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Adsorption Isotherms for the Removal of Heavy Metals from Aqueous Solution Using Groundnut Shell and Rice Husk

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Abstract
Heavy metals are considered as hazardous to the environment due to their toxicity even at low concentration. Batch experiments were conducted to know the potentiality of agricultural byproducts (Groundnut shell, Rice husk and combined adsorbents) on removal of heavy metal ions. It has been found that the percentage of adsorption increases with increase in pH and decreases with the increase in metal ions concentration. The obtained results showed that the adsorption of heavy metals by Rice husk and Groundnut shell were best fitted in Langmuir isotherm than Freundlich isotherm.

Keywords: *Adsorption, copper, lead, langmuir isotherm, Freundlich isotherm*

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INTRODUCTION

Excessive release of heavy metals into the environment due to industrialization and urbanization has posed a great problem worldwide. The presence of heavy metal ions is a major concern due to their toxicity to many life forms. Heavy metals pollution occurs in industrial wastewater such as that produced by metal plating facilities, mining operations, battery manufacturing processes, the production of paints and pigments, and the ceramic and glass industries. Whenever toxic heavy metals are exposed to the natural eco-system, accumulation of metal ions in human bodies will occur through either direct intake or food chains. Even a very small amount can cause severe physiological or neurological damage to the human body. Therefore, heavy metals should be prevented from reaching the natural environment [1].

There are various methods of removing heavy metal ions, and they include chemical precipitation, membrane process, ion exchange, solvent extraction, electrodialysis, and reverse osmosis. These methods are non economical and have many disadvantages such as; incomplete metal removal, high reagent and energy consumption, and generation of toxic sludge or other waste products that require disposal or treatment [2].

Biosorption is a process that utilizes low-cost biosorbent 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. In the recent years many biosorbent materials of agricultural based have been utilized for heavy metal biosorption. These include: coconut husk and shell, sea weeds, bagasse ash, hazelnut shell, peanut hull, tree fern, black gram husk, maize leaf, maize, sun flower waste, coffee beans, *Ficus religiosa* leaves, wheat bran, almond shell, tea waste [3].

Lead

Lead (Pb) is considered as one of the priority metals from the point of view of potential health hazards to human, and it is listed by the Environmental Protection Agency (EPA) as one of 129 priority pollutants [2]. Lead as a pollutant is a major concern as it has been used as one of the raw materials for battery manufacturing, printing, pigments, fuels, photographic materials and explosive manufacturing. The presence of lead in drinking water even at low concentration may cause diseases such as anemia, encephalopathy, hepatitis and nephritic syndrome [4].

Severe lead poisoning can cause encephalopathy, with permanent damage, while moderate lead poisoning result in neurobehavioral and intelligent deficit. Lead poisoning in humans causes severe damage to kidney, nervous system, reproductive system, liver and brain. According to the United States Environmental Protection Agency (USEPA) the maximum permissible limits in wastewater and potable water are 0.1 and 0.015 mg/l for lead (II) [3].

Copper

Copper, an element which has been used by man for years, can be regarded as a longstanding environmental contaminant. Several industries like mining, printing, painting, dyeing, battery manufacture and other industries discharge effluent containing Cu (II) to surface water. For example, copper smelting and mining are major industrial processes that lead to copper contamination of water and soil. Copper is an essential nutrient, required by the body in very small amounts. Short periods of exposure can cause gastrointestinal disturbance, including nausea and vomiting. Use of water that exceeds the permissible level over many years could cause liver or kidney damage. Copper is rarely found in source water, but copper mining and smelting operations and municipal incineration may be sources of contamination.

MATERIALS AND METHODOLOGY

Adsorbent Preparation

Rice husk and Groundnut shell were ground separately and sieved to obtain particle size of 0.6 mm. The sieved adsorbents were washed with distilled water several times to remove dust and kept in an oven at 65°C for 24 h to reduce the moisture content. Then these adsorbents were used for batch experiments.

Adsorbate

Stock solutions of lead (II) were prepared by dissolving 1.59 g of lead nitrate in 1000 ml distilled water. Stock solutions of copper were prepared by dissolving 1 g of copper turnings in 20 mL Nitric acid and then make up into 1000 ml. Different initial concentrations of metal ions were prepared by diluting the stock solutions. The pH was maintained using 0.1 N HCl and 0.1 N NaOH solutions.

Batch Experiments

The experiments were carried out under constant shaking of 100 ml of simulated solutions in conical flasks using heavy rotatory shaking apparatus. Samples were withdrawn after a definite time interval and filtered through Whatman No. 41 filter paper and then measured in ICP. The amount of metal ions adsorbed by adsorbent is calculated using the following equation:

$$Q_e = (Co–Ce)\ V/M \qquad (1)$$

where, Co is the Initial concentrations of the metal ion in solution (mg/L), Ce is the Final concentrations of metal ion solution (mg/L), V is the solution volume (L) and M is the mass of the sorbent (g).

RESULTS AND DISCUSSIONS

General

Adsorption studies were conducted for the removal of lead and copper from aqueous solution. Batch experiments were carried out under different pH, initial concentration of metal ions. The results of the present study are presented in the following section:

Effect of pH

The pH of solution significantly influences the removal of heavy metals; hence it is an important environmental condition for adsorption of Lead and Copper metal ions. With the contact time of 2h batch experiments were carried out at different pH values (3–10) with 30 mg/L of Lead and Copper. Adsorption capacity of Lead and Copper metal ions are shown in Figures 1 and 2, respectively. From Figure 1 it can be observed that 1 g of Rice husk was able to give Lead removal efficiency of 93.78% at pH 6 and Copper removal efficiency of 96.72% at pH 8. Using 1 g of Groundnut shell, the removal efficiency of Lead and Copper was 97.48 and 93.90% at pH 5 and 6, respectively. The study shows that the optimum pH value for the removal of heavy metal ions is 7.

