REVIEW ARTICLE

LEAD (II) REMOVAL FROM WASTEWATER USING MODIFIED BIOCHAR DERIVED FROM RICE HUSKS AND RICE STRAWS

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ABSTRACT

Novel adsorbent was produced from rice husks and rice straw derived biochar. The adsorbent was synthesized by subjecting to pyrolysis agricultural waste and activated the product with thermochemical treatments to enhance its properties. The effects of alkali concentration, process temperature and reaction time on the agricultural waste derived biochar were assessed and results showed that the activation of biochar enhanced its specific surface area by 58.5 to 220.8 square meter per gram. The total pore volume of the biochar also increased from 0.33 cm3 per gram to a maximum of 0.45 cm3 per gram upon activation. The Langmuir equation was used to predict sorption capacity of Lead (Pb^{2+}) by the pristine and thermochemically treated biochar, with maximum sorption 0.25 mol/kg and 1.44 mol/kg, respectively.

INTRODUCTION

Waste disposal had been one of the biggest problem of the modern society. Growing public awareness along with other social issues and scarcity of landsite have lead for scientists and researchers to find ways in combating these issues. Disposal is the main problem but finding valuables out of waste has been the driving force of modern researches. In transforming waste into something sellable, the issue of spending in the disposal of such can be mitigated. Several approach had been suggested in dealing with municipal and agricultural wastes. The most popular are converting these wastes into fuel either in different kinds of means whether by transesterification, gasification, and pyrolysis among several others. In pyrolysis, synthesis gas, bio oil and biochar can be produced. These materials however may not be enough as a saleable material in order to justify the amount of money spent on the process of conversion of waste into these products. Improvements and further process may be needed in order for them to be more profitable. Biochar is the carbonaceous solid byproduct of MSW thermochemical conversion. It is usually rich in nutrients and stable aromatic carbon which makes it suitable for various applications, such as soil amendment, carbon sequestration, pollution mitigation and energy production. Biochar as it is however could not supplant coal as a fuel source and can never replace the performance of other adsorbents.

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But given serious process improvements, it may be a better performing product than most commercial adsorbents like activated carbon which are a lot more expensive. The goal of this research is to be able to activate biochar derived from rice husks and other agricultural wastes so that it can be made suitable as an industrial adsorbent that may be specifically used in wastewater treatment. The improvement and activation of the biochar will be done using chemical and thermal treatment.

MATERIALS AND METHODS

Materials: Rice husks and straws were gathered from nearby farm. Laboratory work were done in CPU College of engineering. All consumables were purchased both online and on a local chemical distributor.

Preparation of Biochar: The biochars used in this work were obtained from two rice residues, straw and husk. All materials were first dried in air and then cut into small pieces (less than 4–5 cm); these were then inserted into a ceramicvessel (370 cm3) that was used in a commercial electric furnace (SOMO-01 Isuzu, Japan). This was charred for 10 h at different temperatures (from 400 to 800 ∘C) at a heating rate of 10 ∘C min−1. After the pyrolysis process, all samples were ground and sieved to less than 0.5 mm in diameter. The biochar yield was calculated as the proportion of the weight of pyrolysis product to the original material. The determination of the volatile matter and ash content was conducted according to the American Society for Testing and Materials (ASTM) D1752-84, which is recommended by the International Biochar

Initiative. The volatile matter was thus determined by measuring the weight loss that follows the combustion of about 1 g of charcoal in a crucible at 950 ∘C. Following the same procedure, the ash content was determined at 750 ∘C. The pH of each mixture (1: 10, w/v ratio) was measured with the MP220 pH meter. Micro- and mesoporosity were evaluated with regard to Iodine and methylene blue (MB) adsorption capacity, respectively, following a previously proposed methodology. The specific surface area was determined using N_2 sorption isotherms run on an automated surface area.

Chemical and thermal activation of biochar: Activation experiments were done by soaking 5 g of biochar with 150 mL of KOH solution with varying concentrations (0.2– 1.0 N). The mixture was then placed in an incubator shaker maintained at a temperature of 35 ºC and a shaking speed of 180 rpm. After 24 h, the activated biochar was filtered and washed with deionized water until the filtrate reached neutral pH. The biochar was then dried overnight, collected and stored in air-tight containers. Thermal activation was carried out by placing the KOH activated biochar in a furnace maintained under an inert N_2 condition and set at a temperature ranging from 400–800 ºC and time from 0.5 to 2.5 hr. After cooling to room temperature, activated biochar was collected and soaked in 0.1 M HCl solution for 2 hr to remove ash and other inorganic impurities. It was then filtered and washed with water until the filtrate had a stable pH. Lastly, the activated biochar was dried at 120 ºC for 24 h and then stored in air-tight containers for future use.

