell

## RESULTS AND DISCUSSIONS

- From **Table 4 To 10**, the results obtained tabulated.
- Graphs plotted for all the results obtained with removal efficiency of biosorbent for a contact period of 24 hours.

- From **Table 4**, it observed that for a contact period of 12 h, the removal efficiency and specific uptake of Cu (II) depends on type and quality of the biosorbent. The percentage removal of Cu (II) using groundnut shell powder as a biosorbent of varied amount from 5 to 50 g/L was 30.4% to 68.2% as represented in **Graph 4**. This shows that with the increase in concentration of biosorbent, the removal efficiency also increased. Further increase for dosage beyond 50 g/L, there was a negligible increase in percentage removal.
- The number of sites available for biosorption depends upon the amount of the adsorbent. The effect of the biosorbent concentration on the removal efficiency of Pb (II) observed from **Table 5** and is presented in **Graph 4**. The metal ions uptake was found to increase linearly with the increasing concentration of the biosorbent up to the biomass concentration of 30 g/L. Beyond this dosage, the increase in removal efficiency was lower. Increasing the biosorbent dosage caused a rise in the biomass surface area and in the number of potential binding sites.
- In heavy metal biosorption, pH is the most important parameter and speciation of metals in the solution is pH dependent. The pH of the solution was varied in the range of 1.0 to 6.3, by using 0.1N HCl and 0.1N NaOH as buffers as shown in table 4.2 and 4.3 and a plot is obtained as shown in graph 4.2 maximum removal of Cu (II) was achieved at pH  $5 \pm 0.01$ , whereas Pb (II) had an optimum pH of  $5 \pm 0.02$ . At pH higher than 6.5 for both metals precipitation occurred, due to this reason biosorption not studied beyond pH of 6.5.
- From **Table-7 and 8**, it observed that the percentage removal of Cu (II) and Pb (II) using groundnut shell powder gradually decreased when the percentage dilution concentration of stock solution increased as shown in **Graph 3**.
- The Freundlich isotherm plotted using  $x/m$  vs.  $C_e$  resulted in a linear plot as shown in graph 4.4. The  $k_f$  values determined from the plot for Cu (II) and Pb (II) found to be 2.738 and 1.03 respectively. The  $n$  values determined from the plot for Cu (II) and Pb (II) found to be 7.69 and 2.78 respectively.
- The  $k_f$  is an indicator of adsorption capacity of the biosorbent used and the slope  $1/n$  gives the adsorption intensity. From the values obtained the adsorption capacity for Cu (II) and Pb (II) is compared as shown in **Table -10**.
- The Langmuir isotherm plotted using  $C_e/(x/m)$  vs.  $C_e$  resulted in linear plot as shown in graph 4.5. The Langmuir isotherm parameters  $a$  and  $b$  were obtained from the plot. The values of  $a$  for Cu (II) and Pb (II) were found to be 15.994 and 40.61 respectively. The values of  $b$  for Cu (II) and Pb (II) found to be 0.13 and 0.07 respectively.
- In order to obtain the biosorption kinetics for Cu (II) and Pb (II), the Lagergren first order and pseudo second order kinetic models applied.
- The Lagergren first order model plotted using time (t) vs.  $\log (q_e - q_t)$  resulted in straight lines as shown in **Graph 4.6**. The value of  $k_1$  and  $q_e$  were determined from the slope intercept of line which is as presented in **Table 11**.
- Pseudo second order kinetic model plotted using  $t/q_e$  vs. time (t) resulted in straight lines as shown in graph 4.7. The values of  $k_2$  and  $q_e$  were determined from the slope intercept of line which is as presented in **Table 11**.
- When the comparison of the two kinetic models conducted, the correlation coefficient ( $R^2$ ) values for Cu (II) were 0.943 and 0.830 respectively, which best fitted in first order kinetic model.
- Whereas the correlation coefficient ( $R^2$ ) values for Pb (II) were 0.943 and 0.993 respectively. Thus, the plot best fitted and followed pseudo second order kinetic model.

