World Academy of Science, Engineering and Technology
International Journal of Environmental and Ecological Engineering
Vol:5, No:12, 2011

Open Science Index, Environmental and Ecological Engineering Vol:5, No:12, 2011 publications.waset.org/9089.pdf

Removal of Ni(II), Zn(II) and Pb(II) ions from Single Metal Aqueous Solution using Activated Carbon Prepared from Rice Husk

Mohd F. Taha, Chong F. Kiat, Maizatul S. Shaharun, Anita Ramli

Abstract**—**The abundance and availability of rice husk, an agricultural waste, make them as a good source for precursor of activated carbon. In this work, rice husk-based activated carbons were prepared via base treated chemical activation process prior the carbonization process. The effect of carbonization temperatures (400, 600 and 800°C) on their pore structure was evaluated through morphology analysis using scanning electron microscope (SEM). Sample carbonized at 800°C showed better evolution and development of pores as compared to those carbonized at 400 and 600°C. The potential of rice husk-based activated carbon as an alternative adsorbent was investigated for the removal of Ni(II), Zn(II) and Pb(II) from single metal aqueous solution. The adsorption studies using rice husk-based activated carbon as an adsorbent were carried out as a function of contact time at room temperature and the metal ions were analyzed using atomic absorption spectrophotometer (AAS). The ability to remove metal ion from single metal aqueous solution was found to be improved with the increasing of carbonization temperature. Among the three metal ions tested, Pb(II) ion gave the highest adsorption on rice husk-based activated carbon. The results obtained indicate the potential to utilize rice husk as a promising precursor for the preparation of activated carbon for removal of heavy metals.

Keywords**—**Activated carbon, metal ion adsorption, rice husk, wastewater treatment.

I. INTRODUCTION

WATER pollution by heavy metals has received wide spread attention for many decades and has been a major cause of concern due to generation of a high toxicological risk for human health, ecosystem, and agriculture. Most of heavy metals are toxic and due to their non-biodegradability and persistence, they tend to accumulate in living organisms causing various diseases and disorders. Ni, Cd, Hg, Zn, Pb are examples of metals that are harmful wastes produced by industries which pose a risk of contaminating groundwater and other water resources [1, 2]. Releasing of these metals leads to poor water quality, insufficient supply of drinking water and complicate the water pre-treatment process for drinking water.

Industrial wastewater, e.g. plating plants, car radiator manufacturing, paint and ink formulation unit, and agricultural sources where fertilizers and fungicidal sprays are intensively used, is the major source of water pollution. Thus, technologies for the treatment and removal of heavy metals from wastewater and prevention of their emission into environment, particularly into surface water, are of particular importance. A variety of treatment processes for metal-contaminated wastewater have been employed including chemical precipitation, chemical oxidation, ion exchange, membrane filtration, chemical reduction electrodeposition and carbon adsorption [1, 3]. These processes usually require high operation and maintenance costs.

Activated carbon has been widely used for the removal of metal ions from fluid streams. Activated carbon is a good adsorbent as it has high surface area and porous structure, high adsorption capacity and a certain degree of reactivity due to the presence of appropriate functional groups [3]. However, production and regeneration of commercial activated carbon is still expensive and increasing attention has been given by researches in many years in order to investigate more economical alternative technologies or adsorbent for the elimination of heavy metals from wastewater. As activated carbon can be produced from any carbonaceous materials that are rich in elemental carbon and low proportion of inorganic components, natural materials or certain easily-available agricultural by-products may have potential to be used as the precursors of activated carbon for heavy metals removal. Research has been conducted on rice husk to produce activated carbon for removal of heavy metals [4, 5]. Considering the availability of agricultural by-products, rice husk is a good alternative for the production of cheap activated carbon as adsorbent.

Rice husk is the by-product of the rice milling industry. Based on about 571 million tonnes rice produced annually which 90 % is produced in developing countries, approximately 140 million tonnes of rice husk available annually for utilization. However, the amount of rice husk available is far in excess of any local uses. It is mainly used as a low-value energy resource, burned in-situ or discarded causing some disposal and environmental problems. The

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utilization of rice husk as the precursor to produce activated carbons that can be used as adsorbents for heavy metals removal from industrial wastewater could alleviate the problems of its disposal and management. It would also add value to this agricultural waste and provide a potentially cheap alternative to existing commercial activated carbons [1, 6].