RESULTS AND DISCUSSION

Effect of process conditions on Total Surface Area: In the investigation of the effect of process parameters in the Total Surface Area of the adsorbents, it was found out that all three parameters namely, reaction temperature, alkali concentration and reaction time, had a profound effect on total surface area. Before activation, the measured surface area of the pristine biochar was found to be 58.5 cm^2 per gram. At its optimum activation process, the biochar was able to increase its total surface area to 220.8 cm^2 per gram. When the effect of the KOH concentration was investigated, the total surface area increases with concentration. However, it is noted that at 0.8N, the achieved SSA is already comparable to that of the SSA achieved at 1.0N KOH. This implies that the ideal concentration for chemical activation is already achieved at 0.8N solution.
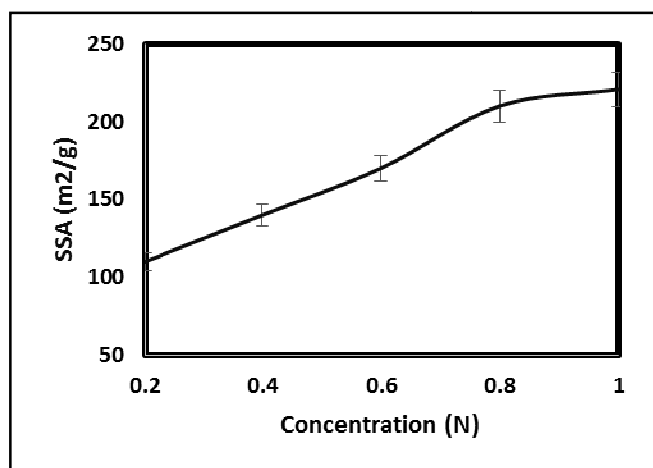
As far reaction time is concerned, not much improvement were made in the total surface area of the activated biochar after 1.5 hrs. There was a steep rise in the SSA of the biochar being activated in reaction time lower than 1.5 hrs but about 1-2% improvement when reaction is prolonged thereafter.
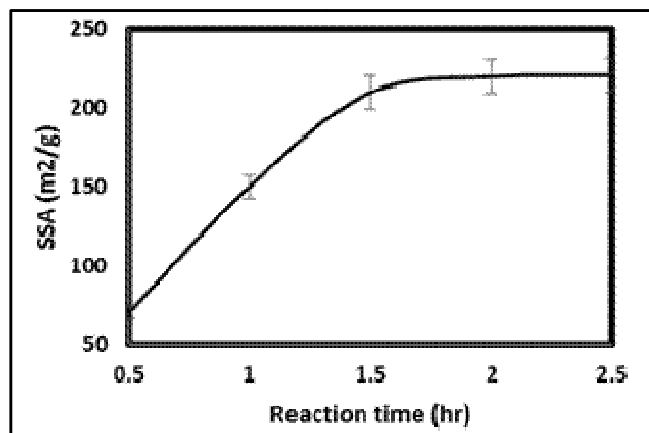

Fig. 2. Effect of Reaction Time on Total Surface Area of Biochar

Also, when the reaction temperature was investigated, it was projected that the ideal reaction temperature was 600 ºC. The SSA at reaction temperatures 700 ºC and 800 ºC are 5-12 cm^2 per gram better but the increase in the energy requirements that may add cost to operating expenses could not be justified, thus 600 ºC has to be the ideal reaction temperature.
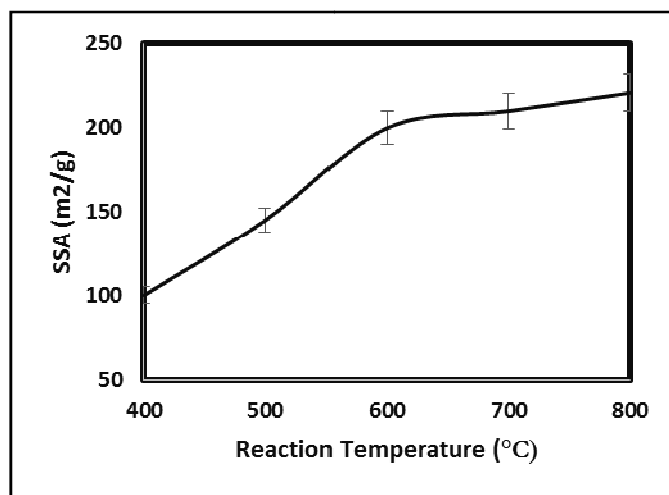