At low pH, high concentrations of H^+ ions were present in solution that competes for vacant adsorption sites of adsorbent. This phenomenon could be confirmed by the observation of sharp increase in the final solution pH of those having low initial pH values. For each hydrolysable metal ion, there was a critical pH range where the metal uptake efficiency increased from a very low level to maximum value. Decreasing trend in uptake was observed above pH 8 due to formation of soluble hydroxyl complexes [5].

Effect of Initial Concentration of Metal Ions

The adsorption experiments were carried out with metal ion concentrations of 20, 40, 60, 80, 100, 120, 140 and 160 mg/L at pH 7 and 8 using 1 g of Rice husk and Groundnut shell. The effects of initial concentration of Lead and Copper are shown in Figures 3 and 4 for Rice husk and Groundnut shell, respectively. Results from these plots indicate that lead removal efficiency decreases from 99.37 to 39.70% and Copper removal efficiency decreases from 97.81 to 70.76% for Rice husk and from 99.18 to 97.17% removal of Lead and 94.56 to 65.38% of Copper for Groundnut shell as the initial concentration of metal ions increased from 20 to 160 mg/ L. Figures 5 and 6 show that removal efficiency by combined adsorbents (Rice husk and Groundnut shell) decreases from 93.90 to 71.50% as the initial concentration of Lead increased from 200 to 450 mg/L and 92.90 to 68.93% as initial concentration of Copper increased from 350 to 600 mg/L.

At low metal ion loads, adsorption involved the high energy sites. Under these conditions, the ratio of number of moles of metal ion to the available adsorption sites was low, and therefore, the amount adsorbed per unit mass increased slowly. With an increase in metal ion load, the higher energy sites would be rapidly saturated and the metal ions would gradually occupy the lower energy sites, resulting in a continuous increase in the amount adsorbed per unit mass [6–11].

Adsorption Isotherms

Experimental isotherms are useful for describing adsorption capacity to facilitate evaluation of the feasibility of this process for a given application, for selection of the most appropriate sorbent, and for preliminary determination of sorbent dosage requirements.

In this work two different models are considered:

- Langmuir
- Freundlich

The equilibrium sorption of lead and copper metal ions was carried out by contacting 1 g of Rice husk and Groundnut shell with 100 mL of different concentration from 20–160 mg/L separately and 1 g of combined adsorbents (Rice husk and Groundnut Shell) with concentration from 200 to 450 mg/L for lead and 350 to 600 mg/L for copper.

