

Removal of Copper from spiked Aqueous Solution Using Activated Carbon of Rice Husk

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Received 21 November 2020; Received in revised form 12 August 2021

Accepted 15 September 2021; Available online 29 September 2022

ABSTRACT

Reprocessing materials as an adsorbent derived from agricultural waste like rice husk has been broadly applied to eliminate hazardous substances from the environment. The main objective of this research was to produce activated carbon from the agricultural waste of rice husk using activating agents like zinc chloride ($ZnCl_2$) (1:2 ratio) and to evaluate the efficiency of copper removal with lower dosage from spiked aqueous solution. The batch adsorption process was dependent on dose, pH, concentration and contact time. Within 10 min for the initial concentration of (1-5mg/L), the copper was removed absolutely (~100%) and the adsorption quantity was good (~20.45mg/g) using 0.25g/L of activated carbon for 100 mL aqueous solution at pH 6. But at the equilibrium state, the copper removal percentage was slightly decreased and obtained (97-100 %). Adsorption isotherm was well fitted with Langmuir ($R^2= 0.9946$) and Freundlich isotherm ($R^2= 0.9979$). Moreover, the kinetic isotherm was closely fitted by the pseudo-second-order model with the regression coefficient ($R^2\sim 1$). So, the activated carbon of rice husk can be used as an adsorbent to effectively reduce copper ion from wastewater.

Keywords: Adsorption; Copper; Rice husk; Wastewater treatment

1. Introduction

Water pollution is a very vital issue for developing countries to save their life. According to the World Health

Organization (WHO), more than three billion people will not have access to safe water by 2025. It observed that in fast growing countries near about 90%

wastewater is undertaken without treatment. Statistical report shows that the minimum 10% population in the world consumes food which is made with wastewater. Pure water is an important part of our life. Water is needed not only for human life but also used for various purposes like agricultural, plant, animal, household and environmental actions. About 90% of surface water is seawater in the oceans but only 3% is pure and just above two thirds of water is ice-covered. The remaining pure water is obtained in groundwater. Small fraction of freshwater is on earth.

Water pollution mixing toxic metals is very dangerous because of toxicity [1]. The toxic metals are distinctive due to their high density and persistence. There are twenty metals as heavy metals in the environment. Some of them are harmful due to their poisonousness and some are non-hazardous [2]. Lead, nickel, copper, cadmium, chromium are more toxic heavy metals. Heavy metals accumulate in the human body, leading to various diseases and disorders. Toxic metals can damage the liver, kidney, brain and central nervous system. Even abortion and neonatal death can be occurred by the severe attack of those metals. Copper can cause vomiting & diarrhea. Only two grams of this metal is enough for anemia. It can damage the liver that can cause death. It has both short & long term effects. In mammals, over exposure of this metal may destroy the kidney [3]. Fishes can also be affected by copper. Some metals were strongly attached with soil like lead and copper. Copper may be found in mushrooms and it can damage the stomach. The main sources of metals are battery manufacturing, ceramic and metal plating industries which produce large quantities of wastewater mixing metals [4].

The common methods used for wastewater treatment are restricted because of technical and financial barriers. Furthermore, it is mainly due to low concentration of toxic metals in aqueous

solution (<100 ppm). For removal of heavy metals from wastewater have some common methods such as ion exchange, adsorption, precipitation and membrane separation [5]. Among those processes, adsorption is one of the efficient methods to remove contaminants from wastewater [6]. The Adsorption process is famous because it reuses biological materials with their major advantages. There are some advantages such as low cost, high efficiency, renewability, minimization of chemical or biological sludge, easy regeneration of bio sorbents and possibility of metal recovery.

Recently, bio- sorption has become an economically popular method as agricultural waste due to their availability, cheap and recycling process [7]. Agricultural waste materials are cost effective adsorbents and easy to handle disposal problems. It can solve waste disposal problems by converting to activated carbon which is used most attractive adsorbents [8]. Natural products like the activated carbon from rice husk can be used as an effective adsorbent for purifying wastewater due to possess medium surface area and pore volume as well as high adsorption capacity with heavy metals. This type of agricultural waste fulfills two purposes such as firstly unusable waste is converted to efficient adsorbent and secondly it can solve wastewater treatment problems in many countries [9].

The two types of biomass are responsible for occurring adsorption methods. One of those is living biomass and another is non-living biomass. *Moringa oleifera*, coconut coir, and rice husk are used as a non-living biomass [10]. In contrast, fungi, yeast and microbial cells are used as a living biomass [11]. The activity of adsorbent depends on its pore volume and surface area. It can be used not only wastewater but also air and gas streams to eliminate contaminants [12, 13]. If the cheap adsorbents are applied, the treatment cost is reduced [14]. Adsorbent of

agricultural waste possess high porous structures [15]. It also contains a large surface area from 1000 m²/g to 2800 m²/g [16]. The quality of activated carbon relied on its pore size. There are three types of pore size according to IUPAC. They are: micro pores (when pore width < 2 nm), meso pores (when pore width 2 nm - 50 nm) and macro pores (when the pore width > 50 nm) [17].