Fig. 3. Effect of Reaction Temperature on Total Surface Area of Biochar

Effect of process conditions on Pore Volume: The pore volume of the biochar was also observed to be dependent of the activation parameters identified in this study. Much like total surface area, KOH concentration, reaction temperature and reaction time also had a significant effect on the pore volume of the biochar. Before activation, pristine biochar only had a pore volume equal to 0.33 cm^3 per gram. At the optimum activation conditions, the pore volume was improved to 0.45 cm^3 per gram. In the chemical activation of the biochar, it was found out that increasing KOH concentration also increases pore volume. It is noted however that the increase in pore volume is minimal between concentrations of 0.8N and 1.0N. This implies that 0.8N KOH concentration is justified as the best concentration for economic purposes.
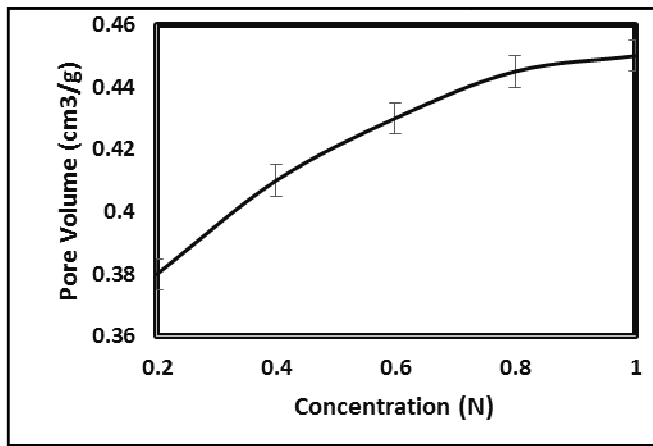

Fig. 1. Effect of KOH concentration on Total Surface Area of Biochar

Fig. 4. Effect of KOH concentration on Pore Volume of Biochar

As far as reaction time is concerned, it is observed that the best pore volume was achieved significantly after 2.5 hrs. This is in contrast to the earlier observed best reaction time for total surface area which was at 1.5hrs. This implies that pore volume needs more time to be improved as compared to the total surface area.
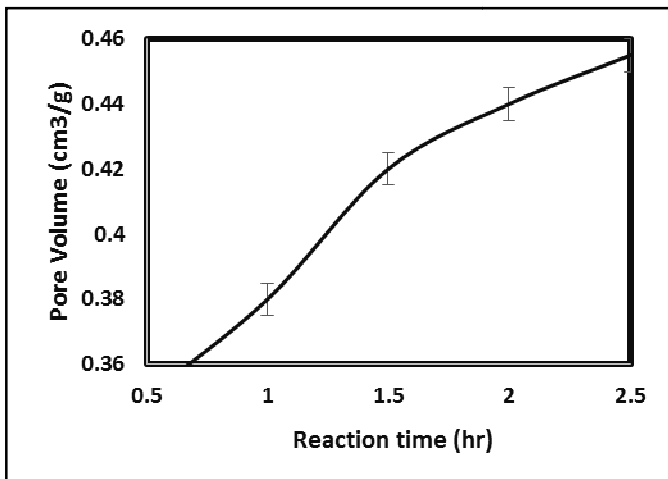

Fig. 5. Effect of Reaction Time on Pore Volume of Biochar

As for the reaction temperature, the maximum pore volume that can be attained is done already at a temperature equal to 600 °C. This is in agreement to the optimum total surface area attained for the same temperature. Increasing the temperature beyond 600 °C has no effect already on the pore volume of the activated biochar.
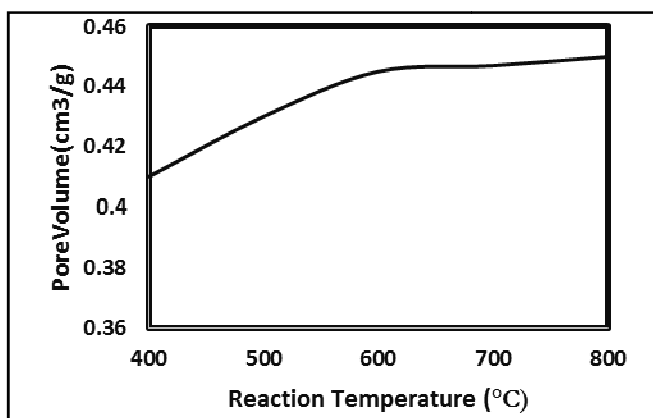

