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Removal of Copper and Zinc Metals from Aqueous System by Using Rice Husk as Low Cost Materials: Original Research

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Abstract

In the present study the adsorption of Cu (II) and Zn (II) ions on rice husk from artificially prepared aqueous solutions of these metal ions was investigated following the batch mode adsorption procedure. Accordingly, the effects of operating parameters such as pH, contact time, and initial concentration of metal ion solution were evaluated. The results so obtained in this study indicated that the optimum conditions for the Cu(II) and Zn(II) ions adsorption were found to be as follows: pH of 6 and 7; contact times of 100 and 125 minutes; and these values were actually determined by setting the initial concentration of 50 mg/L for each metal ion solution. Upon measurements of the residual metal ion concentration using FAAS method, the percent adsorption of both Cu (II) and Zn (II) ions showed significant increase with an increase in each case of the contact time. Furthermore, it was evidently implicated that the binding process of the metal ions on the adsorbent (rice husk) could be affected by change in the pH of both metal ion solutions. In addition the experimental data were analyzed against both Langmuir and Freundlich isotherm for determining the maximum adsorption capacity of the title bioserbent with respect to each of the tested metal ions. The adsorption maxima were calculated on the basis the Langmuir isotherm and found to be 1.93 and 12.98 mg/g for Cu (II) and Zn (II) metal ions respectively. These values are suggested that the rice husk investigated in this study can have a good application potential for the removal of both metal ions (Cu (II) and Zn (II)) from aqueous solutions. In fact, the goal of this work was to develop an inexpensive, highly available, effective metal ion adsorbent from natural waste as alternative to existing commercial adsorbents.

Keywords: adsorption efficiency, adsorption isotherm, batch adsorption, copper, zinc

1. INTROUCTION

Heavy metals are widespread pollutants of the environment and they are non-degradable (Stratton, 1987). It is well perceived that there is a permissible limit of each metal, above which it is generally toxic. Wastewaters commonly have Cu, Ni, Cr, Cd, and Pb. Since all these heavy metals are not biodegradable, their presence in streams and lakes leads to bioaccumulation in living organisms, causing health problems in animals, plants, and human beings (Mehmet *et al.,* 2007). Due to their accumulation through food chain and persistence in nature, it is necessary to remove these toxic heavy metals from wastewater.

At present there are numerous methods in existence for the removal of detrimental metal ions from aqueous solutions (Gabaldon *et al*, 1996) that can make use of either of the conventional and non-conventional technologies. Conventional technologies include: chemical precipitation, ion exchange, membrane separation and adsorption by activated carbon. But, conventional technologies have some drawbacks like high operational cost or disposal of resulting sludge. As a result the effluent treatment in developing countries is expensive (Ahalya *et al.,* 2005). Due to the above drawbacks of conventional technologies, non-conventional (locally available) materials are used for the removal and recovery of heavy metals from industrial wastewater. For example, the adsorption of metals on different microbial and agricultural wastes like treated and untreated mushroom, barley straw, mango seed husk coconut husk, sawdust, sugarcane bagasse and coffee husk *etc.* in different countries has been reported(Kumer, 2006).

Copper and zinc metals are a serious cause of environmental pollution. Therefore, it is necessary to alleviate those ions from industrial effluents. There are different methods for zinc and copper metals treatments have been described by physical and chemical processes. For example, precipitation, coagulation, reduction, membrane processes, ion exchange and adsorption *etc.* However, those techniques have their own inherent limitation such as: less efficiency, sensitive operating conditions, and production of secondary sludge requiring further costly disposal. These disadvantages have resulted in the development of alternative separation technologies. One such alternative method is biosorption (Norton, 2004).

