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Acidically Prepared Rice Husk Carbon for Adsorption of Zn(II) from Aqueous Solution

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Abstract: The aim of the study was to prepare potentially cheaper carbon for the adsorptive removal of Zinc [Zn(II)] from aqueous solution. The adsorption capacity of the prepared carbon to remove Zn(II) from aqueous solution was tested and adsorption mechanism was investigated. Rice husk carbon was prepared by acidic treatment of rice husk. The Acidically Prepared Rice Husk Carbon (APRHC) was characterised in terms of surface area, micropore area, micropore volume, average pore diameter and surface morphology. Adsorption of Zn(II) by APRHC was examined. The influence of operating parameters, namely, pH, initial concentration, contact time and adsorbent dose on adsorption of Zn(II) by the APRHC was evaluated. Batch adsorption tests showed that extent of Zn(II) adsorption depended on initial concentration, contact time and pH. Equilibrium adsorption was achieved in 60 min, while maximum Zn(II) adsorption occurred at pH 3. Langmuir and Freundlich isotherms were studied and the equilibrium adsorption data was found to fit well with the Freundlich isotherm model. Langmuir constants Q° and b were 44 and 0.06 and Freundlich constants K_f and 1/n were 7.31 and 0.38, respectively. Adsorption of Zn(II) by APRHC followed pseudo-second-order kinetics. Being a low-cost carbon, APRHC has potential to be used for the adsorption of Zn(II) from aqueous solution and wastewater in developing countries.

Key words: Adsorption, rice husk carbon, Zn(II), isotherm, kinetics

INTRODUCTION

Heavy metals discharge to the environment has become a point of attention for many researchers due to their toxic and carcinogenic nature. Sources of heavy metals can be natural (such as volcanic activity and weathering of rocks) or anthropogenic (such as electroplating and metal finishing industries, metallurgical industry, tannery, chemical manufacturing, mine drainage, battery manufacturing and landfills leachates). The effluents from these sources contain Zn(II) along with other toxic metals such as chromium, lead, cadmium, nickel, mercury and copper. Zn(II) is an essential trace element for humans and takes part in a number of enzymatic reactions. When concentration of Zn (II) increases above a limit (e.g., the threshold limit value (TLV) for Zn(II) in drinking water is 3 mg L^{-1}), it becomes toxic to man, animals and plants life; causing carcinogenesis, mutagenesis and teratogenesis as a result of its bioaccumulation (Salim *et al*., 2003; ATCDR, 1993). Based on Malaysian Drinking Water Quality Standards, the maximum acceptable limit of Zn(II) is 3 mg L^{-1}, while WHO recommended as 5 mg L^{-1}.

In order to safeguard public health, water and wastewater containing heavy metals must be treated. Several techniques have been suggested for treatment of wastewater containing heavy metals. These include precipitation, coagulation, complexation, ozonation, ion exchange, electroplating and electrodialysis. The problems associated with these techniques are high initial and operational costs, high reagent and energy requirement and the generation of toxic sludge containing heavy metal ions or waste products, which require proper disposal (Volesky, 1990; Pitsari *et al*., 2013).

Adsorption is one of the most effective techniques for the removal of various pollutants including heavy metals from wastewater. Activated carbon is the most widely used adsorbent but the high price of activated carbon limits its use on a large scale (Isa *et al*., 2008). Hence, there is a need to develop low-cost adsorbents that are effective for adsorptive removal of heavy metals. Rice husk is an agricultural waste. It consists of cellulose (32.23%), hemicelluloses (21.34%), lignin (21.44%) and mineral ash (15.05%) (Rahman *et al*., 1997); with high percentage of silica (96.34%) in the mineral ash (Rahman and Ismail, 1993). It is therefore expected that rice

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husk-based adsorbents would be effective in adsorbing heavy metals from aqueous solution. However, the rice husk needs to be modified or treated before being applied for adsorption of heavy metals (Chakraborty *et al*., 2011). Chemical or thermal treatment reduces cellulose, hemicelluloses and lignin crystallinity, leading to an increase of specific area for adsorption (Daffalla *et al*., 2010).