Fig. 6. Effect of Reaction Temperature on Pore Volume of Biochar

Relation of Pore volume and Total Surface Area on Adsorptivity: The reason behind why the effect of process parameters to the total surface area and pore volume was investigated is that the two variables are highly correlated to the performance of the biochar as adsorbents. In the investigation of its adsorptivity using methylene blue as adsorbates, pristine biochar can only adsorb 35% of the Lead (II) in aqueous solution while activated biochar with a reported high total surface area and pore volume can adsorb up to 80%. Figure 7 tells the relationship of the percentage of mineral adsorbed versus the pore volume. At the maximum pore volume after activation of biochar, the maximum percent dye removal was also attained.
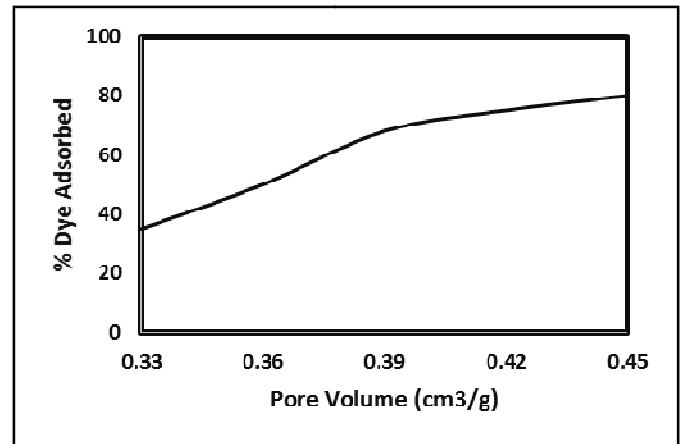

Fig. 7. Effect of Pore volume on the Dye Removal of Biochar

Figure 8 also shows that the higher the total surface area of the adsorbent, the better is the adsorbing capacity of the material. The linear correlation of SSA and percent dye removal suggests that the higher the SSA of the adsorbent, the better would be the adsorbing capacity. It is noted however that in these study, the maximum total surface area attained by the biochar after activation was 220.8 cm2 per gram. It is possible that more than 80% of the mineral will be removed should the total surface area be increased further than the maximum observed value in this study.
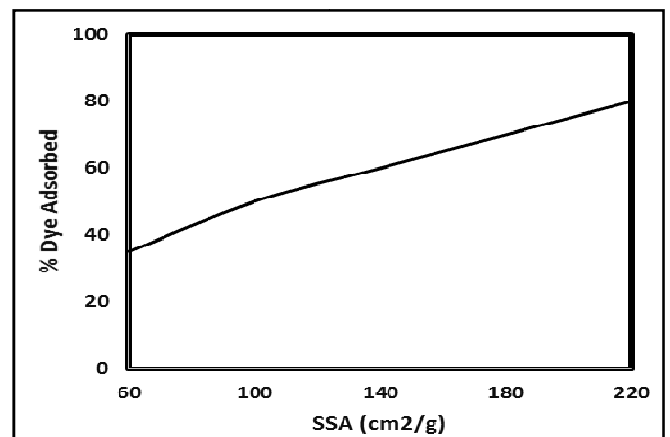

Fig.8. Effect of Total Surface Area on the Dye Removal of Biochar

Conclusion

An adsorbent derived biochar from rice husks and agricultural waste was made after pyrolysis. The results in these study suggested that after thermochemical treatment, the activated biochar is effective in the removal of Lead (II) in aqueous

solution for concentrations up to 80%. It was also noted that the best process parameters in the thermo chemical activation of the biochar were 0.8N KOH as alkali concentration, 600 ºC for reaction temperature and 1.5 hr as the reaction time. The investigation also took note that as the pore volume and the total surface are of the material are increases, so are there adsorbing capacity. These study was able to find out that valuable materials can be made out of waste if they will be prepared properly.

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