

## **An environmental study for adsorption of copper(II) and cadmium(II) from aqueous solution by using rice husk adsorbent**

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### **Abstract**

In this study, rice husk was used as a low cost adsorbent to remove Cu(II) and Cd(II) ions from wastewater by batch method. The main parameters that influencing Cu<sup>2+</sup> and Cd<sup>2+</sup> ions sorption on rice husk such as pH values, amount of adsorbent, contact time and initial heavy metal concentration of wastewater have been studied. The obtained results showed that the percent adsorption of Cu(II) and Cd(II) ions increased with an increase in contact time and dosage of rice husk. The binding process was strongly affected by pH, where the optimum pH for Cu(II) and Cd(II) ions was 6. The experimental data were in high agreement with the pseudo-second-order kinetic model; and analyzed by Langmuir, Freundlich, Tempkin and Dubinin–Radushkevich isotherm models to evaluate the adsorption of Cu(II) and Cd(II) ions on rice husk. The adsorption mechanisms of metal ions onto the rice husk were examined using: Scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR); analysis showed that functional groups provide the major adsorption sites for metal binding. As a conclusion, rice husk could be one of the low cost and effective adsorbent to be used in large amount operation of water treatment.

**Keywords:** Rice husk; Heavy metals; Adsorption; Kinetics; Isothe

## **1. Introduction**

The presence of heavy metal ions is a major concern because their toxicity to many life forms. Heavy metal contamination exists in aqueous wastes of many industries, such as metal plating, mining operations, chloralkali, radiator manufacturing, smelting, alloy industries and storage batteries industries, etc (Kadirvelu et al. 2001). For removal of heavy metals and metalloids, many conventional techniques like chemical precipitation, membrane filtration, ion exchange, carbon adsorption and co-precipitation have been used. But they are not suitable for high concentration of metals and also not cost effective (Demirbas, 2008). In recent years, the need for safe and economical methods for the elimination of heavy metals from contaminated waters has necessitated research interest towards the production of low cost alternatives (Khan et al. 2004). However, adsorption has been universally accepted as one of the most effective pollutant removal process, with low cost, ease in handling, low consumption of chemicals, as well as scope for recovery of value added components through desorption and regeneration of adsorbent (Abdel-Ghani et al. 2007). Rice husk is an agricultural waste material arise in rice producing countries, especially in Egypt. The annual world rice production is approximately 500 million metric tons, of which 10–20% is rice husk. Dry rice husk contains 70–85% of organic matter (lignin, cellulose, sugars, etc.) and the remainder consists of silica, which is present in the cellular membrane (Vempati et al. 1995). In recent years, attention has been focused on the utilization of unmodified rice husk as an adsorbent for the removal of pollutants (Wong et al. 2003). Accordingly, the aim of this work was to evaluate the potential of rice husk as alternative low-cost adsorbents for decontamination of metal ions from aqueous solutions. The adsorption studies were carried out as a function of solution pH, adsorbent dosage, contact time, initial copper (II) and cadmium (II) concentrations and temperature. The equilibrium data were described by the Langmuir, Freundlich, Tempkin and Dubinin–Radushkevich isotherm models as well as determine adsorption kinetics. FTIR and SEM analyses were performed to elucidate the adsorption mechanism(s).

## **2. Experimental**

### **2.1. Materials and chemical solutions**

#### **2.1.1. Adsorbent preparation**

Fresh rice husk was obtained from a local rice mill and the collected rice husk were washed with excess tap water and finally with distilled water in order to remove dust and

particulate materials from the surface, and dried in an oven at 70°C for 24 h. It grinding to powder by using a mixer and sieved to a uniform particle sizes to obtain even intra-particular diffusion of the metal ion (Al-Sultani and Al-Seroury, 2012). For preservation, it was kept in plastic bags and to minimize contact with humidity all these bags were preserved in desiccators until the time of use.

### **2.1.2. Adsorbate**

Stock solutions of Cd (NO<sub>3</sub>)<sub>2</sub> and CuSO<sub>4</sub> at concentration 1000 mg/L were prepared in deionized water. The desired concentrations were prepared through the adequate dilution of stock solution with deionised water. The initial pH was adjusted with concentrated HCl or NaOH. All chemicals are of analytical-grade and were used without further purification. Initial metal concentrations were measured using a flame atomic absorption spectroscopy (Perkin Elmer A Analyst 100). Samples were diluted before the required analysis to set the calibration linear range.

## **2.2. Procedures**

### **2.2.1. Effect of pH**

During the experiment of pH effect, the parameters of temperature, solution volume, adsorbent amount, initial metal ion concentration, and shaking time were fixed at 30°C 10 mL, 0.2 g, 10 mg/L, and 120 mins, respectively. pH was tested for Cd (II) at pH 2, 3, 4, 5, 6, 7 and 8, While, for Cu(II) was at pH 3, 4, 5, 6, 7 and 8 (Prabha and Udayashankara, 2014).

### **2.2.2. Effect of adsorbent amount**

This part of the experiment was performed to verify the effect of biomass weight on sorption process. Different weights of adsorbent rice husk (0.1, 0.2, 0.3, 0.4 and 0.5 g) were mixed and shaken with 10 mL solution of 10 mg/L of Cu(II) and Cd (II) at 30°C and pH 6 for 120 mins (Elham et al. 2010).

### **2.2.3. Effect of contact time**

The effect of contact time was investigated by agitating 0.2 g of adsorbent at pH 6, 30°C in 10 mL, 10 mg/L of Cd(II) and Cu(II) solution over time periods of 10, 15, 30, 45, 60 and 120 mins at constant agitation speed of 130 rpm (Kumar et al. 2010).

### **2.2.4. Effect of initial heavy metal concentration**

In order to assess initial metal concentration, different Cu(II) and Cd(II) concentrations of 10, 20, 30, 40, 50, 60, 70 and 80 mg/L were examined at constant parameters, pH 6 with 0.2 g of adsorbent added into 10 ml solutions for 120 mins (Nour el-din et al. 2008).

### 2.2.5. Effect of temperature

Adsorption process carried out at different values of temperature (25, 30, 35, 40, 45 and 50 °C), at pH 6, 0.2 g adsorbent weight and volume of 10 ml of 10 mg/L for Cd(II) and Cu(II) at 120 mins (Dho and Lee, 2003).

### 2.2.6. Isotherm studies

The extent of removal of heavy metals from aqueous solution depends strongly on the initial metal concentration. In order to assess, equilibrium process of different Cu(II) and Cd(II) varying from 10 to 70 mg/L were examined at constant parameters, pH 6 with 0.2 g of adsorbent, 30 °C and 150 rpm for 6 h.