Rice husk account for about 20 % of the whole rice and contains about 20 % silica. It is insoluble in water, chemically stable and has high mechanical strength. The major constituents of rice husk are cellulose, hemicelluloses, lignin, and mineral components. The content of each constituent depends on rice variety, climatic conditions and the geographic localization. Due its high cellulose and lignin content, rice husk can be utilized as the raw material to prepare activated carbon having highly porous structure in micropores range with high specific surface area [1, 4].

Previous studies have shown the ability of rice husk-based activated carbon for removal of many metal ions and organic molecules from aqueous phase solution [2, 6, 7, 8]. In most cases, rice husk-based activated carbon can be produced using thermal activation and chemical activation. Chemical activation method has been reported to provide a lower process temperature and its yield tends to be greater as burn char is not required [2, 9, 10].

The objectives of this study are to produce a low-cost activated carbon using rice husk and to evaluate the feasibility of using rice husk-based activated carbon for removal of toxic heavy metals from aqueous solution.

II. METHODS

In this work, chemical activation method was adopted in order to convert rice husk into activated carbon that was intended to adsorb Ni(II), Zn(II) and Pb(II) from single aqueous solution. Ni(II), Zn(II) and Pb(II) were selected as they are among the most common metals found in industrial effluents [2, 8]. Rice husk-based activated carbon was prepared from rice husk by NaOH-activation at room temperature and then was carbonized at three different temperatures, i.e. at 400, 600 and 800°C.

A. Preparation of Activated Carbon from Rice Husk

Rice husk was obtained from a rice mill in Malaysia, washed with distilled water and dried in the oven at 80°C for 5 hours. Rice husk was then treated chemically by mixing with 1.0 M NaOH in the ratio of 1:10 (rice husk:NaOH, w/v) at room temperature overnight. Treated rice husk was repeatedly washed with distilled water until the base was undetected in the filtrate. Treated rice husk was then dried at 80°C until its weight attained a constant value followed by grinding and sieving to 63 μm. Treated rice husk was then covered with aluminum foil and placed in alumina crucible. The alumina crucible was capped with an alumina cover to prevent oxidation. The alumina crucible was placed in a furnace and heated up to carbonization temperature (400, 600 and 800°C) with a heating rate of 5°C/min. After 2 hours of carbonization, the furnace was switched of and cooled to room temperature. Rice husk-based activated carbons formed were labeled as RHAC4 (carbonized at 400°C), RHAC6 (carbonized at 600°C) and RHAC8 (carbonized at 800°C).

B. Elemental and Surface Morphology Analyses of Rice Husk-Based Activated Carbons

Raw rice husk, rice husk treated with NaOH and activated carbons prepared from rice husk were analyzed for their elemental analysis (carbon, oxygen and silica content) using field-emission scanning electron microscope/energy dispersive X-Ray (FESEM/EDX, model SUPRA 50). Their morphological characteristics were studied using scanning electron microscope (SEM, model LE01430VP). The total yield (Y_T) of activated carbon obtained was calculated as:

$$Y_T = \left(\frac{\text{Weight of activated carbon obtained}}{\text{Weight of rice husk treated with NaOH}} \right) \times 100 \qquad (1)$$

C. Adsorption Studies

Solution of 25.0 ppm Ni(II) ions was prepared by mixing appropriate amount of $NiCl_2$ (MERCK) with distilled water. The same procedures were applied for the preparation of 25.0 ppm Zn(II) and 25.0 ppm Pb(II) ion solutions using $ZnCl_2$ and Pb $(NO_3)_2$, respectively (MERCK). The adsorption studies were conducted by mixing 0.1 g of rice husk-based activated carbon with 25.0 ml of 25.0 ppm metal ion solution in Erlenmeyer flasks. The flasks were then shaken in the rotary shaker at 150 rpm at room temperature. After shaking for a preset interval time, the mixture was filtered using vacuum filter and the concentration of the metal ions in the filtrate was determined using atomic adsorption spectrometer (AAS, model AA6680). The % metal uptake (% adsorption) and metal uptake capacity (adsorption capacity) at time t, q_t, was then calculated by:

$$\text{\% metal uptake} = \left[\frac{(C_i - C_t)}{C_i} \right] \times 100 \qquad (2)$$

$$q_t = \left[\frac{(C_i - C_t}{W} \right] \times V \qquad (3)$$

where C_i, C_t, W and V are the initial metal ion concentration, metal ion concentration at time t, dry weight of adsorbent used and volume of metal ion solution, respectively.