In this study, rice husk was treated with sulfuric acid to develop an Acidically Prepared Rice Husk Carbon (APRHC). The efficiency of the produced carbon to remove Zn(II) from aqueous solution was tested and adsorption mechanism was investigated. The aim of the study was to develop a low-cost carbon for inexpensive removal of heavy metals.

MATERIALS AND METHODS

Preparation of APRHC: Rice husk was collected from a rice mill and was washed several times with tap water followed by distilled water in order to remove dust and dried in an oven at 105°C for 24 h. The APRHC was prepared as follows (El-Shafey, 2005). The cleaned and dried rice husk (20 g) was weighed in a clean dry beaker of capacity 500 mL. One hundred milliliters of 13 M sulphuric acid were added to the rice husk and the mixture was heated at 175-180°C for 20 min with occasional stirring. The resulting black mixture was allowed to cool in a desiccator to room temperature and then filtered using a Buchner funnel under vacuum. The filtrate was then dried in an oven at 120°C to constant weight and cooled in a desiccator. The resulting APRHC was ground to a finer size of 212-500 μm and used in various adsorption experiments.

Adsorption experiments: Unless specified, batch adsorption experiments were carried out by shaking 100 mL of Zn(II) solution of desired concentration with 0.2 g of APRHC in a conical flask at room temperature (22°C), using an orbital shaker at 150 rpm. After a predetermined contact time, the flask was removed from the orbital shaker and the supernatant was filtered through 0.45 μm membrane filter and analysed for remaining Zn(II) concentration using a spectrophotometer. The effects of pH (1-6), contact time (5-120 min), Zn(II) concentration (20-80 mg L^{-1}) and adsorbent dose (1-6 g L^{-1}) on Zn(II) adsorption were also determined. The pH of the solution was adjusted by 0.1 N NaOH or 0.1 N HCl. Adsorption isotherms and kinetics were studied based on batch equilibrium test using optimum contact time and pH.

RESULTS AND DISCUSSION

Characterisation of APRHC: The values of BET surface area, micropore area, micropore volume and average pore diameter are 58.54 m^2 g^{-1}, 14.53 m^2 g^{-1}, 0.007209 mL g^{-1} and 45.46 Å, respectively. Scanning electron micrograph of APRHC (Fig. 1) shows presence of macro- and micro-pores.

