

Removal of Copper Ions from Synthetic Waste Water Using Some Agricultural Wastes as a Low-Cost Adsorbent

A A Swelam¹, M B Awad¹, A M A Salem¹ and A S El-Feky^{1*}

Chemistry Department, Faculty of Science, Al-Azhar University Cairo, Egypt

Abstract

In the present study, the potential of the raw (RS) and NaOH-Modified Rice Straw (MRS) to remove copper (II) from aqueous solutions was investigated by batch tests under different experimental conditions. The chemical and morphological structures of adsorbents were investigated by scanning electron microscopy (SEM), energy Dispersive Analysis of X-rays (EDAX), element analyzer and Fourier-Transform Infrared spectroscopy (FTIR). The study also investigated the effects of process parameters such as initial Cu (II) concentration, solution pH and temperature. Results of the present study revealed that, the maximum adsorption was about 39.40% and 46.20% for RS and MRS respectively, at pH 4.3, contact time 210 min. and initial concentration is 381.3 mg L⁻¹. Langmuir and Freundlich adsorption isotherms were applicable to the adsorption process and their constants were evaluated. The good correlation coefficient was obtained from pseudo second-order kinetic model, which agreed with conception as the rate-limiting mechanism. Thermodynamic aspects of the adsorption process indicated feasible, spontaneous and endothermic biosorption process. The modified rice straw in comparison, could adsorb Cu (II) ion faster than the unmodified.

Keywords: Rice straw; Adsorption; Copper; Isotherms; Kinetics; Thermodynamics

***Corresponding Author:** A S El-Feky, Chemistry Department, Faculty of Science, Al-Azhar University Cairo, Egypt; E-mail: ahmed.samer@azhar.edu.eg

1. Introduction

The presence of heavy metals in the water environment is a major concern due to their toxic effects since they cause severe health problems to animals and human beings. According to the World Health Organization (WHO), the metals of most immediate concern are aluminum, chromium, manganese,

iron, cobalt, nickel, copper, zinc, cadmium, mercury and lead [1].

Heavy metals as raw materials or catalysts are used widely in many industrial production, such as mining, metallurgy, electrolysis, electroplating and leather [2]. They can be subsequently released into the environment through wastewater, which has become a threat to human and local environment [3]. Because the heavy metals in water are difficult to be biodegraded and tend to accumulate in organisms through the food chain [4], the wastewater containing heavy metals should be treated before discharge..

Various methods for heavy metal removal have been proposed, demonstrated and applied, such as chemical precipitation [5], membrane filtration [6] and ion exchange [7–9]. Compared with treatment methods listed above, adsorption is considered as an efficient method for the removal of heavy metals from waste water with several advantages like no chemical sludge, easy to operate [10] and the process appears to be inexpensive [10–12].

Agricultural wastes are generated in high amounts in Egypt; these products are not used economically. Some of the advantages of using agricultural residues for wastewater treatment include simple technique, little processing requirement, good adsorption capacity, selective adsorption of heavy metal ions which causes environmental issues, low cost, free availability, and easy regeneration [13].

Rice straw is comprised of cellulose, hemi cellulose and lignin that can adsorb heavy metals in aqueous solutions validly [14]. Hence the adsorption of heavy metal ions with waste agricultural materials could provide a novel treatment of both crop residues and heavy metal pollution. In several previous reports, many authors have documented the use of the rice straw for the adsorption of heavy metals [15–17]. Whereas, a lot of previous researchers simply modified rice straw by acid or alkali washing, which just improved the adsorption capacity inconspicuously.

The purpose of this work is to investigate the capability of unmodified (RS) and Modified Rice Straw (MRS) for the removal of Cu (II) from single system. The adsorbents were characterized by Fourier Trans-form Infrared spectra (FTIR), Scanning Electron Microscope (SEM), Energy Dispersive X-ray Analysis (EDXA) and the X-ray Diffraction (XRD. The kinetic and thermodynamic parameters were calculated and the equilibrium data were fitted to some isotherm models to determine the adsorption mechanism.

2. Material and Methods

2.1. Preparation of adsorbent

2.1.a. Rice straw

The natural Rice Straw (RS) used in the present experiments was obtained from a market in Menoufia Country, Egypt. The (RS) was thoroughly washed with a stream of distilled water to remove all dirt and then was dried at 110°C. The dried (RS) were stored in desiccators until used.

2.1.b. Modified rice straw

The Modified Rice Straw (MRS) sample was prepared by alkali treatment. Alkali treatment was carried out by placing the RS sample in contact with NaOH (0.1 M), with constant stirring for 24 h. The liquid/solid ratio was 10 ml/g. It was then filtered,

washed OH⁻ free with distilled water, and dried at 110 °C for 24 h to constant weight. And it was ground and sieved. The particles 0.63 mm was selected and preserved at room temperature in a sealed bottle.

2.2. Preparation of metal-solutions

The Cu (II) stock solution containing 1000 mg/L was prepared by dissolving copper chloride (analytical reagent grade) in distilled water. Copper working solutions in different concentrations was prepared by diluting the Cu (II) stock solution with distilled water.

2.3. Analytical technique

The concentrations of the Cu (II) metal ions were performed using Flame Atomic Absorption Spectrophotometer (FAAS) Vario 6. Elements were determined using an air– acetylene flame.

3. Results and Discussion

3.1. Characterization of adsorbents

3.1.1. Chemical composition

The chemical composition of the rice straw was determined at each stage of treatment and the data are summarized in Table 1.

Table 1: Chemical Characterization of RS and MRS

No.	Chemical Characterization	Samples	
		RS	MRS
1	Moisture Content %	7	6.65
2	Ash Content %	6	13.3
3	Lignin Content %	12.5	13
4	Holocellulose %	75.5	72.8
5	Alpha Cellulose	56	61

3.1.2. FTIR spectra

The rice straw is constituted basically by cellulose, hemicellulose, lignin, extractives, water and mineral ash which are in large amount SiO₂. The lignin is promptly available to interact with cations, by firstly exchanging with protons and subsequently by chelating with the metallic ion.

FTIR spectroscopy was applied to identify the functional groups of rice straw responsible for metal adsorption. To reveal then systematic changes in the spectral features upon reaction with metal ions, FTIR spectra were obtained for the sample before reacting with Cu (II). By comparing the FTIR spectra of outer and inner surface for RS and MRS in table 2 (a, b) and figure 1.