**Table- 4: Percentage removal of Copper (II) using groundnut shell for varying biosorbent dosage**

Biosorbent used	Biosorbent dosage in gm (m)	Concentration of Cu(II) in mg/L		x/m	Percentage removal of Cu(II)
		Initial	Final		
Groundnut shell powder	5	252	175.39	15.32	30.4
	10	252	137.08	11.49	45.6
	15	252	133.05	7.93	47.2
	20	252	126.75	6.26	49.7
	25	252	115.67	5.45	54.1
	30	252	102.31	4.99	59.4
	50	252	80.14	3.44	68.2
	55	252	80.09	3.12	68.2

**Table- 5: Percentage removal of Lead (II) using groundnut shell varying biosorbent dosage**

Biosorbent used	Biosorbent dosage in gm (m)	Concentration of Pb(II) in mg/L		x/m	Percentage removal of Pb(II)
		Initial	Final		
Groundnut shell powder	5	314	130.94	36.612	58.3
	10	314	112.73	20.127	64.1
	15	314	99.224	14.318	68.4
	20	314	86.35	11.38	72.5
	25	314	76.616	9.49	75.6
	30	314	71.59	8.04	77.2
	50	314	69.708	4.88	77.8

**Table- 6: Variation in percentage removal of Copper (II) with pH using groundnut shell**

Biosorbent used	Biosorbent dosage in gm (m)	pH	Concentration of Cu(II) in mg/L		Percentage removal of Cu(II)
			Initial	Final	
Groundnut shell powder	5	1.67	252	226.29	10.2
	5	2.55	252	179.93	28.6
	5	3.94	252	130.79	48.1
	5	5.01	252	93.99	62.7
	5	6.3	252	118.94	52.8

**Table -7: Variation in percentage removal of Lead (II) with pH using groundnut shell**

Biosorbent used	Biosorbent dosage in gm (m)	pH	Concentration of Pb(II) in mg/L		Percentage removal of Pb(II)
			Initial	Final	
Groundnut shell powder	5	1.58	314	245.2	21.9
	5	2.62	314	190.28	39.4
	5	3.5	314	118.38	62.3
	5	5.02	314	104.25	66.8
	5	6.45	314	121.83	61.2

**Table -8: Percentage removal of Copper (II) using groundnut shell for variation in dilution concentration of stock solution**

Biosorbent used	Biosorbent dosage in gm (m)	Dilution Concentration of stock solution (In %)	Concentration of Cu(II) in mg/L		Percentage removal of Cu(II)
			Initial	Final	
Groundnut shell powder	5	0.1	252	141.87	43.7
	5	0.2	504.6	346.25	31.3
	5	0.3	756.2	560.22	25.9
	5	0.4	1008.5	808.40	19.8
	5	0.5	1260.3	1117.6	11.3
	5	0.6	1512.2	1368.3	9.5

**Table -9: Percentage removal of Lead (II) using groundnut shell for variation in dilution concentration of stock solution**

Biosorbent used	Biosorbent dosage in gm (m)	Dilution Concentration of stock solution (In %)	Concentration of Pb(II) in mg/L		Percentage removal of Pb(II)
			Initial	Final	
Groundnut shell powder	5	0.1	314	129.99	58.6
	5	0.2	628.4	369.49	41.2
	5	0.3	942.3	651.13	30.9
	5	0.4	1256.9	979.12	22.1
	5	0.5	1570.1	1359.7	13.4
	5	0.6	1884.2	1746.6	7.3

**Table-10: Isotherm models parameters for biosorption of copper (II) and lead (II)**

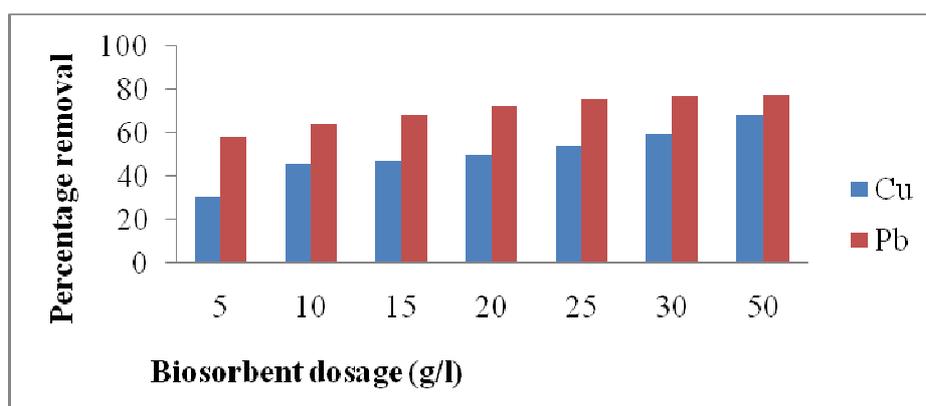
The Freundlich model parameters			
	<b>n</b>	<b>k<sub>f</sub></b>	<b>R<sup>2</sup></b>
Cu	7.69	2.738	0.8786
Pb	2.78	1.03	0.8461

