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Adsorptive removal of Cu (II) using activated carbon prepared from rice husk by ZnCl_2 activation and subsequent gasification with CO_2

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Abstract - Adsorption of Cu (II) onto rice husk based activated carbon (RHAC) was investigated in batch mode with variation in operational parameters such as initial Cu (II) concentration, contact time and adsorbent dosage. Langmuir and Freundlich isotherm models were used to test the adsorption data. Maximum monolayer adsorption capacity of Cu (II) onto RHAC was 112.43 mg/g at 298 K. The pseudo-first-order and pseudo-second-order equations were used to study the adsorption kinetic. It was observed that the adsorption of Cu (II) onto RHAC could best be described by the Langmuir and pseudo-second-order respectively for adsorption equilibrium and kinetic studies.

Index Terms - Activated carbon, Adsorption, Cu (II), Equilibrium; Kinetics, Rice husk

I. INTRODUCTION

Chemical substances such as heavy metals, organic and synthetic compounds generated from industrial activities have resulted in deterioration of the ecosystem due to improper discharge. Unlike other pollutants, heavy metal contamination in the environment poses serious health problems due to their accumulation in living tissues throughout the food chain as non biodegradable pollutants [1]. Sources of heavy metal pollution include textile, electroplating, painting, dyeing and surface treatment industry [2]. The commonly used traditional methods for the treatment of metal containing effluents are chemical precipitation and filtration, chemical oxidation or reduction, electrochemical treatment, reverse osmosis, solvent extraction, ion exchange and evaporation. Several disadvantages are associated with these methods, such as high cost, incomplete metal removal, low selectivity, high energy requirements and generation of toxic slurries that are difficult to eliminate [3]. In recent years, adsorption technique has been used extensively to remove toxic metals from aqueous solution. The adsorbents used in adsorption process were prepared from agricultural by-products, which are cheap and abundantly available. Agricultural wastes such as banana pith [4], mangosteen peel

[5], sawdust [6], sunflower stalks [7], groundnut shells [8] and wheat shell [9] have been used to remove metal ions from water solution.

The objective of this study was to investigate the possible use of chemically activated rice husk as an alternative adsorbent material for removal of Cu (II) ions from aqueous solution. Both Langmuir and Freundlich equations were used to fit the equilibrium isotherm. The adsorption data were also fitted into two simplified kinetic models; pseudo-first-order kinetic and pseudo-second-order kinetic models. The effects of initial Cu (II) concentration and adsorbent dose on the adsorption process were also studied.

II. MATERIALS AND METHODS

A. Material

Rice husk as precursor was obtained from the local rice processing mill in Kepala Batas, Penang, Malaysia. Stock solutions of Cu (II) was prepared by $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Merck, 99% purity) in deionised distilled water. Deionized water was used to prepare all solutions.

B. Preparation of activated carbon

Rice husk was washed with water and subsequently dried at 105°C for 24 h to remove moisture content. The dried RH was ground and sieved to a particle size of 1-2 mm before loading it in a stainless steel vertical tubular reactor placed in a tube furnace. Carbonization step was carried out at 400°C for 30 min under nitrogen (99.99%) flow at flow rate of 150 ml/min. The char produced was mixed with ZnCl_2 at weight ratio of 1:1. Deionized water was then added to dissolve all the ZnCl_2 pellets. The activation step was done using similar reactor as in carbonization step. Once the final activation temperature of 500°C was reached, the gas flow was switched from nitrogen to CO_2 at a flow rate of 150 ml/min for 1.5 h. The activated product was then cooled to room temperature under nitrogen flow. The sample was washed with hot deionized water and hydrochloric acid (0.1M) until the pH of the washed solution reached 6.5-7.

C. Adsorption studies

For batch adsorption studies, 0.3 g of adsorbent were mixed with 100 ml aqueous dye solutions of 50 mg/l initial concentration in 250 ml Erlenmeyer flasks. The mixture was

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agitated at 400 rpm at 30°C until equilibrium was reached. The concentration of Cu (II) solution was determined using a Hanna copper meter (model HI93702). The concentration retained in the adsorbent phase (q_e , mg/g) was calculated by using Eq. (1):

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (1)$$

where C_0 is the initial Cu (II) concentration and C_t is the Cu (II) concentration (mg/L) at any time, V is the volume of solution (L) and W is the mass of the adsorbent (g). Data analysis was carried out using correlation analysis employing least-square method and the sum of error squares (SSE) are calculated using Eq. (2):

$$SSE(\%) = \sqrt{\frac{\sum (q_{e,exp} - q_{e,cal})^2}{N}} \quad (2)$$

where N is the number of data points. Each experiment was conducted in triplicate under identical conditions to confirm the results, and was found reproducible (experimental error within 2%). The percentage removal at equilibrium was calculated as follows:

$$\text{Removal}(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (3)$$

where C_0 and C_e are the liquid-phase Cu (II) concentrations at initial state and at equilibrium (mg/l), respectively.