### 2.3. Calculation of Cu (II) and Cd (II) uptake

The removal efficiency and adsorption capacity given by Yoonaiwong et al. (2011) and analyzed as following Eqs. 1 and 2

$$\text{Metal removal (\%)} = 100(C_0 - C_e)/C_0 \quad (1)$$

The adsorption capacity of metal ion can be analyzed based on the mass balance according as;

$$q_e = (C_0 - C_e) V / m \quad (2)$$

Where  $C_0$  is the initial concentration of metal ions in the solution (mg/L),  $C_e$  is the equilibrium concentration of metal ions in the solution (mg/L),  $V$  is the volume of solution (in liters) and  $m$  is the mass of adsorbent applied in grams.

### 2.4. Fourier Transform Infrared (FTIR) analysis of rice husk.

FT-IR analysis of rice husk was done to predict the functional groups on the walls of the adsorbent responsible for the adsorption process. FTIR spectra were obtained for adsorbent solid samples before and after the adsorption process. The spectra were recorded in Tensor - 27. bruker Transformed Infrared (FTIR). A sample of the adsorbent with the range 400-4000 $\text{cm}^{-1}$ .

### 2.5. Scanning electron microscopy (SEM)

Scanning electron microscope (Model S 3400N, Hitachi, Japan) analysis was also carried out for the dry rice husk particles and different sections in the samples were examined (before and after metals adsorption) for determining the surface morphology.

## 3. Results and discussion

### 3.1. Effect of pH

pH value has large effect in adsorption studies, because it influences not only the activity of functional groups in the adsorbents, but also the metal solution chemistry (Nessim et al. 2011). Results of the effect of pH on adsorption of Cu(II) and Cd(II) are presented in Figure 1. It was found that the total amount of adsorption of Cu(II) and Cd(II) onto rice husk increases with an increase of pH from 3 to 6 and reached a maximum value at pH 6. Many adsorption studies reported pH 5 - 6 as the optimum pH for Cu(II) ions adsorption by various adsorbents (Chen et al. 2012). At low pH (2- 3), more  $H_3O^+$  ions will be available to compete with Cu(II) ions for the adsorption sites of the adsorbents, most of the functional groups are protonated (Al-Jariri and Khalili, 2012). As pH changes, surface charge also changes, and the sorption of charged species is affected (attract ion between the positively charged metal ion and the negatively charged rice husk surface). Furthermore, a lower pH value causes the rice husk surface to carry more positive charges and thus would more significantly repulse the positively charged species Cu(II) in solution (Hengpeng et al. 2012). Adsorption of Cd(II) on the adsorbent depends upon the nature of the adsorbent surface and the species distribution of the metal cation. The solution pH was kept within the pH range of 2 – 6 because the precipitation of metal ion was occurred simultaneously at pH values higher than 6 (Reddy et al. 2010). The primary metal ion species in the pH range studied are  $Cd^{2+}$  and  $CdOH^+$  (Elliott et al. 1982).

### **3.2. Effect of adsorbent amount**

Mass of adsorbent is one of the important parameters in adsorption processes because it determines the capacity of an adsorbent for a given initial concentration of the adsorbate. Figure 2 shows that the adsorption of metals increases gradually with an increase in the amount of rice husk due to the greater availability of metal binding sites of the surface area at higher amount of the adsorbent (Mall et al. 2006). A significant increase in uptake was observed when the dose was increased from 0.1 to 0.5 g for copper ions. While, in cadmium ions the maximum removal was obtained at the adsorbent dose of 0.4 g with percent 97.47 % and the adsorption decreases at higher concentrations of adsorbent (0.5 g), because at high adsorbent amounts cause cell agglomeration and a consequent reduction in intercellular distance and produce 'screen effect' between dense layer of cells, leading to the 'protection' of binding sites from metal ions (Pons and Fuste, 1993).

### **3.3. Effect of contact time**

The effect of sorption time on sorption efficiency has been showed in Figure 3. The plot reveals that the percent of copper and cadmium removal were about 33.84 % of Cu(II) and 30 % of Cd(II) within the first 10 min this is probably due to a larger surface area of the rice husk being available at the beginning for the adsorption of metal ions. The increasing contact time increased the copper and cadmium adsorption and it remained constant after equilibrium was reached in 120 mins, as the binding sites became exhausted, the uptake rate slowed due to competition for decreasing availability of active sites by metal ions. Kumar and Gayathri (2009) reported that, 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.

### **3.4. Effect of initial concentration**

The effect of initial Cu(II) and Cd(II) ions concentration in the range (10 to 70 mg/L) on adsorption was investigated and is shown in Figure 4. It is evident from this figure that the percentage Cu(II) and Cd(II) ions removal decreased with the increase in initial concentration of Cu(II) and Cd(II) ions. The percentage removal decreases from 97.48 to 81.33% for Cu(II) ions ; while, in Cd(II) ions 97.58 to 80.02% at the same contact time and adsorption temperature. A significant amount of metal ions adsorbed at high initial metal concentration can be related to two main factors, namely high probability of collision between metal ions with the adsorbent surface and high rate of metal ions diffusion onto adsorbents surface (Putra et al. 2014). As discussed by Wang et al. (2013), high initial metal concentration accelerates the driving force and reduces the mass transfer resistance of Cu(II) and Cd(II) ions between the aqueous phase and the solid phase.

### **3.5. Effect of temperature**

The effect of temperature on the equilibrium sorption capacity for Cu(II) and Cd(II) ions has been investigated at temperature 20–50 °C with initial heavy metal concentration of 10 mg/l and pH 6. Figure 5 shows the variation of percentage removal with temperature of solution. It can be concluded that the maximum percentage removal of metals has been obtained at 30 °C and reduced with the rise in temperature from 30 to 50 °C. With an increase in temperature above 20 to 30 °C, increasing temperature is known to increase the diffusion rate of adsorbate molecules within pores as a result of decreasing solution viscosity and will also modify the equilibrium capacity of the adsorbent for a particular adsorbate (Al- Qodah, 2006).

Further increase in temperature (above 30 °C) leads to a decrease in the percentage removal. This decrease in adsorption efficiency may be attributed to many reasons: increasing in the relative escaping tendency of the heavy metals from the solid phase to the bulk phase, deactivating the adsorbent surface, and destructing some active sites on the adsorbent surface due to bond ruptures (Meena et al. 2005), or because the weakness of adsorption forces between the active sites of the sorbents and the sorbate species and also between the adjacent molecules of the sorbed phase (Ahmet and Mustafa, 2008).

### 3.6. adsorption isotherm models

The study of adsorption isotherms is fundamental in supplying the essential information required for the design of the sorption process. The adsorption of a substance from one phase to another leads to a thermodynamically defined distribution of that substance between the phases due to the system reaches equilibrium state (Naiya et al., 2009). This distribution can be expressed in terms of adsorption isotherms. In this investigation (Langmuir, 1918, Freundlich, 1906, Tempkin (Tempkin and Pyozhev, 1940) and Dubinin– Radushkevich (Dubinin, 1960) isotherm models were used to analyze the equilibrium data.

