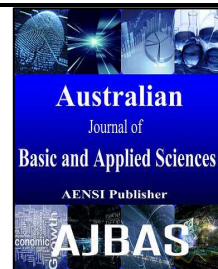




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Rice Husk Derived Activated Carbon for Removal of Zn^{2+} from Aqueous Solution

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ABSTRACT

Background: Rice husk (RH) is one of the agricultural wastes which has a potential as a precursor to prepare activated carbon (AC). It was found that rice husk activated carbon (RHAC) shows good performance for the removal of Zn^{2+} from aqueous solution. **Objective:** This work focuses on characterization of AC produced from RH by using Scanning Electron Microscope (SEM), Fourier transform infrared (FTIR) and N_2 -adsorption analyzer. An attempt was made to study the factors affecting the adsorption of Zn^{2+} from aqueous solution using RHAC such as adsorbent dosage, initial metal concentration and contact time. **Results:** It was shown that adsorption capacity of metal increased up to 85%. **Conclusion:** As conclusion RHAC is a suitable adsorbent for adsorption of Zn^{2+} from aqueous solution. The results obtained also showed that RHAC is an attractive alternative for cheap precursor of AC. RHAC carbonized at 700°C showed better evolution and development of pores as compared to the AC carbonized at 500°C and 600°C.

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INTRODUCTION

Water pollution caused by heavy metals has been a major concern due to their toxicity to many life forms. Heavy metals including silver (As), copper (Cu), nickel (Ni), chromium (Cr), zinc (Zn) and cadmium (Cd) must be removed to a certain levels to meet discharge requirements. Heavy metals can be found in a variety of industries like mining, metal manufacturing and electroplating, dye and paint industry, refinery and photochemicals, as well as fertilizer and pesticides industry (K.M.Y. Nasehir 2010). Therefore, it is mandatory to remove or reduce their concentrations to acceptable levels before being discharge to the environment. The World Health Organization (WHO) suggested a maximum allowable concentration of Zn(II) in drinking water to be 1.5 mg/l (W.M. Antunes 2003). Among the commercial method used to treat wastewater such as chemical precipitation, electrolysis, and ion exchange, adsorption was found to be highly effective, cheap and easy to adapt. Adsorption process as a mean for wastewater treatment has received considerable interest during recent years. In most cases, activated carbon has been used as an adsorbent in industrial wastewater treatment. Its capability to adsorb heavy metals from

wastewater is due to the porous surface structure and high surface area (F.T. Mohd 2011).

Biomass is one of the raw materials commonly used to produce activated carbon. One of the potential biomass that can be utilized as a precursor to produce AC is RH. RH is a waste product from agriculture activity in most countries in Asia and Malaysia. Generally RH consist more than 60% of silica, less than 40% of carbon and mineral composite (A. Dongmin 2011). RH is abundance and only a small part is used as fuel. This creates an environmental problem due to the raising of RH from year to year. Therefore, preparing AC from RH is a one of the valuable material would reduce the disposal problem (L. Tzong-Horng 2009).

MATERIALS AND METHODS

Materials:

RH was obtained from Bernas Rice Factory at Semanggol, Perak. RH was washed using tap water to remove any soil and sand, then it was dried at 90°C for 16 hours (A. Boonpoke 2011). The dried RH was crushed and sieved to obtain the size in the range of 65-300 µm.

Chemical treatment of RH:

The activation process was carried out by soaking 10g of RH with 1M NaOH as activating agent at ratio RH: NaOH of 1:4 at 90 °C for 16 hours. The treated samples were rinsed until neutral pH 6-7 and dried in oven at 90 °C for 16 hours and stored in air tight container.

Preparation of RHAC:

RH treated with NaOH was carbonized at 500, 600 and 700°C in tube furnace under nitrogen flow with heating rate 20°C/min for 1 hour. Activated samples were rinsed with 50% HCl and hot distilled water until neutral (pH 6-7). Then dried in oven at 90 °C for 24hours and stored in airtight container.