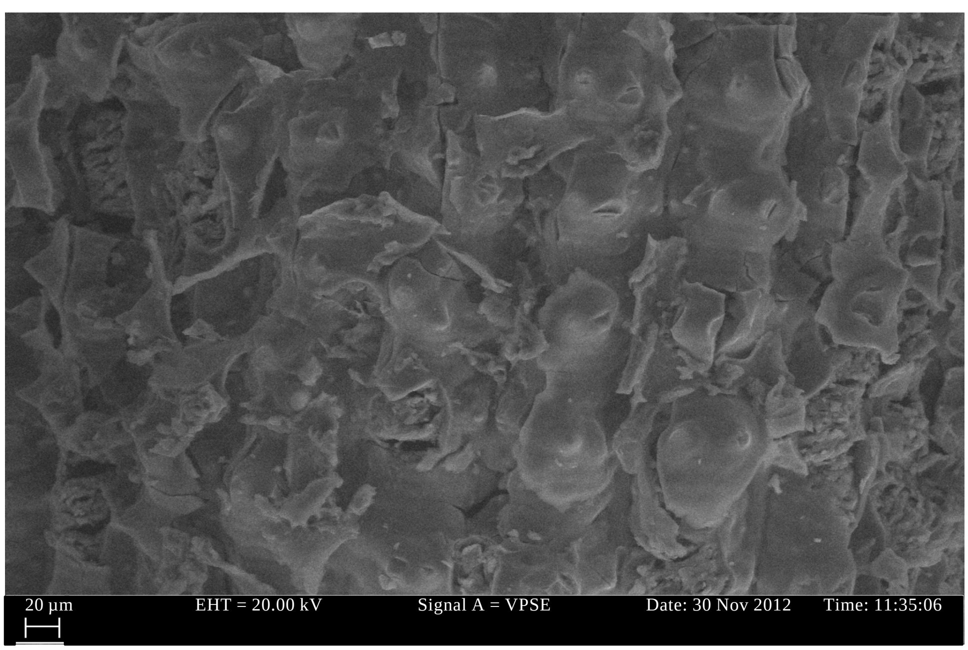

Fig. 1: Scanning electron micrograph of acidically prepared rice husk carbon

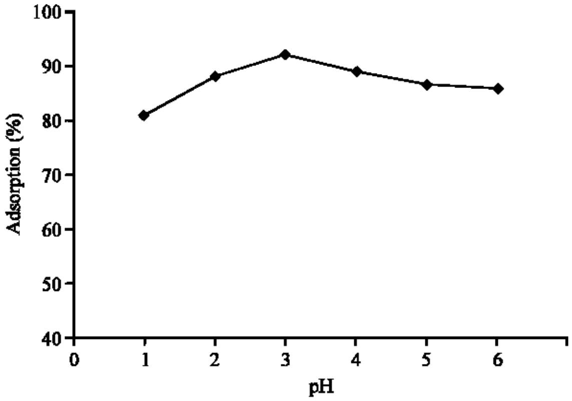

Fig. 2: Effect of pH on adsorption of Zn(II) by acidically prepared rice husk carbon

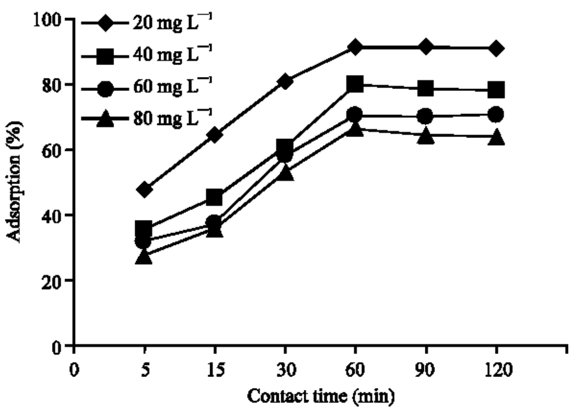

Fig. 3: Effect of contact time on adsorption of Zn(II) by acidically prepared rice husk carbon

Effect of pH: pH of an aqueous solution is one of the important controlling parameters in the adsorption process. In order to investigate the effect of pH on the adsorption of Zn(II) by APRHC, pH of the solution was adjusted. The pH range was chosen as 1-6 to avoid precipitation. It is found that pH affected adsorption of Zn(II). Maximum adsorption of 92% for 20 mg L^{-1} Zn(II) concentration occurred at pH 3 and the results are shown in Fig. 2. Similar observation has been found by Ghorbani *et al.* (2012) for the removal of Zn ion from aqueous solution using polyaniline nanocomposite coated on rice husk. All subsequent adsorption tests were conducted at pH 3.

Effect of contact time and initial Zn(II) concentration: Effect of contact time and initial Zn(II) concentration on adsorption by APRHC is shown in Fig. 3. The contact time was varied in the range 5-120 min at Zn(II) concentrations 20, 40, 60 and 80 mg L^{-1}, APRHC dose of 2 g L^{-1} and pH 3. The extent of Zn(II) adsorption

