*Vietnam Journal of Science and Technology* ***55*** *(4) (2017) 494-502*

DOI: 10.15625/2525-2518/55/4/9124

# EFFECT OF THE CARBONIZATION AND ACTIVATION PROCESSES ON THE ADSORPTION CAPACITY OF RICE HUSK ACTIVATED CARBON

**Hoa Thai Ma[1, 2], Van Thi Thanh Ho[3], Nguyen Bao Pham[2], Dat Chi Nguyen[1],**
**Kieu Thi Diem Vo[4], Hung Cam Ly[3], Tuan Dinh Phan[3, *]**

[1]*Ho Chi Minh City University of Technology - Vietnam National University,*
*268 Ly Thuong Kiet Street, District 10, Ho Chi Minh City*

[2]*Tra Vinh University, 126 Nguyen Thien Thanh Street, Ward 5, Tra Vinh City*

[3]*Ho Chi Minh City University of Natural Resources and Environment,*
*236B Le Van Sy street, District Tan Binh, Ho Chi Minh City*

[4]*Dong Nai Technology University, Nguyen Khuyen Street, Ward Trang Dai, Bien Hoa city*

[*]Email: *pdtuan@hcmunre.edu.vn*

Received: 3 January 2017; Accepted for publication: 28 June 2017

## ABSTRACT

In this study, rice husk was used as a precursor to prepare activated carbon using steam as a physical activation agent. Steam can be used to activate for almost all raw materials. This activation method was followed of the initial carbonization step. The study also investigated the effects of preparation parameters on the adsorption capacity of iodine (I) and methylene blue (MB). These parameters included the range of temperature and time in the carbonization and activation. The initial carbonization, done at temperatures up to 500°C in 60 min., was a highly exothermic process where the temperature was strictly controlled. The creation of the internal surface was done during the activation step with steam at temperatures 800 °C in 30 min., for which the BET (Brunauer, Emmett and Teller) specific surface area was up to 710.8 $m^2$/g. Besides, the I and MB adsorption capacity of the activated carbon were the best that reached 866.0 ± 6.5 and 217.9 ± 1.0 mg/g, respectively, while the I and MB adsorption capacity of carbonization step only reached 311.7 ± 3.4 and 28.7 ± 0.8 mg/g, respectively. The entire synthetic procedure was simple, environmental-friendly and economical-effectively. The application prospect of the activated carbon prepared in this work was much more promising due to its high adsorptive capacity.

*Keywords:* rice husk, carbonization, activation, activated carbon and adsorption capacity.

## 1. INTRODUCTION

Activated carbon with a large adsorption capacity is the carbonaceous material highly needed for various industrial purifications and waste water treatments [1]. The demand for activated carbon (AC) is increasing rapidly with enhanced awareness about environment protection. However, the price of AC is very expensive due to the fact that most of the commercial AC products are derived generally from costly natural materials such as wood or coal. Therefore, the exploration for a cheap and easily available precursor for AC production is of great importance.

There is a growing interest in the production of AC using cheap agricultural and industrial wastes [2]. Several wastes including coffee husks, rice husks, walnut shells, cotton stalks, coconut husks, and corn cobs have been investigating as the activated carbon precursors and are still receiving renewed attention because of their cheap prices and abundant resources. Many of the waste-based AC also enabled comparable or even better performance than the commercial AC in many applications. Consequently, the conversion of cheap biomass wastes into value-added AC not only opens a low-cost path for AC production but also provides an efficient way to reduce the environmental pollution caused by disposing agricultural and industrial wastes [3].

Rice is an important staple food for 3.5 billion people on the world. According to Food and Agriculture Organization of the United Nations (FAO) in 2015, the yield of paddy on the world reached 749.1 million tones and it will tend to increase in the following years. According to statistics rice husk (RH), a by-product from the milling process, made up about 20 % the weight of paddy. Thus, the annual generated RH is about 150 million tons. In Vietnam, it was about approximately 8.94 million tons, equivalent 5.96 % of the world's RH. Currently, the amount of husk is still underused in a reasonable manner especially in developing countries, including Vietnam. Most RH is burned or dumped directly into canals causing environmental pollution. According to the report of Trinh *et al.* [4], rice husk is carbonized at 450 ÷ 520 $^{o}$C, after that the product of this process is activated by over heating at above 700 $^{o}$C in 1.0 to 2.0 hours. The mass ratio of steam and raw material is in the range 0.09 ÷ 0.3. The surface area of obtained activated carbon is 276.68 m$^2$/g. They are fundamental steps to build a manufacturing technological process of domestic rice husk activated carbon production [4].