Characterization Techniques:

The RRH and RHAC obtained before and after the activation are measured by SEM (model LE01430VP), FTIR and N₂-adsorption analyzer. The yield of RHAC is determined using Eq. 2 (L. Tzong-Horng 2009)

$$\text{Yield (\%)} = \frac{\text{mass of activated carbon}}{\text{mass of dried precursor}} \times 100 \dots\dots (\text{Eq. 2})$$

Adsorption studies:

Table 1: Yield of RHAC.

Carbonization temperature (°C)	Yield (%)
500	47.6
600	41.9
700	39.5

The common activating agent used to produce ACs is NaOH, as it would remove silica by forming sodium silicate. This sodium silicate can easily be removed by washing with distilled water due to its high solubility in water. (J. Diaz-Teran 2003, Y.P Guo 2003, A. Perrin 2004, M.A. Lillo-Rodenas 2004, K.Y. Foo 2011). Thus, in this study, NaOH was selected as an activating agent and effect of activation temperature on development of pores was first studied after samples were treated with NaOH.

Table 2 shows textural properties of RHAC prepared at different activation temperatures for 60 mins. The surface area and pore volume increases with increasing temperature from 500 to 700 °C. At temperature 500 °C, the surface area is low because

Table 2: Textural characteristic of RHAC at different activation temperature.

Temperature	500°C	600°C	700°C
BET surface area (m ² /g)	646.0	674.0	890.0
Langmuir surface area (m ² /g)	938.6	973.1	1290.7
Total pore volume (cm ³ /g)	0.3784	0.3517	0.4666
Average pore diameter (nm)	2.24	2.17	2.09

According to the IUPAC classification (K.Y. Foo 2011) the AC prepared from RH with NaOH activation show types I isotherm which shows the characteristics of microporous and mesoporous structures (L. Tzong-Horng 2009) .**Fig. 1** shows the

Adsorption studies were conducted in 250 ml Erlenmeyer flasks containing 0.1-0.5 g AC and a 25 ml solution containing Zn²⁺ with known concentration (10-80 ppm). All the flasks were placed in water bath shaker at shaking speed of 180 rpm. The samples were filtered using filter paper and the residual of Zn²⁺ in aqueous solution was analyzed using Atomic Adsorption Spectrometer (AAS, model AA6680). The Zn²⁺ removal was calculated using Eq. 1.

$$\text{Removal of Zinc (\%)} = \frac{C_o - C_f}{C_o} \times 100 \dots\dots (\text{Eq.1})$$

Where C_o is initial metal concentration and C_f is final metal concentration.

RESULTS AND DISCUSSION

Characterization of RHAC:

The treated RH was carbonized at 500, 600 and 700°C to form RHAC. **Table 1** shows the yield of RHAC where yield decreases as increasing temperature. This is because at higher temperature, more volatile component in the precursor was released and leads to decreasing an activated carbon (F.T. Mohd 2011),(L. Tzong-Horng 2009)].

the pore structure has not properly developed and it was proved that only small reaction occurred between precursor and activating agent (L. Lin 2013). The surface area increases at higher temperatures i.e at 600 and 700°C. It was reported by other researchers (L. Lin 2013) that the maximum surface area of AC prepared from rice husk treated with NaOH was obtained at carbonization temperatures between 700 to 800°C. It is shown in this study that activation temperature of 700 °C gives the maximum surface area and total pore volume are 890 m²/g and 0.47 cm³/g, respectively. This is because of combination effect of the internal heat and pores widening (L. Tzong-Horng 2009).

effect of the activation temperature on the nitrogen adsorption-desorption isotherms of RHAC carbonized at 500, 600, and 700 °C . RHAC carbonized at 700 °C shows the highest values capacities of nitrogen adsorption. When activation

temperature was increased from 500 to 700 °C, it was shown the broad knees isotherms. This result is similar to the previous study which reported AC carbonize at temperature of 500-700 °C produced broad knees isotherms (L. Tzong-Horng 2009). The pores are widened and the pore size distribution

becomes broad due to increase in the adsorbed volumes. This shows that development of the pore structure of AC strongly depends on the activation temperature. In this study, 700 °C is the optimum temperature for activation of RH.