#### 3.6.1. Langmuir isotherm model

Langmuir adsorption isotherm (Langmuir, 1918) applied to equilibrium adsorption assuming a monolayer adsorption onto the surface of the adsorbent with a finite number of identical sites. The isotherm is presented by the following equation:

$$q_e = q_{\max} bC_e / (1 + bC_e) \quad (3)$$

where  $q_e$  (mg/g) is the observed adsorption capacity at equilibrium,  $q_{\max}$  (mg/g) is the maximum adsorption capacity corresponding to the saturation capacity (representing total binding sites of biomass),  $C_e$  (mg/L) is the equilibrium concentration and  $b$  (L/mg) is a coefficient related to the affinity between the sorbent and sorbate ( $b$  is the energy of adsorption). The linear relationship can be obtained by plotting  $(1/q_e)$  vs.  $(1/C_e)$ :

$$1/q_e = 1/(bq_{\max}C_e) + 1/q_{\max} \quad (4)$$

In which  $b$  and  $q_{\max}$  are determined from slope and intercept, respectively. The different adsorbents can be compared by its respectively  $q_{\max}$  values which are calculated from fitting the Langmuir isotherm model to actual experimental data. 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 (Webber and Chakravarti, 1974).

$$R_L = 1 / (1 + bC_e) \tag{5}$$

Where:  $C_e$  is the initial concentration  $b$  is the constant related to the energy of adsorption (Langmuir Constant).  $R_L$  value indicates the adsorption nature to be either unfavourable if  $R_L > 1$ , linear if  $R_L = 1$ , favourable if  $0 < R_L < 1$  and irreversible if  $R_L = 0$ . From the data calculated in Table (1), the  $R_L$  is greater than 0 but less than 1 indicating that Langmuir isotherm is favourable. The obtained results demonstrates that the Langmuir isotherm model is able to fit the sorption of Cu(II) and Cd(II) by rice husk with the correlation coefficient " $R^2$ " of 0.95 and 0.98, respectively. And the maximum monolayer coverage capacity ( $q_{max}$ ) from Langmuir Isotherm model was determined to be 133.34 mg/g for Cu(II) ions while, for Cd(II) ions 41.15 mg/g. The Langmuir constant ( $b$ ) which is related to the heat of adsorption was found to be 0.07 and 2.56 for uptake of Cu(II) ions and Cd(II) ions, respectively as shown in Fig (6) and Table 1,  $R_L$  (the separation factor) is 0.45 and 0.19 for Cu(II) and Cd(II) ions respectively, indicating that the equilibrium sorption was favourable.

### 3.6.2. Freundlich adsorption isotherm

The Freundlich isotherm assumes a heterogeneous surface with non-uniform distribution of adsorption heat over the surface (binding sites are not equivalent) or a multilayer adsorption (Freundlich, 1906). The mono-component Freundlich isotherm equation is given by:

$$q_e = K_f C_e^{1/n} \tag{6}$$

Where  $K_f$  is the Freundlich isotherm constant related to the sorption capacity and  $n$  is the constant related to affinity of metal ions on adsorbent. The Freundlich model can be easily linearised by plotting it in a logarithmic form:

$$\log q_e = \log K_f + 1/n \log C_e \tag{7}$$

By plotting  $\log q_e$  vs.  $\log C_e$ , the constant  $n$  and  $K_f$  can be determined from the slope and intercept, respectively. The linearized Freundlich isotherms acquired for Cu(II) and Cd(II), are presented in Figure 7 and Table 1. The experimental data obeyed the Freundlich model, as confirmed by the high determination coefficient ( $R^2$  more than 0.96).

The 'n' value of Freundlich equation could give an indication on the favorability of sorption and the  $n$  values were found to be greater than unity for adsorbent of both Cu(II) and Cd(II). According to (Kadirvelu and Namasivayam, 2000),  $n$  values between 1 and 10 represent beneficial adsorption.

### 3.6.3. Tempkin isotherm

Tempkin isotherm assumes that the heat of adsorption decreases linearly with the coverage because adsorbent adsorbate interaction (Piccin et al. 2011). The Tempkin isotherm has generally been applied in the following linear form:

$$q_e = B \ln A_T + B \ln C_e \quad (8)$$

$$B = RT/b \quad (9)$$

Where:  $A_T$  (L/g) is Tempkin isotherm constant,  $b$  (J/mol) is a constant related to heat of sorption,  $R$  is the gas constant (8.314 J/mol K) and  $T$  the absolute temperature (K). A plot of  $q_e$  versus  $\ln C_e$  enables the determination of the isotherm constants  $K_T$ ,  $b$  from the slope and intercept. From the Tempkin plot shown in Fig (8) and Table (2), the following values were estimated:  $A_T = 3.71$  and  $1.12$  L/g,  $B = 10.64$ ,  $8.83$  J/mol for Cu(II) and Cd(II), respectively, and the  $R^2 = 0.45$  for Cu(II) while, for Cd(II)  $R^2 = 0.87$ .

#### 3.6.4. Dubinin–Radushkevich (D–R) isotherm

Dubinin–Radushkevich isotherm is generally applied to express the adsorption mechanism with a Gaussian energy distribution on a heterogeneous surface (Gunay et al. 2007). He assumed that the characteristics of the sorption curves are related to the porosity of the adsorbent. Table 2 and Figure 9 summarizes the corresponding isotherm parameters, and the linear form of the isotherm can be expressed as follows:

$$\ln q_e = \ln Q_D - B_D \varepsilon^2 \quad (10)$$

Where  $Q_D$  is the theoretical maximum capacity (mol/g),  $B_D$  is the D–R model constant ( $\text{mol}^2/\text{kJ}^2$ ),  $\varepsilon$  is the Polanyi potential and is equal to

$$\varepsilon = RT \ln(1 + 1/C_e) \quad (11)$$

The mean energy of sorption,  $E$  (kJ/mol), is calculated by the following equation  $E = 1/\sqrt{2B_D}$  (12)

Where:  $R$ ,  $T$  and  $C_e$  represent the gas constant (8.314 J/mol K), absolute temperature (K) and adsorbate equilibrium concentration (mg/L), respectively. One of the unique features of the Dubinin-Radushkevich (DRK) isotherm model lies on the fact that it is temperature-dependent, which adsorption data at different temperatures are plotted as a function of logarithm of amount adsorbed  $\ln q_e$  vs.  $\varepsilon^2$  the square of potential energy, all suitable data will lie on the same curve, named as the characteristic curve (Foo and Hameed, 2010). From the linear plot of DRK model,  $q_D$  was determined to  $37.77$  and  $39.01$  mg/g for Cu(II) and Cd(II) ions respectively. Moreover, the mean free energy,  $E = 2 \times 10^{-7}$  for Cu(II) ions while for Cd(II) ions  $E = 1.25 \times 10^{-9}$  KJ/mol indicating a physisorption process and the  $R^2 < 0.73$ .