III. RESULTS AND DISCUSSION

A. Elemental and Surface Morphology Analyses of Rice Husk-Based Activated Carbon

Rice husk treated with NaOH having particle size of 63 μm was carbonized at 400, 600 and 800°C to form rice husk-based activated carbon. The yield obtain is tabulated in Table 1. As expected, the weight of the samples decreased after carbonization process due to loss of volatile matter.

TABLE I
YIELD OF RICE HUSK-BASED ACTIVATED CARBON

Carbonization temperature (°C)	Yield (%)
400	36.8
600	36.6
800	34.0

Fig. 1 reveals changes in main components of the five samples analyzed. Generally, treatment of rice husk with NaOH and an increased in the carbonization temperature increased the amount of carbon but reduced the amount of oxygen and silica content. The silica content reduced significantly after treating with 1.0 M NaOH as compared to raw rice husk. This could be due to leaching of silica, the most abundant inorganic element in rice husk, from the external epidermis of the structure of the husk when the rice husk is treated with solution of NaOH. NaOH reacts with silica forming sodium silicate (Na_2SiO_3) which can be removed by adequate water-washing as it is soluble in water [9, 10]. The carbon content of activated carbon increased with increasing of carbonization temperature but the oxygen content showed the opposite trend. This can be explained by the fact that during carbonization, the destruction of cellulose and hemicelluloses of rice husk take place causing the volatile matter to vaporize. As carbonization temperature increases, more volatile matter will be vaporized, thus increases the content of carbon but reduces the oxygen content in rice husk activated carbon. The carbon content becomes constant when only the non-volatile flammable component remained in the rice husk-based activated carbon after all the volatile matter is driven off [11].

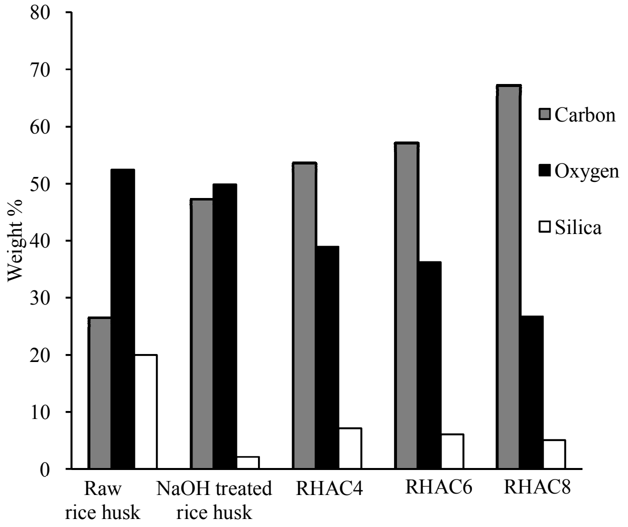

Fig. 1 Carbon, oxygen and silica content of raw rice husk, treated rice husk and activated carbon prepared from rice husk

Samples were analyzed using Scanning Electron Miscroscope (SEM) to study the morphological features of raw rice husk, rice husk treated with 1.0 M NaOH and rice husk-based activated carbon. Their scanning electron micrographs, as shown in Fig. 2 – 3, verified the effect of NaOH treatment on rice husk which significantly affect the surface area and pores structure development. As compared to scanning electron micrograph of the raw rice husk, rice husk treated with NaOH showed the evidence for the formation of pores. Fine pores were created in the interior structure of the treated rice husk which is consistent with the theory that the chemical treatment process will produce high porous cellulose-silica material. These pores formed and remained on the husk's outer epidermis as the results of reaction between silica and NaOH producing sodium silicate. Sodium silicate is easily removed by water-washing. During the activation process, sodium hydroxide can also decomposes the lignin and other mineral components in the husk causing swelling in the organic composition. Entering the interior of carbon tissue by NaOH or activating agent is favorable as this increases the specific surface area as well as pore volume which are stably created in the carbon composite [7, 10, 12].