Rice husk consists of cellulose (32.24%), hemicelluloses (21.34%), lignin (21.44%) and mineral ash (15.05%) as well as high percentage of silica in its mineral ash. It is insoluble in water, has good chemical stability and mechanical strength making it a good adsorbent material for treating heavy metals from wastewater. It is used to treat heavy metals in the form of either untreated or modified form (Esteghlalian *et al.,* 1997). The FTIR spectra of raw rice husk show the following peaks; at 796cm^{-1} due to C–H bending vibration; at 1076cm^{-1} due to C–O stretching vibration; at 1646cm^{-1} is due to N-H stretching vibration; at 1735cm^{-1} is due to C=O stretching; at 2855cm^{-1} due to C–H stretching vibration and a broad peak at 3430cm^{-1} due to O–H stretching (Panda *et al.*, 2010). The mechanism of sorption for the raw and modified forms of rice husk is linked to the role played by the essential stretching functional groups like hydroxyl (-OH), carboxylic acid (-COOH), carbonyl (C=O), Si-O-Si, Si-OH, aromatic and phenolic groups existing in the sorbent. Such functional groups can be increased in concentration and/or can be created by the action of chemical modifiers (Gordon *et al*., 1999). The adsorption capacity of treated rice husk to remove Cu (II) and Zn (II) ions from aqueous solution was reported by researchers. But, there is a research gap on adsorption efficiency of untreated rice husk for removing Cu (II) and Zn(II) ions from aqueous solution.

2. MATERIALS AND METHODS

Apparatus and instruments

The apparatus used in this study were: pH meter (MP 220) to measure pH of the solution, AAS (GBC 932 plus) to measure metal ion concentration, Mechanical shaker (Orbital shaker SO1, UK) to agitate the sample, Electronic balance (OHAUS, Switzerland) for weighting, Desiccator (Nikko Japan super dry SD-504) to keep a sample less humid, Electrical mill (IKA WERKE) to grind sample, Erlenmeyer flask, Whatman No.42 filter paper, Sieve, and Hot air oven to dry sample.

Chemicals and reagents

Analytical grade reagents; $CuSO_4 \cdot 5H_2O$ (Himedia Laboratories Pvt. Ltd), $ZnSO_4.7H_2O$ (Laboratory reagent, India) were used to prepare standard solutions of the metals studied. Concentrated HNO_3 (S.d.fiNE-CHEM LimiTEd MUMBAI 400030), NaOH (IP241HPUK UN), HCl (Blulux Laboratories (p) Ltd- 121001), NaCl (UN1-CHEM S34900-3I) were also used.

Experimental Procedure

Cleaning of laboratory equipment- all the sample containers were thoroughly washed with detergent, rinsed with distilled water before soaking in 10% HNO_3 for about 24 hours. Containers were finally rinsed with de-ionized water before being used for sampling.

Rice husk collection and preparation-the rice husk was collected from rice mill using plastic bags. Then, the raw rice husk was cleaned by distilled water and dried at 100°C for 24 h in a hot air oven before ground by electrical mill and allowed to pass through 250µm sieve.

Preparation of adsorbate solutions-1000 mg/L stock solutions of Cu (II) and Zn (II) ions were prepared by dissolving 3.93g of $CuSO_4.5H_2O$ and 4.4g of $ZnSO_4.7H_2O$ respectively in de-ionized water. Then, a few drops of 0.1M HNO_3 were added to each stock solution to prevent the precipitation of Cu^{2+} and Zn^{2+} by hydrolysis. Finally, the required working solutions were taken by pipeting a known amount of the stock solutions in to Erlenmeyer flask and diluting using the required amount of de-ionized water.

Batch Mode Adsorption Studies- batch mode adsorption studies for individual metal ions were carried out at 25 ± 1^0C and 20g/L of adsorbent dosage. The effects of different parameters such as adsorbate concentration, contact time, and pH were studied. The batch mode adsorption studies were carried out in 250 mL Erlenmeyer flask and the flask was shaken for a prescribed length of time by orbital shaker. Then, thorough filtration using filter paper was done. Finally, the amount of Cu^{2+} and Zn^{2+} ions remaining in solution in each case was determined by FAAS.