D. Adsorption kinetic models

The pseudo-first-order kinetic equation is expressed as [26]:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

where q_e and q_t are the adsorption capacities at equilibrium and at time t , respectively (mg/g). k_1 is the rate constant for pseudo-first order adsorption (min^{-1}). A plot of $\ln (q_e - q_t)$ against t at various concentrations and temperatures resulted in graphs with negative slopes. k_1 and q_e are calculated from the slopes and intercepts respectively.

The pseudo second order kinetic equation is expressed as [27].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

Plots of t/q_t versus t gave linear graphs from which q_e and k_2 were estimated from the slopes and intercepts of the plot.

E. Adsorption Equilibrium Models

Langmuir isotherm assumes monolayer adsorption into a surface containing a finite number of adsorption sites which

are uniform for adsorption with no trans-migration of adsorbate in the plane of surface. The linearized form of Langmuir adsorption model is expressed as [28]:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_o} + \frac{1}{Q_o b} \quad (6)$$

where C_e is the dye concentration in the solution at equilibrium (mg/l), Q_e is the Cu (II) concentration of C-RHAC at equilibrium (mg/g), Q_o is the monolayer adsorption capacity of RHAC (mg/g) and b is the Langmuir adsorption constant (lm/g). A plot of C_e/Q_e against C_e gave a straight line with a slope $1/Q_o$ and an intercept of $1/Q_o b$.

The linearized form of Freundlich model is represented by [29].

$$\log q_e = \frac{1}{n} \log C_e + \log k_f \quad (7)$$

where q_e is the amount Cu (II) adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/l); k_f and n are constants incorporating the factors affecting the adsorption capacity and the degree of non-linearity between the solute concentration in the solution and the amount adsorbed at equilibrium respectively. Plots of $\log q_e$ versus $\log C_e$ gave linear graphs.

F. Characterization of RHAC

The surface morphology of the samples was examined using a scanning electron microscope (JEOL, JSM-6460 LV, Japan). Proximate analysis was carried out using thermogravimetric analyser (Perkin Elmer TGA7, USA) and elemental analysis was performed using Elemental Analyzer (Perkin Elmer Series II 2400, USA). The surface area, pore volume and average pore diameter of the RHAC were determined by nitrogen adsorption isotherm at 77 K using Micromeritics ASAP 2020 volumetric adsorption analyzer. The surface area of the sample was determined using Brunauer-Emmett-Teller (BET) equation. The total pore volume was estimated to be the liquid volume of nitrogen at a relative pressure of 0.98.

III. RESULTS AND DISCUSSION

A. Effect of initial Cu (II) concentration and contact time

The adsorption capacity of Cu (II) increased with time and attained a maximum value at 45 min and thereafter, it reached a constant value indicating that no more Cu (II) ions were further removed from solution as shown in Fig. 1. By increased in initial concentration of Cu (II) solution from 25 to 200 mg/l, the amount adsorbed increased from 14.34 to 71.87 mg/g. This may be attributed to an increase in the driving force of the concentration gradient with the increase in the initial Cu (II) concentration in order to overcome all mass transfer resistance of Cu (II) ions between the aqueous and solid phases. Therefore, a higher initial concentration of Cu (II) ions may increase the adsorption capacity [10].

