

ISSN: KHOA HỌC TỰ NHIÊN VÀ CÔNG NGHỆ 1859-3100 Tập 15, Số 3 (2018): 89-99 HO CHI MINH CITY UNIVERSITY OF EDUCATION JOURNAL OF SCIENCE

> NATURAL SCIENCES AND TECHNOLOGY Vol. 15, No. 3 (2018): 89-99

Email: tapchikhoahoc@hcmue.edu.vn; Website: http://tckh.hcmue.edu.vn

STUDYING THE PREPARATION OF ACTIVATED CARBON FROM MACADAMIA NUT SHELLS BY CHEMICAL ACTIVATION WITH NaOH IN METHYLENE BLUE TREATMENT APPLICATION

Doan Nguyen Hoang Anh, Pham Mai Ly^{*}, Dao Minh Trung

Thu Dau Mot University Received: 11/01/2018; Revised: 06/3/2018; Accepted: 26/3/2018

ABSTRACT

Study on preparation of activated carbons by chemical activation with NaOH using the impregnatio ratio of 3:1 (NaOH:char) from Macadamia nut shell in terms on temperature and time. The research result showed that Methylene Blue (MB) absorption at optimum temperature and time of 300°C and 90 minutes was 205,68 mg and the removal efficiency was 97,59% corresponding to the color reduction from 349,67 Pt-Co to 8,4 Pt-Co. This results showed that activated carbons prepared from Maccadia nut shells and chemical activation with NaOH had the capable of color treatment in textile wastewater.

Keywords: activated carbon, macadamia nut shells, MB absorption. TÓM TẮT

Nghiên cứu điều chế than hoạt tính từ vỏ hạt Mắc-ca sử dụng tác nhân hoạt hóa NAOH ứng dụng xử lí Metylen Blue

Nghiên cứu điều chế than hoạt tính bằng cách kích hoạt hóa học với NaOH theo tỉ lệ ngâm 3:1 (NaOH:than) từ vỏ hạt Mắc-ca theo hai yếu tố về nhiệt độ và thời gian. Kết quả nghiên cứu cho thấy tại nhiệt độ và thời gian tối ưu là 300°C và 90 phút, than hoạt tính đạt được độ hấp phụ Methylen Blue (MB) là 205,68mg và hiệu suất loại bỏ 97,59% tương ứng với độ màu giảm từ 349,67 Pt-Co xuống còn 8,4 Pt-Co. Qua kết quả nghiên cứu cho thấy, than hoạt tính được điều chế từ vỏ hạt Mắc-ca và kích hoạt hóa học với NaOH có khả năng xử lí màu trong nước thải dêt nhuôm.

Từ khóa: than hoạt tính, vỏ Mắc-ca, hấp phụ màu Methylen Blue.

1. Introduction

Activated Carbons are well-known as a highly adsorbent material and are used in many water treatment fields [1], [2]. The adsorption capacity of activated carbon is

^{*} Email: *mt.lypham@gmail.com*

influence by many factors such as structural characteristic, surface chemistry functional groups [3], surface area, ash content... [4]. In face, activated carbons are prepared from two main sources, that are coal and agricultural waste such as coconut shells coal [5], husk [6], bamboo coal [7].

In Vietnam, Macadamia are growing in the North West and Tay Nguyen areas in recent years. By 2020 years, there are 10.000 ha of land that can be used to plant Macadamia [8]. According to the report of [9], each ton of nut shells can emit 70 - 77% of the shells in annual years. Most of shells are considered as waste products, only a few are used as fuel [10], [11].

However, according to the research report [12], [13], [14] showed that the Macadamia shells had many attractive features to prepare activated carbon such as Carbon content (47 - 49%), carbon content of Macadamia was higher than one of bamboo coal (45,53%) [15] and they equaled with carbon content in coconut shell coal (48,63%) [15]. In addition, the shells contained 46,52% oxygen; 6,10% hydrogen; 0,36% nitrogen and ash content was only 0,22% [12], the above characteristics showed that Macadamia has the potential to be activated carbon.

Activated carbons preparation process from Macadamia nut shell was activated with various agents such as CO_2 or water vapor [16], [17], [18]; KOH and ZnCl₂ [19, 20]; NaOH [11] and H₃PO₄ [21].