Burning RH gives 14–20 % ash which contains 80–95 % silica and minor amounts of metallic elements [5]. RH is little commercial value and not useful to feed either humans or animals because it contains high content of silicon dioxide [6] which is dissolved in hot concentrated alkali [7].

The activation of AC includes of physical and chemical methods. By physical activation, AC is obtained after two steps: the first is carbonization, which is the pyrolysis of carbonaceous materials at high temperature (500 - 1000 $^{o}$C) in an inert atmosphere to eliminate maximum amounts of oxygen and hydrogen elements; the second is the thermal activation at the same temperature in the presence of an oxidizing gas such as steam, carbon dioxide or both [8]. Chemical activation involves impregnation of raw materials with such chemicals as $H_3PO_4$, KOH, NaOH, or $ZnCl_2$, etc. These chemicals are dehydrating agents that can influence the pyrolytic decomposition and retard the formation of tars during the carbonization process, thereby increasing the yield of AC [9].

In general, AC is produced by carbonizing the raw materials prior to steam activation. The carbonization process leaves an imprint effect on the final product and the careful selection of carbonization process is enriching the carbon content and creating an initial porosity in the char. The activation process further develops the porosity and creates some ordering of the structure to generate a highly porous solid as final product [10].

The alkali treatment of raw material can greatly increase the BET surface area and total pore volume of the produced AC [11, 12]. It is highly necessary to advance the alkali treatment technology for AC or to develop a utilization technology for the generated waste solution.

The aim of this study is to explore the temperature and time conditions of carbonization and activation process of producing AC from RH with the raw material treatment by alkaline. That promises to leverage agricultural by-product to produce AC using for environmental treatment.

## 2. MATERIAL AND METHODS

### 2.1. Raw material

RH from a rice mill at Tra Vinh province was used as raw material. Then it was washed thoroughly with distilled water to remove soil and dust, then dried at 105 $^{o}$C in an oven for 24 hours.

### 2.2. Experiment procedures

The dried rice husk was impregnated with 2M NaOH solution with the ratio of RH: NaOH = 1:8 and stirred at least 1 hour at 100 $^{o}$C.

After the basis solution was drained, the RH was washed with distilled water until the filtrate was neutral, and then dried at 105 $^{o}$C for 24 hours.

For approximately 40 g of the dried rice husks were placed in a quartz reactor which was inserted into a vertical electric heating furnace. The whole system was purged nitrogen gas to remove the oxygen. Then the reactor was heated at 400 – 550 $^{o}$C in the presence of nitrogen flow with a heating rate of 10 $^{o}$C/min. and was held at this temperature for 1 hour. There after the temperature was raised to 750 – 850 $^{o}$C. After the activation temperature was reached, the gas was switched to steam and sample was kept under this condition for 30 – 90 min. before it was finally cooled in nitrogen flow (shown in Fig.1.).

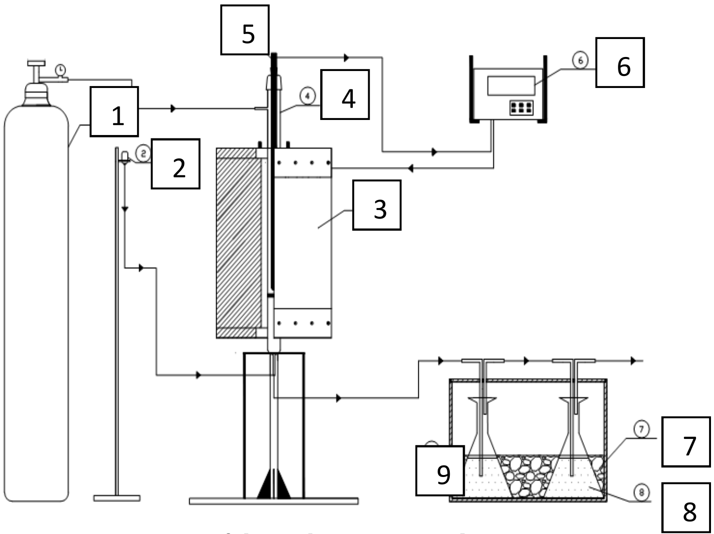


*Figure 1.* Diagram of the carbonization and activation process.