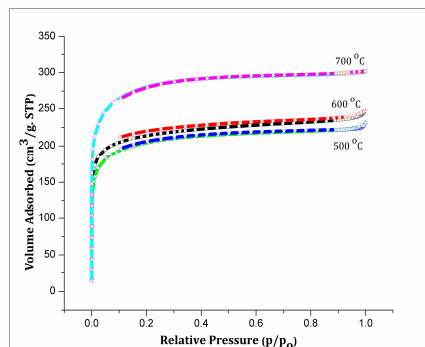


Fig. 1: Nitrogen isotherm of RHAC.

Based on **Fig. 2**, it was shown the RHAC contain majority of mesopores and micropores (< 2nm).

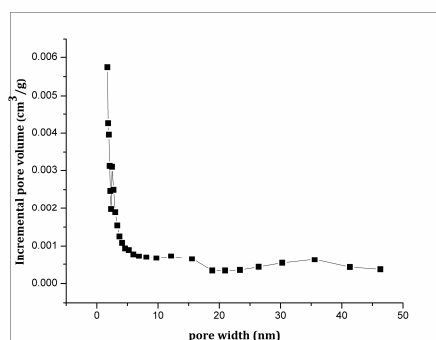


Fig. 2: Pore size distribution of RHAC carbonize at 700 °C.

RHAC was analyzed using Scanning Electron Microscope (SEM, model LE01430VP) to study the surface morphology between RRH and RHAC. From **Fig. 3** it can be seen that the surface of RRH was rough, uneven, and undulating. Pre-treatment of RH with NaOH give significant effect to the surface area and pore development. NaOH also can break down the lignin and mineral components in the RH during the activation process. The treatment of RH with NaOH leads to better pore development in the activated carbon because of reaction between silica and NaOH. This is lead to the formation of sodium silicate which is it can easily dissolved in water. NaOH as activating agent can enters the inner surface of carbon and this could increase the surface area and pore volume (Tzong 2004, J.W. Shao 2009, N.S. Awwad 2010)].

Fig. 4 shows the surface morphology of RHAC carbonized at 700 °C. It can be seen that more uniform pores were developed after carbonization at 700 °C. Formation of pores occurs after

carbonization due to the termination of non-carbon elements and volatile matters (L.A. Rahman 2004). High surface area and porous structure of RHAC come from these well-developed pores (L. Xuegang 2011). This also proved by other researchers which stated that formation of pores would give good adsorption of metal ions because metals ions would be trap in the pores structure (F. Qinggi 2004).

Fig. 5 shows the FTIR spectrum of RRH and RHAC respectively. A broad band in the region 3396 cm^{-1} may be assigned to O-H hydroxyl groups (Y. Guo 2007). The new peak at 2921 cm^{-1} in spectrum of RRH is C-H vibrations of aliphatic carbon or can also be attribute to $-\text{CH}_2$ or $-\text{CH}_3$ deformation (L. Tzong-Horng 2009),(V.C. Srivastava 2006),(A. Mubeena 2010)..

After carbonizing the RH in a N_2 atmosphere at 700 °C, most of peaks disappear due to the decomposition of volatile matter. Activation of RH with NaOH shows most of the bands disappear completely due to the removal of ash in carbons. The

removal of ash in carbon was also reported in previous study (L. Tzong-Horng 2009).

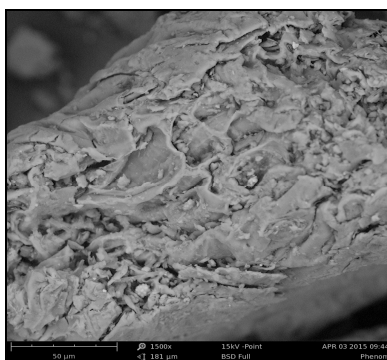


Fig. 3: SEM micrographs of RRH.

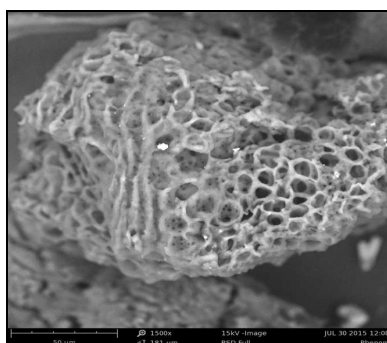


Fig. 4: SEM micrographs of RHAC carbonized at 700 °C.