The commercial activated carbon is used as powder and granular form but it is a costly process. Powdered form is applied to liquid media which are sizes of 15-25 µm. On the other hand, granular adsorbents are mostly applied for both in liquid and gas media. Those types of activated carbon can be used in medicine [18], pharmaceutical [19] and wastewater treatments [20].

Activated carbon derived from Agricultural wastes like rice husk, coconut coir have lignocellulosic compounds as major constituents. They also have other polar functional groups such as alcohols, aldehydes, carboxylic, ketones and ether groups [21]. These functional groups can bind toxic metals by donating electrons [22]. Most of the plants such as neem, rice, and *Moringa oleifera* have binding properties. The heavy metals chelation property of adsorbents can be developed by chemically activating agents like zinc chloride. It also can develop pore size and surface area of activated carbon. Activating agents such as sodium carbonate (Na₂CO₃), sulphuric acid (H₂SO₄), and potassium carbonate (K₂CO₃), zinc chloride (ZnCl₂), phosphoric acid (H₃PO₄) are commonly used to produce activated carbon by chemical activation [23]. These agents can inhibit tar improvement and decrease the volatile matter growth of impregnated precursors. The activating agents support the improvement of the carbon porosity through degradation mechanisms and dehydration [24].

2. Materials and Methods

2.1 Sample collection and preparation

Rice husk was collected from Mohammadpur, Magura, Bangladesh. The rice husk was sun dried for 6 hours then it was washed with distilled water to remove dirt from its surface and dried in an oven at 110 °C for 13 hours. The raw materials were reduced into smaller particle sizes using a mortar and pestle as well as a blender. The sample (100 g) was then chemically activated using a zinc chloride (10 % ZnCl₂) solution to soak (char with chemical 1:2 ratio) for 16 hours. Then the sample was dried in the oven at 110 °C for 12 hours. It was ground and sieved at 400 µm. Then the sample was kept in the desiccator for further use. The husk was placed in the furnace at 700 °C with heating rate of 10 °C/min for 60 min. During the carbonization process, purified nitrogen was flown. It was cooled to a normal temperature. This activated carbon sample was washed severally with distilled water. The carbonized sample was soaked in 500 mL 0.5M HCl for 1 hour due to removing CaO or mineral. The sample was washed repeatedly with distilled water for removing free acid. The washed sample was dried in the oven at 110 °C for 18 hours. These were then sieved with a sieve 400 µm. The produced activated carbon was stored in a polypropylene bottle. These prepared activated carbon was used for these experiments.

2.2 Instrumentation

Functional groups on the surface of adsorbents were determined using Fourier-transform infrared spectroscopy (PERKIN ELMER FTIR Model 1600, USA). The initial & final metal concentration of aqueous solution was obtained using Atomic absorption spectrophotometer (AAS-240 FS AA, USA). Micro porosity of the outer surface of adsorbents and pore size were obtained using Scanning electron microscope (SEM-HITACHI SU 6600, Japan) and Brunauer-Emmett-Teller (BET:

BELSORP-MINI, Japan). Water distillation (2108, GLF, Germany), pH meter (3510, Genway), Shaker (UK.), analytical balance (CP 2245, Sartorius, USA.), oven, furnace and blinder were used during this study.

2.3 Preparation of spike aqueous solution

All chemicals were analytical grade obtained from Merck, Germany. Standard solution and stock solution of metal (copper) was obtained by dissolving metal salt in deionized water. A 9.333 g of copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ > 99%) was dissolved in 1 L volumetric flask of water to make 1000 mg/L of metal salt solution as 1000 mg/L of stock solution. The working solutions were obtained by diluting the stock solutions. From the 1000 mg/L of stock solution, 1 mL, 2 mL, 3 mL, and 5 mL of salt separately were mixed with requiring 1000 mL of water to get 1 mg/L, 2 mg/L, 3 mg/L, and 5 mg/L of working solutions. Other chemicals are 0.5 M hydrochloric acid (HCl ~70%), 0.5 M nitric acid (HNO_3 ~70%), 1N sodium hydroxide (NaOH), 0.05 M sodium nitrate (NaNO_3 buffer), (10%) zinc chloride ZnCl_2 .

2.4 Adsorption experiments

This study was conducted by adding 0.25 gm/L activated carbon in 100 mL spiked aqueous solutions. Flasks with adsorbents were placed in a shaker at room temperature (25 ± 2 °C) with 200 rpm speed for 2 hours. The pH was controlled at 6 using 0.1N NaNO_3 buffer solution to get best adsorption capacity of adsorbents for this experiment but to observe the effect of pH of the solution were adjusted ranging from 2-8 by 0.1N (HCl & NaOH) solutions. Then after 10, 20, 40, 60 and 120 minutes the samples were taken and filtered with filter paper. They were analyzed using Atomic Adsorption Spectrophotometer (AAS). According to Eq. (2.1), the amount of adsorbate adsorbed on the adsorbent at any time, q_t (mg/g) was calculated and the

percent removal of adsorbate was evaluated as

$$q_t = (C_0 - C_e)V/W, \quad (2.1)$$

where C_0 and C_e (mg/L) are the concentrations of solution at initial and at equilibrium time, respectively. V is the volume of the solution (L) and W is the mass of adsorbent used (g).

$$\% \text{Removal} = (C_0 - C_e) \times 100 / C_0. \quad (2.2)$$

2.5 Adsorption equilibrium models

Adsorption isotherms are probably the best techniques to calculate the amount of adsorbate from solution. It can retain and remain in the solution after equilibrium. This also provides the design of adsorption systems. It expresses the external properties and attraction of the adsorbent for different pollutants. They can also be used to relate the adsorptive capabilities of the adsorbent for varieties of pollutants.