(Note: 1: Nitrogen gas tank, 2: water bottle, 3: reactor, 4: quartz reaction vessel, 5: temperature sensor, 6: temperature control, 7: ice, 8: acetone solution, 9: tank insulation).

The carbonization and activated carbon product was analyzed with I and MB adsorption capacity by GB-T 12496.8-1999 and GB-T 12496.10-1999 standard. Scanning electron micrographs of samples was also observed.

The recovery of AC was calculated by the formula:

$$\text{The recovery of AC (\%)} = \frac{w_{AC}}{w_{RH}} * 100$$

here $w_{AC}$ is weight of AC; $w_{RH}$ is weight of RH.

### 2.3. Determination of the adsorption capacity

The iodine adsorption capacity was determined by GB-T 12496.8-1999 standard.

The methylene blue adsorption capacity was determined GB-T 12496.10-1999 standard.

The I and MB adsorption capacity was calculated by the following equation:

$$The\ adsorption\ capacity\left(\frac{mg}{g}\right) = \frac{w_i - w_t}{w_M}$$

where $w_i$ is the initial mass of iodine or methylene blue before adsorption process and $w_t$ is the mass of iodine or methylene blue after adsorption process (mg), $w_M$ is the mass of sample (g).

All of determinations were performed in triplicate.

## 3. RESULTS AND DISCUSSION

### 3.1. Effect of the carbonization temperature

The ranges of temperature from 400 to 550 $^{o}$C in 60 min. were conducted which are causing the I and MB adsorption capacity of char varied from 46.2 to 311.7 and 16.6 to 28.7 mg/g, respectively. A maximal I and MB adsorption capacity reached 311.7 ± 3.4 mg/g and 28.7 ± 0.8 mg/g, respectively which was observed at 500 $^{o}$C in 60 min. as shown in Fig. 2.

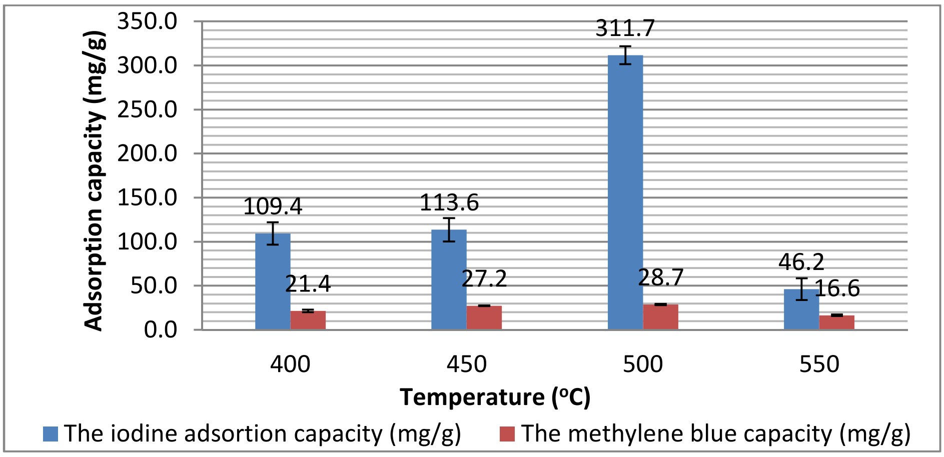


*Figure 2.* The effect of the carbonization temperature on the I and MB adsorption capacity.

This was not only because the main reaction of carbonization was actively proceeded with the increase of carbonization temperature, but also because RH showed the reduction of adsorption characteristics due to the contraction and sintering of char at high temperatures [13] (above 500 $^{o}$C). Therefore, the temperature condition at 500 $^{o}$C was chosen to produce char which was used as feedstock for activation process to increase the efficiency of carbonization process.

