Journal of Science and Technology ***54*** *(1A) (2016) 277-284*

PREPARATION OF ACTIVATED CARBON FROM SUGARCANE BAGASSE USING $ZnCl_2$ FOR THE REMOVAL OF Cu (II) ION FROM AQUEOUS SOLUTION: APPLICATION OF RESPONSE SURFACE METHODOLOGY (RSM)

Van Thuan Tran, Bui Thi Phuong Quynh, Thanh Khoa Phung, Giang Ngoc Ha, Thi Thuong Nguyen, Long Giang Bach*

NTT Institute of Hi-Technology, Nguyen Tat Thanh University, 300A Nguyen Tat Thanh, District 4, Ho Chi Minh City, Vietnam

*Email: *blgiangntt@gmail.com*

Received: 31 August 2015; Accepted for publication: 26 October 2015

ABSTRACT

This study aimed at preparing low cost activated carbon (AC) from sugarcane bagasse by $ZnCl_2$ activation and evaluating the effects of synthesis conditions and variables using the response surface methodology (RSM) approach for the adsorption of Cu (II) ion from aqueous solution by the synthesized ACs. From the analysis of variance (ANOVA), the most influential factors including activation temperature, impregnation ratio and activation time on each experimental design response were investigated. The optimized conditions for preparation of AC and removal of Cu (II) ions were identified with the activation temperature of 673 K, impregnation ratio of 1.5 and activation time of 35.2 minutes. An optimized conditions based–test experiment with 48.8 % of AC yield and 92.3 % Cu (II) ion removal was observed.

Keywords: sugarcane bagasse, activated carbon; response surface methodology (RSM).

1. INTRODUCTION

Copper (II) contamination in groundwater source adversely affects living species, ecological systems as well as psychological health of human. Conventional copper (II) ion elimination processes including chemical precipitation, ion exchange, solvent extraction, ultra filtration, reverse osmosis and membrane filtration exposed some disadvantages such as economically inefficient technique and safe ineligibility [1]. Among well–known adsorbents, AC is much paid attention due to their high adsorption capacity for inorganic and organic pollutants. However, synthesis of AC is a large challenge because of its high cost. Therefore, unsophisticated protocol for preparation of activated carbon from available and inexpensive raw materials of agricultural byproducts is an essential solution. Sugar bagasse towards sustainability is emerged as a prospective raw material for preparation of AC because thousands tons of bagasse residue releases from surrounding sectors in Vietnam after the process of refined sugar manufacture. In order to achieve highly micro-porous crystalline, AC preparation could be performed by two main steps including chemical activation and carbonization. In the chemical activation process, dehydrating reagents, such as zinc chloride, potassium hydroxide, potassium carbonate, sodium hydroxide, phosphoric acid and sulfuric acid are utilized to inhibit the formation of unwanted tar and to increase yield, micro-porosity, surface area of AC [2]. Among the chemical activation agents, zinc chloride ($ZnCl_2$) is considered as an efficient chemical with respect to AC preparation because of excellent heavy metal removal efficiency in wastewater [3]. Moreover, $ZnCl_2$ contributed to creation of both higher micro–porous structure and greater surface area. In the carbonization process, pyrolysis implementing in the inert atmosphere facilitates volatile emission and produces a material constituted mainly of micro– and meso–porous activated carbon [4]. Optimization of AC preparation requires a large number of independent experiments to increase precision and reliability of method. Therefore, modification of a mathematic technique is necessary to decrease number of experimental runs and to search for optimal conditions for expected responses. The response surface methodology (RSM) based on design of experiments (DOE) and analysis of variance (ANOVA) permits to assess the statistical correlation of several factors. Furthermore, RSM can evaluate the compatibility of predicted and actual models [5]. In this study, application of RSM was utilized to analyze effects of independent variables including activation temperature, impregnation ratio and activation time on AC yield and Cu (II) ion removal from aqueous solution. In addition, identification of optimized RSM based–conditions of micro–porous AC preparation from sugarcane bagasse and Cu (II) ion elimination were also studied simultaneously. And hence, application of optimized conditions for experimental investigation was observed.

2. MATERIALS AND METHODS

2.1. Production of AC

Sugarcane bagasse samples were collected from local sugarcane juice shops in Ho Chi Minh city, Vietnam was initially washed with hot distilled water several times in prior to dry under sunlight. The material was then ground and separated in particles with diameters approximately 1.0 mm. Proximate analysis (TCVN 5253:90, TCVN 9297:2012) gives the content of moister, ashm volatiles and fixed carbon were 11.2 %, 2.55 %, 57.4 % and 28,.85 %, respectively.