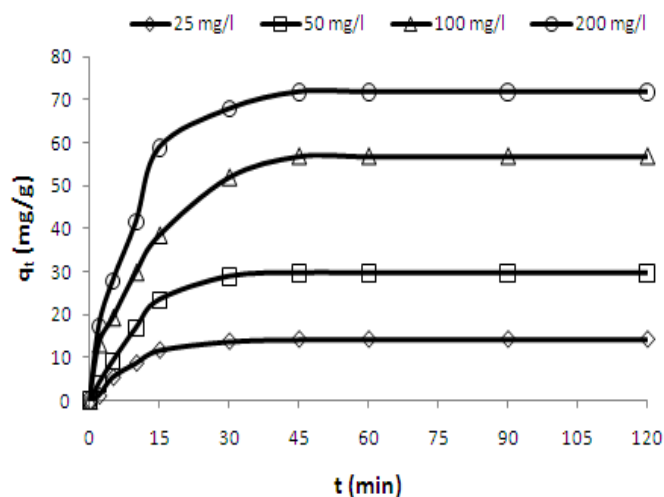


Figure 1: Effect of initial concentration on the adsorption of Cu (II) by RHAC.

The experimental data for the adsorption of Cu (II) onto RHAC with the kinetic models were used to evaluate the controlling mechanism of adsorption processes. Values of $Q_{e, \text{exp}}$, $Q_{e, \text{calc}}$, k_1 , R^2 and SSE (%) are given in Table 1 and Table 2 for pseudo first-order and pseudo first-order kinetic models, respectively. The higher the correlation coefficients (R^2) values and lowest SSE values confirmed that the adsorption data were well represented by pseudo-second-order kinetic for the entire adsorption process.

B. Effect of RHAC dosage on Cu (II) adsorption

Adsorbent dosage is an important parameter because it determines the capacity of an adsorbent for a given initial concentration of the adsorbate. The effect of adsorbent dosage was studied on Cu (II) ion removal from aqueous solutions by varying the amount of RHAC from 0.5 to 3.0 g/l, while keeping other parameters (agitation speed and contact time) constant. Fig. 2 showed that the amount of Cu (II) ion adsorbed increased from 19.98 to 84.02 mg/g for RHAC as the adsorption dosage was decreased from 3 to 0.5 g/l.

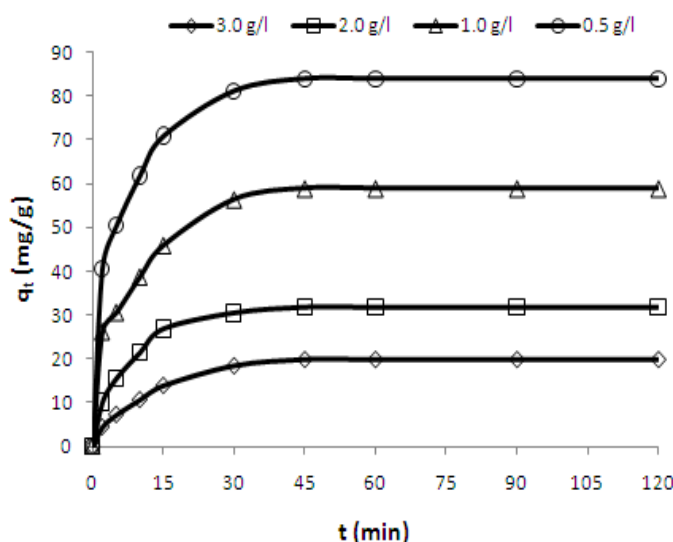


Figure 2: Effect of adsorbent dosage on the adsorption of Cu (II) by RHAC.

The decrease in unit adsorption with increase in the dosage of adsorbent was due to adsorption sites remaining unsaturated during the adsorption process [11]. The kinetic parameters calculated from the kinetic models are shown in Table 1 and 2. The experimental data fitted well with the pseudo second-order kinetic model ($R^2 > 0.99$).

TABLE 1
PSEUDO FIRST-ORDER KINETIC PARAMETERS

	$Q_{e, \text{exp}}$ (mg/g)	$Q_{e, \text{calc}}$ (mg/g)	k_1 (1/min)	R^2	SSE (%)
C_0 (mg/L)					
25	14.34	13.65	0.0296	0.94	0.345
50	29.65	34.56	0.0479	0.93	2.455
100	56.79	63.68	0.0576	0.92	3.445
200	71.87	81.43	0.0684	0.95	4.780
m_i (g/L)					
0.5	84.02	83.67	0.0511	0.92	0.185
1.5	58.89	65.63	0.0652	0.98	3.370
2.0	31.77	38.81	0.0785	0.96	3.520
3.0	19.98	27.32	0.0849	0.93	3.670