2.5.1 Langmuir isotherm

The Langmuir isotherm indicates that the adsorption procedure will only take place at specific homogeneous sites on the adsorbent surface. Basically, once the adsorbate is attached on the site. Therefore, no more adsorption can take place at that site. It relates the adsorption of molecules on a solid surface. This equation is valid for monolayer sorption onto a solid surface. It is concluded that the adsorption process is monolayered in nature. The isotherm indicates that monolayer adsorption might occur on the surface of the adsorbent created with homogeneous adsorption patches. The Langmuir equation is based on assumptions as stated by (Desta, & Lucia, 2013):

- i) Monolayer adsorption onto a surface containing a fixed adsorption site.
- ii) No shifting of adsorbate in the plane surface.

iii) Sorption stops as adsorption sites are filled.

The Langmuir isotherm equation is stated by

$$q_e = Q_0 K_L C_e / (1 + K_L C_e) \quad (2.3)$$

The linear form of Langmuir isotherm equation is given by Eq. 4

$$C_e/q_e = 1/Q_0 K_L + C_e/Q_0, \quad (2.4)$$

where C_0 and C_e are the initial & equilibrium concentration of adsorbate (mg/L) respectively. Other sides, q_e is the amount of solute bind on adsorbent (mg/g), Q_0 is the maximum binding ability of activated carbon (mg/g). The Langmuir adsorption constant is K_L (L/mg). The constant value can be determined from the linear plot of (C_e/q_e) versus C_e .

Dimensionless separation factor (R_L) can be defined as

$$R_L = 1/(1 + K_L C_0), \quad (2.5)$$

where R_L value suggested that the adsorption process to be unfavorable when ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$).

2.5.2 Freundlich isotherm

Adsorption can occur on a surface of adsorbents through a multilayer adsorption mechanism in accordance with the Freundlich isotherm. This isotherm is used for heterogeneous surface substances. The adsorption intensity of the adsorbent is calculated by this isotherm. The isotherm model is expressed by Eq. (2.6):

$$q_e = K_f C_e^{1/n}, \quad (2.6)$$

where at equilibrium, q_e & C_e is the amount of pollutant bind onto adsorbent (mg/g) and concentration of adsorbate (mg/L) respectively. Besides, K_f is the Freundlich constant, (mg/g) (L/mg). $1/n$ and n are the Freundlich heterogeneity factors. The equation can be expressed in the linear form by taking the logarithmic:

$$\log q_e = \log K_f + 1/n \log C_e. \quad (2.7)$$

From the equation, if the plot of $\log q_e$ versus $\log C_e$ is obtained, a straight line indicating Freundlich isotherm well fitted. Where the slope and intercept can be determined from the linear plot. The value of n can be a favorable when $1 < n < 10$.

2.6 Adsorption kinetics models

The adsorption kinetics shows the rate of adsorbate uptake on activated carbon which regulates the equilibrium time. In order to select the optimum conditions for adsorption, the adsorbate adsorb kinetics is important. The kinetic parameters are important to predict the adsorption rate. These parameters are as follows: the effects of initial concentration, contact time, pH and adsorbent dosage. In fact, kinetic models are useful in determining the significance of diffusion mechanisms inside the adsorbent particles. The adsorption techniques will be influenced by the physical and chemical characteristics of the adsorbent. The kinetic data can be well-fitted to either the pseudo-first or second order kinetic models.

2.6.1 Pseudo-first-order kinetic model

This model has been widely used for the prediction of adsorption kinetics. The model is defined as in Eq. (2.8):

$$dq_t/dt = k_1 (q_e - q_t). \quad (2.8)$$

Here, q_e is the amount of solute adsorbed at equilibrium, (mg/g), q_t is the amount of solute bind with adsorbent at time, (mg/g). Where k_1 is the rate constant of pseudo-first order sorption (1/h). Integrating equation (9) for the boundary conditions $t = 0$ to t and $q_t = 0$ to q_t , gives the following equation:

$$\log(q_e - q_t) = \log q_e - k_1 t / 2.303. \quad (9)$$

Elimination of the logarithm constant as in Eq. (2.10), below.

$$\log(q_e - q_t) = \ln q_e - k_1 t. \quad (2.10)$$

The graph of $\ln(q_e - q_t)$ and t provides a slope of k_1 and $\ln q_e$ as the intercept.

