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Original Article

PREPARATION OF RICE STRAW ACTIVATED CHARCOAL BY 2-STEP H_3PO_4 ACTIVATION

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ABSTRACT

Objective: To determine optimal conditions required for activated charcoal production from rice straw with high quality for medical and pharmaceutical applications using chemical activation process.

Methods: Effects of different pretreatment protocols in 2-step H_3PO_4 activation of Thai rice straw on adsorption properties, pore structure, and surface chemistry were investigated. The rice straw was carbonized at 400 °C for 2 h. The obtained charcoal was then impregnated with 85% H_3PO_4 in the ratio of 1:4 w/v for 24 h, followed by carbonization at 500, 600 and 700 °C for 1 h.

Results: The results indicated that the 2-step H_3PO_4 activation, impregnating and carbonization at 700 °C was more efficient in producing activated charcoal because of showing the highest iodine adsorption (629 mg/g), methylene blue adsorption (198 mg/g) and Pb^{2+}ions adsorption (64.19%). The adsorption capacity on iodine, methylene blue, and Pb^{2+} ions were compared. The results showed that rice straw activated charcoal was most efficient highest to adsorb Pb^{2+} ions. This adsorption capacity was higher than that of the commercial medical-grade activated charcoal.

Conclusion: The rice straw activated charcoal which was prepared by 2-step H_3PO_4 activation tends to be potential for medical and pharmaceutical applications.

Keywords: Rice straw, Activated charcoal, Phosphoric acid.

INTRODUCTION

The production of rice is the largest sector of rice straw in Thailand. Rice straw, as a waste material has been widely utilized in various fields, such as feeding of animals, the raw material for paper industry, organic fertilizer, construction materials, compost manure, fuel, potential for ethanol production, and precursors for activated charcoal [1-3]. Burning of rice fields after harvesting is a common practice for disposal of rice straw and for preparing the land for cultivation. During the burning of rice straw, carbon dioxide is emitted into the atmosphere causing air pollution, traffic disturbance and environmental problems [5].

Activated charcoal, also called activated carbon or activated coal, has become one of the most important and most widely used adsorbents due to its highly developed internal porosity and large surface area, enabling high adsorption capacity [6]. United States Pharmacopeia (USP) reported that activated charcoal is the residue obtained by the destructive distillation of various organic materials, then treated to increase its adsorptive power [7]. Activated charcoal has been used as a universal antidote in the treatment of poisonings since 1830. According to the adsorption capacity, it has been used as a non-specific gastrointestinal (GI) decontaminant in poisoning (including excessive gas, diarrhea, peptic ulcers and deodorizing of ostomies). In addition, activated charcoal has been used to reduce the severity of diarrhea and for the abatement of odor from ostomies, both subjectively and qualitatively [8-9]. In many cases, it has often been used as emergency home care, such as carbon-containing sorbents modified with mineral and trace elements such as zinc, iron, potassium and magnesium used as entering sorbents during intoxications and other disturbances [9]. Chang *et al.*(2014) used potassium hydroxide (KOH) as an activating agent to produce activated carbon from rice straw utilized as the carbofuran remover from environmental water [10]. Hsu *et al.* (2009) prepared charcoal from rice straw and investigated for the removal of hexavalent chromium (Cr (VI)) from the water. Rice straw-based carbon might be effectively used at low pH for the treatment of Cr (VI) contaminated water [11].

The demand of activated charcoal has been increasing in various industries, especially in medicinal and pharmaceutical fields, requiring a huge amount of raw materials. Therefore, the objective of this research is to achieve production of high quality activated charcoal with high adsorption capacity from rice straw for medicinal and pharmaceutical applications.

MATERIALS AND METHODS

Preparation of rice straw activated charcoal

Rice straw was collected from the Chiang Mai Rice Research Center, Chiang Mai, Thailand. The rice straw was cut into small pieces, dried, ground and sieved to collect the 60-mesh particle size. The rice straw material was carbonized at 400 °C for 2 h. and then impregnated using 85% phosphoric acid in the ratio of 1:4 w/v for 24 h at room temperature. After that, the impregnated material was carbonized at 500, 600 and 700 °C for 1 h. The obtained activated charcoal was washed with boiled water to remove residual acid until the filtrated to be a neutral and finally washed with distilled water. The neutral activated charcoal was then dried at 110 °C for 24 h, cooled in a desiccator and stored for characterization.