As can be seen in Fig. 3, carbonization process resulted in the creation of many fine pores in the interior structure of the thermally decomposed husk whereby samples carbonized at 800°C developed more uniform pores compared to samples carbonized at 400°C and 600°C. These figures also show the formation of porous biosorbent from rice husk and evolution on the pores structures with different sizes and shapes. Development of pores after carbonization is expected due to elimination of most non-carbon elements and volatile matters such as nitrogen and oxygen leaving behind highly carbonaceous materials [9]. These well-developed pores contribute to the large surface area and porous structure of rice husk activated carbon [13]. Many studies shown that the development of pores would give better adsorption capability for metal ions as metals ions tend to trap in the pores structures [14].

B.Adsorption Studies

The adsorption experiments were conducted for different contact times with fixed amount of adsorbent and metal ion concentration. Fig 4 – 9 represent the variation in percentage removal and adsorption capacity of Ni(II), Zn(II) and Pb(II) with contact time at room temperature on rice husk-based activated carbon. It is obvious that as the carbonization temperature increased, the capacity of rice husk-based activated carbon to remove Ni(II), Zn(II) and Pb(II) from single a queous solution increased as well. This could be to the higher porosity obtained at higher carbonization temperature which correlate well with the obvious development of pores in the rice husk shown by SEM micrographs as carbonization temperature was increased from 400°C to 600°C and from 600°C to 800°C.

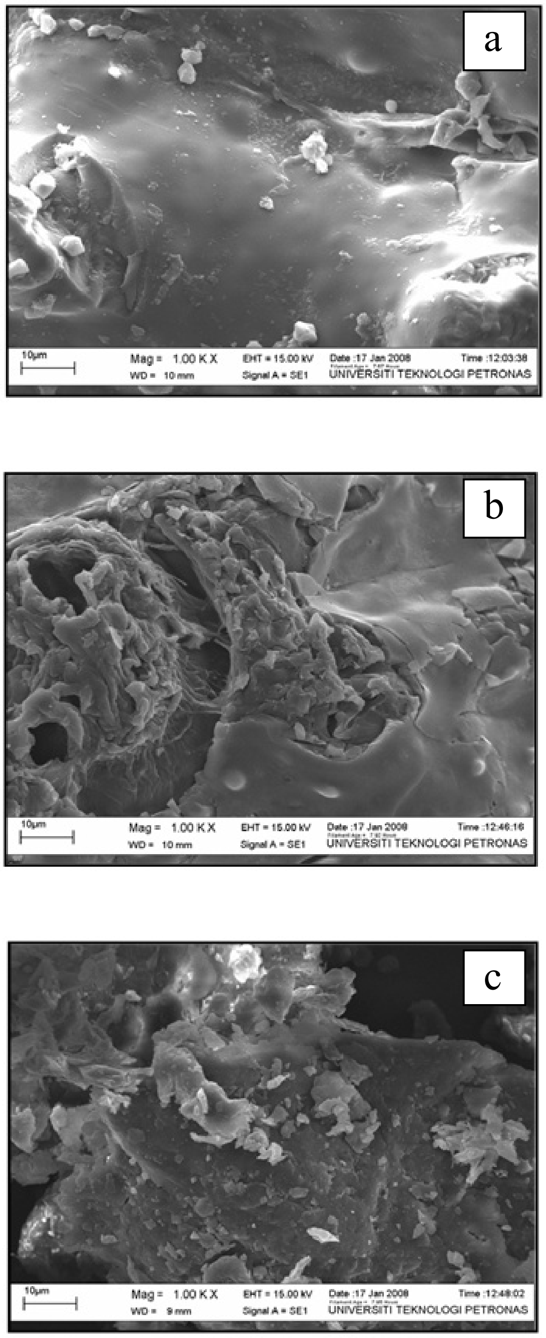

Fig. 2 Morphology of (a) raw rice husk, (b) rice husk treated with 1.0 M NaOH (c) NaOH treated rice husk grinded to 63 µm