2.6.2 Pseudo-second-order kinetic model

In contrast, the pseudo-second-order equations forecast the performance over the whole range of adsorption. It is an adsorption mechanism being the rate controlling step. The pseudo-second-order equations at equilibrium can be expressed as Eq. (2.11):

$$dq_t/dt = k_2 (q_e - q_t)^2. \quad (2.11)$$

Here, q_e is the amount of solute adsorbed at equilibrium, (mg/g), q_t is the amount of solute bind of adsorbent at time, (mg/g). Where, k_2 is the rate constant of pseudo-second-order sorption (g/h.mg). Then integrating Eq. (2.12) for the boundary conditions $t = 0$ to t and $q_t = 0$ to q_t , provides the below equation:

$$1/(q_e - q_t) = 1/q_e + k_2 t. \quad (2.12)$$

That is integrated rate law for a pseudo-second-order reaction. Here, Eq. (2.13) can be rearranged to gain linear form:

$$t/q_t = 1/k_2 q_e^2 + t/q_e. \quad (2.13)$$

The linear graph of t/q_e Vs t provides $1/q_e$ the slope and $1/k_2 q_e^2$ as the intercept.

3. Results and Discussion

3.1 Proximate analysis

By this report of rice husk (precursor) defines the distribution of its elemental contents as shown in Table 1. It was observed that the volatile matter of 15.5% of rice husk were more than other contents. The moisture content of 1.3% of rice can be lost as a vapour from adsorbents during heating with high temperature. The ash content, fixed carbon and yields of the sample were 7.25%, 75.95% and 16.4 %, respectively. Fixed carbon content gives information of the amount of char formation in the thermochemical conversion process. It is the solid combustible residue that remains after the volatiles matter drive off. The higher the fixed carbon, the higher the char production in the thermochemical conversion process as a product yield. The yield is usually defined as final weight of activated carbon produced after activation, washing, and drying, divided by initial weight of raw material, both on a dry basis. From this data table obtained an outline about the properties and components of rice husk (precursor). So, chemically activating agents like zinc chloride was effective to remove inorganic elements of minerals from precursors.

Table 1. Proximate analysis of rice husk adsorbents.

Parameter	Value (%)
Volatile content	15.5
Moisture content	1.3
Ash content	7.25
Fixed carbon	75.95
Yields	16.4

According to an analysis report, the minerals are considered as contaminants such as Ca, Na, K, Al, N, P, Si, Zn and Fe. Due to purifying the prepared activated carbon and removing the contaminants, the acid solution is generally used during washing part and in further treatment. These inorganic elements could be eliminated from precursors of agricultural products with HCl, H₂SO₄, HF or ZnCl₂ treatment in order to diminish the ash content.

3.2 Characterization of activated carbon

ZnCl₂ altered the carbonization behavior of rice husk, converted the contained minerals into soluble salts and established skeletal pore structure at the pre-carbonization period. ZnCl₂ plays an important role in porosity development at different stages. When ZnCl₂ was introduced to the precursor during the impregnation process, the partial structure of rice husk was destroyed. Then, ZnCl₂ developed micro pores abundantly and reduced the formation of graphitized carbon during the activation phase. However, using the acid treatment, some of the minerals are removed from the structure and raise to the surface area and carbon porosity [25]. Therefore, acid treatment was confirmed to increase the surface area and porosity of activated carbon. Carbonization at 700 °C can develop basic microstructure of porosity. The developed pores are prone to be filled with tarry products which are produced during pyrolysis. The higher temperature of carbonization supports the removal of tarry and disorganized matter, thereby eliminating constrictions and forming a more accessible pore structure. Besides tarry products, mineral oxides were also present in the ash matrix which usually blocked the pores structures. The development of more surface area and pores in activated carbon-treated ZnCl₂ with acid solution is likely to be due to the elimination of impurities on the surface and in the pores. Activated carbon can contain mineral matter up to 15

% in the form of ash content, which clogs up the pores [26]. (Fig. 1) shows a plotted graph for the pore size distributions of rice husk activated carbon, based on these data. As can be seen from this plot, singular sharp peaks were detected in the range of 20 to 40 Angstrom (Å) (or 2 to 4 nm).

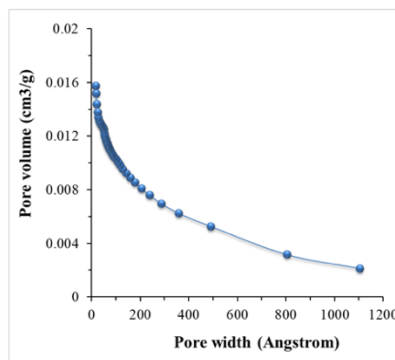


Fig. 1. Pore size distribution of rice husk.

About 75 % of the pores had diameters within the mesopores range (pore diameter range of 10 -180 Å) for rice husk. Hence, the activated carbon is a mesoporous material. This suggests the prepared activated carbon would be very absorptive to wastewater. In inert conditions, carbonization could yield a meso pore carbon of a very narrow pore size distribution. Carbon with narrow pore size distributions is stable in structure and could increase practical parameters such as BET surface area and V_0 total micro pore volume [27].

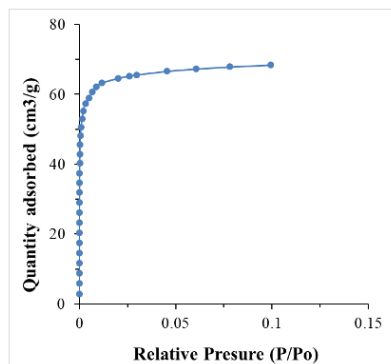


Fig. 2. Adsorption isotherm of rice husk.