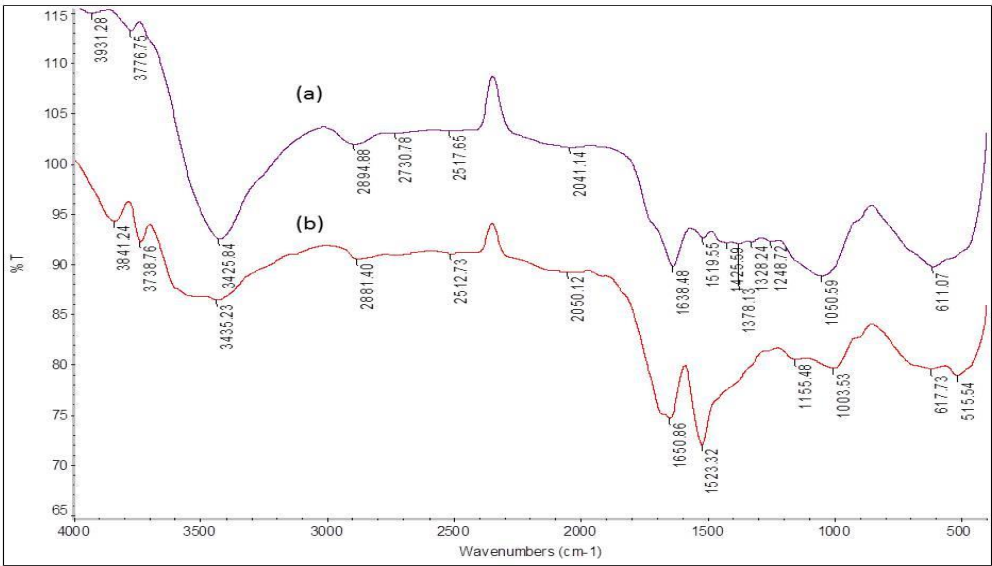
Table 2a: FTIR for outer surface of RS and MRS

FTIR Peak	Outer surface		Assignment	Reference
	RS	MRS		
1	$\approx 3300\text{ cm}^{-1}$	Shift to $\sim 26\text{ cm}^{-1}$	Stretching vibration of $-\text{OH}$ groups	[18], [19]
2	$\approx 2925 \pm 1\text{ cm}^{-1}$		Vibration of the carbon-hydrogen bonds superimposed onto $-\text{OH}$ broad band	[18], [19]
3	$\approx 1738\text{ cm}^{-1}$	Disappear	The vibration of carbonyl from carboxylic groups in ester linkage	[20]
4	$\approx 1626 \pm 4\text{ cm}^{-1}$	Shift slightly	$-\text{OH}$ groups	[18], [19]
5	$\approx 1539\text{ cm}^{-1}$	Disappear	The vibration of carbonyl from carboxylic groups in ester linkage	[20]
6	$\approx 1217\text{ cm}^{-1}$	Disappear	Vibration of silica bonds	[21]
7	$786 \pm 5\text{ cm}^{-1}$	Disappear	Vibration of silica bonds	[18]

Table 2 b: FTIR for inner surface of RS and MRS

FTIR peak	Inner surface		Assignment	Reference
	RS	MRS		
1	$\approx 3273.5 \pm 57\text{ cm}^{-1}$	Shift to 49 cm^{-1}	Hydrogen bonded $-\text{OH}$ in cellulose fibers	[18], [19]
2		$\approx 2919 \pm 0.5\text{ cm}^{-1}$	C–H vibration bond	[19]
3		$\approx 1614 \pm 19\text{ cm}^{-1}$	$-\text{OH}$ vibration bond	[18], [19]
4		$1201\text{--}1156\text{ cm}^{-1}$	Vibration range of silica bonds	[20]
5	790 cm^{-1}	Disappear	Vibration range of silica bonds	[20]

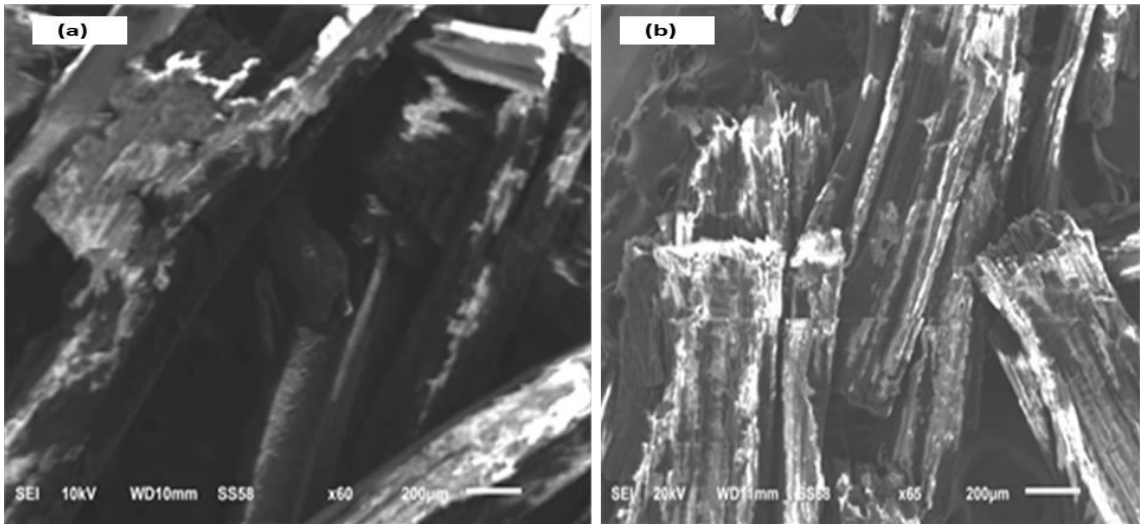
Figure 1: FTIR spectra for (a) RS and (b) MRS before adsorption.



3.1.3. Scanning Electron

Scanning Electron (SEM) micrographs of untreated and treated rice straws are shown in Fig. 2(a,b). As shown in Figure 2 (a, b) the surface roughness of the outer and inner surfaces of rice straws change significantly after alkali treated with NaOH. Changes started to be substantial when the rice straws were treated with NaOH. These include wearing of asperities on the outer surfaces and particle cracking which suggests the weakening of the rice straws due to increase in brittleness. The result of Scanning Electron Microscopy (SEM) also shows that rice straw is a porous material [22].

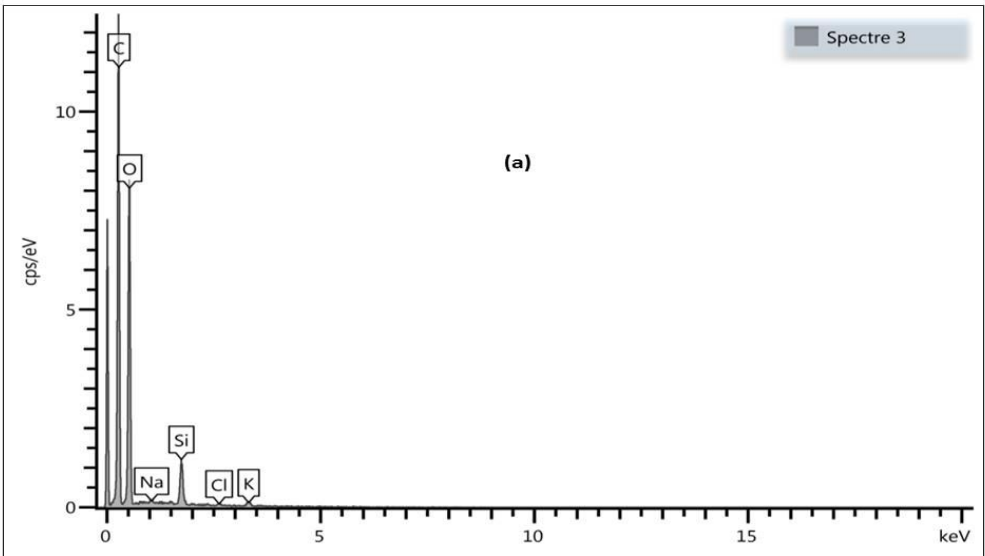
Figure 2: SEM image for (a) RS and (b) MRS before adsorption