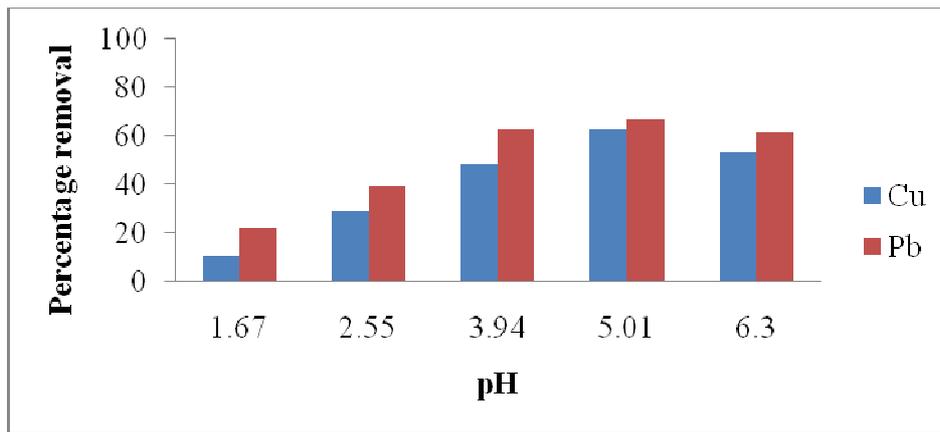
The Langmuir model parameters			
	<b>b</b>	<b>a</b>	<b>R<sup>2</sup></b>
Cu	0.13	15.994	0.7702
Pb	0.07	40.61	0.9308

**Table -11: Kinetic models parameters for biosorption of copper (II) and lead (II)**

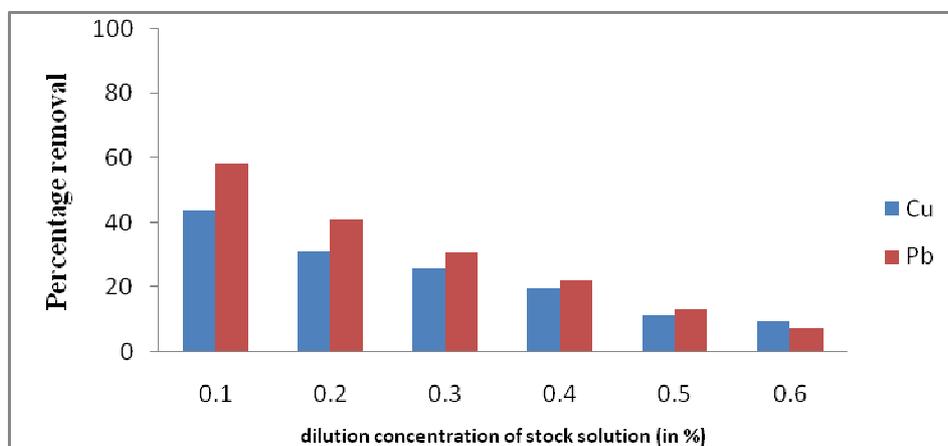
The Lagergren first order model parameters			
	<b>k<sub>1</sub>(min<sup>-1</sup>)</b>	<b>q<sub>e</sub> (mg g<sup>-1</sup>)</b>	<b>R<sup>2</sup></b>
Cu	0.0025	5.90	0.943
Pb	0.0375	5.298	0.986

The pseudo second order model parameters			
	<b>k<sub>2</sub>(g mg<sup>-1</sup> min<sup>-1</sup>)</b>	<b>q<sub>e</sub> (mg g<sup>-1</sup>)</b>	<b>R<sup>2</sup></b>
Cu	0.033	14.097	0.830
Pb	0.00625	28.45	0.993