Thus, in this study, activated carbons was prepared from Macadamia nut shells by chemical activation with NaOH. In addition, Bio-activated carbons were investigated Methylene Blue adsorption capacity in textile wastewater.

2. Experimental

2.1. Materials

- Research subjects: Methyllen Blue ($C_{16}H_{18}CIN_3S.3H_2O$, 99%, China) has a concentration of 25mg/L (corresponding to 349,67 Pt-Co, TCVN 6185:2005).

- Research chemicals: $Na_2HPO_4.12H_2O$ (98%, China), KH_2PO_4 (98%, China), NaOH (96%, China). HCl 1N (China).

- Research materials: Macadamia nut shells are harvested in Lam Dong province.

- Research equipment: Jartest. This equipment is produced with a six - place multiple stirrer system. The turbine-type stirrer consists of a plat panel in the same vertical, that are placed in 1 L beaker for the same type of waste water. They operate by a gear-box, that can be used to adjust spin speed.

2.2. Experimental methods

2.2.1. Part 1: Preparation of bio-activated carbon from Macadamia nut shells

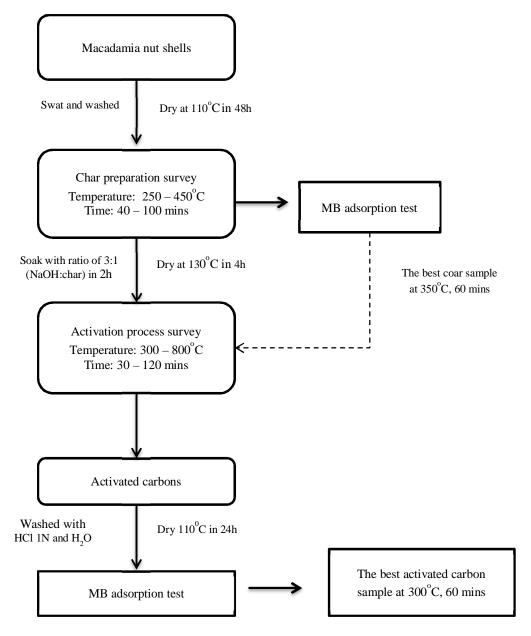


Fig 2.1. The layout of experiments to prepare activated carbon

2.2.2. Part 2: Survey of methylene Blue absorption ability

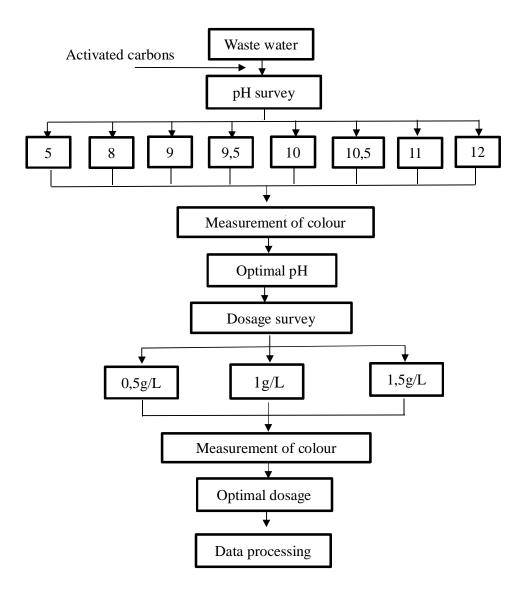


Fig 2.2. Layout of Methylene Blue treatment experiments by activated carbon

2.3. Evaluation methods

- Determination of pH by Mettler Toledo equidment (2017).
- Determination of colour by TCVN 6185:2005.
- Determination of surface observation by Scanning Electron microscope (SEM).

- Determination of functional groups by Fourier Transformation Infrared Spectrometer (FT-IR).

- Determination of Methylene Blue absorption index by GB/T 12496.10 – 1999 Standard.