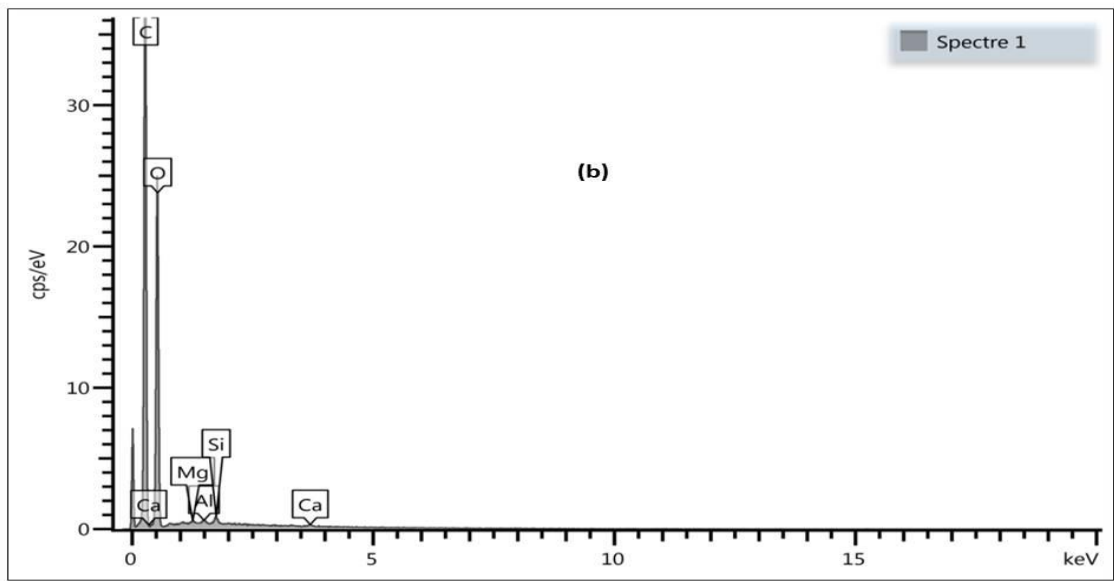
3.1.4. EDXA Spectra

Figure 3 (a, b) shows the EDXA spectra of RS and MRS adsorbents before adsorption with Cu (II) respectively. Figure 3 (a, b), indicates the presence of major constituents – carbon and oxygen in the two samples adsorbents. It was suggested that toxic metals including Cu (II) had been adsorbed on the surface of MRS successfully. Moreover, after loading with toxic copper, a distinct increase of silica peak intensity could be found. This phenomenon might be derived from the alkali treatment.

Figure 3: EDXA for (a) RS



(b) MRS before adsorption

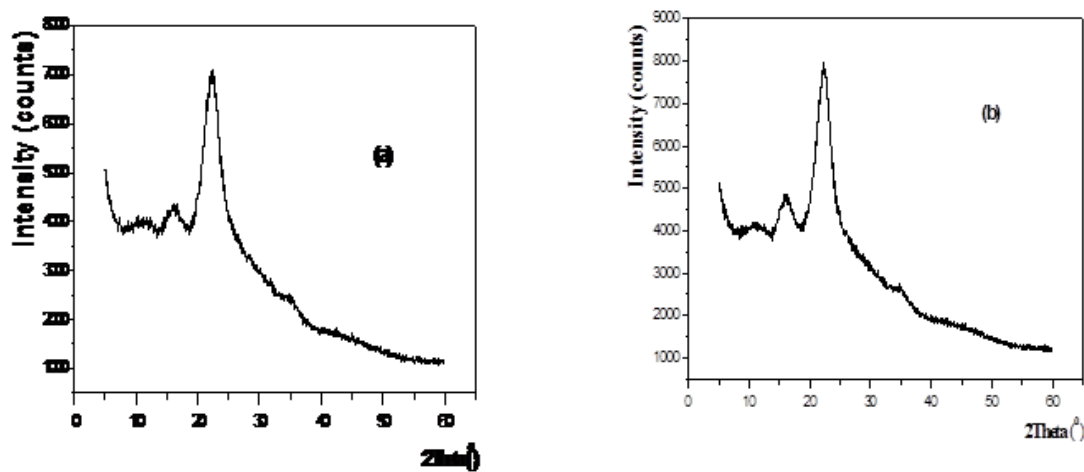


3.1.5. X-ray Diffraction

Figure 4 (a, b) shows the X-ray diffraction patterns of RS and MRS biosorbents powder. Diffraction peaks corresponding to crystallinity were not observed, whereas, amorphous form is identified in the biosorbent. The amorphous nature of the biosorbents suggested that the metal ion could more easily penetrate into the surface of the two biosorbents on the amorphous. Optimization of Cu (II) biosorption by chemically modified rice straw.

Fig

Figure 4: XRD for (a) RS and (b) MRS before adsorption

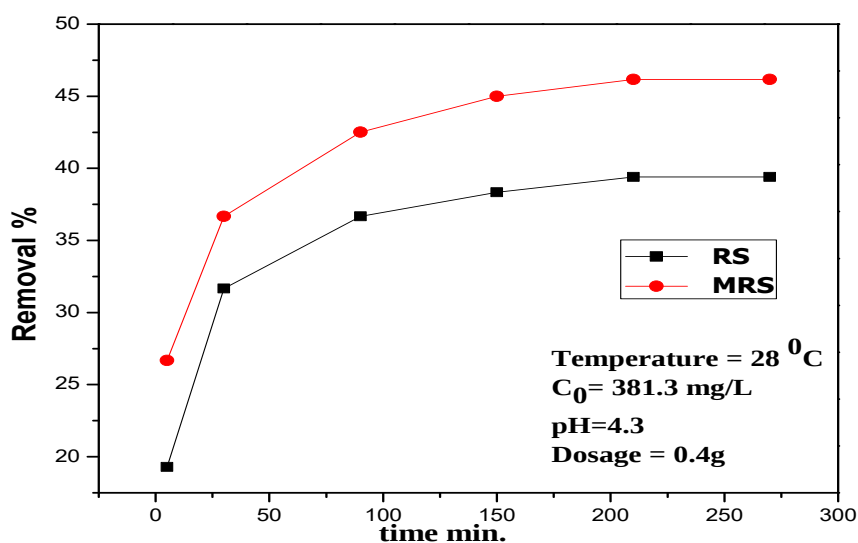


3.2. Effect of contact time

The rate at which adsorption take place is most important when designing batch adsorption experiments. Consequently, it is important to establish the time dependence of such systems under various process conditions. The experimental runs measuring the effect of contact time on the batch adsorption of metal solution containing 381.3mg/l of Cu(II) at 28°C and initial pH value 4.3 is shown in Figure 5.