TABLE 2
PSEUDO SECOND-ORDER KINETIC PARAMETERS

	$Q_{e, \text{exp}}$ (mg/g)	$Q_{e, \text{calc}}$ (mg/g)	k_1 (1/min)	R^2	SSE (%)
C_0 (mg/L)					
25	14.52	0.0428	8.801	0.997	0.090
50	30.14	0.0049	4.308	0.996	0.245
100	57.31	0.0026	8.385	0.995	0.260
200	72.81	0.0017	8.781	0.998	0.470
m_i (g/L)					
0.5	85.35	0.0021	14.825	0.993	0.665
1.5	59.88	0.0035	12.138	0.996	0.495
2.0	33.42	0.0067	6.763	0.999	0.825
3.0	21.34	0.0089	3.553	0.998	0.68

C. Adsorption Equilibrium Studies

Values of adsorption isotherm parameters at 298 K are shown in Table 3. Comparing the R^2 values, the adsorption data fits Langmuir isotherm well compared to Freundlich isotherm. It shows the homogeneity of the material as well the possibility of monolayer adsorption of Cu (II). The values of n greater than one indicates that the adsorption is favorable.

TABLE 3
LANGMUIR AND FREUNDLICH ISOTHERM PARAMETERS

Langmuir isotherm			Freundlich isotherm		
Q_0 (mg/g)	b (L/mg)	R^2	k_f (mg/g)	n	R^2
112.43	0.0146	0.99	18.437	6.341	0.954

D. RHAC Characteristics

The BET surface area, total pore volume and average pore diameter of the prepared activated carbon were found to be 604.34 m²/g, 0.41 cm³/g and 2.75 nm, respectively. The average pore diameter of 2.75 nm indicates that the RHAC prepared was in the mesopores region. During the activation,

CO₂ gas molecules used as activating agent diffuse into the carbon structure thus increases the CO₂-carbon reaction, thereby developing more pores on the sample. From the SEM micrograph, the rice husk surface texture was undulating with very little pores as shown in Fig. 3(a). After activation process, pores were developed with homogeneous distribution on the RHAC surface (Fig. 3(b)).

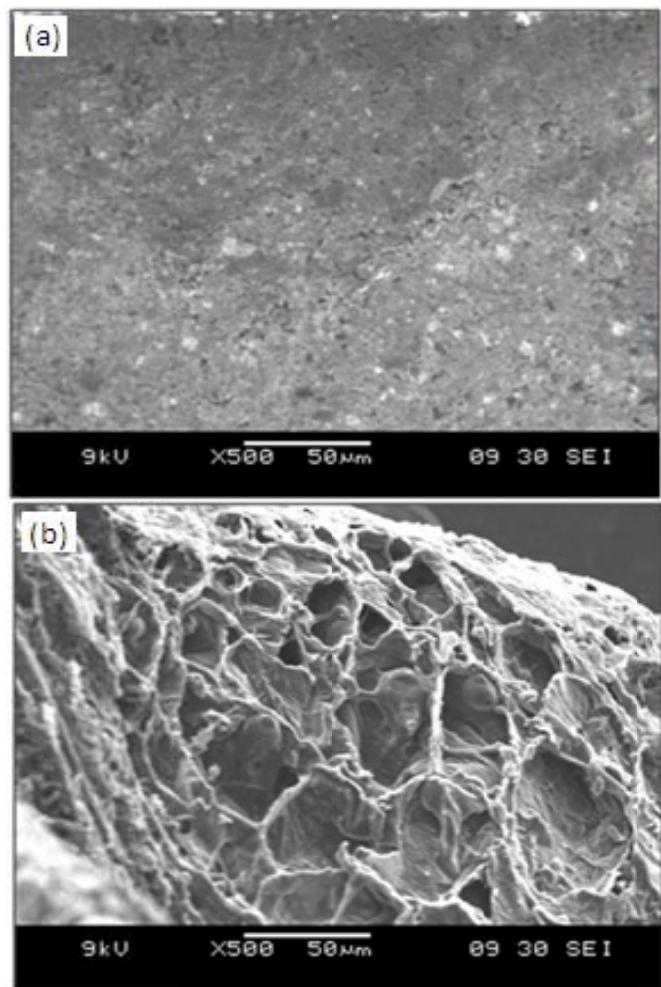


Figure 3: Scanning electron micrographs; (a) Rice husk, (b) RHAC (magnifications: 500x)

The results for proximate and ultimate analysis of the samples are tabulated in Table 4 and Table 5, respectively. The rice husk was found to be high in volatile matter and moderate carbon content, indicating the suitability of rice husk to be used as precursor for activated carbon preparation. After undergoing activation process, the volatile matter content decreased significantly whereas the fixed carbon content increased in activated sample.