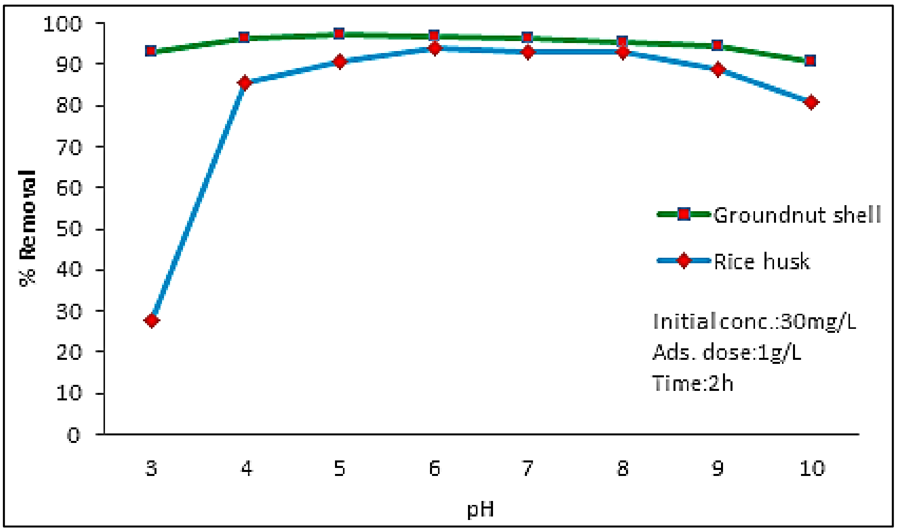

Fig. 1: *Effect of pH on Lead Removal by Rice Husk and Groundnut Shell.*

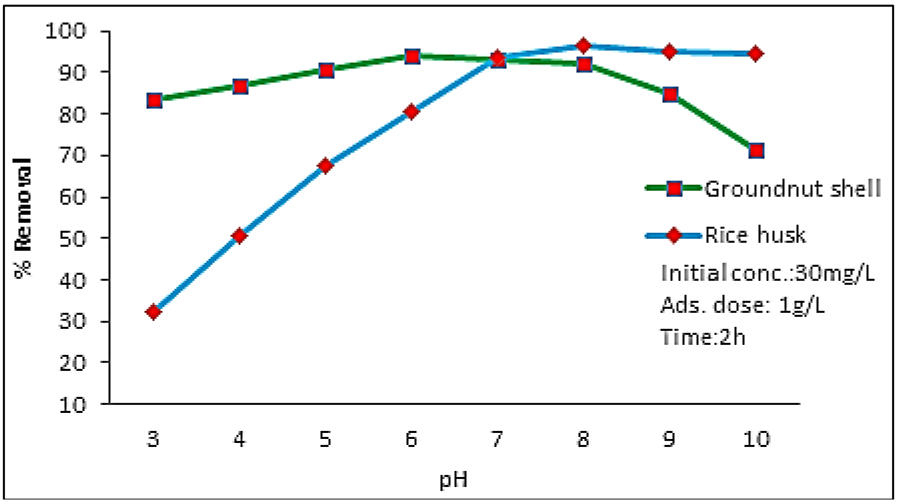

Fig. 2: *Effect of pH on Copper Removal by Rice Husk and Groundnut Shell.*

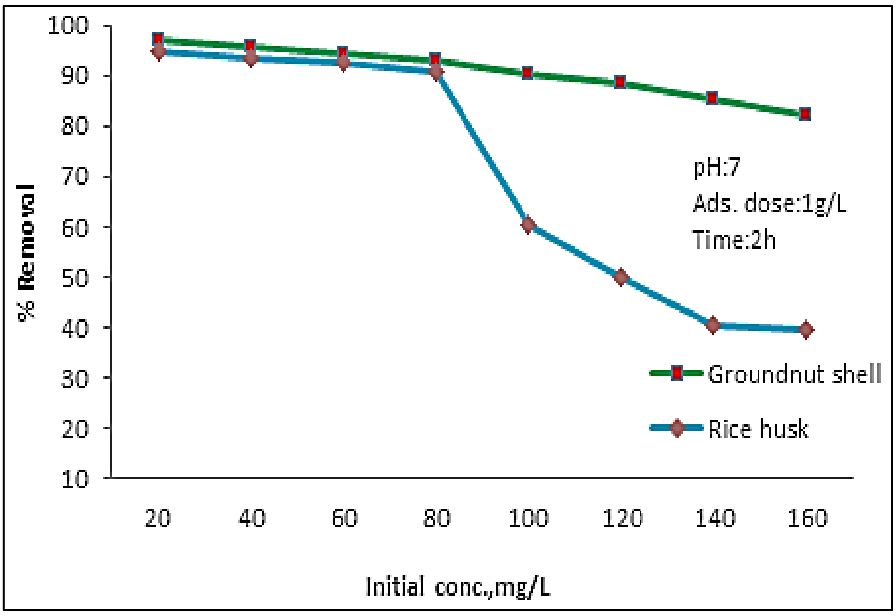

Fig. 3: *Effect of Initial Concentrations on Lead Removal by Rice Husk and Groundnut Shell.*

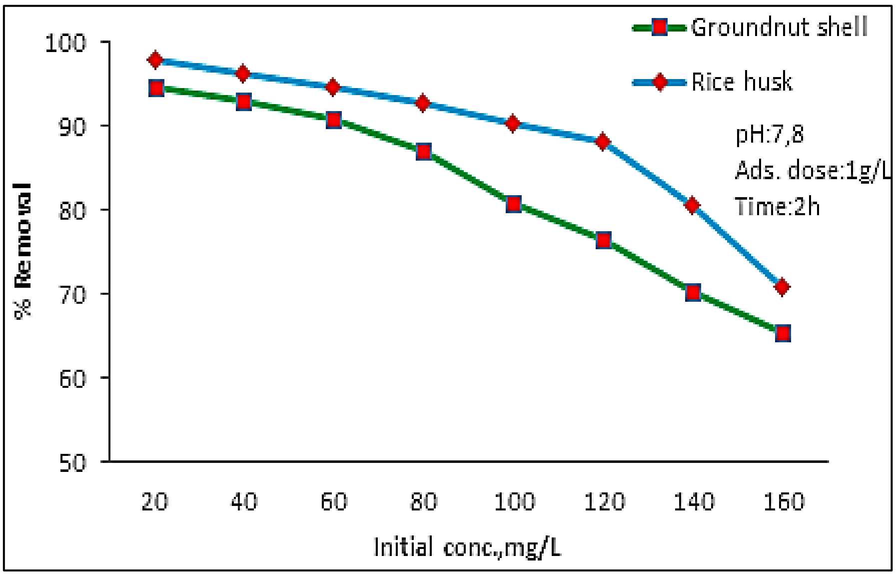

Fig. 4: *Effect of Initial Concentrations on Copper Removal by Rice Husk and Groundnut Shell.*

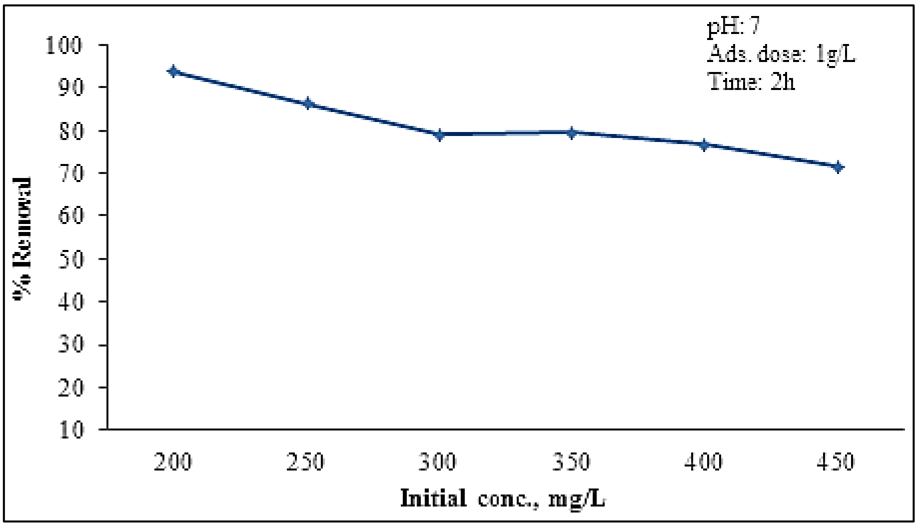

Fig. 5: *Effect of Initial Concentration on Lead Removal by Combined Adsorbents.*