The adsorption of Cu (II) increased with increasing contact time and became almost constant for ~3.5 h for both RS. and MRS. After ~3.5, the % removal was negligible hence all experiments were carried out at equilibrium time of 3.5 h. Higher adsorption efficiency of MRS than RS could be attributed to available absorbing site (Surface functional groups) on the adsorbent surface [23].

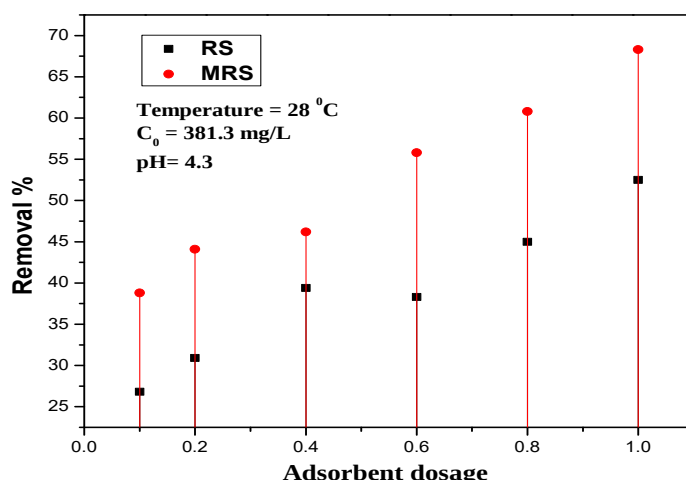
Figure 5: Effect of contact time on the removal of Cu (II) by RS and MRS



3.3. Effect of adsorbent dosage

The adsorbent weight is an important parameter in adsorption studies because it determines the capacity of adsorbent for a given initial concentration of metal ion solution. To study the influence of the liquid to solid ratio on the retention of copper, three different values have been taken by varying the adsorbent amount of both RS and MRS while keeping the volume of the metal solution constant as shown in Figure 6, where it can be seen that the adsorption increases with the increase in the amount of the adsorbents doses from 0.1 to 1.0g. This can be explained by a greater availability of the exchangeable sites or surface area at higher amount of the adsorbent. The RS has adsorption ability for Cu (II), the removal percentage of Cu (II) from 26.8% to 52.5% and for MRS, the removal percentage of Cu (II) is 38.8% and 68.3%, respectively [24,25]. The data clearly shows that the MRS is more effective than RS for removal of Cu (II) from aqueous solution.

Figure 6: Effect of amount of adsorbent on the removal of Cu (II)



3.4. Effect of initial metal ion concentration

The metal uptake mechanism is particularly dependent on the initial heavy metal concentration. The adsorption capacity of Cu(II) for RS increased from 12.8 mg/g to 28 mg/g with the increasing initial Cu (II) concentration from 127.1 mg/L to 889.7 mg/L. And the uptake of Cu (II) for MRS increased from 11.5 mg/g to 19.6 mg/g with initial Cu (II) concentration ranging from 127.1 mg/L to 889.7 mg/L (Figures not shown). Actually, as the initial concentrations of Cu (II) increased, the driving force became higher as well, the accessibility of the heavy metal ions to the binding sites of the RS and MRS are relatively high with increased initial concentration, the ions exchange frequently and the uptake of heavy metals becomes more and more [26-29].

This may be due to, at low concentrations, copper ions are adsorbed by specific active sites, while at higher concentrations; lower adsorption yield is due to the saturation of adsorption sites. Though an increase in metal uptake was observed, the decrease in percentage adsorption may be attributed to lack of sufficient surface area to accommodate much more metal available in the solution. This appears to be due to the increase in the number of ions competing for the available active sites on the surface. In addition, typical mass-transport controlled kinetics of pollutants removal by the rice straw is another factor which control removal rate of copper and at higher concentrations, more metal ions are left in solution [30].

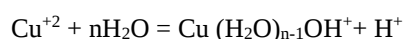
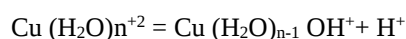
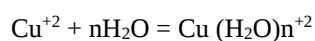
3.5. Effect of initial pH

The pH of the solutions has been identified as the most important variable governing metal adsorption. This is partly due to the fact that hydrogen ion (H^+) themselves is strong competing ions and partly that the solution pH influences the chemical speciation of the functional groups on to the adsorbent surfaces. In order to

evaluate the influence of this parameter on the adsorption, the experiments were carried out at different initial pH values. The pH range was chosen as 1.8– 4.6 in order to avoid metal hydroxides, which has been estimated to occur at $pH > 4.9$ for $Cu(OH)_2$.

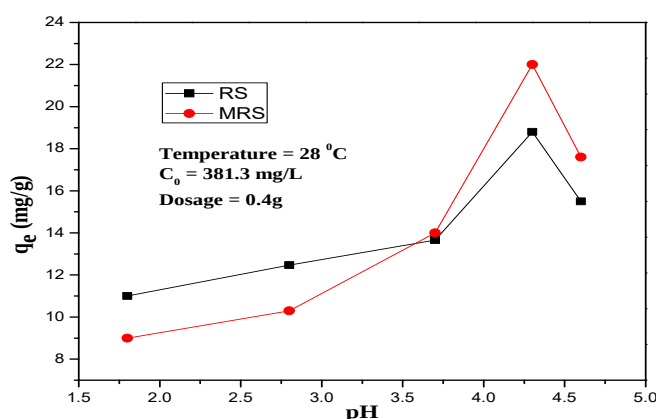
At higher pH values a slight decrease of adsorption for Cu (II) could be suffering hydrolysis, starting at pH higher than 4.9, forming $Cu(OH)_2$, which promotes a reduction of the adsorption capacity, due to the diminution of the formal charge of the metallic ion.[31]

The effect of pH on adsorption efficiencies are shown in Figure 7. It can observed from Figure 7 that the removal of Cu (II) increase with increasing solution pH and a maximum value was reached at an equilibrium pH of around 4.3 for RS and MRS. The same trend has also been reported in the removal of Cu (II) ions by other vegetable materials [32-34]. The low degree of adsorption at low pH values can be explained by the fact that at low pH values the $[H^+]$ ion concentration is high and therefore protons can compete with the lead cations for surface sites, since at low pH, Cu (II) are present in solution as Cu^{+2} free cations. The process involved for Cu (II) adsorption are proposed by Greenwood and Earnshaw, 1997 [35] as the following.