3. Results and discusstion

3.1. Results of Activated Carbon preparation from Macadamia nut shells

3.1.1. Survey of temperature affecting activation process

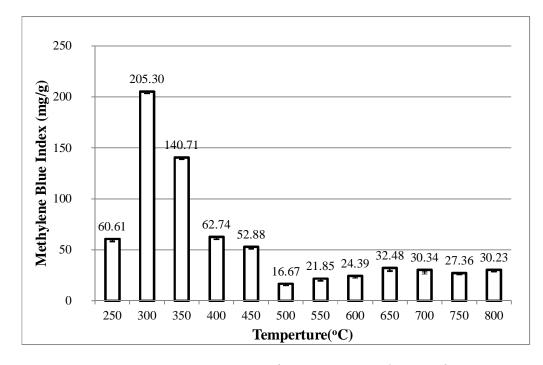


Fig 3.1. Optimum temperature determination results according to Methylene Blue Absorption

From Fig 3.1 showed that temperature was determinated in increasing range from 250 to 800°C and time in 90 minutes. After this survey, the maximum MB absorption reached 300°C và MB index reached 205,3mg MB/ g than.

This research results showed that absorption capacity of activated carbons that were activeated by NaOH was higher than some materials from previous study results such as study of [22] showed that the garlic shell materals were used to absorb MB with 82,64mg/g or the research results using tea leaves in the research of [23], the absorption was 85,16mg/g. In addition, the study results of [24] researched absorption capacity of husks that reaching 40,59mg/g and the research results of [25] showed that orange peel adsorption reached 18,60mg/g or the research of [26] with report about fly ash material was 75,52mg/g.

Thus, this above research results showed that activated carbon was found optimum temperature at 300°C with the best absorption efficient.

3.1.2. Survey of reaction time affecting activation process

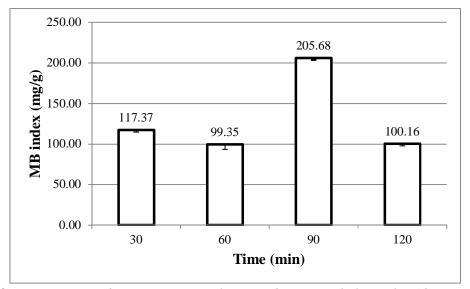


Fig 3.2. Optimum time determination results according to Methylene Blue Absorption

From research results in Fig 3.2, the time was surveyed in range of 30, 60, 90 and 120 minutes at optimum temperature (300° C). This results showed that absorption decreased from 117,37 mg/g (at 30 minutes) to 99,35 mg/g (at 60 minutes). When the heating time increased to 90 minutes, the adsorption increased dramatically 205,68 mg/g and continued to decrease to 100,16 mg/g at 120 minutes. Thus, the research results showed that 300 °C and 90 mins were optimal parameters to achieve the best MB absorption ability.

Comparation with some of previous study results such as the study results of [27] showed that activated carbon prepared from rubber waste was be used to remove MB from aqueous solution and the efficiency reached 49 mg/g; the research results of [28] researched MB adsorption capacity of coir pith carbon material 5,87 mg/g or based on the results of [29] reported on cereal grains's capacity with absorption of 26,3mg/g and in 2007 years, the study of [30] successfully investigated the adsorption capacity of fallen phoenix tree's leaves with the adsorption up to 89,7mg/g; according to the research results of [31], the MB removal capacity of Hazel nut shell reached 38,22 mg/g.

Thus, This study results showed that activated carbon with NaOH chemical activation had MB absorption capacity higher than those studies.

The research results was determinated optimal parametes at 300°C and 90 mins and the removal ability was 205,68 mg/g corresponding to 1g char absorp 205,68 mg MB.

3.2. The treatment capacity survey results of activated carbon on Methylene Blue 3.2.1. Survey optimum pH for treatment process

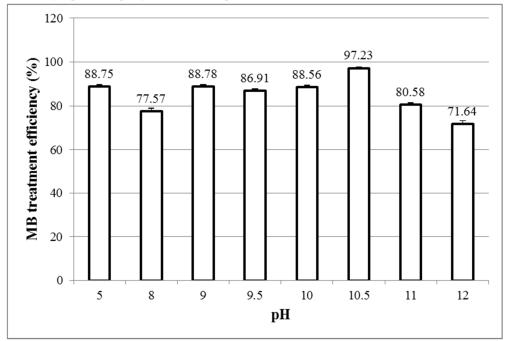


Fig 3.3. Optimum pH determination results according to the MB treatment efficient