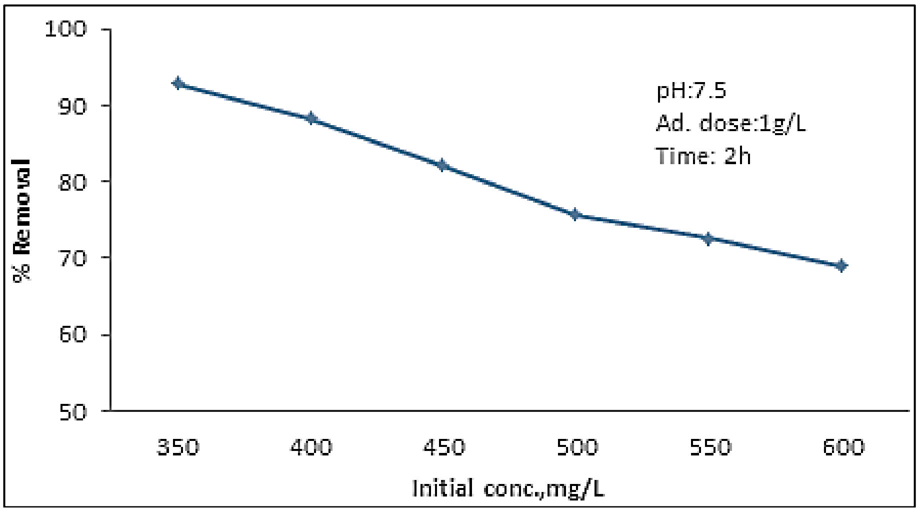

Fig. 6: *Effect of Initial Concentration on Copper Removal by combined Adsorbents.*

Langmuir Adsorption Model

The Langmuir model assumes the surface of the sorbent to be homogenous and the sorption energies to be equivalent for each sorption site. The essential characteristics of the Langmuir model can be expressed in terms of a dimensionless constant and separation factor or equilibrium parameter, R_L. Langmuir adsorption describes quantitatively the formation of a monolayer of adsorbate on the outer surface of the adsorbent, and after that, no further adsorption takes place. Thereby, the Langmuir represents the equilibrium distribution of metal ions between the solid and liquid phases. The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface [9–13].

Based upon these assumptions, Langmuir represented the following equation:

$$Q_e = q_{max} [K_L C_e / 1 + K_L C_e] \quad (2)$$

Langmuir adsorption parameters were determined by transforming the Langmuir Eq. (2) into linear form:

$$C_e / Q_e = 1/Q_{max} + C_e / Q_{max} \quad (3)$$

where, Ce is the equilibrium concentration of adsorbate (mg/L), Qe is the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g), Q_{max} is the Langmuir constants related to adsorption capacity (mg/g), K_L is the rate of adsorption (L/mg).

The values of q_{max} and K_L were computed from the slope and intercept of the Langmuir plot of C_e/Q_e versus C_e. The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L, which is a dimensionless constant referred to as separation factor or equilibrium parameter

$$R_L = 1/ [1+ (1+K_L C_o)] \quad (4)$$

where, C_o is the initial concentration (mg/L), K_L is the constant related to the energy of adsorption (Langmuir constant), R_L value indicates the adsorption nature to be either

$R_L > 1$: unfavorable
$R_L = 1$: Linear
$0 < R_L < 1$: Favorable
$R_L = 0$: irreversible

In the present study Langmuir isotherm plots of C_e/q_e versus C_e for the removal of lead and copper metal ions from aqueous solution using Rice husk, Groundnut shell and combined adsorbents have been shown in Figures 7–12, respectively. The value of R_L lies between 0 and 1, hence the adsorptions of lead and copper on Rice husk, Groundnut shell and combined adsorbents are favorable [2].

Freundlich Adsorption Model

Freundlich adsorption is commonly used to describe the adsorption characteristics for the heterogeneous surface. Freundlich model was chosen to estimate the adsorption intensity of the sorbent towards the sorbate. The empirical equation proposed by Freundlich as follows:

$$Q_e = K_f C_e^{1/n} \quad (5)$$

where, K_f is the Freundlich isotherm constant (mg/g) (dm^3/g), n is the adsorption intensity, C_e is the equilibrium concentration of adsorbate (mg/L), Q_e is the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g).

Taking logs and rearranging the Eq. (5) as follows:

$$\text{Log } Q_e = \text{Log} K_f + 1/n \text{ Log } C_e \quad (6)$$

The constant K_f is an approximate indicator of adsorption capacity, while 1/n is a function of the strength of adsorption in the adsorption process. These constants can be obtained by appropriate plot of Log Q_e against Log C_e [2].

If n value lies between one and ten, this indicates favorable adsorption process. n=1, the Freundlich isotherm becomes linear isotherm and indicates that all sites on the adsorbent have equal affinity for the adsorbate. Value of n>1 indicates that affinities decreases with increasing adsorption density.

In this study, Freundlich isotherm plots of Log q_e versus Log C_e for the removal of lead and copper metal ions on Rice husk, Groundnut shell and combined adsorbents have been shown in Figures 13–18, respectively. From the data in Tables 1–4 show that the values of n lies between 0 and 1, hence adsorptions are favorable.