On the other hand, as pH increases, there is a decrease in positive surface charge (since the deprotonation of the sorbent functional groups could be occurs, which results in a lower electro static repulsion between the positively charged metal ion and the surface of MRS, favoring adsorption than its RS.

Figure 7: The effect of pH on the removal of Cu (II) by RS and MRS



3.6. The distribution ratio (D)

Distribution ratio D for copper ions was determined by the batch method at different temperature systems (301, 313 and 323K). The distribution ratio, D , is defined as the ratio of metal ion concentration on the adsorbent to that in the aqueous solution and can be used as a valuable tool to study Cu (II) ion mobility. The distribution ratio (D)

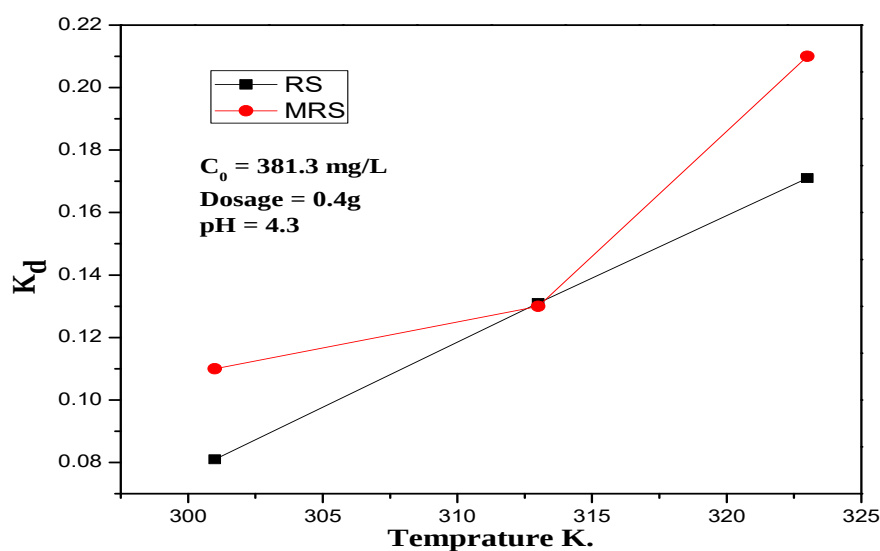
is defined by the following relationship [36, 37]:

$$K_d = \frac{(I-F)}{500 \text{ mg}} \times \frac{50 \text{ ml}}{F}$$

Where I is the volume of EDTA used before treatment of metal ion-exchange. F is the volume of EDTA consumed by metal ion left in solution phase.

High values of the distribution ratio (as in aqueous-MRS systems), indicate that the metal has been retained by the solid phase through sorption reactions, while lower values of D (as in aqueous-RS systems), indicate that a large fraction of the metal remains in solution. Figure 8 shows that the distribution ratio (D) values increase with the increase in temperatures of copper solutions. The rapid metal sorption has significant practical importance, as this will facilitate with the small amount of resin to ensure efficiency and economy.

Figure 8: The effect of distribution coefficient on adsorption of Cu (II)



3.7. Adsorption Isotherm

When the adsorption is at the state of equilibrium, the results were then fitted to the Langmuir [38] and Freundlich [39] isotherm model. The Langmuir model is effective in monolayer adsorption on surfaces and the Freundlich model is valid for non-ideal multilayer adsorption. These two models can be expressed by the following equations (1, 2):

$$\text{Freundlich } \log q_e = \log K_F + \frac{1}{n} \log C_e \quad \text{----- 1}$$

$$\text{Langmuir } \frac{C_e}{q_e} = \frac{1}{K_L Q_{\max}} + \frac{C_e}{Q_{\max}} \quad \text{----- 2}$$

Where q_e (mg/g) is the amount of uptake at equilibrium time; C_e is the equilibrium concentration (mg/L), K_F and n are constants related to adsorption. $Q_{\max}$ (mg/g) is the maximum metal uptake of Langmuir isotherm; K_L is the equilibrium coefficient.

Freundlich constant K_F is related to temperature [38], value of n is correlated with the favorability of adsorption $n > 1$ indicates favorable adsorption isotherm [40].

The Langmuir equation is also used to obtain R_L , the dimensionless equilibrium parameter or the separation factor [41, 42] from the expression (3):

$$R_L = 1 / (1 + K_L C_0) \quad \text{----- 3}$$

The values of b in the Langmuir model suggested whether the isotherm is unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$) [43].

The linear Freundlich and Langmuir plots are obtained by plotting (i) $\log q_e$ vs. $\log C_e$ and (ii) C_e/q_e vs. C_e , respectively, from which the adsorption coefficients could be evaluated.

Experimental data are fitted with both Langmuir and Freundlich adsorption isotherm model. Based on the experimental results, presented in (Figs. not shown), the parameters in the Langmuir and Freundlich adsorption isotherm model were determined and along with the regression coefficient R^2 presented in Table 3.

From table 3, the R^2 of the Langmuir isotherm model were higher than those of Freundlich isotherm model, which indicates the experimental data fitted to Langmuir isotherm model better for both RS and MRS, accordingly, the adsorbed metal ions were on the active sites in the form of mono-molecules.

Table 3: Adsorption isotherm parameters for (6 mmol/L) of Cu (II) on RS and MRS in aqueous solution.

Rice Straw	Langmuir parameters				Freundlich parameters		
	Q_{max} (mg/g)	K_L (L/mg)	R_L	R^2	n	K_F (mg/g)	R^2
RS	10.7	10×10^{-3}	0.72	0.98292	0.87	9772.4	0.97208
MRS	14.0	0.013	0.17	0.99026	1.2	1862.1	0.97368

3.8. Adsorption kinetic studies

The kinetics of Cu (II) adsorption was evaluated by applying three common models: the pseudo-first order [44], the pseudo-second order [45] and Weber Morris models [46] .The pseudo-first-order model was applied to depict the adsorption of liquid/solid system based on solid capacity [47]. The pseudo-second-order kinetic model was used for explaining the adsorption mechanism of rate-controlling steps [48] which can be expressed as follows (4, 5, 6, 7):

Pseudo-first-order $\log(q_e - q_t) = \log q_{e,1} - k_1 t$ ----- 4

Pseudo-second-order $\frac{t}{q_t} = \frac{1}{k_2 q_{e,2}^2} + \frac{t}{q_{e,2}}$ ----- 5

$h = k_2 q_{e,2}^2$ ----- 6

Weber Morris models $q_t = K_{int} t^{0.5}$ ----- 7

Where :

k_1 is the Lagergren adsorption rate constant (min^{-1}) .

k_2 is the pseudo-second-order adsorption rate constant ($\text{g}/(\text{mg h})$).

q_e and q_t are the amounts of Co(II) absorbed (mg/g) at equilibrium and time t .

h is the initial adsorption rate ($\text{mmol}/(\text{g min})$).

k_{int} is the intraparticle diffusion rate coefficient ($\text{g mg}^{-1} \text{min}^{1/2}$).