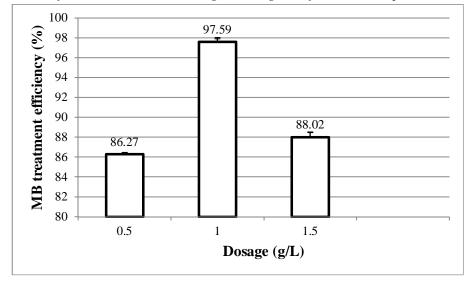
The study results on MB treatment ability in Fig 3.3 showed that pH was ranged from 5 to 12 [32, 33] corresponding to the lowest efficiency at pH = 12 (71,64%) and the highest efficient at pH = 10,5 (97,23%). There by, pH value of 10,5 is pH range with the highest treatment efficiency.

According to the study results of [34] and [35] they explained that pH had influence on MB absorption capacity of activated carbon material. When the pH in solution was adjusted at low-level, colour treatment ability of activated carbon would work on the protonation of functional groups and through electrostatic repulsion, MB was readily removed from solution. When solution was adjusted with high pH, surface of activated carbon was negatively charged, so they would be based on electrostatic attraction and hydrogen bonds to remove colourants.

Treatment ability of activated carbon in this study with the 97,23% efficient was higher than some of previous study results such as the research results of [36] showed that

the colour removal efficiency of sawdust was only 74% and the report results of [29] investigated the adsorption capacity of chaff and reached 84%, at the same pH.

Thus, activated carbon prepared from Macadamia nut shells with NaOH chemical activation in this study had the best MB removal ability at pH = 10.5 with 97,23%.



3.2.2. Results of activated carbon's dosage investigation for treatment process

Fig 3.4. Optimum dosage determination results according to the MB treatment efficient

The results of dosage (from 0.5 - 1.5 g/L) [37] survey in Fig 3.4 showed that the highest MB removal efficiency of 97,59% with 1 g activated carbon /L waste water. According to the research results of [34] suggested that the pore size and activated carbon dosage were two factors that significantly influence to MB absorption ability. The increasing amount of absorbed surface area, the absorption capacity would be increased significantly.

Comparation to some previous studies such as the research results of [36] showed that after 30 minutes, MB treatment efficiency of activated carbon prepared from sawdust reached 35,8% when using H₂SO₄ chemical agent and 22,8% when using with formaldehyde agent. This proved that the treatment ability of activated carbon in this study was better than some material in previous studies.

This research results showed that activated carbon prepared from Macadamia nut shells and NaOH chemical agent had MB treatment capacity with 97,59% for the assimed wastewater in the laboratory with a concentration of 25 mg/L corresponding to 349,67 Pt-Co.

3. Conclution

Research results showed that bio-activated carbon material was successfully prepared from Macadamia nut shells by chemical activation with NaOH at 300°C and 90 minutes operation parameters, MB index of this material reached 205,68mg/g corresponding to the MB treatment efficiency at pH = 10,5 and amount of 1g/L was 97,59%.

Activated carbons were prepare from Macadamia nut shell and chemical activation with NaOH had the high removal efficient, therefore, in order to increase the application ability in wastewater treatment of activated carbons, it is necessary to investigate on other pollutants treatment ability in wastewater.

In addition, this new bio-materials can be researched on the desorption of material and the improvement of activated carbon by degererated methods to improve the environmental quality of industrial wastewater.

* Conflict of Interest: Authors have no conflict of interest to declare.