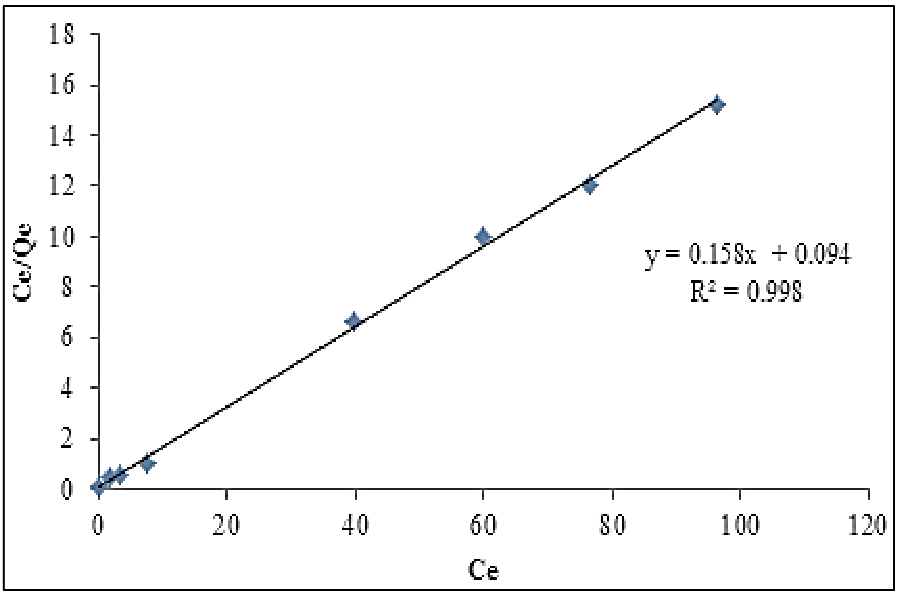

Fig. 7: *Langmuir Isotherm for the Adsorption of Lead on to Rice Husk.*

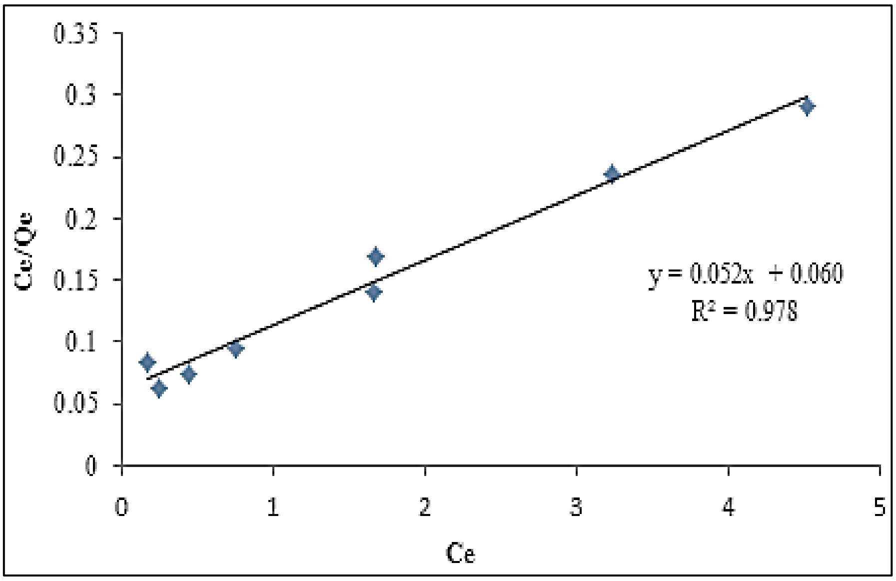

Fig. 8: *Langmuir Isotherm for the Adsorption of Lead on to Groundnut Shell.*

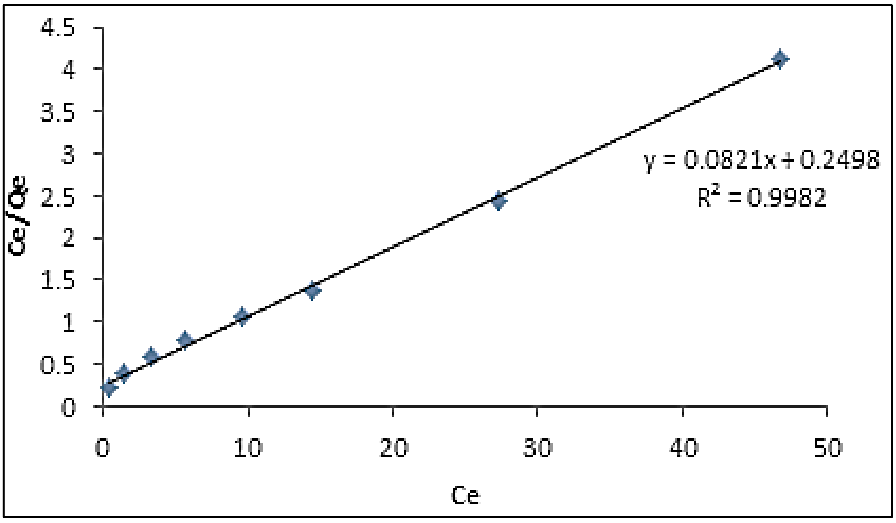

Fig. 9: *Langmuir Isotherm for the Adsorption of Copper on to Rice Husk.*