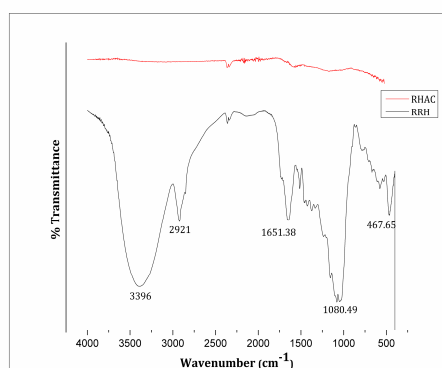


Fig. 5: FTIR spectrums of RRH and RHAC.

Removal of Zn^{2+} :

1) Effect of adsorbent dose (m):

The effect of adsorbent dosage on the Zn^{2+} uptake is shown in **Fig. 6**. Adsorbent dosage was varied from 0.02 to 0.10g. The figure shows the adsorption of Zn^{2+} increases with increasing of adsorbent dosage start 0.08 to 0.12 g. The percent removal increase up to 89 % at 0.10 g and very small increase until 0.12 g of adsorbent.

2) Effect of initial metal ion concentration:

The effect of initial metal concentration on Zn^{2+} removal at adsorbent dosage (0.1g 25ml⁻¹), pH (6.5) and stirring speed of 180 ppm at $27 \pm 1^\circ C$ is shown

in **Fig. 7**. The removal of Zn^{2+} increases with increasing initial metal concentration until it reach a maximum value at 80 ppm and it remains constant until 100 ppm. At low concentration, the ratio of available surface to the initial metal concentration is low. Thus, the removal metal ions are low. When initial metal concentration increases, the ratio of available surface to the initial metal concentration is higher, hence the percentage removal becomes higher. Therefore, an increase in initial concentration of Zn^{2+} causing the adsorption uptake of Zn^{2+} also increases. The maximum Zn^{2+} removal at 80 ppm is 90%. This result shows that, the removal of Zn^{2+} is

influence by the initial metal concentration (B. Manjeet 2009).

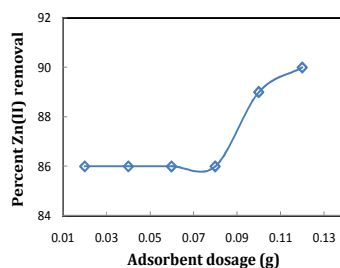


Fig. 6: Effect of adsorbent dosage on the removal of Zn²⁺ by RHAC carbonized at 700 °C.

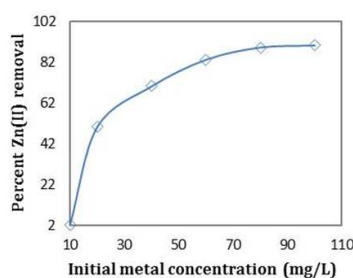


Fig. 7: Effect of initial metal concentration on the removal of Zn²⁺ by RHAC carbonized at 700 °C.

3) Effect of contact time:

The relationship between contact time and the removal of Zn²⁺ from aqueous solution using RHAC is shown in **Fig. 8**. The effect of contact time was studied at temperature 37 °C for 80 min. At the first 40 min, the removal of Zn²⁺ is 84 %, but further increase in contact time gradually decreases the Zn²⁺

removal due to the desorption of Zn²⁺ from the AC surface (E. Bernard 2013), but after 60 min the Zn²⁺ removal approached equilibrium until 80 min. This experiment shows that different contact times give different percent removal of zinc ion to attained equilibrium.

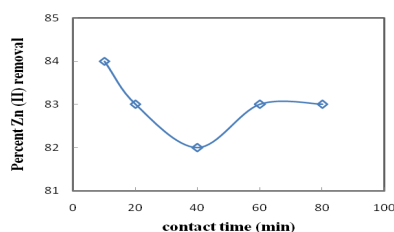


Fig. 8: Effect of initial contact time on the removal of Zn²⁺ by RHAC carbonized at 700 °C.

Conclusion:

As conclusion, RHAC is a suitable adsorbent for the removal of Zn²⁺ from aqueous solution. RHAC shows high potential as an attractive alternative precursor for the preparation of AC. RHAC carbonized at 700 °C showed better evolution and development of pores as compared to the ones carbonized at 500 and 600 °C.

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