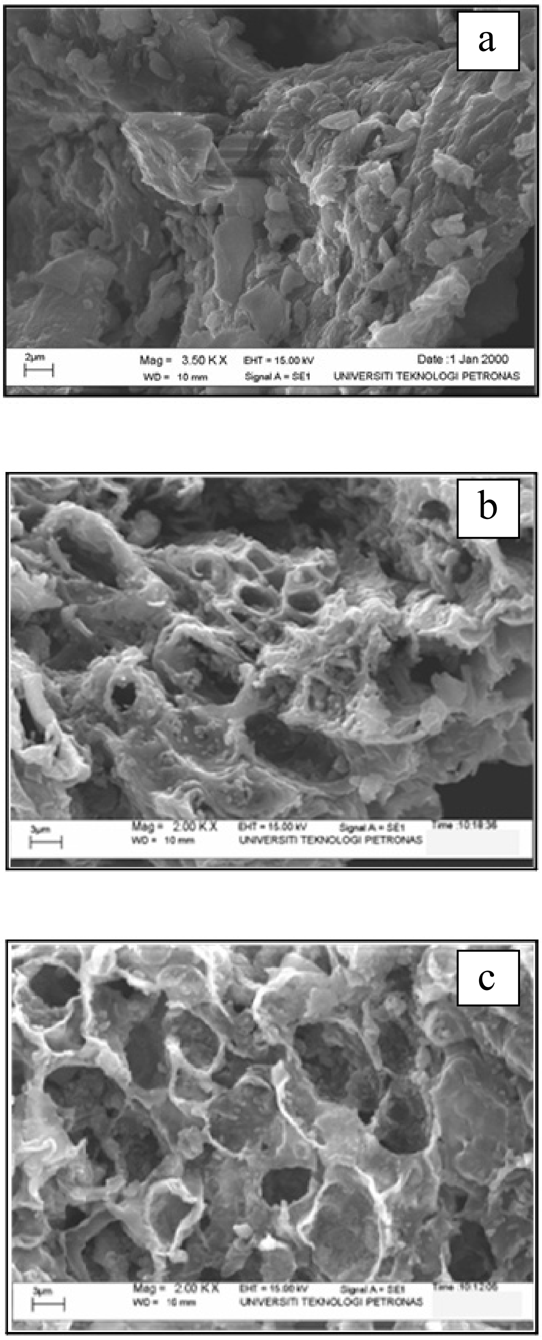

Fig. 3 Morphology of rice husk-based activated carbon (carbonized at different temperature), (a) RHAC4 (b) RHAC6 (c) RHAC8

Generally the rate of adsorption was very fast at the initial stages and there was no significant change in the extent of adsorption when the system reached equilibrium. As expected, due to better pores development, RHAC8 performed better in removing Ni(II) from aqueous solution compared to the ones carbonized at 400°C and 600°C. The adsorption profile of Ni(II) by on rice husk-based activated carbon showed that the uptake of Ni(II) was very rapid in the first 30 min and only slight variations on the adsorption results were obtained after 45 min of contact time. The adsorption of Ni(II) by RHAC8 reached equilibrium faster than RHAC4 and RHAC6 whereby the equilibrium was attained in 60 min.

Adsorption of Zn(II) and Pb(II) ions showed similar trend as shown in Fig. 5 and 6. The adsorption behavior indicates that rice husk-based activated carbon has a potential as metal extraction agent for Ni(II), Zn(II) and Pb(II) from single aqueous solution. The results obtained clearly show that the ability of rice husk-based activated carbon to remove

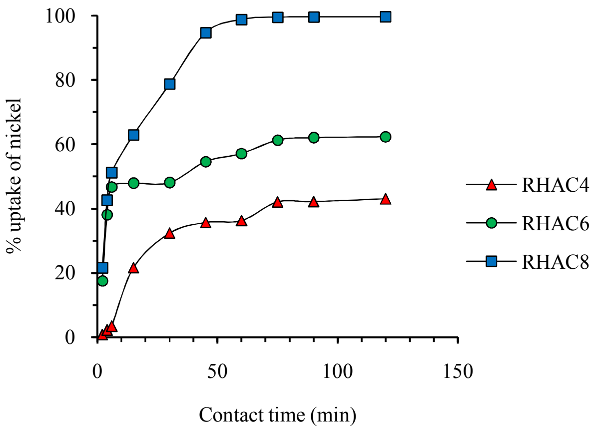

Fig. 4 Ni(II) ion adsorption profile at room temperature on RHAC4, RHAC6 and RHAC8