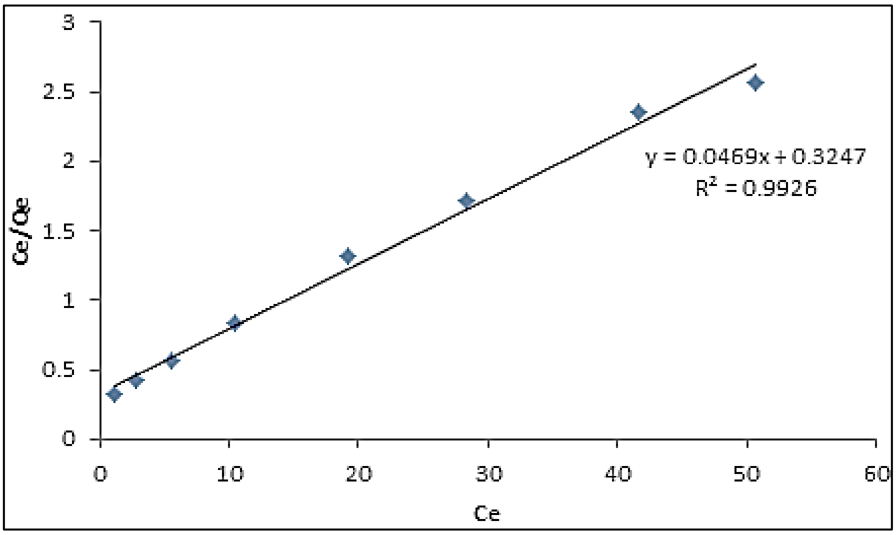

Fig. 10: *Langmuir Isotherm for the Adsorption of Copper on to Groundnut Shell.*

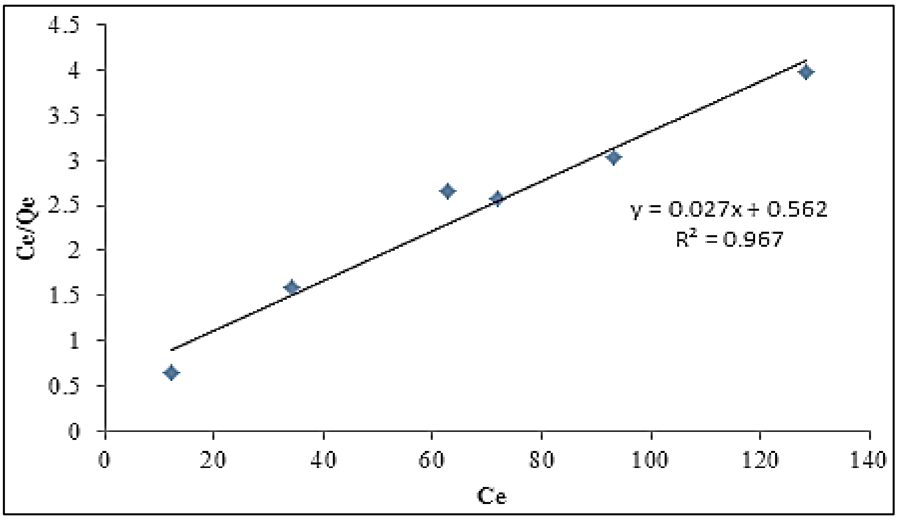

Fig. 11: *Langmuir Isotherm for the Adsorption of Lead on to Combined Adsorbents.*

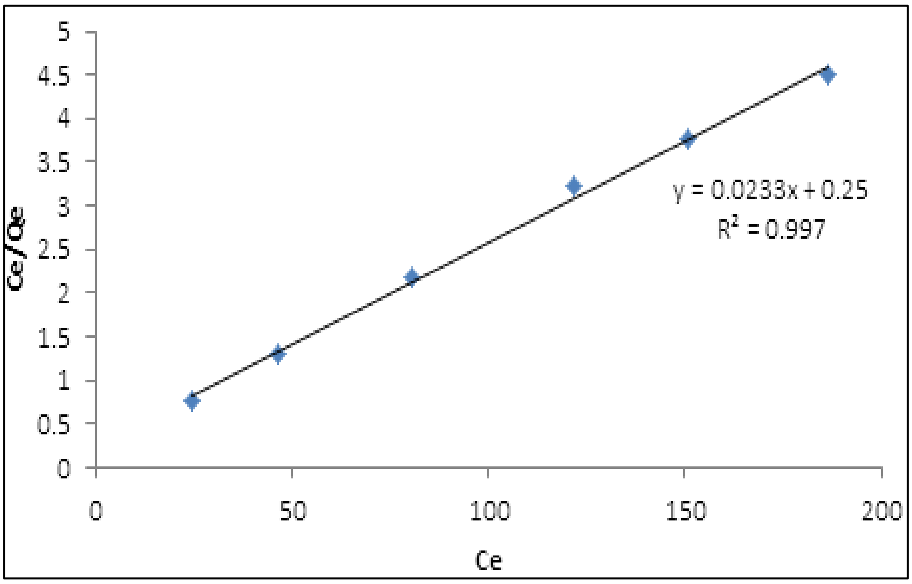

Fig. 12: *Langmuir Isotherm for the Adsorption of Copper on to Combined Adsorbents.*