The results showed that the best correlation coefficients were, in decreasing order, Freundlich > Langmuir > D-R > Tempkin models for Cu(II), while for Cd(II) Langmuir > Freundlich > D-R > Tempkin models

### 3.7. Adsorption kinetics

In the kinetic models, it is normally assumed that the overall rate of adsorption is exclusively controlled by the adsorption rate of the solute on the surface of the adsorbent. The adsorption kinetics is commonly modeled with the pseudo-first-order and pseudo-second-order kinetics.

The pseudo-first order is given by the following equation Ho et al. (2000).

$$\text{Log}(q_e - q_t) = \log q_e - k_1 t / 2.303 \quad (13)$$

Where  $q_e$  and  $q_t$  ( $\text{mg} \cdot \text{g}^{-1}$ ) are the adsorption capacity at equilibrium and time  $t$ , respectively.  $K_1$  ( $\text{min}^{-1}$ ) is the rate constant of pseudo-first-order adsorption. When values of  $\log(q_e - q_t)$  are linearly correlated with  $t$ , we have a good fit for the pseudo-first-order reaction. Values of  $k_1$  and  $q_e$  are determined from the slope and intercept of the kinetic model, respectively. On the other hand, the pseudo-second order is given by the following formula.

$$t/q_t = 1/k_2^2 q_e^2 + t/q_e \quad (14)$$

Where  $k_2$  ( $\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ ) is the pseudo-second-order rate constant of sorption. Plots of  $t/q_t$  against  $t$  should give a linear relationship from which the values of  $q_e$  and  $k_2$  can be determined from the slope and intercept, respectively. Conformity between the experimental data and model-predicted values was expressed by the coefficient of determination ( $R^2$  values close or equal to 1). The experimental results of the heavy metals uptake,  $q_t$ , versus time were fitted to the above mentioned models by the method of nonlinear regression. The results are shown in Table (3 and 4) and Figures. (10 and 11). It was found, in this study, that pseudo-first-order kinetic models were ruled out because their correlation coefficients ( $R^2$ ) for the present experimental data were too small (less than 0.38) for both copper and cadmium ions. Experimental data, however, are closely aligned with the second-order equation because the determination coefficient were more than 0.98. The second-order rate parameter  $q_e$  indicated that this model was successful in estimating  $q_e$  because the experimental values of  $q_e$  agree with the  $q_e$  (calculated).

### 3.8. FTIR Spectrum

FTIR analysis was carried out in order to identify the different functional groups present in rice husk for copper ions (Figures 12 & 13) which were responsible for adsorption

process. The peaks appearing in the FTIR spectrum were assigned to various functional groups according to their respective wavenumbers as reported in literatures. The analysis of the FTIR spectra indicates broad band at 3416 and 3415  $\text{cm}^{-1}$  (ranging from 3200 to 3600  $\text{cm}^{-1}$ ) before and after adsorption, representing -OH group due to inter- and intramolecular hydrogen bonding of polymeric compounds such as alcohols or phenols as in pectin, hemicelluloses, cellulose and lignin (Iqbal et al. 2008) and -NH groups (Sheng et al. 2004). The bands observed at about 2925 $\text{cm}^{-1}$  before adsorption and 2926  $\text{cm}^{-1}$  after the adsorption around (2906.73-2927.94 $\text{cm}^{-1}$ ) could be assigned to symmetric or asymmetric -CH stretch of methyl, methylene and methoxy groups (Feng et al. 2008). The existence of the peak registered at 1712  $\text{cm}^{-1}$  before adsorption represents the stretching vibration of C=O bonds, which originates from non-ionic carboxyl groups (-COOH, -COOCH<sub>3</sub>) and may be denoted by carboxylic acids or corresponding esters (Li et al. 2007), and after adsorption this band was disappearance which indicated that further degradation were occurred after adsorption. The peak at 1651 $\text{cm}^{-1}$  before and after adsorption indicates C=O stretching (Yoonaiwong et al. 2011) and N-H stretching vibrations as well as indicate to the C=C stretching which might be attributed to the presence of lignin aromatic bond (Florido et al., 2009). Which C=C stretching vibrations between (1541.12-1697.36 $\text{cm}^{-1}$ ) indicative of alkenes and aromatic functional groups (Cherifi et al. 2009). Moreover, the band at 1511 and 1518  $\text{cm}^{-1}$  can be connected the -NH band at 1516-1535  $\text{cm}^{-1}$  (Sheng et al. 2004). The values which appeared in the region between 605 and 1086  $\text{cm}^{-1}$  are finger print of symmetric bond. From FTIR study, the formation of new absorption bands, the change in absorption intensity, and the shift in wavenumber of functional groups could be due to interaction of ions of dyes with active sites of adsorbents. Results from this study suggest, carbonyl, hydroxyl and amine are the main adsorption sites in rice husk.

### 3.9. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is a powerful technique that can be used to investigate binding of metals to seaweed (Yang, 2007).

The morphology of rice husk surface was analyzed by scanning electron microscopy before and after copper ions loading (Figures.13, a & b). The cells before exposure were fine, well shaped and had certain dimensions. After exposure to metals the SEM analysis is clearly indicated the presence of lot of irregular surface, swollen, highly porous structure of the RH sample studied and their surface becomes meanders after exposure to metals ions solution. This may be due to changes in surface morphology are usually related to disruption of the cross-

linking between the metal ions and negatively charged chemical groups, e.g. carboxyl groups, in the cell wall (Romera et al. 2007), and evidence the increase surface adsorption of metals.

#### 4. Conclusions

The adsorption of copper and cadmium ions by rice husk were investigated and found to be dependent on the pH solution, initial concentration, contact time and temperature. The maximum removal of copper and cadmium ions were attained at pH 6 at 30°C, using heavy metals concentration of 10 mg/L. The adsorption isotherm data could be well fitted by both Langmuir equation and Freundlich equation. The adsorption kinetic was described well by the pseudo-second-order model. Data of the IR spectrum confirmed the presence of some functional groups in the biomass of rice husk. The relatively low cost and high capabilities of the rice husk make it potentially attractive adsorbent for the removal of Cu (II) and Cd (II) from wastewater.