REFERENCES

- [1] Samorn Hirunpraditkoon., T. Nathaporn, R. Anotai, and N. Kamchai, "Adsorption capacities of activated carbons prepared from Bamboo by KOH Activation," *International Journal of Chemical*, vol. 5, pp. 447 481, 2011.
- [2] Tzong-Horng L. and S.-J. W. W, "Characteristics of microporous/mesoporous carbons prepared from rice husk under base- and acid-treated conditions," *Journal of Hazardous Materials*, vol. 171, pp. 693 - 703, 2009.
- [3] Yan-Juan Z., X. Zhen-Jiao, D. Zheng-Kang, L. Meng, and W. Yin, "Effects of steam activation on the pore structure and surface chemistry of activated carbon derive from bamboo waste," *Applied Surface Science*, vol. 315, pp. 279 286, 2014.
- [4] A. Kwaghger and J.S. Ibrahim, "Optimization of conditions for the preparation of activated carbon from mango nuts using HCl," *American Journal of Engineering Research*, vol. 2, pp. 74 - 85, 2013.
- [5] M. Kobya, "Removal of Cr (VI) from aqueous solutions by adsorption onto hazelnut shell activated carbon: kinetic and equilibrium studies," *Bioresource technology*, vol. 91, pp. 317-321, 2004.
- [6] N. S. Awwad, H.M.H. Gad, M.I. Ahmad, and H.F. Aly, "Sorption of lanthanum and erbium from aqueous solution by activated carbon prepared from rice husk," *Colloids and Surfaces B: Biointerfaces*, vol. 81, pp. 593-599, 2010.
- [7] S. Y. Wang, M.H. Tsai, S.F. Lo, and M.J. Tsai, "Effects of manufacturing conditions on the adsorption capacity of heavy metal ions by Makino bamboo charcoal," *Bioresource Technology*, vol. 99, pp. 7027-7033, 2008.
- [8] Bộ Nông Nghiệp và PTNT, "Cây Mắc ca hiện trạng và định hướng phát triển," ed, 2015.

- [9] E. S. Penoni, R. Pio, F.A. Rodrigues, L.A.C. Maro, and F.C. Costa, "Analysis of fruits and nuts of macadamia walnut cultivars," *Ciência Rural*, vol. 41, pp. 2080-2083, 2011.
- [10] F. Caturla, M. Molina-Sabio, and F. Rodriguez-Reinoso, "Preparation of activated carbon bu chemical activation with ZnCl2," *Great Britain*, vol. 29, pp. 999 - 1007, 1991.
- [11] A. C. Martins, O. Pezoti, A.L. Cazetta, K.C. Bedin, D.A.S Yamazaki, G.F.G. Bandoch, et al., "Removal of tetracycline by NaOH-activated carbon produced from macadamia nut shells: kinetic and equilibrium studies," *Chemical Engineering Journal*, vol. 260, pp. 291-299, 2015.
- [12] C. A. Toles, W.E. Marshall, and M.M. Johns, "Phosphoric acid activation of nutshells for metals and organic remediation: process optimization," *Journal of Chemical Technology and Biotechnology*, vol. 72, pp. 255-263, 1998.
- [13] S. O. Bada, R.M.S. Falcon, L.M. Falcon, and M.J. Makhula, "Thermogravimetric investigation of macadamia nut shell, coal, and anthracite in different combustion atmospheres," *Journal of the Southern African Institute of Mining and Metallurgy*, vol. 115, pp. 741-746, 2015.
- [14] T. P. Xavier, T.S. Lira, M.A. Schettino Jr, and M.A.S. Barrozo, "A STUDY OF PYROLYSIS OF MACADAMIA NUT SHELL: PARAMETRIC SENSITIVITY ANALYSIS OF THE IPR MODEL," *Brazilian Journal of Chemical Engineering*, vol. 33, pp. 115-122, 2016.
- [15] W. M. A. W. Daud and W.S.W. Ali, "Comparison on pore development of activated carbon produced from palm shell and coconut shell," *Bioresource Technology*, vol. 93, pp. 63-69, 2004.
- [16] Orellana Salazar and Gerardo Nelson, "Estudio comparativo de la adsorción de oro mediante carbón activado empleando soluciones lixiviadas con cianuro y tiourea en franromec sAA," 2016.
- [17] J. A. Conesa, M. Sakurai, and M.J. Antal, "Synthesis of a high-yield activated carbon by oxygen gasification of macadamia nut shell charcoal in hot, liquid water," *Carbon*, vol. 38, pp. 839-848, 2000.
- [18] Bae Jun-Seok and Su Shi, "Macadamia nut shell-derived carbon composites for post combustion CO 2 capture," *International Journal of Greenhouse Gas Control*, vol. 19, pp. 174-182, 2013.
- [19] A. Ahmadpour and D.D. Do, "The preparation of activated carbon from macadamia nutshell by chemical activation," *Carbon*, vol. 35, pp. 1723-1732, 1997.
- [20] M. J. B. Evans, E. Halliop, and J.A.F. MacDonald, "The production of chemically-activated carbon," *Carbon*, vol. 37, pp. 269-274, 1999.
- [21] Jagtoyen Marit and Derbyshire Frank, "Activated carbons from yellow poplar and white oak by H3PO4 activation," *Carbon*, vol. 36, pp. 1085-1097, 1998.
- [22] B. H. Hameed and A.A. Ahmad, "Batch adsorption of methylene blue from aqueous solution by garlic peel, an agricultural waste biomass," *Journal of hazardous materials*, vol. 164, pp. 870-875, 2009.
- [23] M. T. Uddin, Md. A. Islam, S. Mahmud, and Md. Rukanuzzaman, "Adsorptive removal of methylene blue by tea waste," *Journal of Hazardous Materials*, vol. 164, pp. 53-60, 2009.