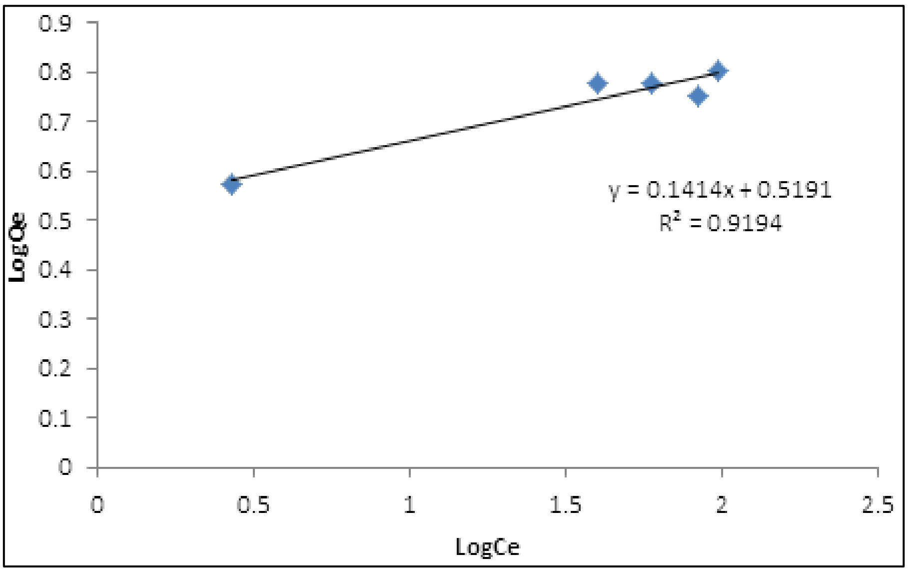

Fig. 13: *Freundlich Isotherm for the Adsorption of Lead on to Rice Husk.*

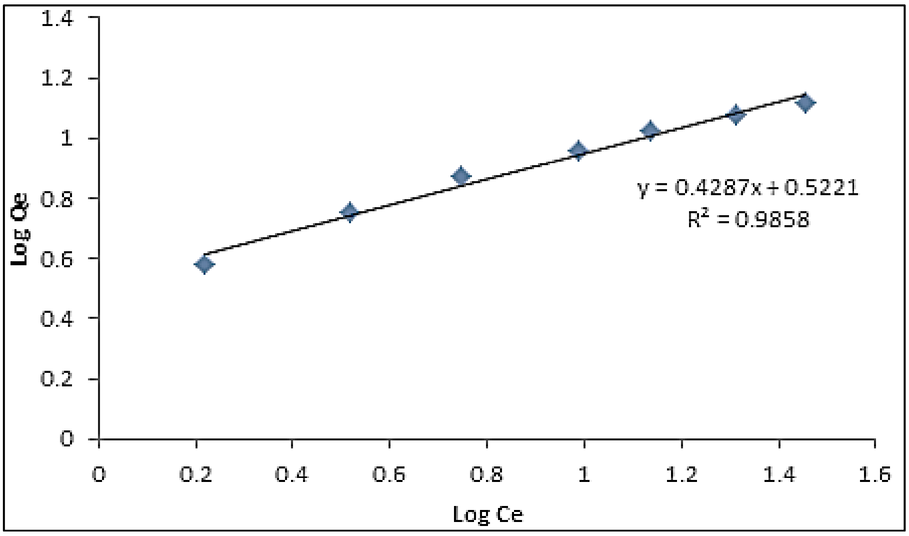

Fig. 14: *Freundlich Isotherm for the Adsorption of Lead on to Groundnut Shell.*

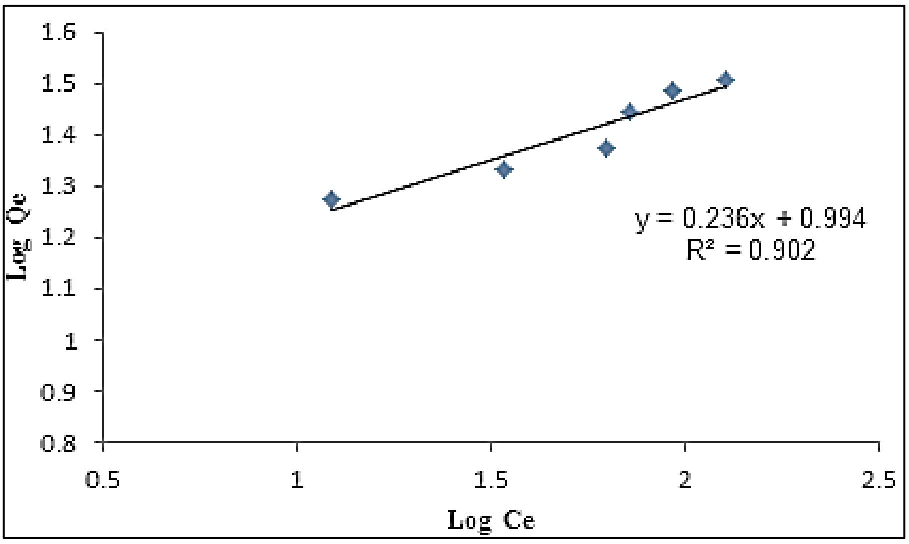

Fig. 15: *Freundlich Isotherm for the Adsorption of Lead on to Combined Adsorbents.*