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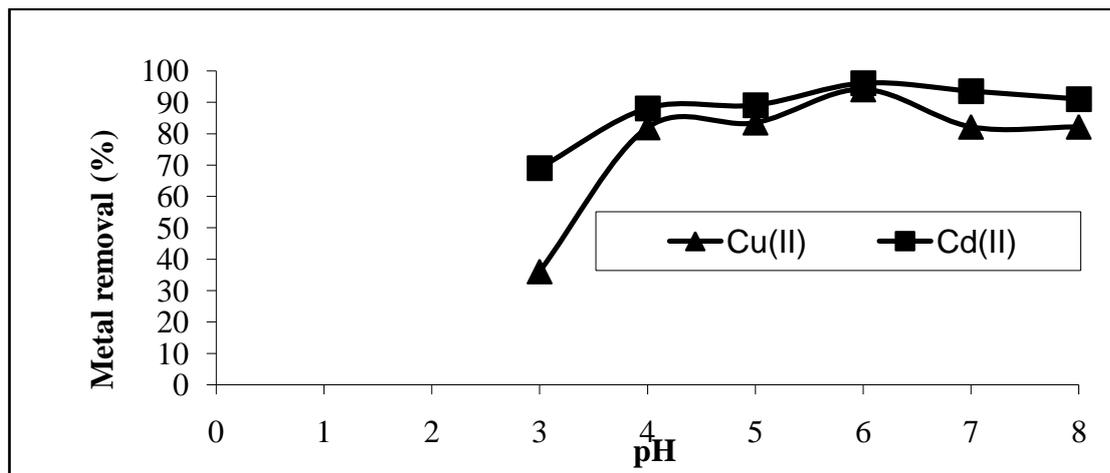
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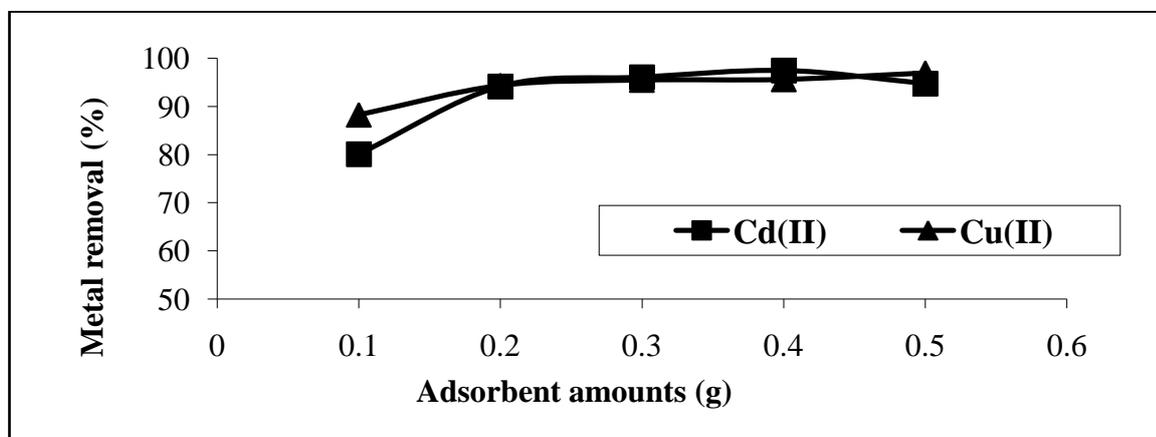
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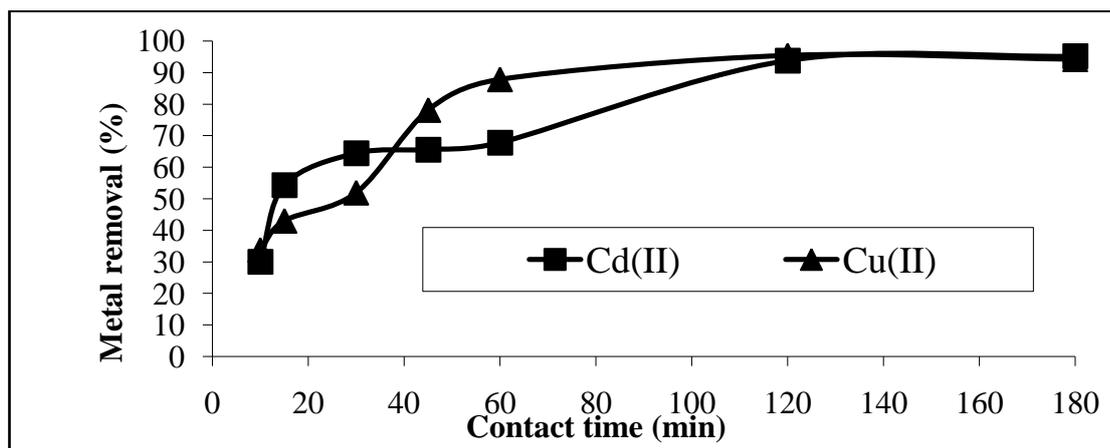
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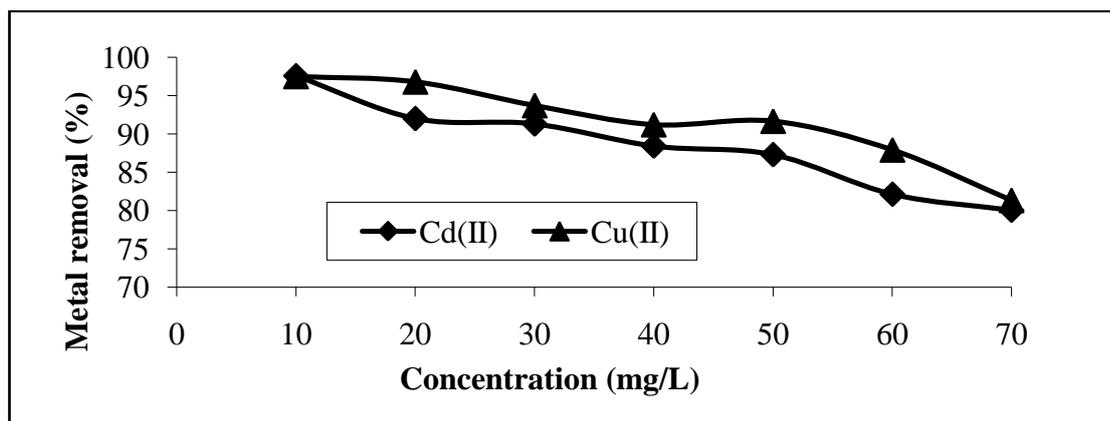
**Figure 1.** Effect of pH values on copper and cadmium ions sorption