Impregnation agent, $ZnCl_2$ (anhydrous, impurity of 98 %), was purchased from Sigma–Aldrich. The ACs were synthesized by a continuous two-step procedure. In the chemical activation protocol, dried sugarcane bagasse of 3.0 g was soaked with $ZnCl_2$ solution, with different impregnation ratios (IR), at room temperature for 24 h. Then the resulting bagasse was dried at 80 ^{o}C for 24 h. The received $ZnCl_2$–impregnated sugarcane bagasse was heated at 500 ^{o}C for 1 h (the heating rate of 10 ^{o}C/min) followed by cooling down for 6 h. The char was repeatedly washed with deionized water in order to eliminate Zn residual followed by drying at 80 ^{o}C. The AC yield was quantified by the following equation:

$$\text{Yield (\%)} = w_c.100/w_o \tag{1}$$

where, w_c and w_o are the weight of activated carbon (g) and the weight of dry precursor (g), respectively.

2.2. Batch adsorption experiments

The adsorption of aqueous Cu(II) ions by the synthesized ACs were conducted following a procedure described in the previous work [6]. In a typical experiment, 250 mg of activated carbon sample was poured into 50 mL of aqueous solution containing 50 ppm initial Cu (II) ion in 100 mL Erlenmeyer flask around 30 ^{o}C. The mixture then was agitated with rate of 350 rpm for 2 h. Finally, the undissolved solid was separated using filtered paper. The residual Cu (II) concentration was confirmed by ICP–MS and calculated as follows:

$$Cu\ (II)\ removal\ (\%) = (C_o - C_f).100/C_o \tag{2}$$

where, C_o and C_f are Cu (II) ion concentrations of initial state and after stirring for 2 h (ppm), respectively.

2.3. Experimental design and response surface methodology (RSM)

RSM thoroughly analyses experimental variables that significantly influence on response results based on numerous specified runs [7]. However, central composite design (CCD) can decrease the number of experimental trials needed to evaluate multiple parameters and their interaction [8]. Herein, respond surface with CCD was utilized to determine the interrelating effects of three input variables consist of activation temperature (x_1), impregnation ratio (x_2) and activation time (x_3) on two output variables including AC yield (y_1) and Cu (II) ion elimination (y_2). The fluctuation of investigated levels between -α and + α were also observed (Table 1).

Table 1. Independent variables matrix and their encoded levels.

No	Independent factors	Code	Levels				
			-α	-1	0	+1	+α
1	Activation temperature (K)	x_1	605	673	773	873	941
2	Impregnation ratio (–)	x_2	0.16	0.5	1.0	1.5	1.84
3	Activation time (min)	x_3	9.5	30	60	90	110.5

The center variables (encoded 0) are utilized to determine the experimental error and the reproducibility of the data. The margin points including the low (encoded -1), high (encoded +1) and rotatable (encoded $\pm\alpha$) levels are also manipulated. In additional, CCD matrix for three independent variables (k = 3) enumerates the 2^k factorial experiments, 2k axial experiments and six replication experiments as following formula:

$$N = 2^k + 2k + c = 2^3 + 2.3 + 6 = 20 \tag{3}$$

where, N is defined as total number of experiments for three independent variables (k = 3). Two response values were AC yield (y_1) and Cu (II) elimination (y_2) dealing with the mathematical correlation between the three independent variables that approximated by the quadratic polynomial regression equation as given by equation:

$$y = \beta_o + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k}\sum_{j=1}^{k} \beta_{ij} x_i x_j + \sum_{i=1}^{k} \beta_{ii} x_i^2 \tag{4}$$

where, y is the predicted response; x*i* and x*j* are the independent variables. The parameter β_o is the model constant; β_i is the linear coefficient; β_{ii} is the second–order coefficient and β_{ij} is the interaction coefficient.

2.4. Analysis of variance (ANOVA)

ANOVA was used to assess the considerable contribution of variables and their interaction between the process variables and the responses. The plot of three-dimensional graph leads to the generation of surface response applied for the prediction of best operating conditions according to P–values and F–values. Application of Design – Expert ® version 9.0.5.1 (DX9) statistical software program (Stat–Ease Inc., Minneapolis, USA) with ANOVA could evaluate the signification, confidence and reliability of model, ultimately.

3. RESULTS AND DISCUSSION

3.1. Preliminary assessment and regression model equation with Design-Expert version 9.0.5.1

The preparation variables such as activation temperature, activation time and IR ratio are well known to greatly affect on the formation of pores, pore volume, pore size, pore distribution and thus leading to changes in related parameters such as surface area and carbon yield of the resulting activated carbons. According to results of experimental matrix and values of observed responses (Table 2), it is obvious that AC preparation strongly depends on both activation temperature and activation time while Cu (II) ion elimination much depends on two factors including activation temperature and impregnation ratio. For example, at the fixed IR of 1.0 and activation time of 60 min, when the activation temperature increased from about 600 K to 773 K, the elimination of Cu(II) ion increased nearly two times presumably due to significant enhancement of the surface area and pore volume. Additionally, it was observed that the higher activation temperature led to significant decrease in the carbon yield as resulted from the enhanced gasification. Generally, the visible fluctuation rage is 28.4 – 51.1 (%) for AC yield and 21.6 – 91.2 (%) for Cu (II) ion removal. The maximum percentage of AC yield obtained 51.1% (entry 1) and the largest Cu (II) ion elimination efficiency reached 91.2 % (entry 3). Furthermore, the Design Expert 9 (DX9) program can predict AC yields and Cu (II) concentration removal based on observed results as shown in equal (5) and (6), respectively.