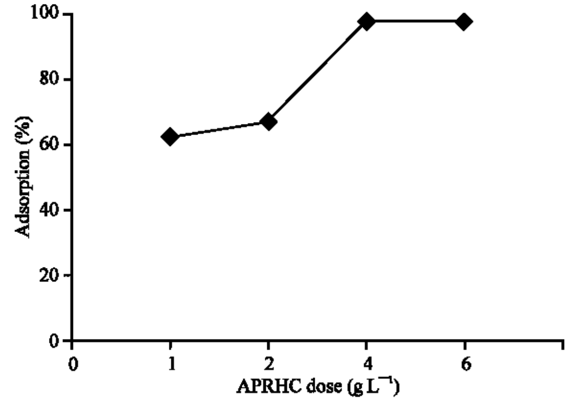

Fig. 4: Effect of APRHC dose on adsorption of Zn(II) by acidically prepared rice husk carbon

increased as the initial Zn(II) concentration decreased and as the contact time increased. Equilibrium adsorption was attained in 60 min. A contact time of 60 min has also been reported for the adsorption of Zn(II) by bed sediments (Jain, 2001). A contact time of 60 min was used in further adsorption tests.

Effect of APRHC dose In order to assess the APRHC dose on Zn(II) adsorption, an experiment was conducted under optimum conditions (contact time 60 min and pH 3). The effect of APRHC dose (1-6 g L^{-1}) on adsorption of Zn(II) is shown in Fig. 4. The adsorption was found to increase with APRHC dose and maximum adsorption of 97.2% for 80 mg L^{-1} Zn(II) concentration occurred at 4 g L^{-1}.

Adsorption isotherm: In a solid-liquid system during adsorption, the distribution ratio of the solute between the solid and the liquid phase is a measure of the position of equilibrium. The preferred form of representing this distribution is to express the solute adsorbed per unit weight of the solid (q_e) as a function of equilibrium concentration (C_e) at a fixed temperature. This type of expression is known as an adsorption isotherm (Weber, 1972). The Langmuir and Freundlich adsorption isotherms are represented in Eq. 1 and 2, respectively:

$$q_e = \frac{Q^{\circ} b C_e}{1 + b C_e} \quad (1)$$

$$q_e = K_f C_e^{1/n} \quad (2)$$

where, Q° is the amount of solute adsorbed per unit weight of adsorbent in forming a monolayer on the surface (monolayer adsorption capacity), b is a constant related to the energy of adsorption, K_f is the Freundlich

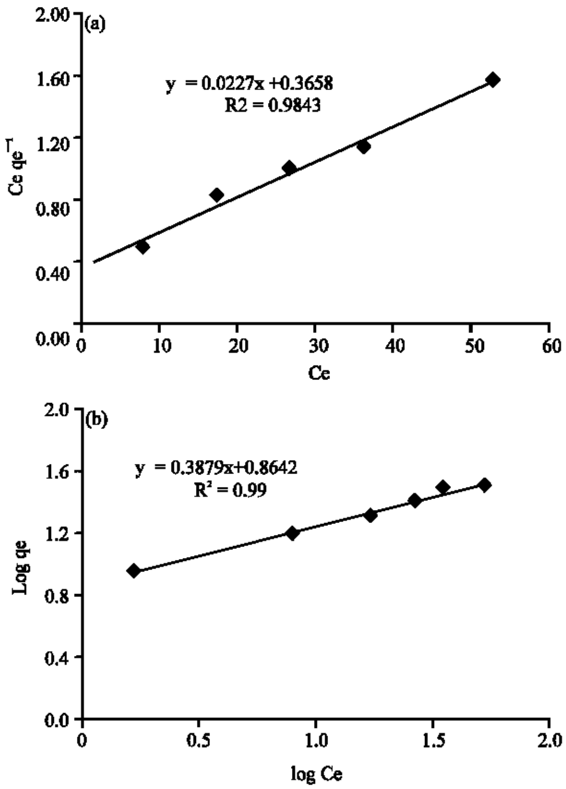

Fig. 5(a-b): (a) Langmuir isotherm and (b) Freundlich isotherm for Zn(II) adsorption acidically prepared rice husk carbon