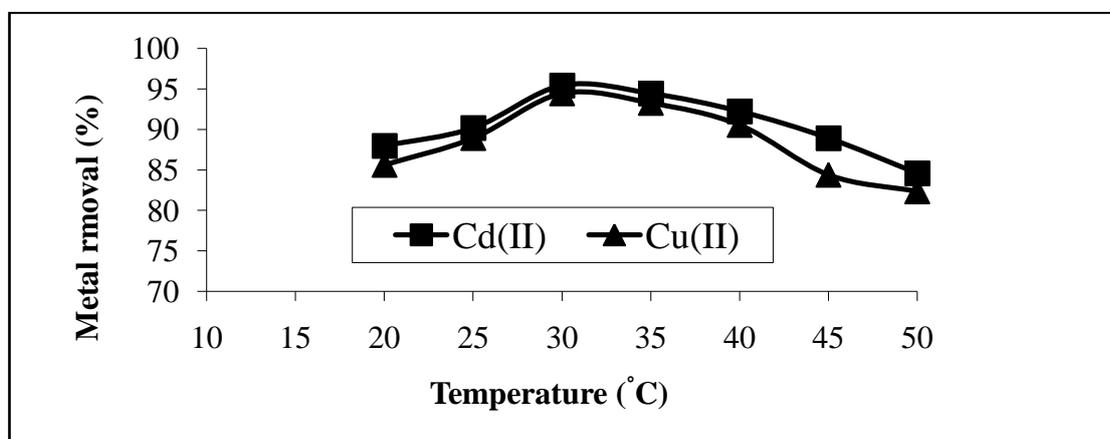
**Figure 2.** Effect of adsorbent amounts on percentage uptake of copper and cadmium ions sorption



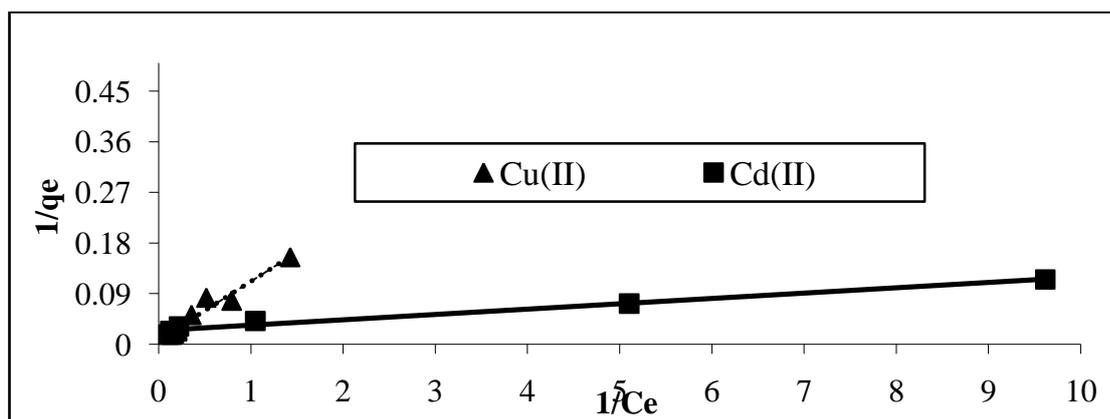
**Figure 3.** Effect of contact time on percentage uptake of upper and cadmium ions sorption



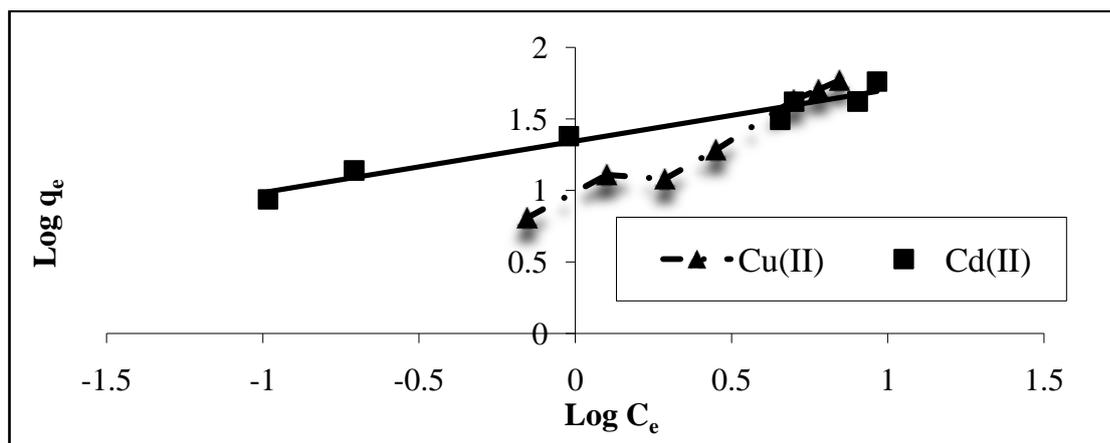
**Figure 4.** Effect of initial metal ion concentration on percentage uptake of copper and cadmium ions sorption



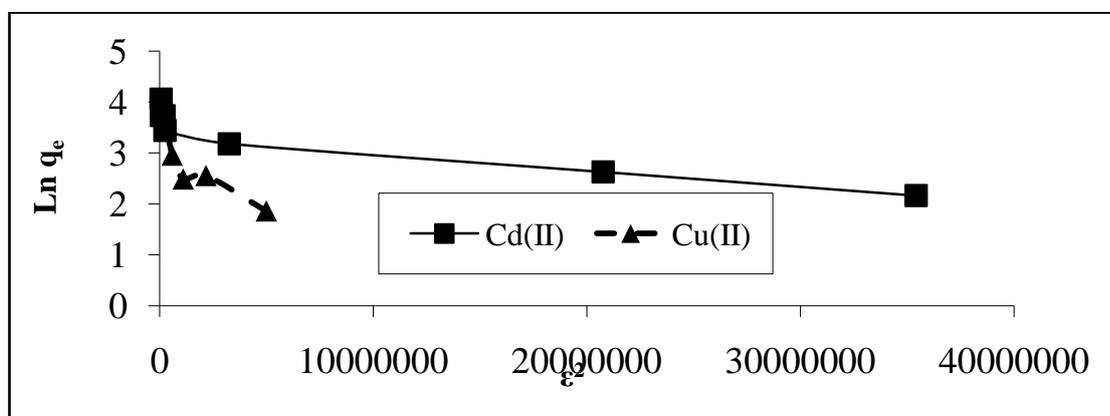
**Figure 5.** Effect of temperature on percentage uptake of copper and cadmium ions sorption