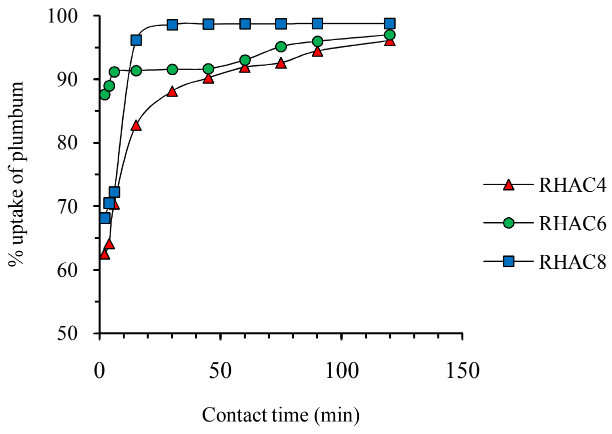

Fig. 5 Pb(II) ion adsorption profile at room temperature on RHAC4, RHAC6 and RHAC8

Pb(II) ion is better than Ni(II) and Zn(II) ions. However, further study need to be conducted to investigate the selectivity of rice husk activated carbon towards Ni(II), Zn(II) and Pb(II) ions when these metal ions are present together in aqueous solution. Since adsorption capacities of sorbents varies depending on the treatment on sorbent material and experimental conditions, it is advised that the reported sorption capacities should be taken as the values that can be achieved under a specific set of conditions and not as maximum sorption capacities [6]. Table 2 represents the adsorption capacities (or removal percentage) of rice husk-based activated carbon developed in this study.

TABLE II
ADSORPTION CAPACITY OF RICE HUSK-BASED ACTIVATED CARBON AND REMOVAL PERCENTAGE OF METAL ION

Adsorbate	Sorbent material	Adsorption capacity (mg/g)	Removal percentage (%)
Ni(II)	RHAC4	2.69	43.0
	RHAC6	3.88	62.0
	RHAC8	6.23	99.7
Zn(II)	RHAC4	5.28	84.6
	RHAC6	5.38	86.0
	RHAC8	6.17	98.8
Pb(II)	RHAC4	6.01	96.1
	RHAC6	6.06	97.0
	RHAC8	6.17	98.8

Metal ion concentration is 25.0 ppm

Generally, from the results of adsorption behavior for Ni(II), Zn(II) and Pb(II) ions, the metal ions adsorbed occupied a large number of pores at the beginning of adsorption process. As the contact time increased, the pores were filled and the rate of metal adsorption became slower gradually and reached a plateau. This behavior reflects the fact that the adsorption is a surface phenomenon and that the surfaces are readily accessible to the metal ions in the solution [14]. It also suggests the occurrence of a rapid external mass transfer followed by a slower internal diffusion process which could be the rate determining step.

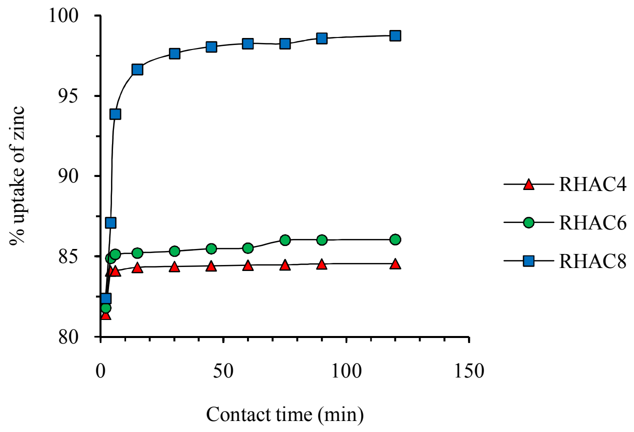

Fig. 6 Zn(II) ion adsorption profile at room temperature on RHAC4, RHAC6 and RHAC8