Fig. 2 demonstrates the adsorption isotherms of rice husk. The shapes of the adsorption isotherm are a reflection of the pore size distribution in adsorbent samples. It can be suggested that the isotherms of rice husk resemble a combination of type I with prominent hysteresis loops of type H₄, which occur in the region of 0.02 to 0.08 P/Po. This displays the higher degree of meso porosity contained in carbons [28]. Fig. 2 shows a less steep Type I isotherm with a sharp “knee” form at the low relative pressure and a regular increase in nitrogen gas (N₂) adsorb at the higher pressure. The regular increase in N₂ adsorb occurred beyond P/Po > 0.02, thus presenting the heterogeneous micro porosity and growth of small size meso porosity. Zinc chloride treatment increased the adsorbed amount of nitrogen for rice husk in the region of 0 to 0.1 P/Po. Isotherms presented with a steep adsorption at very low relative pressures (P/Po = 0 to 0.02) characteristic of micro porous structures [29]. The hysteresis loop type H₄ considered the presence of mesoporous particles. Rice husk exposed the higher adsorption of the series in the low-pressure region. Acid treatment improved the quantity adsorbed at low relative pressures. Rice husk adsorbs almost more N₂, which indicates a higher surface area. The sloped-up plateau started at P/Po > 0.02. The increase in N₂ bind at the other pressures indicated the rise of micro pore diameter and development of meso porosity [29].

3.2.1 Surface morphology

The surface chemistry is a very important part of activated carbon for analyzing. Fig. 3 shows the SEM micrographs of the rice husk before and after adsorption under 1000x

magnifications. These micrographs presented the morphological changes of the carbon materials during carbonization and activation processes after adsorption. After carbonization was performed under inert conditions. Pore development in the char during pyrolysis was essential. It would increase the surface area and pore volume of the activated carbon after the activation process [30]. Only ZnCl₂ used for rice impregnated samples can have a better porous structure development. The BET surface area and pore volume of this activated carbon derived from rice husk were 271.85m²/g and 0.1217 cm³/g, respectively. The introduction of ZnCl₂ enlarged the difference between the morphology on the surface of the char and of the activated carbon. The reactions between ZnCl₂ and carbon took place due to the diffusion effect. In Fig. 3 for rice husk, more heterogeneous and irregular shape pore structures were filled up by copper. More pores were advanced and were closed to each other. The heat was carried into the molecules which can create more pores in the activated carbon [31]. Okman et al., 2014, [32] observed spongy-like structures with many small cavities in the grape seed based activated carbon which was impregnated with K₂CO₃. As can be observed in Fig. 3, the presence of small white particles of various sizes attached to the surface of the activated carbon. The white particles were believed to be the residues of zinc salt (from ZnCl₂). A similar finding was observed by [33] while making the activated carbon from banana peel. This indicates that the traces of zinc salts residues are present in the carbon matrix even though a serious washing procedure with the combination of HCl and distilled water was applied.

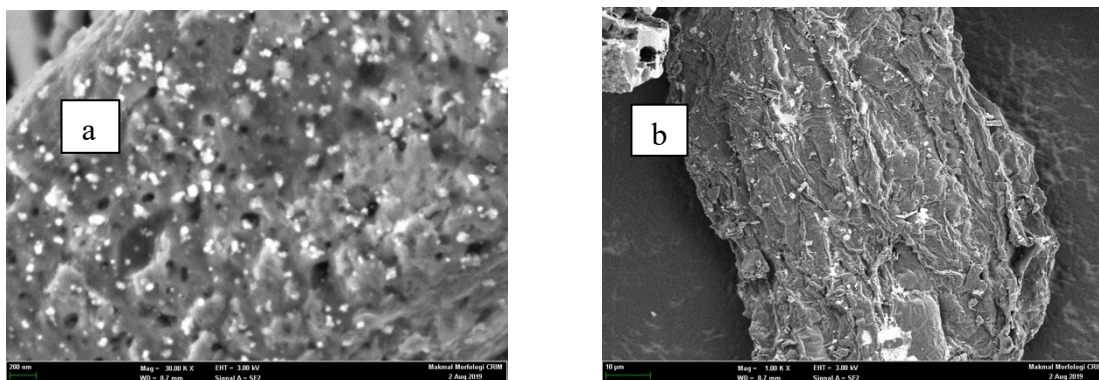


Fig. 3. SEM micrograph (a) before adsorption and (b) after adsorption of Rice husk.

3.3 Equilibrium studies

Fig. 4 shows an equilibrium curve of copper for the rice husk activated carbon. The comparison of adsorption capacity of different metals among our activated carbon and others (AC) derived from rice husk is shown in Table 2.