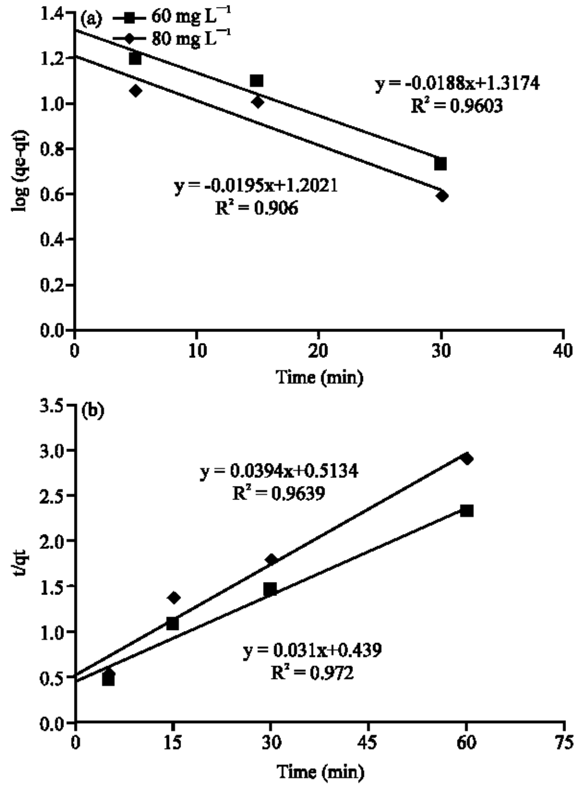

Fig. 6(a-b): (a) Pseudo-first-order kinetic plot and (b) Pseudo-second-order kinetic plot of Zn(II) adsorption by acidically prepared rice husk carbon

constant (adsorption capacity) and 1/n represents the adsorption intensity of Zn(II) by adsorbent or surface heterogeneity.

Linear forms of the Langmuir isotherm ($C_e/q_e = 1/(bQ^\circ)+C_e/Q^\circ$) and the Freundlich isotherm ($\log q_e = \log K_f+(1/n) \log C_e$) were fitted to the adsorption data; shown in Fig. 5a and b, respectively. Langmuir constants Q° and b were 44 and 0.06 and Freundlich constants K_f and 1/n were 7.31 and 0.38, respectively. The Freundlich isotherm model gave better fit of the experimental data than Langmuir isotherm model.

Adsorption kinetics: For adsorption kinetics, the experimental data of Zn (II) adsorption by APRHC were applied to the two commonly used models, i.e., the pseudo-first-order and pseudo-second-order kinetic models. The linear form of the pseudo-first-order model is written as in Eq. 3:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{3}$$

and the linear form of the pseudo-second-order model is in Eq. 4:

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{t}{q_e}\right) \tag{4}$$

where, q_e and q_t are the amounts of metal ion adsorbed (mg g^{-1}) at equilibrium and any time t, respectively, k_1 is the equilibrium rate constant for pseudo-first-order kinetics (min^{-1}) and k_2 is the equilibrium rate constant for pseudo-second-order kinetics [g (mg^{-1} min^{-1})]. Plots of log (q_e-q_t) versus t and of t/q_t versus t are presented in Fig. 6a and b, respectively. The experimental data fitted better to pseudo-second-order kinetic model than pseudo-first-order kinetic model, based on high R^2 for pseudo-second-order kinetic model. Hence, it is concluded that the adsorption of Zn (II) by APRHC is chemisorption. Similar observations have been reported for removal of Zn(II) using carbonaceous sorbent chemically prepared from rice husk (El-Shafey, 2010), Van apple pulp (Depci *et al*., 2012) and marine green algae (Kumar *et al*., 2007).

CONCLUSION

Acidically prepared rice husk carbon was found effective in the adsorption of Zn(II) from aqueous solution and maximum adsorption occurred in 60 min at pH 3. Freundlich isotherm model fitted the experimental data better than Langmuir isotherm model. Langmuir constants Q° and b were 44 and 0.06 and Freundlich constants K_f and 1/n were 7.31 and 0.38, respectively. The pseudo-second-order kinetic model fitted the experimental data well, indicating chemical adsorption of Zn(II). Being a low-cost agricultural by-product, rice husk is a good source for the preparation of rice husk carbon that can be employed as an effective adsorbent for the removal of Zn(II) and potentially for other heavy metals from aqueous solution and wastewater in developing countries.

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