Determination of Metal Ions by FASS- for calibration purpose, standards and blank (de-ionized water) were run in flame atomic absorption spectrometer before the analysis of the samples. Then, the concentration of each metal ion was determined from the calibration curve. Finally, removal efficiency was calculated by using the relationship.

$$\text{Adsorption (\%)} = ((C_o - C_e)/C_o) \times 100$$

Where; C_o and Ce are the initial and equilibrium concentration of adsorbate respectively.

The adsorption capacity of the rice husk was calculated based on the following equation:

$$q_e = (C_o - C_e) \times V/m$$

Where; q_e is the adsorbed metal ion on the sorbent, m is the weight of sorbent; V is the volume of metal ion solution.

3. RESULTS AND DISCUSSION

3.1. The Optimum Condition for Cu (II) and Zn (II) Ions Removal by Rice Husk

Effect of contact time

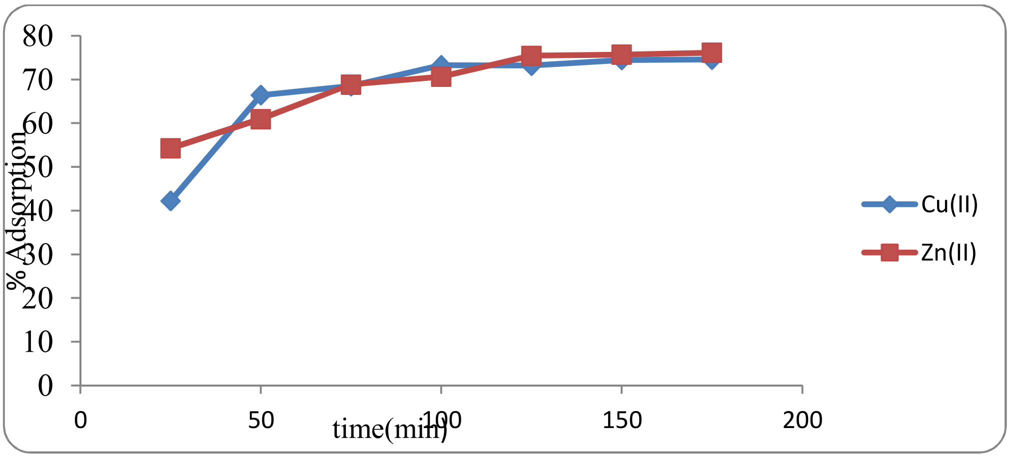

Figure 1: Cu (II) and Zn (II) ions adsorption efficiency (%) at various contact time (C_o = 50 mg/L, adsorbent dosage =20g/L, solution pH = 6 and 7, agitation speed = 150 rpm and 200rpm respectively).

The plots in figure 1 reveal that the percentage rates of both copper and zinc adsorption have rapidly increased at the beginning. This may be due to larger surface area of the husk being available at beginning for the adsorption of Cu^{2+} and Zn^{2+} ions. As the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles. With the progressive occupation of these sites, the process becomes slower. This is in accordance with the observations in other similar studies (Nadeem *et al*., 2010). If one observes the appendix tables 4 and 5, almost 73.24 ± 0.07% Cu (II) ions were removed in first 100 minutes. In the case of Zn (II), 75.44 ± 0.030% of the ions were adsorbed in first 125 minutes. Therefore, 100 minutes for Cu (II) and 125 minutes for Zn (II) ions can be taken as sufficient agitation times for attaining equilibrium.

Effect of pH

Evidences show that the pH of solution affects the solubility of metal ions and concentration of the counter ions on the functional groups of the biomass cell walls. This is partly due to the fact that hydrogen ions (H^+) themselves are strong competing ions and partly that the solution pH influences the chemical speciation of the functional groups onto the adsorbent surfaces. At low pH, due to high positive charge density and protons on the surface sites during uptake of metal ions, electrostatic repulsion will be high resulting in lower removal efficiency as electrostatic repulsion decreases with increasing pH. Thus enhancement of metal ion adsorption is noted (Taty-Costodes *et al*., 2003).