The parameters of two models were summarized in (Table not shown). As shown in Figures (9, 10), the values of R^2 for both RS and MRS higher in pseudo-second-order (0.99938 and 0.99878) showed better fitting results to the adsorption than the pseudo-first-order kinetic model (0.95721 and 0.98984). for this, the pseudo-second-order gave an excellent adaption to the data, which could be explained that the adsorption process of Cu(II) were mostly controlled by chemisorption behavior [49, 50].

Intra particle diffusion model (Weber Morris):

The adsorbate transport from the solution phase surface of the adsorbent particles may be controlled either by one or more steps, e.g. film or external diffusion, pore diffusion, surface diffusion and the adsorption on the pore surface, or a combination of more than one steps. In a rapidly stirred batch adsorption, the diffusive mass transfer can be related by an apparent diffusion coefficient which will fit the experimental sorption rate data. Generally, a process is diffusion controlled if it is dependent upon the role at which components diffuse towards one another. If the Weber, Morris plot of q_t versus $t^{0.5}$ gives a straight line passes through origin, then the adsorption process is controlled by intra particle diffusion only.

The mathematical dependence of fractional uptake of the adsorbate is obtained if the adsorption process is considered to be influenced by diffusion in the cylindrical and convective diffusion in the adsorbate solution. It is assumed that the external resistance to mass transfer surrounding the particles is significant only in the early stage of the adsorption. Our results indicated that, the straight line of the plots do not pass through origin, suggesting that

adsorption proceeds from boundary layer mass transfer across the interface to the intra particle diffusion within the pores of adsorbent [51]. This indicates the mechanism of Cu (II) adsorption by rice straw and its modified are complex and both, the surface adsorption as well as intraparticle diffusion contribute to the rate determining step.

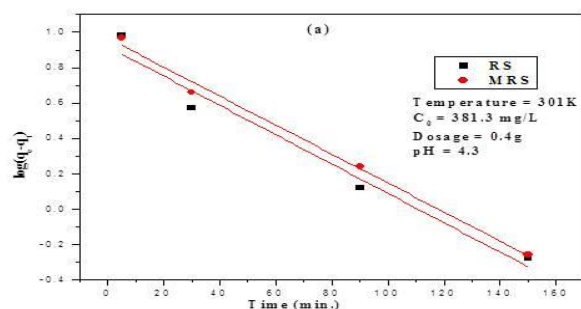


Fig. 9 Pseudo first order plot for the Cu(II) adsorption by RS and MRS.

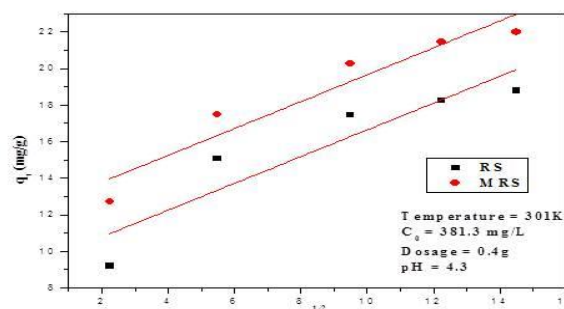
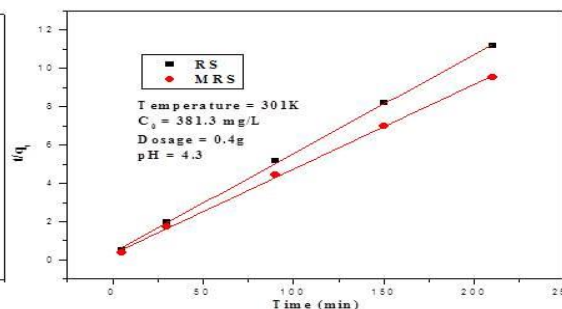


Fig. 11 Weber plot for the Cu(II) adsorption by RS and MRS.

3.9. Effect of temperature and Calculation Thermodynamic parameters

The amount of adsorption as a function of temperature was (Fig. not shown). Results indicate that the amount of Cu(II) adsorption increase for RS from 39.4% to 57.9% and for MRS from 46.2% to 62.3% when the temperature are in the range of 301–323 K, which might be due to the accelerated diffusivity of metal ions from the external layer into the micro pores of the rice straw with the increasing temperature [52].

The thermodynamic parameters such as ΔG^0 , ΔH^0 and ΔS^0 can better describe the adsorption mechanism. The relationship of them can be expressed as follows (8, 9):

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (8)$$

$$\Delta G = \Delta H - T\Delta S \quad (9)$$

Where ΔG^0 (kJ/mol) is adsorption free energy, ΔH^0 (kJ/mol) is adsorption enthalpy, ΔS^0 (kJ mol⁻¹K⁻¹) is adsorption entropy; R(8.314J/(mol K)) is universal gas constant, T (K) is temperature, K_d value is known as the distribution coefficient of the adsorbate, is equal to (q_e/C_e) . ΔH^0 and ΔS^0 were slope and intercept of the linear relationship of K_d versus $1/T$. The results of the adsorption of Cu (II) onto RS and MRS were calculated according to Eqs. (8,9). Table 4 shows the parameters of thermodynamics for RS and MRS, results indicated that ΔG^0 were all negative at different temperatures, its absolute values increased with the rise of temperature, which suggested that the adsorption of Cu (II) could happen spontaneously. ΔH^0 stayed positive values all the time, indicating that the reaction was endothermic and ΔS^0 also maintained positive values, which inferred that the adsorbent had good affinity for Cu (II) [53].

The values of the activation energy (E_a) and sticking probability (S^*) were estimated from the experimental data. They were calculated using a modified Arrhenius type equation related to surface coverage as expressed in equations (10, 11):

$$\theta = 1 - \frac{C_e}{C_0} \quad (10)$$

$$S^* = (1 - \theta) \exp\left(-\frac{E_a}{RT}\right) \quad (11)$$

The sticking probability, S^* , is a function of the adsorbate/adsorbent system under consideration and is dependent on the temperature of the system. The parameter S^* indicates the measure of the potential of an adsorbate to remain on the adsorbent indefinitely.

Table 4 also indicated that the values of $S^* \leq 1$ for RS and MRS, hence the sticking probability of the Cu(II) ion onto the two adsorbent systems are very high. The apparent activation energy (E_a) and the sticking probability (S^*) are estimated from the plot (Fig. not shown). The positive values of the apparent activation energy E_a also indicated that the higher solution temperature favors the adsorption process and also the adsorption process is endothermic in nature [54].