TABLE 4
PROXIMATE ANALYSIS OF RICE HUSK AND RHAC

Sample	Proximate analysis (%)			Ash
	Moisture	Volatile	Fixed Carbon	
Rice husk	4.2	58.0	21.7	16.1
RHAC	2.1	19.9	63.2	24.8

Similar trend was observed for the elemental analysis where the carbon content increased up to 78.2% for RHAC. This was due to the pyrolytic effect at high temperature where most of the organic substances have been degraded and discharged both as gas and liquid tars leaving a material with high carbon purity [12]. The elemental analysis of RHAC indicated a reduction of hydrogen content to a value less than 5.0% which is due to the ruptured organic molecular chains after undergoing carbonization and physiochemical activation process [13]. Besides, there is also no significant change in nitrogen content in the raw rice husk and the RHAC prepared. This result is in agreement with the work of Tay et al. [14] in preparing activated carbon from waste biomass by chemical activation of K₂CO₃ and KOH.

TABLE 5
ELEMENTAL ANALYSIS OF RICE HUSK AND RHAC

Sample	Elemental analysis (%)			
	C	H	N	others
Rice husk	38.1	8.3	0.8	52.8
RHAC	78.2	4.7	0.6	16.5

The FTIR spectrum of RHAC is shown in Fig. 4. The main functional groups are O-H vibration stretching at bandwidth 3390-3842 cm⁻¹, C=C stretching in aromatics or carbonyl groups at bandwidth 1622-1640 cm⁻¹, C-H out-of-plane bending in benzene derivative vibrations at bandwidth 615-800 cm⁻¹, the skeleton C=C vibrations in aromatic rings at bandwidth 1458 cm⁻¹ and C-O-H twist broad at bandwidth 419-495 cm⁻¹, C-O-C stretching is attributed to esters (R-CO-O-R), ether (R-O-R) or phenol group at bandwidth 1000-1165 cm⁻¹ and C=O stretching from ketones, aldehydes or carboxylic groups at bandwidth 2375-2385 cm⁻¹. The FTIR spectra obtained were similar with those reported in studies carried out on commercial granular activated carbons prepared from cherry stones [15].

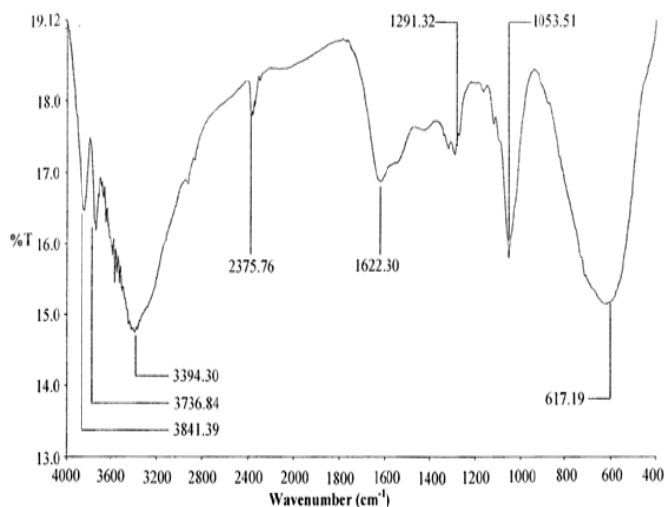


Figure 4: FTIR spectrum of RHAC

IV. CONCLUSIONS

The adsorption of Cu (II) on RHAC was found to be dependent on initial Cu (II) concentration, contact time and

adsorbent dosage. Adsorption process revealed that the initial uptake was rapid and equilibrium was achieved in 45 min. The optimum parameters for this study were 50 mg/l of Cu (II) concentration and 3 g/l of adsorbent dosage. Experimental results indicated that the pseudo-second-order reaction kinetic provided the best description of the adsorption data. Isothermal study indicated that adsorption data correlated well with Langmuir isotherm model. This study demonstrated that RHAC could be used as an effective adsorbent for the treatment of wastewater containing Cu (II) ions.

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