Characterization of rice straw activated charcoal

Iodine adsorption

The adsorption performance of activated charcoal was characterized by iodine adsorption. The iodine adsorption efficiency was compared with commercial medical-grade activated charcoal. The iodine number was determined according to the certified method of American Society for Testing and Materials (ASTM D4607-94) [12].

Methylene blue adsorption

The methylene blue adsorption efficiency was compared with the commercial medical-grade activated charcoal. The methylene blue number was determined according to the Japanese Industrial Standards Committee standard (JIS) [13]. Briefly, the activated charcoal samples were mixed with methylene blue solution in conical flasks.

The solution was quickly shaken for 10 s. Further, added 50 ml of methylene blue solution to achieve equilibrium. The solution was then shaken for 30 min until adsorption was completed and a state of equilibrium was reached, filtered and determined by a UV/Vis spectrometer at 663 nm.

Heavy metal adsorption

Pb^{2+} ions were selected for determining heavy metal adsorption performance of the activated charcoal. Standard solutions of lead nitrate ($Pb(NO_3)_2$) was prepared at 50, 100, 200, 400, and 600 ppm for the standard curve. The mixture of 0.25 g of the selected activated charcoal and 25 ml of standard lead nitrate solution at a concentration of 1000 ppm was prepared. The mixtures were stirred for 1 h at a room temperature. Then, the solutions were filtered. The concentrations of Pb^{2+} were measured by AAS at a wavelength of 217 nm, respectively. Percentage of removal of heavy metal was calculated as follow:

$$\text{Removal (\%)} = (C_o - C_e)/C_o \times 100$$

Where C_o and C_e are the concentrations of the heavy metal solution at initial and equilibrium (mg/l) respectively.

Determination of surface chemistry

The surface functional groups of activated charcoal were determined by Fourier transforms infrared (FT-IR) spectra analysis.

Determination of pore structure

The pore structure was recorded by scanning electron microscope (SEM) JEOL JSM-5910LV.

Statistical analyses

Results were expressed as average values of three replicates ±standard deviation (SD).

All statistical analysis was conducted using SPSS (version16). p value were considered as significant.

RESULTS AND DISCUSSIONS

Iodine adsorption and methylene blue adsorption of obtained charcoal from phosphoric acid (H_3PO_4) activation

The iodine adsorption and methylene blue adsorption are common methods for determination of the porous structure of activated charcoal. The number of micropores inside activated charcoal had a profound effect on iodine adsorption because the small particle of iodine molecule (0 to 20 Å, or up to 2 nm) could be adsorbed inside the micropores of activated charcoal [12]. Therefore, the value of iodine number exhibited the microporous structure. Some activated charcoal had a mesopore (2 to 5 nm) structure which adsorbs medium-sized molecules such as methylene blue. Thus, the quantity of methylene blue which is adsorbed into activated charcoal also indicated the mesoporous structure [13]. The activation temperatures of H_3PO_4 activation on iodine and methylene blue adsorption value are presented in table 1.

Table 1: The activation temperatures of 500, 600 and 700 °C of obtained activated charcoal from H_3PO_4 activation on iodine and methylene blue adsorption value

Activation temperatures (°C)	Iodine number (mg/g)	Methylene blue number (mg/g)
500	403±4.35^{d}	152±0.08^{D}
600	488±6.03^{c}	163±0.04^{C}
700	629±6.64^{b}	198±0.15^{B}
Commercial medical-grade activated charcoal	1009±1.62^{a}	359±0.18^{A}

Results are presented as means±SD, n=3.