Table 4: Thermodynamic parameters for (6mmol/L) of Cu(II) on RS and MRS in aqueous solutions

Rice Straw	Temp.K	ΔG (kJ/mol)	ΔS (J/mol k)	ΔH (KJ/mol)	S^*	E_a (KJ/mol)
RS	301	-25.2	83.67	31.59	1.48×10^{-3}	15.13
	313	-26.2	-	-	-	-
	323	-27.0	-	-	-	-
MRS	301	-21.8	72.63	27.76	1.54×10^{-3}	14.84
	313	-22.7	-	-	-	-
	323	-23.4	-	-	-	-

Cost of Adsorbents

The production of rice straw in Egypt is about 4.7 million ton annually. The adsorbent material used in this study is generally available at a relatively cheap rate, 100 L.E. /ton for rice straw. The treatment of 1m^3 of wastewater with RS would cost approximately 31.25 L.E [55].

Conclusions

The adsorption properties of Cu^{2+} by untreated rice straw and alkali treated rice straw were examined in this experiment. The results obtained from the present investigation reveal that:

- The rice straw which is abundantly available and can be easily converted into good adsorbent by using simple method of activation, such as activation with alkali.
- Rice straw is an environmentally friendly potential adsorbent for toxic metals. This work examined the efficiency of

this adsorbent in removal of some metal ions from aqueous solution. The present investigation shows that the rice straw is an effective and inexpensive adsorbent for the removal of Cu (II).

- As the material is a waste product, the use of activated rice straw as adsorbent would also solve their disposal problem.
- The concentration of copper metal ions from 127.1 mg/L to 889.7 mg/L.
- It was found that the percentage removal of toxic copper ions was dependent on the dose of low cost adsorbent and adsorbent concentration.
- The contact time necessary for maximum adsorption was found to be 3.5 hours.
- The optimum pH range for toxic copper ions adsorption was 1.8– 4.6.

References

1. El-Sayed G.O., H.A. Dessouki, S.S. B. Ibrahim (2010). Biosorption of Ni (II) and Cd (II) ions from aqueous solutions onto rice straw, Chem. Sci. J. 9: 1-11.
2. Božić D, Gorgievski M, Stanković V, Štrbac N, Šerbula S, Petrović N (2013). Adsorption of heavy metal ions by beech sawdust Kinetics, mechanism and equilibrium of the process. Ecological Engineering 58: 202–206.
3. XU M Y, YIN P, LIU X G, TANG Q H, QU R J, XU Q (2013). Utilization of rice husks modified by organo multi phosphonic acids as low-cost absorbents for enhanced adsorption of heavy metal ions. Bioresource Technology 149: 420–424.
4. SAYGIDEGER S, GULNAZ O, ISTIFLI E S, YUCEL N (2005). Adsorption of Cd(II), Cu(II) and Ni(II) ions by *Lemna minor* L: Effect of physicochemical environment . Journal of Hazardous Material 126(1–3) : 96–104.
5. Jain C., M. Sharma (2002). Adsorption of cadmium on bed sediments of river Hindon: adsorption models and kinetics. Water Air Soil Poll 137: 1–19.
6. Pagana A., S. Sklari, E. Kikkinides, V (2008). Zaspalis, Microporous ceramic membrane technology for the removal of arsenic and chromium ions from contaminated water. Microporous Mesoporous Mater 110 150–156.
7. Al Abdulgader H., V. Kochkodan, N. Hilal (2013). Hybrid ion exchange–pressure driven membrane processes in water treatment. A review, Sep. Purif. Technol 116: 253–264.
8. Comstock S.E., T.H. Boyer (2014). Combined magnetic ion exchange and cation exchange for removal of DOC and hardness, Chem Eng J 241: 366–375.
9. Chérif M., I. Mkacher, L. Dammak, A.B. Salah, K. Walha, D. Grande, V.Nikonenko (2015). Water desalination by neutralization dialysis with ion-exchange membranes: flow rate and acid/alkali concentration effects. Desalination 361: 13–24.
10. Ali I., M. Asim, T.A. Khan (2012). Low cost adsorbents for the removal of organic pollutants from wastewater. J Environ Manag. 113: 170–183.
11. Ahmaruzzaman M., V.K. Gupta (2011). Rice husk and its ash as low-cost adsorbents in water and wastewater treatment, Ind. Eng. Chem. Res 50: 13589–13613.
12. Mohan D., K.P. Singh, V.K. Singh (2008). Wastewater treatment using low cost activated carbons derived from agricultural byproducts-a case study. J.Hazard Mater. 152: 1045–1053.
13. Osman H.E., R.K. Badwy, H.F. Ahmad (2010). Usage of some agricultural By-Products in the removal of some heavy metals from industrial wastewater. J Phytology 2(3): 51-62 : 2075-6240.
14. Sharma R., B. Singh (2013). Removal of Ni (II) ions from aqueous solutions using modified rice straw in a fixed bed column. Bioresour Technol 146 : 519–524.
15. Pan J., J. Jiang, R. Xu (2013). Adsorption of Cr (III) from acidic solutions by crop straw derived biochars. J Environ Sci 25 : 1957–1965.
16. Hameed B., M. El-Khaiary (2008). Kinetics and equilibrium studies of malachite green adsorption on rice straw-derived char, J. Hazard. Mater. 153: 701–708.
17. Rocha C.G., D.A.M. Zaia, R.V.d.S. Alfaya, A.A.d.S. Alfaya (2009). Use of rice straw as biosorbent for removal of Cu(II), Zn(II), Cd (II) and Hg (II) ions in industrial effluents. J Hazard Mater 166: 383–388.
18. Congcong S., C. Chen, T. Wen, Z. Zhao, X. Wang, A. Xu (2015). J.Colloid and Interf Sci 456: pp. 7-14.
19. Lichun F., C. Shuang, F. Liu, A. Li, Y. Li, Y. Zhou, H. Song (2014). J Hazard Mater 272: pp. 102-111.
20. Nabi S.A. , Mohammad Shahadat, Rani Bushra, A.H. Shalla, A. Azam (2011) .Colloids and Surfaces B: Bio interfaces 87 : 122–128.
21. Asif A. K., S. Shaheen; Solid State Sciences, 16 (2013), 158-167.
22. Johar N., Ishak Ahmad, Alain Dufresne (2012). Industrial Crops and Products 37 : 93–99.
23. El-Said A.G. (2010). Biosorption of Pb(II) Ions from Aqueous Solutions Onto Rice Husk and its Ash. Journal of American Science 6 (10).
24. Ahsan Habib, Nazrul Islam, Anarul Islam and A. M. Shafiqul Alam (2007). Removal of Copper from Aqueous Solution Using Orange Peel, Sawdust and Bagasse. Pak J Anal Environ. Chem Vol. 8, No. 1 & 2: 21- 25.
25. Asrari, Elham, Tavallali, Hossein, Hagshenas and Mahnoosh (2010). Removal of Zn(II) and Pb (ii) ions using rice husk in food industrial wastewater. J Appl Sci Environ Manage 14(4): 159-162.