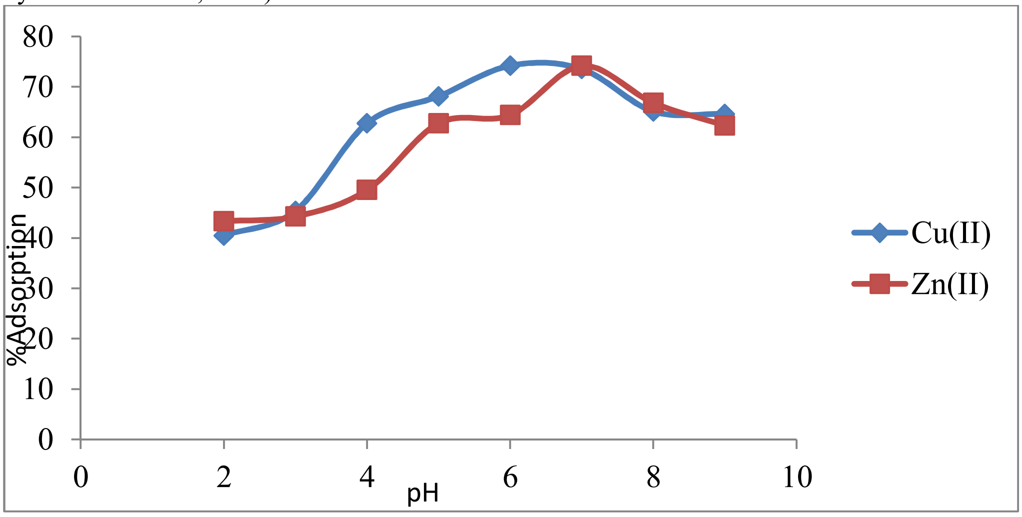

Figure 2: Effect of pH on Cu (II) and Zn (II) ions adsorption efficiency (%) (C_o = 50 mg/L, adsorbent dosage = 20g/L, time =100min and 125min, agitation speed = 150 rpm and 200rpm respectively).

The plots in figure 2 depict that the adsorption efficiency of both Cu (II) and Zn (II) ions onto the surface of biosorbent (RH) increases as the pH of the metal ion solution increases. In both cases the increase in adsorption is gradual up to pH 3, but it becomes drastic after this pH. The trend continues until the maximum adsorption values of 74.21 ± 0.080% (at pH 6) and 74.17 ± 0.075% (at pH 7) were attained for Cu (II) and Zn (II) ions respectively. These values were taken to be the optimum amounts of metal ions that could be removed from the respective solution via adsorption on the RH surface.

pH (below 3), there was excessive protonation of the active sites of the rice husk surface that might have prohibited the formation of links between the Cu (II) or Zn (II) ions and the active sites. At moderate pH values of 3 to 6 for copper and 3 to 7 for zinc, most of the linked H^+ ions were supposed to be released from the active sites and this resulted in an increase in the amount of metal ions adsorbed. The peak percentage adsorptions of Cu (II) and Zn (II) were attained at pH 6 and 7 respectively. After optimum pH, the observed decrease in adsorption of Cu (II) ions may be attributed to the fact that the Cu (II) ions in solutions might begin to precipitate as $Cu(OH)_2$. At higher pH values (7 to 9) the OH^- ions may compete for Zn(II) ions with the active sites on the surface of the adsorbents causing a decrease in the adsorption rate of Zn(II) ions there by the Zn(II) ions to begin precipitating as $Zn(OH)_2$.