### 3.2. Effect of the carbonization time

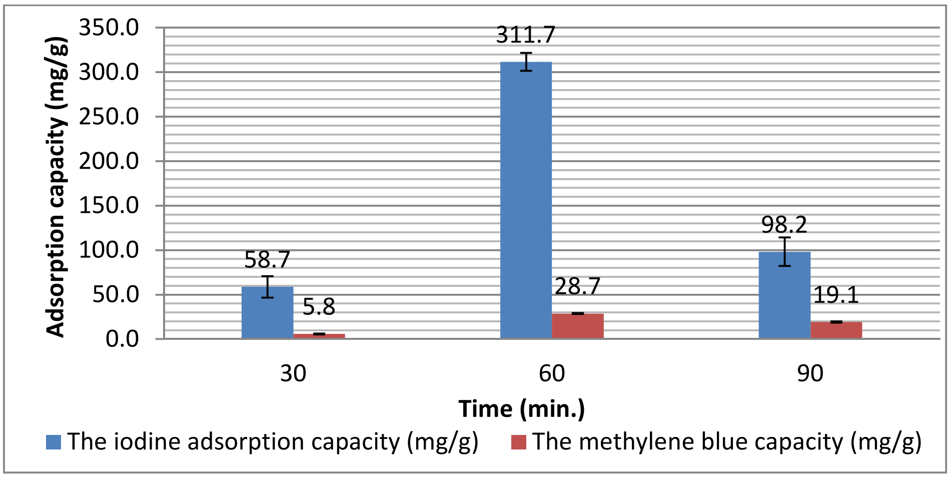


*Figure 3*. The effect of carbonization time on the I and MB adsorption capacity.

The carbonization time had a significant effect on the efficiency of carbonization process. The ranges of the time from 30 to 90 min. were conducted which caused the change of I and MB adsorption capacity of char from 58.7 to 311.7 mg/g and 16.6 to 28.7 mg/g, respectively. The maximal I and MB adsorption capacity values reached 311.7 mg/g and 28.7 mg/g, respectively which was observed at 500 $^{o}$C in 60 min. as shown in Fig.3. It was explained as follows: when reaction has started for 60 min., the pores were sintered during the increase of thermal exposure time, thus decreased the adsorption characteristics. This result was similar to the observations by other researchers [14]. Therefore, the carbonization condition at 500 $^{o}$C and 60 min. was chosen to produce char which was used as feedstock of activation process.

### 3.3. Effect of activation temperature

The activation of char was the most important stage of the production process of AC, since this stage increased porosity and specific surface area of the product. In general, there were three types of pores to be developed in the solid, that were micropore (< 2 nm), mesopore (2 ÷ 20 nm) and macropore (> 50 nm). The size of the formed pores would effect the porosity, the total surface area available for adsorption and most importantly, it determined the size of molecules that could diffuse into the pore of solid. Thus development of an appropriate pore structure was necessary if the AC was produced for a particular application [10]. The experiments were conducted with superheated-steam at 750, 800 and 850 $^{o}$C. The AC product was tested for the I and MB adsorption capacity. The results were shown in Fig. 4. It was pointed out that at 800 $^{o}$C, the sample possessed the largest adsorption capacity, clearly indicating that the pore volume mostly increased under this activation condition. Comparatively, as the activation temperature was lower than 800 $^{o}$C, the char was only partially activated [11], leading to undeveloped porosity and hence lower surface area.

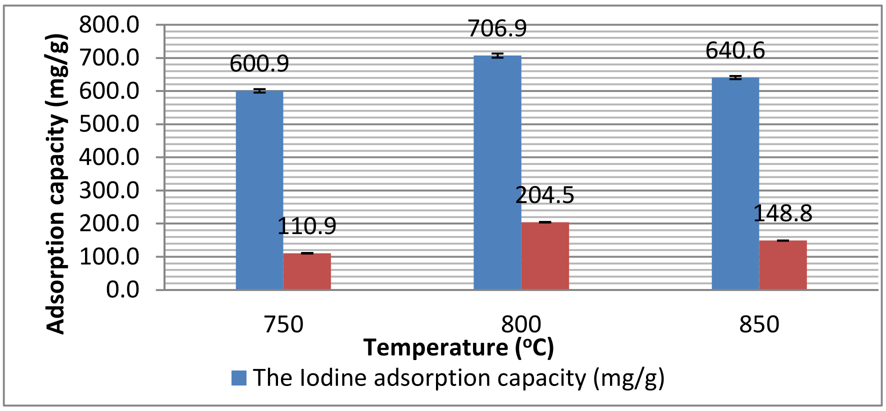


*Figure 4*. The effect of activation temperature on the I and MB adsorption capacity.