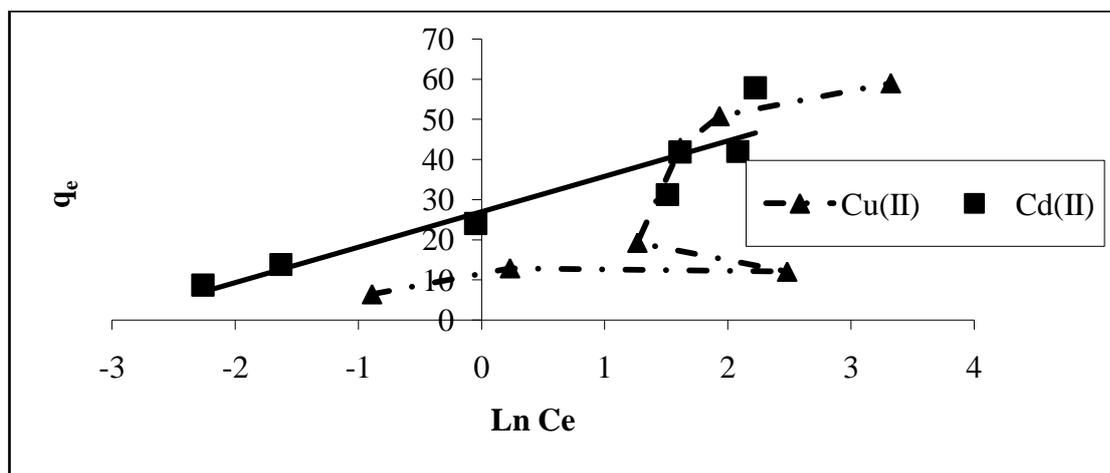
**Figure 6.** Langmuir isotherms plot for the sorption of Cu(II) and Cd(II)



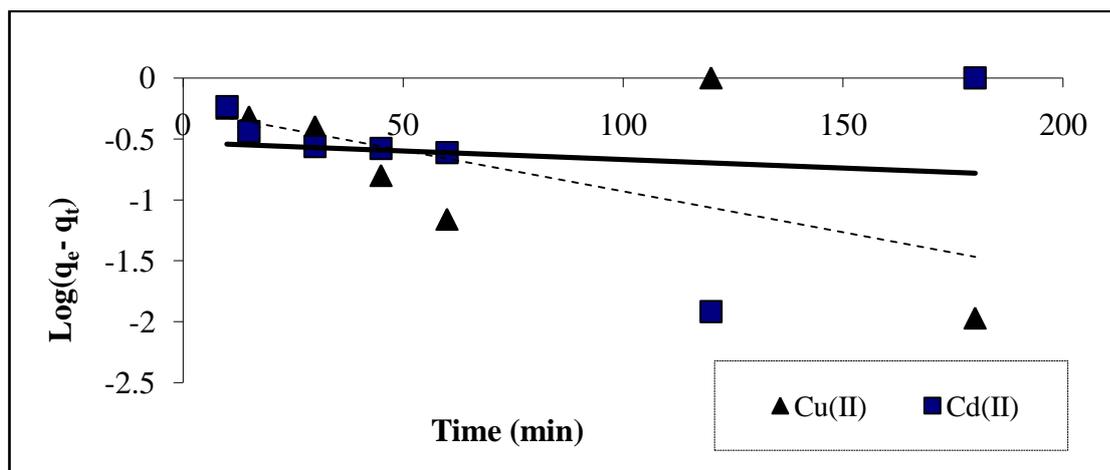
**Figure 7.** Freundlich isotherms plot for the sorption of Cu(II) and Cd(II)



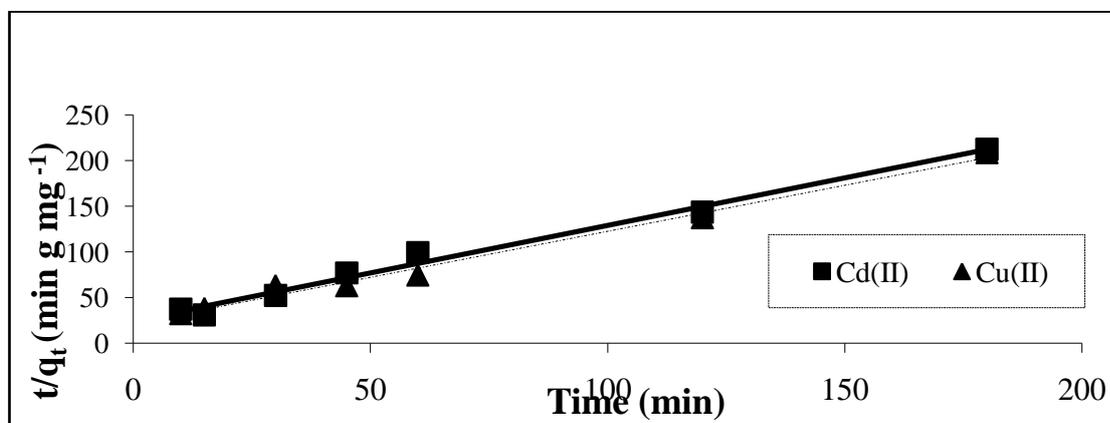
**Figure 8.** Dubinin-Radushkevich isotherms plot for the sorption of Cu(II) and Cd(II)



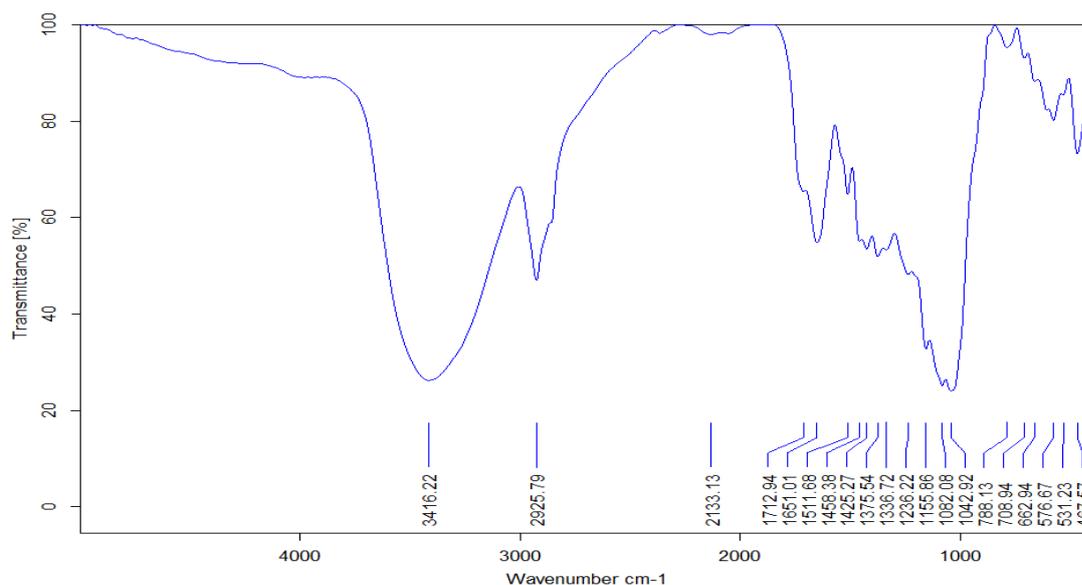
**Figure 9.** Tempkin isotherms plot for the sorption of Cu(II) and Cd(II)