Effect of initial concentration of metal ion

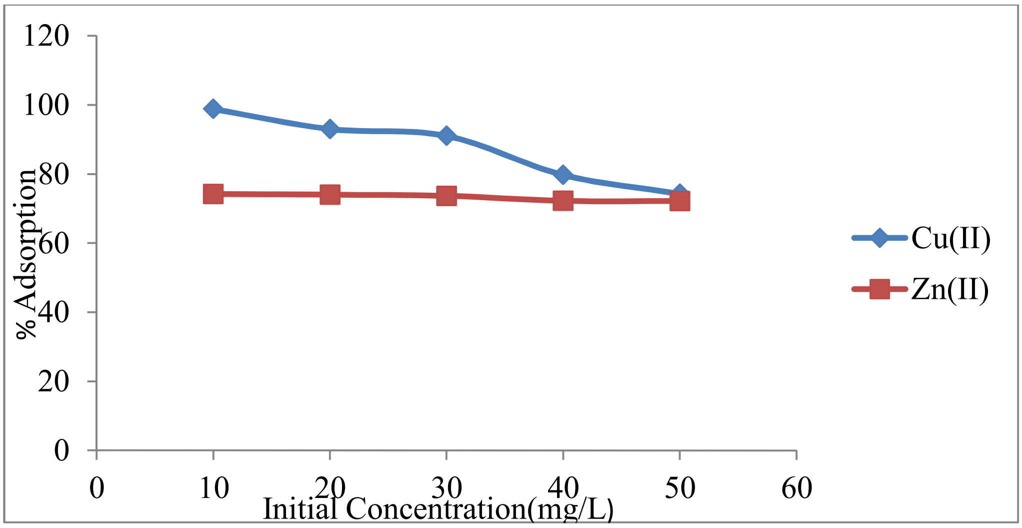

Figure 3: Effect of initial concentration on Cu (II) and Zn (II) ions adsorption efficiency (%) (Adsorbent dosage = 20g/L, time = 100 min and 125min, solution pH = 6 and 7, agitation speed = 150 rpm and 200 rpm respectively).

The results obtained in this regard are shown in figures 7 and 8, and accordingly an increase in the initial concentration of each of Cu (II) and Zn (II) ions leads to an increase in the adsorption capacity of the ions by RH. However, the percentage adsorption of copper and zinc ions on the adsorbent decreased from 98.79 ± 0.010% at 10 mg/L to 74.24 ± 0.055% at 50 mg/L for Cu(II) ions and 74.20 ± 0.10% at 10 mg/L to 72.13 ± 0.011% at 50 mg/L for Zn(II) ions. This is in agreement with the results obtained by Ragheb (2007) for heavy metals removal by low-cost adsorbents. Though an increase in metal uptake was observed, the decrease in percentage biosorption may be attributed to lack of sufficient surface area to accommodate much more metal ions available in the solution. But, in case of low concentrations of metal ions the ratio of the initial number of moles of each of Cu (II) and Zn (II) ions to the available surface area is large. In consequence, all Cu (II) and Zn (II) ions present in the solution could have interacted with the binding sites and thus the percentage adsorption became higher than those observed at higher initial copper and zinc ion concentrations.

3.2. Adsorption Isotherms

The Langmuir model assumes monolayer coverage of adsorbent surface and no interaction of adsorbate in the plane of the adsorbent surface. The empirical Langmuir equation is written as

$$q_e = q_m K_a C_e/(1+K_a C_e) \quad \text{(Langmuir, 1918)}$$

Where; q_e is the amount adsorbed per unit mass of adsorbent (mg/g), Ce the equilibrium concentration of the adsorbate (mg/L), q_m the equilibrium sorption capacity for complete monolayer (mg/g) and Ka the sorption equilibrium constant (L/mg).