Similarly, however, when the activation temperature was higher than 800 $^{o}$C, violent gasification reactions might cause a part of the micropore structure to be destroyed by collapsing or combining together, resulting in the reduction of micro-porosity and accordingly the increase of mesopore volume [15]. Other similar explanations, the gradually enhanced reaction between steam and carbon resulted in more developed pore structures. When the activation temperature was over 800 °C, the reactions between steam and carbon started to be diffusion- controlled and thus caused a nonhomogeneous reaction in the particle, resulting in the reactions mainly on their external surfaces that had little contribution to the pore generation. Furthermore, the reaction between steam and carbon became too violent to widen the pores and cause some micropores to be converted into mesopores and macropores, decreasing the specific surface area and total pore volume. Beside the influence of the increasing temperature, the ash formation also increased, resulting in a decrease of surface area. Pore widening and pore collapse could also occur and resulted in a decrease of surface area [16]. That was demonstrated by the fact that the AC activated at 850 °C had a smaller micropore volume than that activated at 800 °C. That meant the AC activated at 850 °C had a smaller micropore volume than that activated at 800 °C [3]. This led to the best adsorption capacity of I and MB at 800 $^{o}$C as 706.9 mg/g and 204.5 mg/g, respectively, as shown in Fig. 4.

However, at the condition, the recovery of AC was slightly lower than that activated at 750 $^{o}$C as shown in Table 1. It might be due to the reaction between steam and carbon, resulting in the carbon loss at higher treatment temperature and longer residence time [17].

*Table 1*. Effect of activation conditions on the recovery of AC.

| | **Temperature ($^{o}$C)** | | | **Time (min.)** | | | |
|---|---|---|---|---|---|---|---|
| | 750 | 800 | 850 | 20 | 30 | 60 | 90 |
| **Recovery of AC, %** | 18.7±0.2 | 17.0±0.4 | 5.2±0.1 | 43.0±0.5 | 23.8±0.3 | 17.0±0.2 | 3.0±0.4 |

### 3.4. Effect of activation time

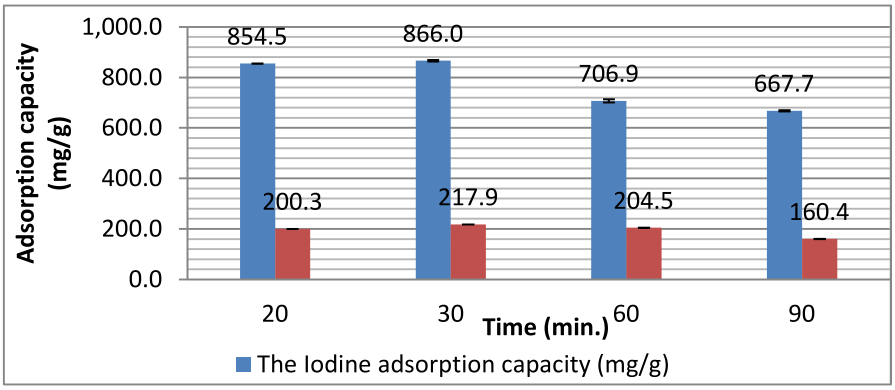
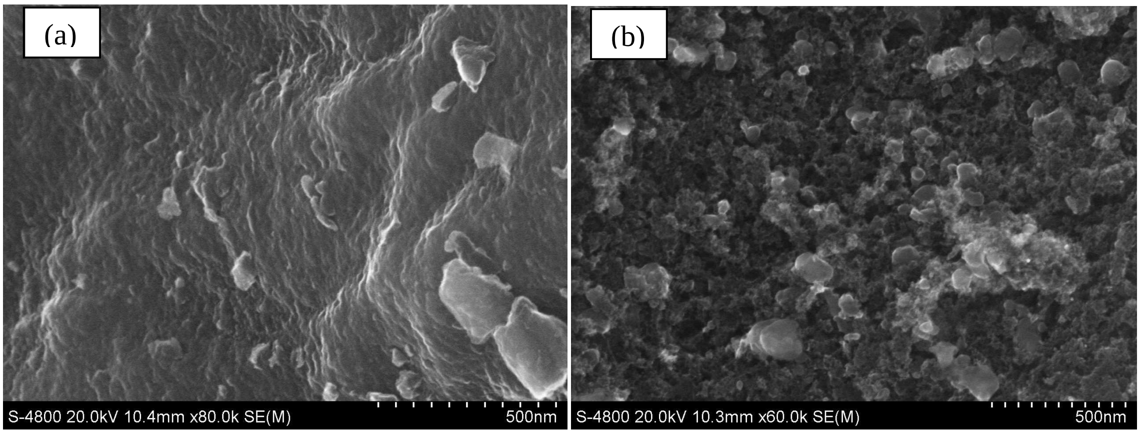