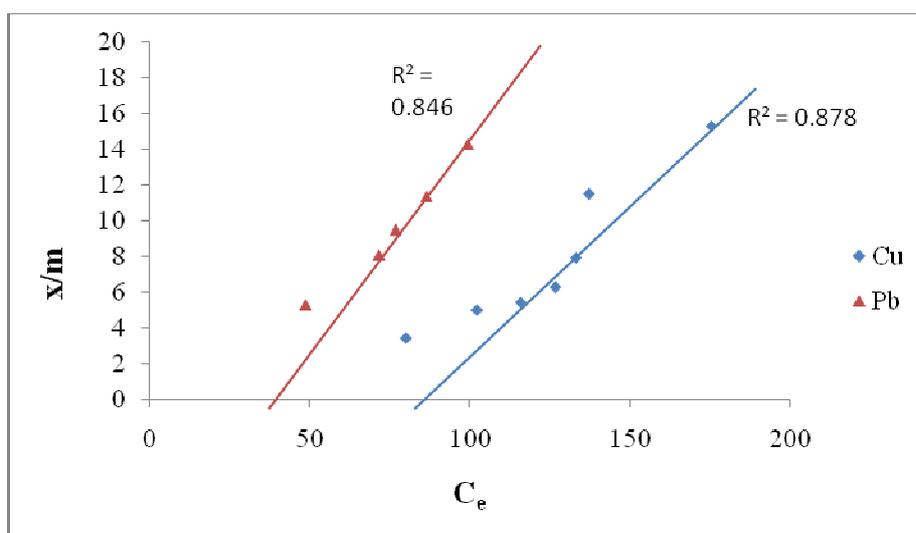
**Graph-1: Percentage removal of Cu (II) and Pb (II) using groundnut shell for varying biosorbent dosage**



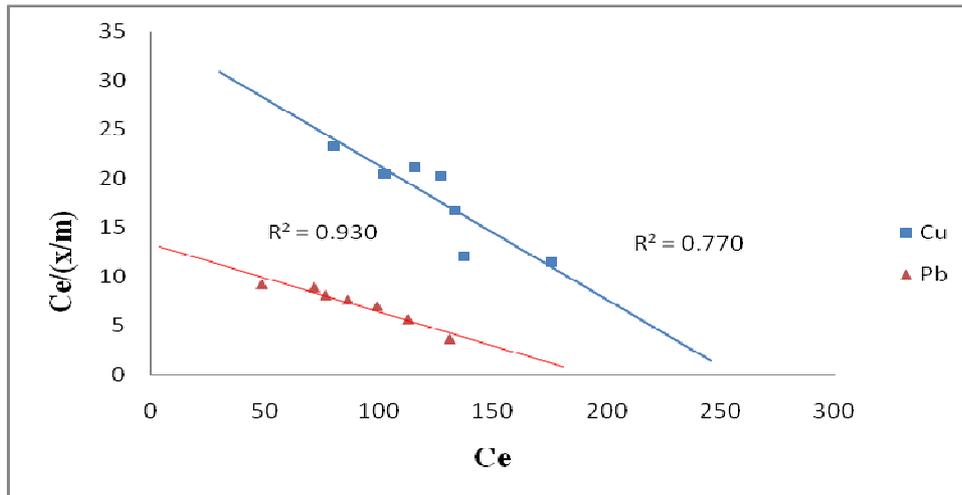
**Graph-2: Percentage removal of Cu (II) and Pb (II) using groundnut shell for pH variation**



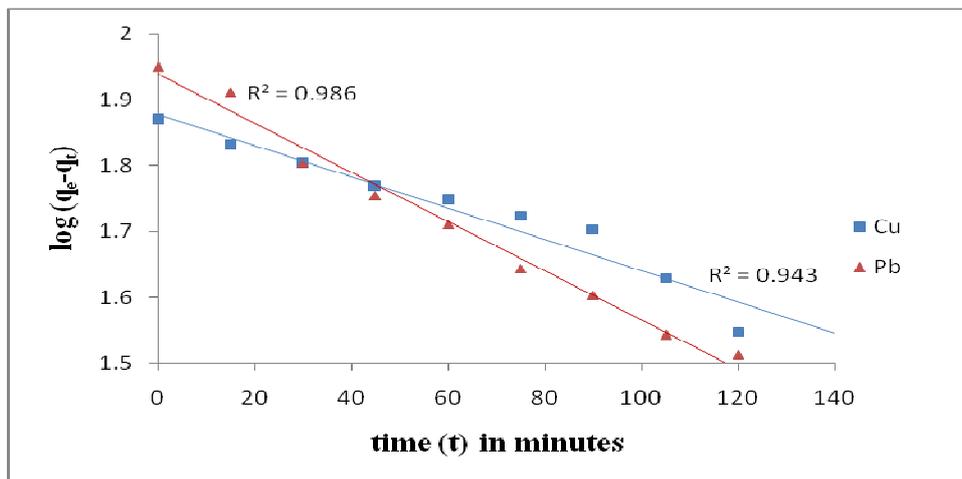
**Graph- 3: Percentage removal of Cu (II) and Pb (II) using groundnut shell for variation in dilution concentration of stock solution**