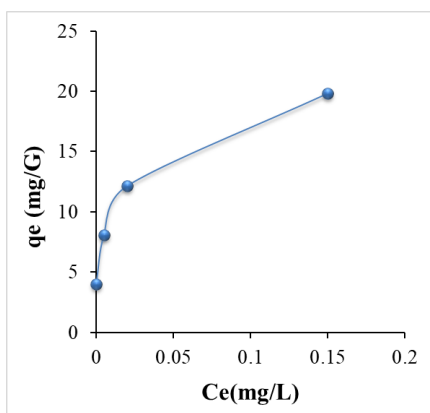


Fig. 4. Equilibrium plot for rice husk

The copper curve shows a concave downward shape due to high affinity between adsorbate and activated carbon. The contaminant metal was cationic form. The adsorption mechanism could be caused the result of ion exchange or electrostatic forces due to the presence of an oxygen-containing group (COOH) on the surface of adsorbents.

So, with increasing the oxygen containing group of adsorbents, the quantity of adsorbate also increased. The amount of adsorbate ranged from 3.98 mg/g to 20.45 mg/g within 10 mins for ranging initial concentration (1-5) mg/L of copper salt solution. It was observed where final concentration obtained zero ($C_f=0$) and after 120 min the quantity of adsorbate ranged from 3.98 mg/g to 19.84 mg/g, respectively.

Therefore, at 700 °C activation temperature and char : zinc chloride with ratio (1:2), the activated carbon showed optimum adsorptive capacity. The results showed a rapid uptake of adsorbate molecules onto the surface of the adsorbent during the first 10 minutes, and then slight desorption and slower uptake through to 120 minutes. The reason for this behavior is that the adsorptive site becomes loaded as molecules adhere to the surface of the carbon structure. The values however greatly depend on the equilibrium concentration of the effluent with the adsorbent. Fig. 4 shows that the equilibrium curve for Cu^{2+} adsorptive capacity of rice husk was more due to the use of zinc chloride as a chemical activating agent in this study.

Table 2. Comparison of adsorption capacity of different metals among our activated carbon and others (AC) derived from rice husk.

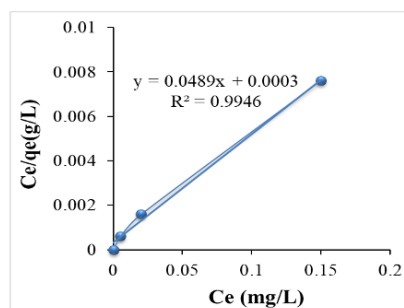
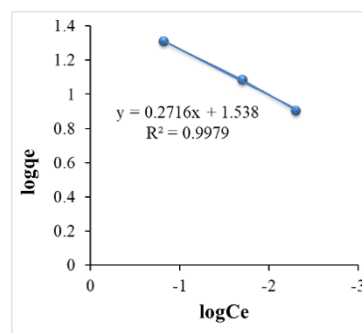
Adsorbents	Adsorbate	Adsorption Capacity (mg/g)	References
Rice husk (AC)	Cu (II)	29	[34]
Rice husk (AC)	Cu (II)	4.77	[35]
Rice husk (AC)	Cd (II)	11.12	[36]
Rice husk (AC)	As (III)	1.22	[37]
Rice husk (AC)	Ni (II)	8.86	[38]
Rice husk (AC)	Cu (II)	19.84	This article

3.4 Adsorption studies

Langmuir isotherm expressed monolayer of the metal ions are designed on adsorbent. The experimental q_{\max} for rice husk was found to be 20.45 for Cu comparable with theoretically calculated q_{\max} as given in Table 3. The higher value of K_L describes the affinity of the adsorbent to adsorb metal ions. The value of q_{\max} can also be considered as the total number of active sites of adsorbents for adsorption. It acts as a natural antioxidant like some other plants which were reported as natural sources of antioxidants [39]. The plot of $\log q$ against $\log C_e$ obtained the constant K_f and $1/n$. K_f indicates the strength of adsorption. A lower value of K_f designates more adsorption. Another constant, $1/n$, indicates the adsorption intensity. Data would be favourable when n value is ($1 < n < 10$). Rice husks were closely fitted with Langmuir isotherm and Freundlich isotherm. The mean adsorption energy (E) can describe adsorption properties. It can be calculated from the D-R isotherm model as shown in Fig. 7. If the values of $E < 8$ kJ/mol, it follows physical adsorption. When the value of E ranges from 8-16, it follows chemical adsorption. The adsorption energy values from Table 2 suggest that rice husk indicated a chemical adsorption for copper (rice, $E = 8.2$) metal ions.

The experimental data were fitted into Langmuir and Freundlich isotherm and represented in Figs. 5 and 6. For the Langmuir isotherm, the plot of C_e/q_e

against C_e showed a linear relationship with $R^2 = 0.9946$ of rice husk. For Freundlich isotherm, the plot of $\log q_e$ against $\log C_e$ also shows a linear relationship with $R^2=0.9979$ of rice. The Freundlich plot and the Langmuir plot were fitted favorably well with the isotherms of rice husk because the value of R_L obtained from slope was 0.0012 for rice [favorable when ($0 < R_L < 1$)]. For Freundlich isotherm, a value of n ($3.68 > 1$) for rice (favorable when $1 < n < 10$) obtained represents a favorable condition following the works of [40].