Copper adsorption isotherm

Table 1: The results of Cu (II) ions adsorption isotherm

Initial concentration C_o (mg/L)	Final concentration C_e (mg/L)	Adsorption capacity (q_e) (mg/g)	C_e/q_e	Log C_e	Log q_e
10	0.12	0.49	0.24	-0.92	-0.30
20	1.40	0.93	1.50	0.14	-0.03
30	2.70	1.36	1.98	0.43	0.13
40	8.11	1.59	5.10	0.90	0.20
50	12.88	1.85	6.96	1.10	0.26

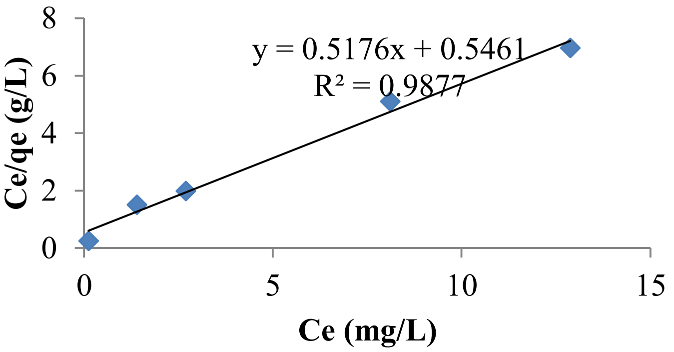

Figure 4: Langmuir adsorption isotherms for Cu (II) ions

The linear form Langmuir isotherm is given by the following equation (Langmuir, 1918)

$$C_e/q_e = 1/K_a q_m + C_e/q_m$$

Another linear form can be obtained by dividing the above equation by C_e. By plotting C_e/q_e against C_e, a straight line is obtained having a slope $1/q_m$ and intercept $1/K_a q_m$. From the Langmuir equation, the maximum adsorption capacity (q_m) by RH was 1.93 mg/g. The essential characteristics of Langmuir isotherms can be expressed in terms of dimensionless equilibrium parameter K_L (Juang, *et al.*, 1997).

$$K_L = 1/(1+K_a C_o) \quad .$$

Where; C_o is initial metal ion concentration in solution (mg/L), K_a is Langmuir constant related to adsorption energy.

$$K_L = 1/(1+0.94C_o), \text{ so } 0 < 1/(1+0.94C_o) < 1, \text{ because } C_o > 0$$

The value of K_L indicates a favorable adsorption. This means that rice husk is a favorable adsorbent for the removal of Cu (II) ions from aqueous solutions.

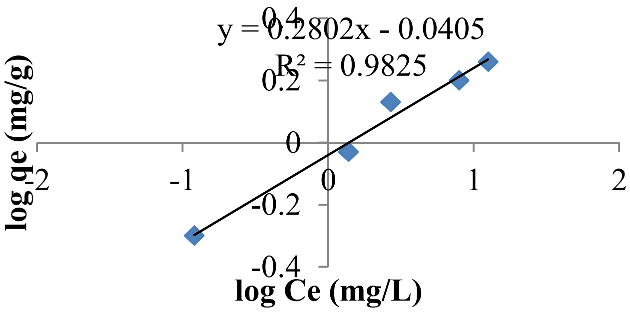

Figure 5: Freundlich adsorption isotherm for Cu (II) ions

The Freundlich equation is expressed as:

$q_e = K_F Ce^{1/n}$ Where; K_F and n are adsorption capacity and intensity respectively.

The linear form Feundlich isotherm is given by the following equation;

$$\text{Log } qe = \log K_F + 1/n \log Ce$$

Plotting log q_e versus log C_e, a straight line is obtained with a slope of 1/n and intercept of log K_F. The value of 1/n shows the concentration of solute adsorption. If the value of 1/n is close to 1, it shows that just a little concentration change can relatively affect the adsorption. Besides, n value can indicate the capacity of adsorption and the adsorbent dose. If n is more than 1, it means the adsorbent can effectively adsorb the solute (Freundlich, 1906). Using Freundlich equation the values of 1/n and n were calculated 0.280 and 3.57, respectively. Since the values of 1/n lie between 0 and 1 and n > 1, it indicates that the rice husk can adsorb Cu (II) ions effectively.