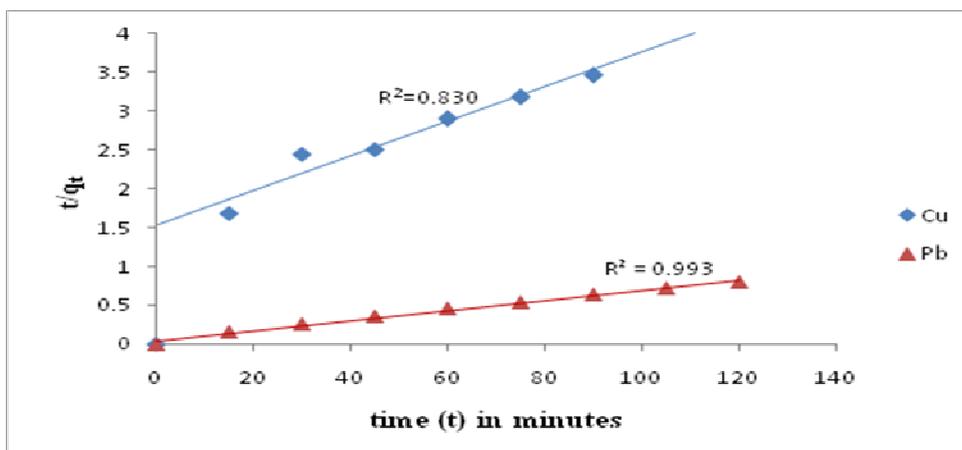
**Graph- 4: Freundlich isotherm using groundnut shell**



Graph 5: Langmuir isotherm using groundnut shell



Graph 6: Lagergren first order model using groundnut shell



Graph 7: Pseudo second order model using groundnut shell

## CONCLUSIONS

- The removal efficiency for Cu (II) and Pb (II) using groundnut shell powder as biosorbent are 68.2% and 77.8% respectively. The optimum dosage for maximum copper (II) and lead (II) are 50 g and 30 g respectively.
- By comparing the results obtained, for 12 hours contact time with groundnut shell powder showed substantial increase in Cu (II) and Pb (II) removal.
- The pH was found to be the most important factor affecting the biosorption potential. Results obtained showed that, maximum adsorption was achieved in acidic range.
- From adsorption isotherms plotted for the results obtained showed that, the efficient removal of Cu (II) best fitted in Freundlich isotherm rather than Langmuir isotherm. Whereas the efficient removal of Pb (II) best fitted in Langmuir isotherm rather than Freundlich isotherm.
- From the biosorption kinetic study models plotted for the results obtained showed that, Cu (II) and Pb (II) best fitted in Lagergren first order model and pseudo second order kinetic model respectively.
- Heavy metals removal using groundnut shell is a low cost wastewater treatment and can be effectively used in small scale treatment plants.
- Transportation and storage problems for biosorbent are negligible.

## REFERENCES

1. Nilanjana Das, R.Vimala and P.Karthika 2008, "Biosorption of heavy metals-An overview", *Indian Journal of Biotechnology*, 2008, 1, 159-169.
2. Nasim Ahmad Khan, Shaliza Ibrahim and Piarapakaran Subramaniam 2004, "Elimination of Heavy Metals from Wastewater Using Agricultural Wastes as Adsorbents", *Malaysian Journal of Science*, 2004, 23, 43 – 51.
3. Amit Bhatnagar and A K Minocha 2006, "Conventional and non-conventional adsorbents for removal of pollutants from water", *Indian Journal of chemical technology*, 2006, 13, 203-217.
4. Anna Witek Krowiak, Roman G Szafran and Szymon Modelski, "Biosorption of heavy metals from aqueous solutions onto peanut shell as a low-cost biosorbent", *Journal of Desalination*, 2011, 265, 126–134.
5. Suleman Qaiser, Anwar R. Saleemi and Muhammad Umar, "Biosorption of Pb (II) and Cr (VI) on groundnut hull: Equilibrium, kinetics and thermodynamics study", *Electronic Journal of Biotechnology*, 2009, 12 4.

**\*Corresponding Author: Kiran B.M;** Department of Environmental Engineering,  
AIT, Chikkamagalur, India