**Fig. 5.** Langmuir plot for copper adsorption of rice husk.**Fig. 6.** Freundlich plot for copper adsorption of rice husk.

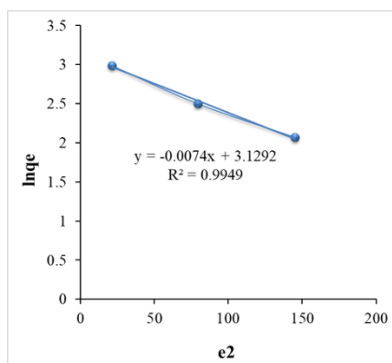


Fig. 7. Dubinin-Radushkevich plot for Copper adsorption of Rice husk.

Table 3. Comparison table for Langmuir, Freundlich and Dubinin-raduchkevich of rice husk activated carbon.

Heavy Metal	Langmuir model			Freundlich model			Dubinin-Radushkevich		
	R ²	q _{max} (mg/g)	K _L (L/mg)	R ²	1/n	K _f ((mg/g)(mg/L) ^{1/n})	R ²	q _{max} (mg/g)	E (kJ/mol)
Cu	0.995	20.45	162.97	0.998	0.272	1.54	0.99	22.87	8.2

According to [41], if the linearity was achieved and the line passes through the origin, it indicates the internal diffusion is the slowest step in the adsorption process. From Fig. 9, graph lines for copper of rice husk were not linear and did not pass through the origin. It is indicated that the adsorption process was controlled by film diffusion. From Fig. 8 this finding, the pseudo-second order favored the adsorption process with a regression correlation ($R^2 \sim 1$) for rice while the pseudo first order kinetic coefficient R^2 got 0.12. The correlation coefficients were well fitted for pseudo-second order contrast of first order and inter-particle diffusion. Therefore, the adsorption and kinetics of Cu^{2+} ions could be well approximated by the second order model. According to [41], acid-treated activated carbon can remove more pollutant from wastewater. From Table 3, it can be concluded that adsorption quantity (19.84) and regression correlation $R^2 \sim 1$ for rice husk were indicative of a good result.

3.5 Adsorption kinetic studies

All constant values of adsorption kinetics of rice husk for copper adsorption are shown in Table 4. There are significant differences for the adsorption quantity (q_e) values between experimental 19.84 and calculative values 1.64 of rice husk activated carbon, respectively, for pseudo-first-order equation. On the other hand, the experimental values (q_e) 19.84 and calculative values 19.80 of rice husk were close for pseudo-second-order models.

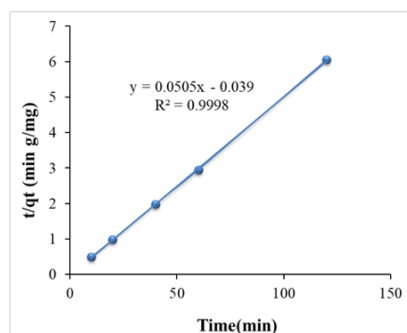


Fig. 8. Pseudo-second order of rice for copper kinetic adsorption.

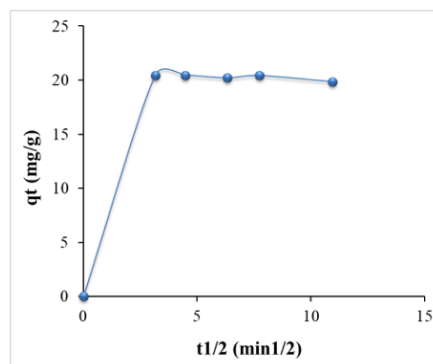


Fig. 9. Intraparticle diffusion for copper adsorption of rice husk.

3.6 Effect of Initial concentration

The effect of initial concentration for the removal of copper from wastewater using activated carbon rice husk is shown in Fig. 11. The initial concentration was set at 1, 2, 3, 5 mg/L. It can be seen from the

graph that increasing the initial concentration caused the removal percentage of copper from aqueous solution was decreased but the adsorption capacity of activated carbon also was increased.

Table 4. 1st, 2nd order and inter-particle diffusion constant values comparison of activated carbon.

Heavy Metal	q_{exp} mg/g	First Order		Second Order			Intra-Particle Diffusion		
		R^2	q_{qal} mg/g	k_1 (min^{-1})	R^2	q_{qal} mg/g	k_2 (g/mg/min)	k_d ($mg/l min^{-1/2}$)	R^2
Cu	19.84	0.12	1.64	0.004	0.999	19.80	0.065	0.073	0.72

Within 10 min for all initial concentration (5mg/L), the copper was removed completely (100%) using rice husk and the adsorption quantity was 20.45 mg/g. but after 120 min at equilibrium state, copper removal percentage was slightly decreased and 97% of rice husk for 5 mg/L concentration of copper. This type of pattern suggests that it can be possible due to monolayer formation of pollutant on the adsorbent surface [29]. From the result, it suggests that the removal percentage of rice husk for copper was greater due to possessing a larger surface area and pore volume in activated carbon. It was proved that metals can be removed from wastewater using activated carbon [42].