The results exhibited the highest iodine adsorption value which was achieved at 700 °C. The activated charcoal prepared by 2-step H_3PO_4 activation 500, 600 and 700 °C gave the iodine adsorption value of 403±4.35, 488±6.03 and 629±6.64 mg/g, respectively. The commercial medical-grade activated charcoal exhibited the iodine adsorption value of 1009±1.62 mg/g. In addition, the activation with H_3PO_4 is more effective in iodine adsorption, which is capable of developing a structure with a microporous structure. It can be concluded here that the surface area available to iodine increased with an increase in the activation temperature which was found that the activation developed fine microporous structure. According to Marsh and Rodriguez-Reinoso, when increased the activation temperature, phosphoric acid hydrolyzes the glycosidic linkages of hemicellulose and cellulose, and it cleaves aryl ether bonds in lignin that include dehydration, degradation, and condensation [10]. Similar results have been reported by other researchers [11-12]. Therefore, the optimum value of carbonization temperature was considered as 700 °C for H_3PO_4 activation.

The results indicated that the activation of straw rice charcoal with H_3PO_4 had less effect on the adsorption capacity of methylene blue. It can be concluded here that the chemical activation formed smaller pore size than the methylene blue molecule. The methylene blue molecule could not enter into the pores of activated charcoal. Thus, due to a high amount of iodine value, the obtained activated charcoal prepared by 2-step H_3PO_4 activation showed the microporous structure.

Determination of pore structure

Fig. 1 illustrates the morphology of obtained activated charcoal from 2-step H_3PO_4 activation. It was found that the creation of the pores during the activation process is implemented to widen the diameters of the pores, the inner part of rice straw activated charcoal created the micro porous structure.

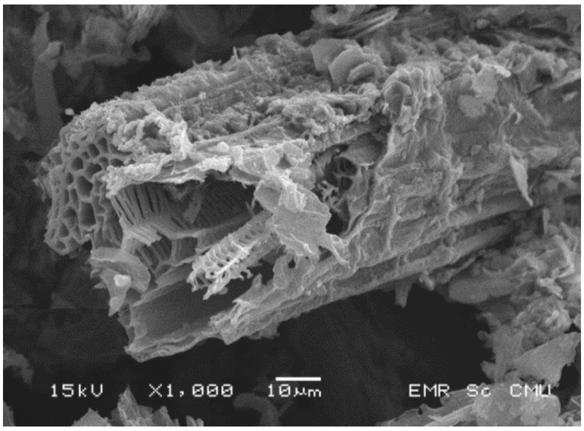

Fig. 1: SEM image of rice straw activated charcoal

Determination of surface chemistry

Fig. 2 shows the FT-IR spectra of the rice straw activated charcoal prepared by 2-step H_3PO_4 activation. All of the rice straw activated charcoals exhibited an absorption band at 1577-1574 cm^{-1} assigned of stretching vibration in carbonyl groups (C=O). The rice straw is activated charcoals carbonized at 500 and 600 °C showed the decomposition of the hydroxyl group (O-H). When the temperature increased to 700 °C, it showed an absorption band at 3418 cm^{-1} assigned to stretching vibration of a hydroxyl group (O-H). The absorption band at 1061 cm^{-1} assigned to C-O stretching vibration of alcohols [16, 17].

The results obtained from 2-step H_3PO_4 activation agreed with the studies by Puziy *et al.* (2005), they reported that the absorption band at 1300-900 cm^{-1} showed characteristic of phosphorus and phospho- carbonaceous compounds that represent from phosphoric acid activation. The absorption band at 1180 cm^{-1} may be assigned to the stretching vibration of hydrogen-bonded P=O groups that were obtained from phosphates or polyphosphates, the O–C stretching vibration in the P–O–C (aromatic) linkage and to P=OOH. The absorption band at 1085 cm^{-1} could be due to