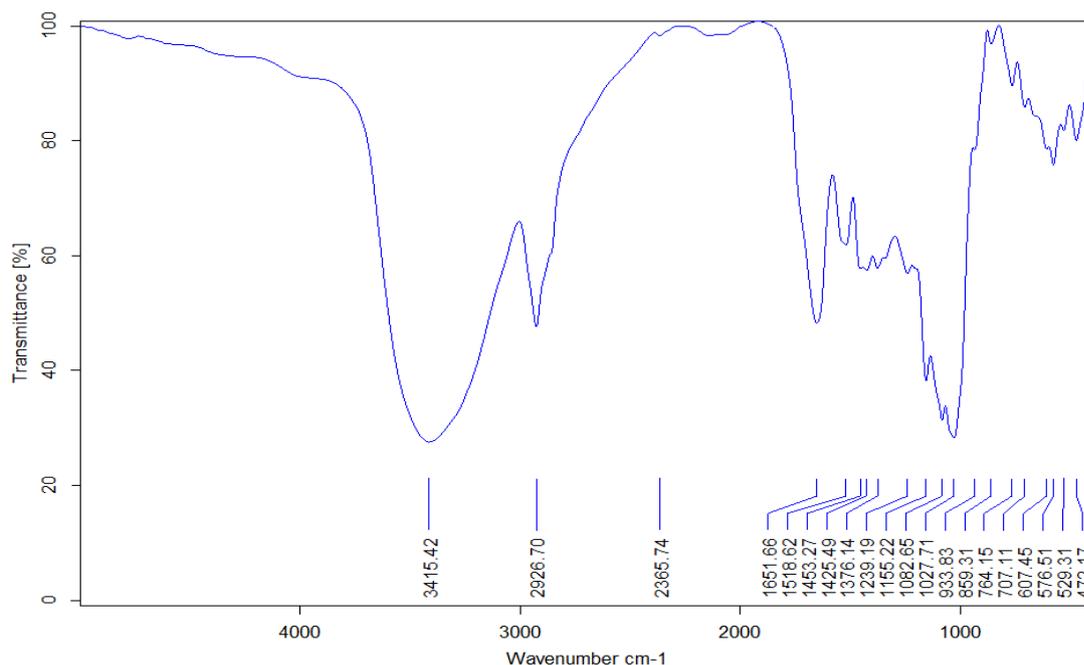
**Figure 10.** Pseudo-first order plot for the sorption of Cu(II) and Cd(II) ions



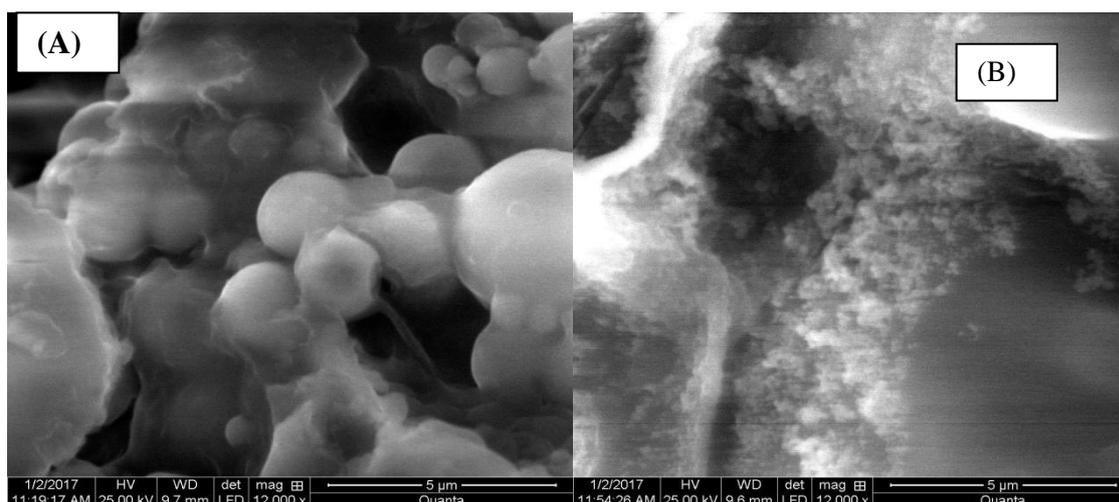
**Figure 11.** Pseudo-second order plot for the sorption of Cu(II) and Cd(II) ions



**Figure 12.** IR spectrum before adsorption of Copper



**Figure 13.** IR spectrum after adsorption of Copper



**Figure 14** SEM micrograph (12000) of rice husk cell wall (A-left) before and (B- right) after metal adsorption from aqueous solution

**Table 1.** Parameters for plotting langmuir and freundlich adsorption isotherms

Metal ions	Langmuir Isotherm				Freundlich Isotherm		
	R <sup>2</sup>	q <sub>max</sub> (mg/g)	B (L/mg)	R <sub>L</sub>	R <sup>2</sup>	n	K <sub>f</sub> (mg/g)
Cu(II)	0.948	133.34	0.07	0.45	0.960	1.04	8.489
Cd(II)	0.978	41.15	2.56	1.84	0.956	0.38	2.7 × 10 <sup>-4</sup>

**Table 2.** Parameters for plotting Dubinin-Radushkevich and Tempkin adsorption isotherms

Metal ions	Dubinin-Radushkevich				Temkin		
	R <sup>2</sup>	E (kJ/mol)	q <sub>D</sub> (mg/g)	B <sub>D</sub> (mol <sup>2</sup> /K <sup>2</sup> )	R <sup>2</sup>	A <sub>T</sub> (L/mg)	B
Cu(II)	0.722	2 × 10 <sup>-7</sup>	37.78	4 × 10 <sup>-7</sup>	0.491	3.70	10.64
Cd(II)	0.873	1.25 × 10 <sup>-9</sup>	39.01	4 × 10 <sup>-8</sup>	0.871	1.117	8.83

**Table 3.** Comparison between the adsorption rate constants with Pseudo-first-order

Metal ions	Pseudo-first-order rate equation			
	R <sup>2</sup>	q <sub>e</sub> (mg/g)	k <sub>ad</sub> (min <sup>-1</sup> )	q <sub>e</sub> _exp.(mg/g)
Cu(II)	0.384	0.552	-0.0154	0.873
Cd(II)	0.021	0.295	-3.224 × 10 <sup>-3</sup>	0.846

**Table 4.** Comparison between the adsorption rate constants with Pseudo-second-order rate equations

Metal ions	Pseudo-second-order rate equations			
	R <sup>2</sup>	q <sub>e</sub> , cal.(mg/g)	K (g mg <sup>-1</sup> min <sup>-1</sup> )	q <sub>e</sub> _exp.(mg/g)
Cu(II)	0.989	0.993	0.0461	0.878
Cd(II)	0.987	0.959	0.0436	0.846