3.7 Effect of pH

These studies were conducted ranging pH 2-8 of solution. It shows that with increasing the pH values, the metal removal percentage also increased and at pH 6 the maximum removal percentage was obtained. The adsorption performance of activated carbon can be affected by the pH of solution. If the pH value was low, the outer surface of adsorbents collected many positive charges, which provided a greater static repulsion force. If pH is increased, the static repulsion forces reduced, and heavy metal adsorption improved. At pH lower than 5, Cu (II) mainly exists as Cu^{2+} but at a

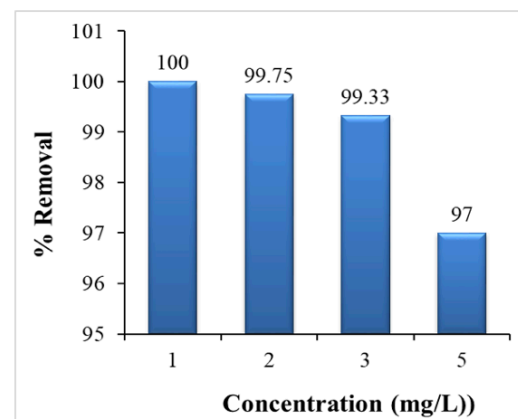
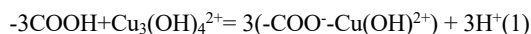


Fig. 10. Adsorption removal (%) for Copper of Rice.

higher pH range of 7-11 the predominant species of Cu (II) is $Cu_3(OH)_4^{2+}$. At around a pH of 6 there is a very small fraction of $Cu_2(OH)_2^{2+}$ present in the solution. The higher adsorption rate for rice husk activated carbon at a pH 6 can be explained by the mechanism of electrostatic force. At $pH > pH(zpc)$ (4.9) for adsorbents, the surface of the adsorbent is negatively charged which carries an electrostatic force between the metal cations $Cu_2(OH)_2^{2+}$ and active sites of adsorbent. At a lower pH, the adsorbent surface contains a positive charge and H^+ ion in the solution inhibits the approach of the metal cations and less adsorption occurs. On the other hand, the acidic carboxylic group on surface of adsorbents can conduct adsorption of metal

ions by an ion exchange mechanism which is shown in the equation below



It was concluded that at pH level 6, the removal of copper ion was better for rice husk due to containing $\text{Cu}_2(\text{OH})_2^{2+}$ form.

3.8 Effect of adsorbent dosage

The effect of adsorbent dosage was carried out ranging from 5 mg to 50 mg of activated carbon during removal of copper ion adsorption from 100 ml aqueous solution as shown in Fig. 12. This figure shows that with increasing the adsorbent dosage, the removal of metal ion also improved from about 16% to 100% for copper. After reaching 0.025 g of adsorbent dosage, the adsorption process also reached equilibrium state. The removal percentage of pollutants improved from aqueous solution with the improving dosage [43]. This can be obtained to have an available active part of adsorbents for complexation of heavy metal [44]. Further increasing the adsorbent dose cannot show significant improvement in removal adsorption. This may have occurred due to reaching the equilibrium state between binding adsorbate and unabsorbed adsorbate in the adsorption process.

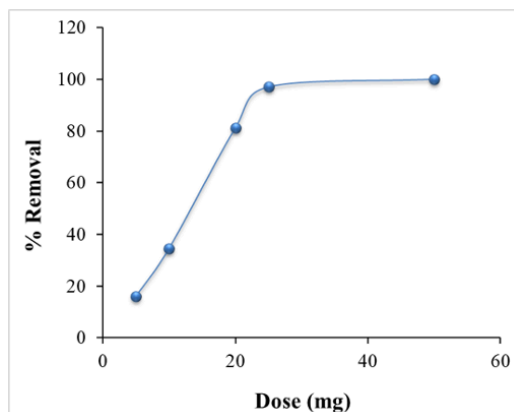


Fig. 11. Effect of dosage for copper adsorption of rice.

4. Conclusion

From the study of activated carbon, the adsorbent of rice husk proved effective for the removal of copper ion from spiked aqueous solution. It was found that the highest adsorption efficiency of activated carbon was 100% for concentration of solution (1 mg/L) and 97% for concentration of solution (5 mg/L) using 100 mL spiked aqueous solution at pH 6 while the suitable dosage was 0.25g/L. This research indicates that the use of ZnCl_2 as a well activating agent along with the pyrolysis under inert condition which played a vital role in producing natural husk into well-advanced porosity activated carbon. However, the prepared activated carbon contained deposits of ZnCl_2 and inorganic constituents on the surface. Several cleaning processes removed some of these deposits to develop porosity. The HCl treatment on the prepared activated carbon managed to reduce the remaining minerals. For this reason, it developed a highly porous carbon structure. These data proved that rice husk waste has potential as a precursor cheap and highly efficient activated carbon. The Langmuir and Freundlich isotherms models were closely fitted with the experimental data. On the other hand, a pseudo-second order isotherm with a regression correlation R^2 of 0.999 for Cu was well achieved. It was therefore concluded that zinc chloride as a chemical activating agent can be effectively used to produce activated carbon for removal of heavy metals like copper from wastewater.

Acknowledgements

This research was partially supported by Universiti Sains Islam Malaysia.

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