26. Amarasinghe B., R. Williams (2007). Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater. *Chem Eng. J* 132: 299–309.
27. Chen S., Q. Yue, B. Gao, Q. Li, X. Xu (2011). Removal of Cr(VI) from aqueous solution using modified corn stalks: characteristic, equilibrium, kinetic and thermodynamic study. *Chem Eng J* 168: 909–917.
28. Sarı A., M. Tuzen (2008). Biosorption of total chromium from aqueous solution by red algae (*Ceramium virgatum*): equilibrium, kinetic and thermodynamic studies. *J Hazard Mater* 160: 349–355.
29. Anirudhan T., S. Jalajamony, P. Suchithra (2009). Improved performance of a cellulose-based anion exchanger with tertiary amine functionality for the adsorption of chromium (VI) from aqueous solutions. *Colloids Surf Physicochem Eng Aspects* 335: 107–113.
30. Bojic A, Purenovic M, Bojic D (2004). Removal of chromium (VI) from water by microalloyed aluminium based composite in flow conditions. *Water SA* 30: 353–359.
31. Low K.S., C.K. Lee, S.C. Liew (2001). Sorption of Cadmium and Lead from aqueous solution by spent frain, proce. *Biochem* 36: 1-5.
32. Taty-Costades V.C., H. Fauduet, C. Porte, A. Delacroix (2003). Removal of Cd(II) and Pb(II) ions, from aqueous solutions by adsorption onto saw dust of pinus sylvestris. *J Hazard Mater* 105:121-142.
33. Saeed A., M. Iqbal, M.W. Akhtar (2005). Removal and recovery of lead (II) from single and multi metal (Cd, Cu, Ni, Zn) solution by crop milling waste (black gram musk). *J Hazard Mater* 117: 65-73.
34. Goel J., K. Kadirvelu, C. Rajagopal V.K. (2005). Garg. Removal of lead (II) from aqueous solution by adsorption on carbon aerogel using a response surface method ological approach. *Ind Eng. Chem. Res* 44(7): 1987-1994.
35. N.N. Greenwood, A. Earnshaw (1997). *Chemistry of the Elements*, 2nd ed., Butterworth-Heinemann, Oxford: p. 1217.
36. Hyoe Takata, Tatsuo Aono, Keiko Tagami, Shigeo Uchida (2016). *Science of the Total Environment*. Volume 543 Part A, 1 February: Pages 315–325.
37. Paolo Trincherio, Scott Painter, Hedieh Ebrahimi, Lasse Koskinen, Jorge Molinero, Jan-Olof Selroos (2016). *Computers & Geosciences*. Volume 86 January: Pages 55-63.
38. Mary Jenish Barnabas, Surendran Parambadath, Aneesh Mathew, Sung Soo Park, Ajayan Vinu, Chang-Sik Ha; *Journal of Solid State Chemistry*, 2016, 233, 133–142.
39. Rout P.R., P. Bhunia, R.R. Dash (2014). Modeling isotherms, kinetics and understanding the mechanism of phosphate adsorption onto a solid waste: ground Burnt Patties. *J Environ Chem Eng* 2:1331–1342.
40. Chen Y., D. Zhang (2014). Adsorption kinetics, isotherm and thermodynamics studies of flavones from *Vaccinium bracteatum* Thunb leaves on NKA-2 resin. *Chem Eng J*.
41. Ghasemi M., M. Naushad, N. Ghasemi, Y. Khosravi-fard (2014). Adsorption of Pb (II) from aqueous solution using new adsorbents prepared from agricultural waste: adsorption isotherm and kinetic studies. *J Ind Eng Chem* 20: 2193–2199.
42. Hall K.R., L.C. Eagleton, A. Acrivos, T. Vermeulen (1966). *Ind Eng Chem Fundam* 5: 212–223.
43. Juang R.S., F.C.Wu, R.I. Tseng (1997). *Environ Technol* 18: 535–542.
44. Kim I., M. Saif Ur Rehman, J.-I. Han (2014). Fermentable sugar recovery and adsorption potential of enzymatically hydrolyzed rice straw, *J Clean Prod* 66:555–561.
45. Božić D., M. Gorgievski, V. Stanković, N. Strbac, S. Serbula, N. Petrović (2013). Adsorption of heavy metal ions by beech sawdust—kinetics, mechanism and equilibrium of the process. *Ecol Eng* 58: 202–206.
46. Moaaz K. Seliem, Sridhar Komarneni, Mostafa R. Abu Khadra (2016). *Microporous and Mesoporous Materials* 224 : 51-57.
47. S.A.M. Idris (2015). Adsorption, kinetic and thermodynamic studies for manganese extraction from aqueous medium using mesoporous silica. *J Colloid Interface Sci* 440: 84–90.
48. L. Zhou, Y. Wang, Z. Liu, Q. Huang (2009). Characteristics of equilibrium, kinetics studies for adsorption of Hg (II), Cu (II), and Ni (II) ions by thiourea-modified magnetic chitosan microspheres. *J Hazard Mater* 161: 995–1002.
49. Ghasemi N., P. Tamri, A. Khademi, N.S. Nezhad, S.R.W. Alwi (2013). Linearized equations of pseudo second-order kinetic for the adsorption of Pb (II) on pistacia atlantica shells. *IERI Procedia* 5: 232–237.

50. Zhou C., Q. Wu, T. Lei, I.I. Negulescu (2014). Adsorption kinetic and equilibrium studies for methylene blue dye by partially hydrolyzed polyacrylamide/cellulose nanocrystal nanocomposite hydrogels. Chem Eng J 251 : 17–24.

51. Srivastava V.C., M.M. Swamy, I.D. Mall, B. Prasad, I.M. Mishra (2006). Adsorptive removal of phenol by baggase fly ash and activated carbon equilibrium, Kinetics and thermodynamics. Colloid surf A: Physiochem Eng Aspects 272: 89-104.

52. S. Kizito, S. Wu, W.K. Kirui, M. Lei, Q. Lu, H. Bah, R. Dong (2015). Evaluation of slow pyrolyzed wood and rice husks biochar for adsorption of ammonium nitrogen from piggery manure anaerobic digestate slurry. Sci Total Environ 505: 102–112.

53. Yunhai Wua., Yiang Fanb, Meili Zhangb, Zhu Mingb, Shengxin Yangb, Aynigar Arkinb, Peng Fang (2016). Functionalized agricultural biomass as a low-cost adsorbent: Utilization of rice straw incorporated with amine groups for the adsorption of Cr (VI) and Ni (II) from single and binary systems. Biochemical Engineering Journal 105: 27–35.

54. B.Singh, S. K.Das (2013). Colloids and Surf. B: Biointer 107: 97– 106.

55. Nagwa Nawar (2013). Removal of Heavy Metals Fe^{3+} , Mn^{2+} , Zn^{2+} , Pb^{2+} and Cd^{2+} from Wastewater by Using Rice Straw as Low Cost Adsorben. Academic Journal of Interdisciplinary Studies Vol 2 No 6.