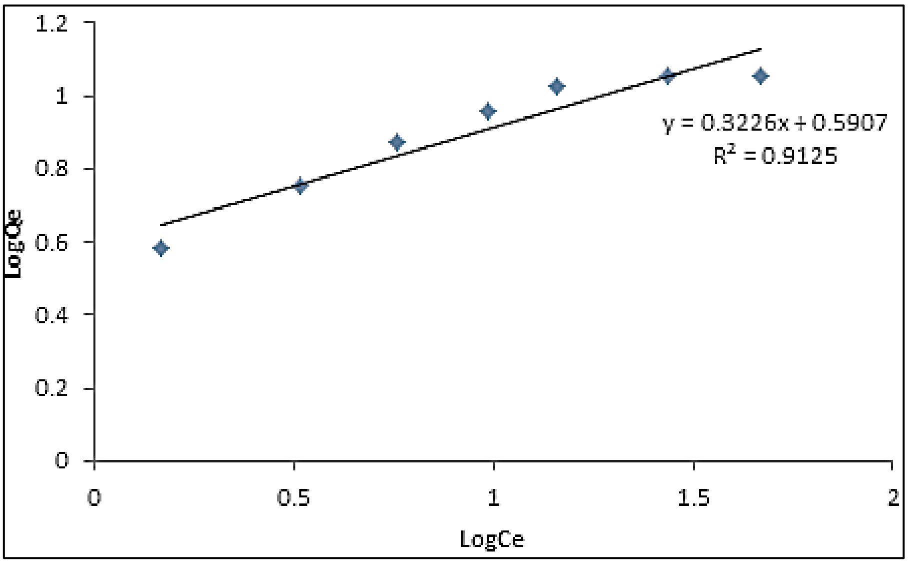

Fig. 16: *Freundlich Isotherm for the Adsorption of Copper on to Rice Husk.*

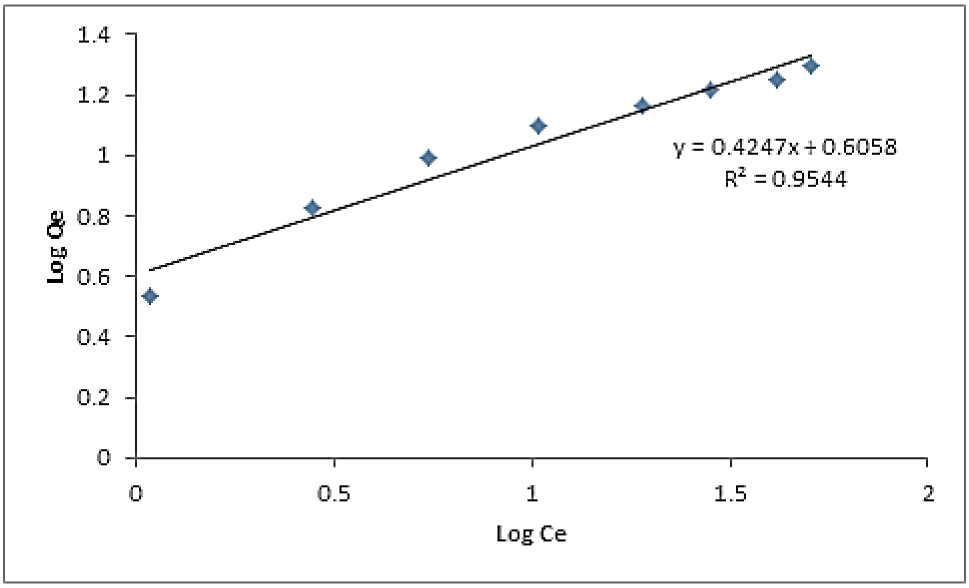

Fig. 17: *Freundlich Isotherm for the Adsorption of Copper on to Groundnut Shell.*

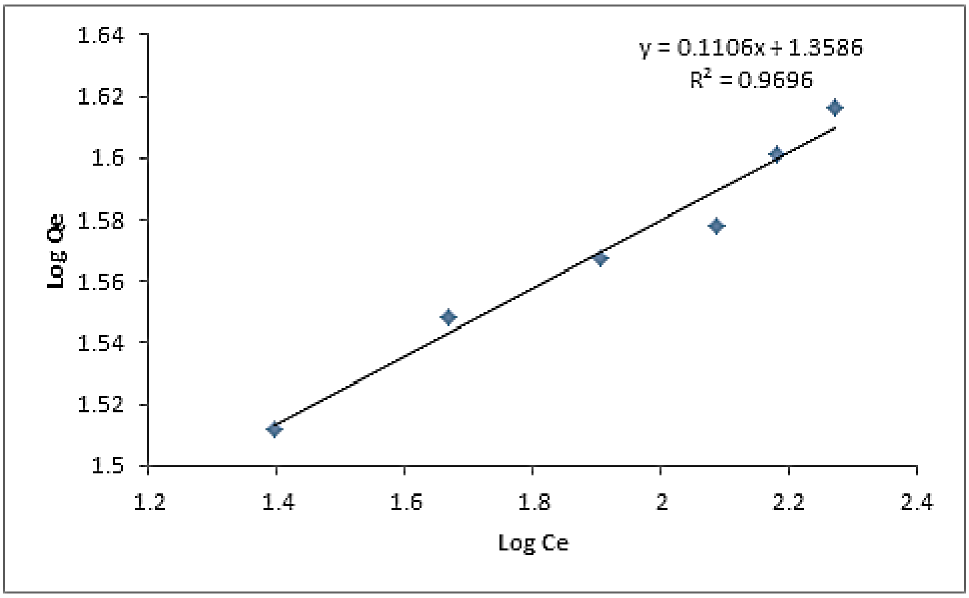

Fig. 18: *Freundlich Isotherm for the Adsorption of Copper on to Combined Adsorbents.*

Table 1: *Langmuir Isotherm Constants for Lead Adsorption by Rice Husk, Groundnut Shell and Combined Adsorbents.*

Adsorbents	**Langmuir Isotherm**			
	Q_m (mg/g)	**K_L**	**R^2**	**R_L**
Rice husk	6.330	0.595	0.998	0.078
Groundnut shell	15.151	5.197	0.990	0.0095
Combined adsorbents	37.030	20.815	0.967	0.00024

Table 2: *Freundlich Isotherm Constants for Lead Adsorption by Rice Husk, Groundnut Shell and Combined Adsorbents.*

Adsorbents	**Freundlich Isotherm**		
	K_f (mg/g) (L/mg) $^{1/n}$	**n**	**R^2**
Rice husk	3.572	7.092	0.919
Groundnut shell	3.327	2.336	0.985
Combined adsorbents	9.863	4.237	0.902

Table 3: *Langmuir Isotherm Constants for Copper Adsorption by Rice Husk, Groundnut Shell and Combined Adsorbents.*

Adsorbents	Langmuir Isotherm			
	Q_m (mg/g)	K_L	R^2	R_L
Rice husk	12.195	3.037	0.998	0.0161
Groundnut shell	20.83	6.438	0.997	0.0077
Combined adsorbents	43.478	10.869	0.997	0.0003

Table 4: *Freundlich Isotherm Constants for Copper Adsorption by Rice Husk, Groundnut Shell and Combined Adsorbents.*

Adsorbents	Freundlich Isotherm		
	K_f (mg/g) (L/mg) $^{1/n}$	n	R^2
Rice husk	1.146	3.105	0.912
Groundnut shell	4.093	2.415	0.945
Combined adsorbents	22.803	9.090	0.969

CONCLUSION

Batch experiments were conducted to know the potentiality of Rice husk and Groundnut shell as adsorbents for the removal of heavy metals (lead and copper) from synthetic wastewater. Based on the results and discussions the following conclusions have been derived:

- The maximum removal efficiency of heavy metal ions using Rice husk and Groundnut shell was obtained at pH range of 6–8 and 5–6, respectively.
- The contact time necessary for maximum adsorption was found to be 2 h.
- From the adsorption isotherm the efficient removal of heavy metals best fitted in Langmuir isotherm than Freundlich isotherm.
- As low cost adsorbents Rice husk and Groundnut shell can be efficiently used for removal of heavy metals without giving any chemical treatment for adsorbents.

Scope for Future Studies

On the basis of knowledge gained from the present study, the following suggestions have been made for future work:

- Using same adsorbents, other heavy metal`s removal studies can be made.
- Batch adsorption can be carried out for various particle size and temperature.

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