*Figure 5.* The effect of activation time on the iodine and methylene blue adsorption capacity.



*DA Micropore Volume = 0.001 cc/g*

*Pore Radius (mode)= 9.800e + 00 Å*

*DA Micropore Volume = 0.471 cc/g*

*Pore Radius (mode)= 8.700e+00 Å*

*Figure 6.* SEM micrographs of the AC treated at 500 °C/60 min. (a),
and of the char treated at 800°C/30 min. (b).

According to Fig. 5. there were the significant effects of the activation time on the I and MB adsorption capacity. At 800 °C in 30 min. the I and MB adsorption capacity of AC reached the highest values as 866.0 ± 6.5 and 217.9 ± 1.0 mg/g, respectively. Those values were much higher than 311.7 ± 3.4 and 28.7 ± 0.8 mg/g, respectively, received by carbonization step. Besides, the specific surface area by BET method of 710.8 $m^2$/g and the micropore volume of 0.471 cc/g have figured out a sharp increase in comparison with the char micropore of 0.001 cc/g. The results were in good agreement with the earlier reports [16, 18]. It could be explained that during early stage of the activation process, the development of mesopores was less significant but it rapidly increased thereafter. The continuous development of mesopores and the expense of micropores were the typical characteristics of steam activation [19]. Besides, the high I and MB adsorption capacity indicated the high degree of activation (typical range 500 ÷ 1200 mg/g) and the relationship with the micropore content. At higher temperature and longer activation time, the adsorption decreased. That might be due to a partly reduction of micropores. Besides, the recovery percentage of AC had the tendency to decrease with the increase of temperature or retention time as shown in Table 1. From these results, it could be inferred that a significant amount of micropores was formed in the AC sample and it was generally agreed among investigators [20] that the adsorption capacity of AC largely depended on the amount of micropores presented in the solid. AC adsorption capacity was proportional to the quantity of the micropore volume in the material. Fig.6. showed that the activation significantly increased with the amount of AC micropores (a) in comparison with that of char (b).

## 4. CONCLUSION

The effect of process parameters on the I and MB adsorption capacity have been investigated. The results showed that temperature and retention time of the carbonization and activation process effect significantly to the adsorption capacity. Based on the experimental data, the best conditions were identified for carbonization as temperature of 500 $^{o}$C, retention time of 60 min. and for activation as 800 $^{o}$C and 30 min, respectively. At those conditions, the I and MB adsorption capacity were 866.0 ± 6.5 mg/g and 217.86 ± 1.0 mg/g, respectively. Besides, its specific surface area by BET method was 710.8 $m^2$/g. It was proved that the steam activation method to produce AC from RH was a highly effective one.

***Acknowledgement.*** This work was financially supported by the Ministry of Natural Resources and Environment (MONRE) through the Project coded 2015.04.19.