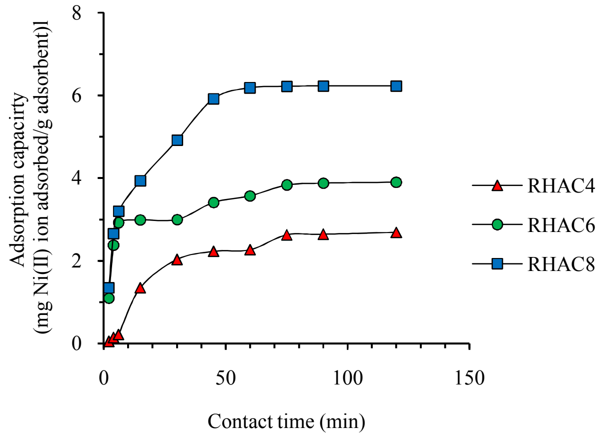

Fig. 7 Adsorption capacity of RHAC4, RHAC6 and RHAC8 towards Ni(II) ion

The slower internal diffusion process could be due to the slow diffusion of the adsorbed metals from the surface film into the micropores which are the least accessible sites for adsorption [15]. This could also be due to the difficulty of metal ions to occupy the remaining vacant surface sites due to repulsive forces between metal ions and bulk phase [16].

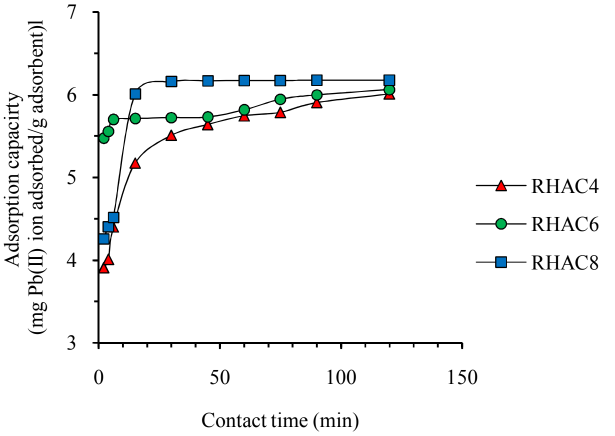

Fig. 8 Adsorption capacity of RHAC4, RHAC6 and RHAC8 towards Pb(II) ion

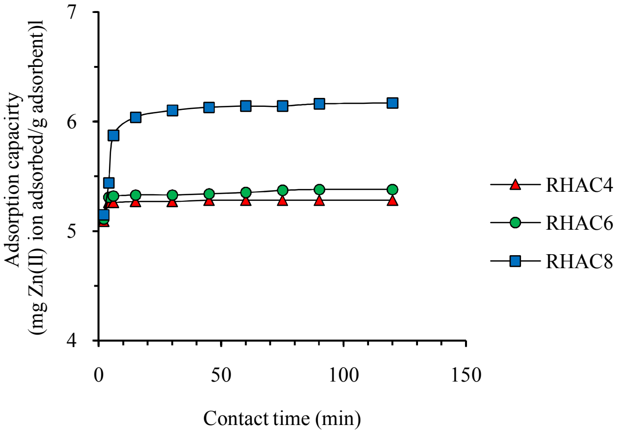

Fig. 9 Adsorption capacity of RHAC4, RHAC6 and RHAC8 Zn(II) ion

IV. CONCLUSIONS

Based on the results obtained, it can be concluded that rice husk-based activated carbon is a suitable adsorbent for the adsorption of Ni(II), Zn(II) and Pb(II) ions from single metal aqueous solution. The adsorption rate and adsorption capability are considerably fast and high, respectively, making rice husk based activated carbon is a very attractive alternative for cheap adsorbent material. RHAC4, RHAC6 and RHAC8 have different adsorption rate and adsorption capacity that could be due to different pores development. From surface morphology analysis, RHAC8 showed better evolution and development of pores as compared to others. This in turn contributes to better pore size and pore volume that would give RHAC8 a better adsorption capacity for Ni(II), Zn(II) and Pb(II) ions than the ones carbonized at 400 and 600°C. Indicated by adsorption capacity, rice husk-based activated carbon adsorb Pb(II) ion from single metal aqueous solution better than Ni(II) and Zn(II) ions.

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