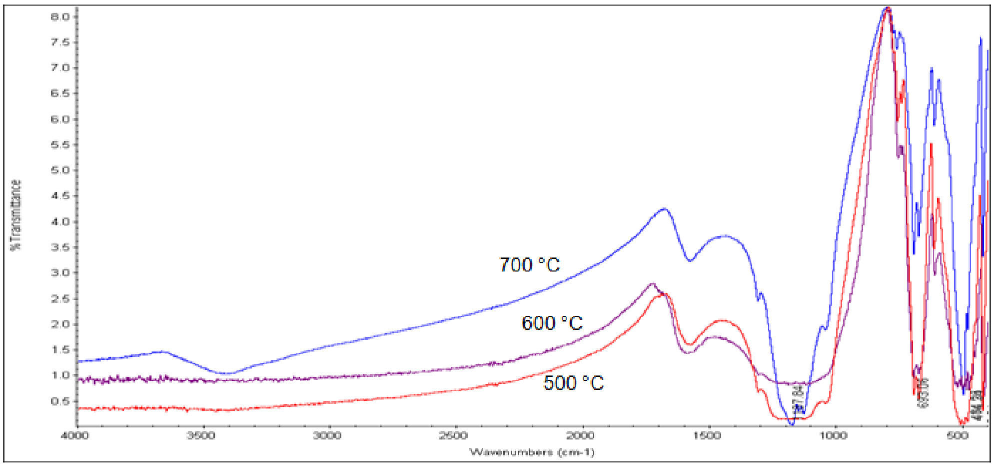

Fig. 2: FT-IR spectra of rice straw activated charcoal obtained from 2-step H_3PO_4 activation at 500, 600 and 700 °C

Determination of heavy metal adsorption

The adsorption of Pb^{2+} ions on activation temperature of 2-step H_3PO_4 activation is shown in fig. 3.

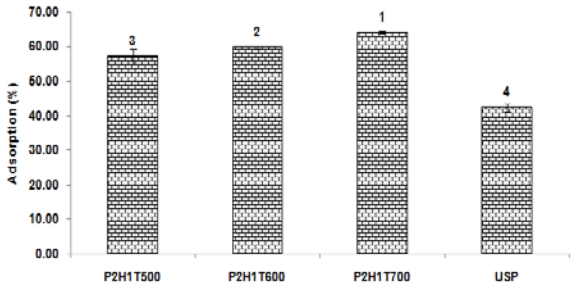

Fig. 3: The adsorption of Pb^{2+}ions of 2-step H_3PO_4 activation at 500, 600 and 700 °C (P2H1T500, P2H1T600 and P2H1T700, respectively) and activated charcoal USP grade (USP)

The results indicated that the adsorption of Pb^{2+} ions of activated charcoal which was obtained from 2-step H_3PO_4 carbonization temperatures at 500, 600 and 700 °C were 57.05, 59.62 and 64.19 %, respectively. The results exhibited the highest iodine adsorption value which was achieved at 700 °C. Moreover, the obtained rice straw activated charcoal gave the good results of Pb^{2+} ions more than commercial medical-grade activated charcoal (USP), which showed the percentage adsorption was 42.30 %. It can be concluded that the obtained rice straw activated charcoal prepared by 2-step H_3PO_4 activation showed the higher Pb^{2+}ions adsorption than commercial medical-grade activated charcoal.

The reaction of metal ion adsorption on the surface of rice straw activated charcoal can be explained that the rice straw is activated charcoal consist of carbonyl (C=O) on the surface. When the activated charcoal dissolves in an aqueous solution, the reaction of acidic groups occurs through ionization and creates positively-charged sites (H^+ ion). The H^+ lions are adsorbed to the negatively-charged $C\text{-}O^-$sites of the carbon surface in an aqueous phase. These negatively-charged sites interact with the Pb^{2+} ions. Therefore, these functional groups could form surface complexes with Pb^{2+}ions and increase the adsorption efficiency of Pb^{2+}ions of the rice straw activated charcoal which were similar to previous studies from Bansal and Goyal [19].

Additionally, Mihajlovic *et al.* (2014) described that the metal ion adsorption on the surface of activated charcoal strongly depends on electric charge, hydrated ionic radious, hydration energy and metal electronegativity [20]. According to Faur-Brasquent *et al.* (2002), the influence on maximum adsorption capacities depends on porosity, electronegativity and ionic radius [21].

CONCLUSION

The 2-step activation by impregnation using phosphoric acid as activating agents in the ratio of 1:4 w/v, followed by carbonization process at 500, 600 and 700 °C were more efficient highest to adsorbed Pb^{2+} ions. This adsorption capacity was higher than that of the commercial medical-grade activated charcoal, and then the rice straw can be used as a suitable material for the production of high quality activated charcoal which makes them more suitable for Pb^{2+} ions adsorption. The microstructures of the activated charcoal, observed by SEM, agreed with the result of iodine adsorption.

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CONFLICT OF INTERESTS

Declare none

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