## REFERENCES

1. Dąbrowski A., Podkoscielny P., Hubicki Z., Barczak M. - Adsorption of Phenolic Compounds by Activated Carbon, A Critical Review. Chemosphere **58** (2005) 1049-70.
2. Paraskeva P., Kalderis D., Diamadopoulos E. - Production of Activated Carbon from Agricultural by Products. J. Chem.Technol. Biotechnol. **83** (2008) 581-592.
3. Yang J., Yu J., Zhao W., Li Q., Wang J. and Xu G. - Upgrading Ash-Rich Activated Carbon from Distilled Spirit Lees, Industrial & Engineering Chemistry Research **51** **(**2012) 6037−6043Liou T.H. - Preparation and characterization of nano-structured silica from rice husk, Mat Sci Eng. A **364** (2004) 313-323.
4. Trinh D.V. Cao T. N., Bui H. X., Phạm B. T., Nguyen P. T. D. - Technology for activated carbon production from rice husks, Proceedings of the 9th Conference of Science and Technology, Hochiminh City University of Technology, Hochiminh City, 2007, pp. 1-4 (in Vietnamese).
5. Liou T. H. - Preparation and characterization of nano-structured silica from rice husk, Mat Sci Eng. A **364** (2004) 313-323.
6. Ebaid R. A., El-Refaee I. S. - Utilization of rice husk as an organic fertilizer to improve productivity and water use efficiency in rice fields, Proceedings of the 8th African Crop Science Society Conference, El-Minia, Egypt, 1923 (2007).
7. Greenwood N. N., Earnshaw A. - Chemistry of the Elements. Oxford: Pergamon Press, 1984, 393–99. ISBN 0-08-022057-6.
8. Bouchelta C., Medjram M. S., Bertrand O., Bellat J. P. - Preparation and characterization of activated carbon from date stones by physical activation with steam. J Anal Appl Pyrolysis **82** (2008) 70-77.

9. Hassan A. F. and Youssef A. M. - Preparation and characterization of microporous NaOH-activated carbons from hydrofuoric acid leached rice husk and its application for lead(II) adsorption. Carbon Letters **15** (2014) 57-66.
10. Daud WMAW, Ali WSW, Sulaiman MZ - The effects of carbonization temperature on pore development in palm-shell-based activated carbon. Carbon **38** (2000) 1925–1932.
11. Liou T., Wu S. - Characteristics of Microporous/mesoporous Carbons Prepared from RH under Base- and Acid-treated Conditions. J. Hazard. Mater. **171** (2009) 693-703.
12. Yang J. A., Qiu K. Q. - Development of High Surface Area Mesoporous Activated Carbons from Herb Residues. Chem. Eng. J. **167 (**2011) 148-154.
13. Jung D. and Chun Y. - Characteristics on Carbonization and Steam Activation of Sewage Sludge. The Open Process Chemistry Journal **2** (2009) 12-19.
14. Ahmadpour A., Do D. D. - The preparation of active carbons from coal by chemical and physical activation. Carbon **34** (1996) 471-479.
15. Chen Y., RuZhai S., Liu N., Song Y., An Q., Song X. – Dye removal of activated carbons prepared from NaOH-pretreated rice husks by low-temperature solution-processed carbonization and $H_3PO_4$ activation. Bioresource Technology **144** (2013) 401–409.
16. Kalderis D., Bethanis S., Paraskeva P., Diamadopoulos E. - Production of activated carbon from bagasse and rice husk by a single-stage chemical activation method at low retention times. Bioresource Technology **99** (2008) 6809–6816.
17. Kruse A., Funke A., Titirici M.M. - Hydrothermal conversion of biomass to fuels and energetic materials. Curr. Opin. Chem. Biol. **17** (2013) 515–521.
18. Sindhu M., Begum K. M. M. S., and Sugashini S. - A comparative study of surface modification in carbonized rice husk by acid treatment, Desalination and Water Treatment **45** (2012) 170-176.
19. Rodriguez-Reinoso F. In: Lahaye J., Ehrburger P., editors - Fundamental issues in control of carbon gasification reactivity. Netherlands: Kluwer Academic (1991), pp. 71.
20. Tounsadi H., Khalidi A., Farnane M., Abdennouri M., Barka N. - Experimental design for the optimization of preparation conditions of highly efficient activated carbon from Glebionis Coronaria L. and heavy metals removal ability, Process Safety and Environment Protection **102** (2016) 710-723.