- [24] V. Vadivelan and K.V. Kumar, "Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk," *Journal of colloid and interface science*, vol. 286, pp. 90-100, 2005.
- [25] G. Annadurai, R.S. Juang, and D.J. Lee, "Use of cellulose-based wastes for adsorption of dyes from aqueous solutions," *Journal of hazardous materials*, vol. 92, pp. 263-274, 2002.
- [26] P. Janos, H. Buchtova, and M. Rýznarová, "Sorption of dyes from aqueous solutions onto fly ash," *Water research*, vol. 37, pp. 4938-4944, 2003.
- [27] G. San Miguel, G.D. Fowler, and C.J. Sollars, "Adsorption of organic compounds from solution by activated carbons produced from waste tyre rubber," *Separation science and technology*, vol. 37, pp. 663-676, 2002.
- [28] D. Kavitha and C. Namasivayam, "Experimental and kinetic studies on methylene blue adsorption by coir pith carbon," *Bioresource Technology*, vol. 98, pp. 14-21, 2007.
- [29] R. Han, Y. Wang, P. Han, J. Shi, J. Yang, and Y. Lu, "Removal of methylene blue from aqueous solution by chaff in batch mode," *Journal of Hazardous Materials*, vol. 137, pp. 550-557, 2006.
- [30] R. Han, W. Zou, W. Yu, S. Cheng, Y. Wang, and J. Shi, "Biosorption of methylene blue from aqueous solution by fallen phoenix tree's leaves," *Journal of Hazardous Materials*, vol. 141, pp. 156-162, 2007.
- [31] M. Doğan, H. Abak, and M. Alkan, "Biosorption of methylene blue from aqueous solutions by hazelnut shells: equilibrium, parameters and isotherms," *Water, air, and soil pollution*, vol. 192, pp. 141-153, 2008.
- [32] Hamdaoui Oualid, "Batch study of liquid-phase adsorption of methylene blue using cedar sawdust and crushed brick," *Journal of Hazardous Materials*, vol. 135, pp. 264-273, 2006.
- [33] H. Mittal, N. Ballav, and S.B. Mishra, "Gum ghatti and Fe 3 O 4 magnetic nanoparticles based nanocomposites for the effective adsorption of methylene blue from aqueous solution," *Journal of Industrial and Engineering Chemistry*, vol. 20, pp. 2184-2192, 2014.
- [34] M. Ghaedi, S.H. Heidarpour, S.N. Kokhdan, R. Sahraie, A. Daneshfar, and B. Brazesh, "Comparison of silver and palladium nanoparticles loaded on activated carbon for efficient removal of Methylene blue: Kinetic and isotherm study of removal process," *Powder Technology*, vol. 228, pp. 18-25, 2012.
- [35] B. Y. Gao, Q.Y. Yue, Y. Wang, and W. Z. Zhou, "Color removal from dye containing wastewater by magnesium chloride," *Journal of Environmental Management*, vol. 82, pp. 167 - 172, 2005.
- [36] V. K. Garg, M. Amita, R. Kumar, and R. Gupta, "Basic dye (methylene blue) removal from simulated wastewater by adsorption using Indian Rosewood sawdust: a timber industry waste," *Dyes and pigments*, vol. 63, pp. 243-250, 2004.
- [37] R. Malik, D.S. Ramteke, and S.R. Wate, "Adsorption of malachite green on groundnut shell waste based powdered activated carbon," *Waste management*, vol. 27, pp. 1129-1138, 2007.