Zinc adsorption isotherms

Table 2: The results of Zn (II) ions adsorption isotherm

Initial concentration C_o (mg/L)	Final concentration C_e (mg/L)	Adsorption capacity (q_e) (mg/g)	C_e/q_e	Log C_e	Log q_e
10	2.58	0.37	6.97	0.41	-0.43
20	5.20	0.74	7.02	0.71	-0.13
30	7.90	1.10	7.18	0.89	0.04
40	11.10	1.44	7.70	1.04	0.15
50	13.93	1.80	7.73	1.14	0.25

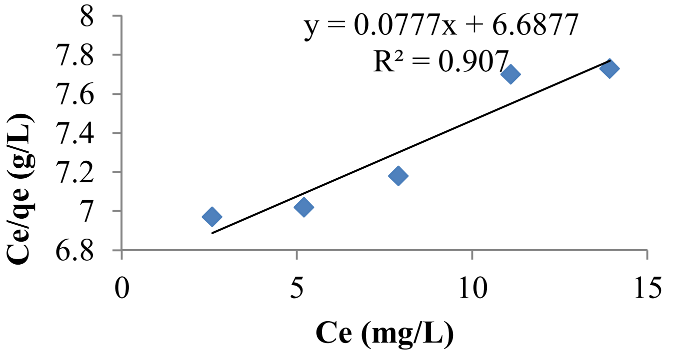

Figure 6: Langmuir adsorption isotherm for Zn (II) ions

The maximum adsorption capacity (q_m) of the rice husk was calculated as 12.98 mg/g. From the experiment;

$$K_L = 1/(1+0.011C_o), \text{ so } 0 < 1/(1+0.011C_o) < 1, \text{ because } C_o > 0$$

The value of K_L indicates a favorable adsorption. This implies that rice husk is a favorable adsorbent for the removal of Zn (II) ions from aqueous solutions. Therefore, the adsorption of Zn (II) ions on rice husk is feasible.

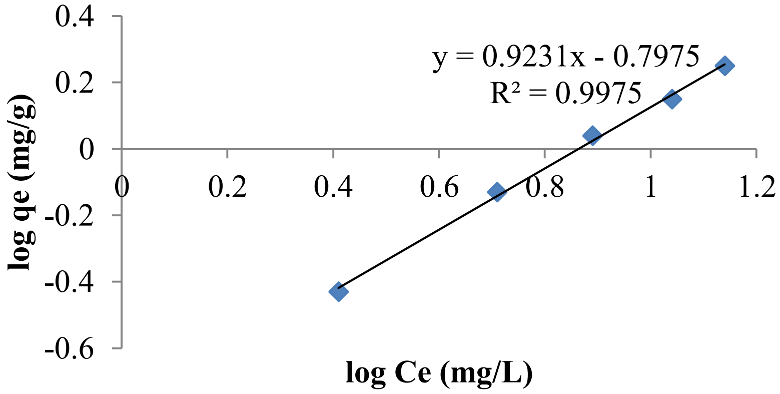

Figure 7: Freundlich adsorption isotherm for Zn (II) ions

The values of 1/n and n were obtained as 0.923 and 1.083 respectively. Since the values of 1/n lie between 0 and 1 and n > 1, it indicates that the rice husk can also adsorb Zn (II) ions effectively. The adsorption of Zn (II) ions on rice husk better fitted to the Freundlich model than to the Langmuir model as the correlation coefficients (R^2) are found to be 0.997 and 0.907 respectively. Therefore, Zn (II) adsorption on rice husk was characterized by heterogeneity of surfaces (supporting surfaces of different affinity).

CONCLUSION

It is obvious that many industries are releasing their effluents directly to the water bodies without pretreatment, it might be due lack of efficient or economically feasible means. Adsorption is a strong choice for removal of heavy metals from the wastewater. The rice husks are an agricultural waste substance. A simple and cost effective treatment procedure was proposed for the removal of heavy metals through the adsorption on rice husk. Removal of copper and zinc ions by rice husks has been shown to depend significantly on the pH, initial metal ion concentration, and contact time. In general Rice husk is effective and low cost adsorbent for removal of Cu (II) and Zn (II) ions from aqueous solution.

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