$$y_1 = 43.57 - 5.84x_1 - 0.58x_2 - 4.15x_3 - 0.92x_1^2 - 0.092x_2^2 - 0.48x_3^2 + 0.013x_1x_2 - 2.46x_1x_3 - 0.46x_2x_3 \quad (5)$$

$$y_2 = -948.4 + 2.26x_1 + 317.2x_2 + 0.8x_3 - 13.10^{-4}x_1^2 - 14x_2^2 - 35.10^{-4}x_3^2 - 0.36x_1x_2 - 3.10^{-4}x_1x_3 - 0.2x_2x_3 \quad (6)$$

Table 2. Experimental matrix: values of observed and predicted responses.

Entry	Independent factors (coded)			Experiment (ICP–MS)		Prediction (DX9)	
	x_1 (K)	x_2 (-)	x_3 (min)	y_1 (%)	y_2 (%)	y_1 (%)	y_2 (%)
1	673	0.5	30	51.1	56.0	49.7	44.3
2	873	0.5	30	42.3	64.2	43.0	66.8
3	673	1.5	30	49.0	91.2	49.5	87.6
4	873	1.5	30	44.4	45.6	42.7	38.6
5	673	0.5	90	46.8	46.8	47.3	48.9
6	873	0.5	90	32.3	69.0	30.6	67.8
7	673	1.5	90	47.0	88.4	45.2	81.0
8	873	1.5	90	28.4	21.6	28.6	28.5
9	605	1.0	60	50.3	45.0	50.8	54.1
10	941	1.0	60	30.5	32.8	31.1	28.8
11	773	0.16	60	44.0	64.0	44.3	65.7
12	773	1.84	60	41.5	65.6	42.3	69.0
13	773	1.0	9.5	48.9	62.0	49.2	70.6
14	773	1.0	110.5	34.4	69.4	35.2	66.0
15	773	1.0	60	45.2	82.2	43.6	77.3
16	773	1.0	60	43.7	81.4	43.6	77.3
17	773	1.0	60	44.0	76.6	43.6	77.3
18	773	1.0	60	44.4	74.2	43.6	77.3
19	773	1.0	60	43.1	74.4	43.6	77.3
20	773	1.0	60	42.3	79.4	43.6	77.3

3.2. Response surface methodology (RSM)

Analysis of variance (ANOVA) of the quadratic polynomial regression model was utilized to identify the signification of input variables and output variables as well as relationship between the responses and the independent factors. Moreover, compatibility of such model was evaluated by correlation coefficients and adequate precision. According to data of Table 3, the ANOVA results revealed that the quadratic models at 95 % confidence level were statistically significant.

Table 3. ANOVA for response surface regression model of AC yield and Cu (II) removal.

Source	Degree of freedom	y_1, AC yield (%)			y_2, Cu (II) ion removal (%)		
		Sum of squares	F value	P value	Sum of square	F value	P value
Model	9	770.87	70.44	<0.0001^{s}	5851.96	11.91	0.0005^{s}
x_1	1	466.28	383.45	<0.0001^{s}	2884.96	52.81	<0.0001^{s}
x_2	1	4.58	3.76	0.0844^{n}	2747.71	50.31	<0.0001^{s}
x_3	1	235.29	193.49	<0.0001^{s}	62.58	1.15	0.3123^{n}
x_1^2	1	12.28	10.10	0.0112^{s}	2308.92	42.28	<0.0001^{s}
x_2^2	1	0.12	0.10	0.7575^{n}	176.96	3.24	0.1054^{n}
x_3^2	1	3.34	2.74	0.1320^{n}	146.30	2.68	0.136^{n}
$x_1 x_2$	1	0.0012	0.001	0.9751^{n}	2548.98	46.67	<0.0001^{s}
$x_1 x_3$	1	48.51	3.76	0.0001^{s}	6.48	0.12	0.7384^{n}
$x_2 x_3$	1	1.71	193.49	0.2659^{n}	62.72	1.15	0.3118^{n}
LOF^{a}	5	9.36	4.72	0.0791^{n}	435.85	6.26	0.0499^{s}
PE^{b}	4	1.59	–	–	55.68	–	–

^{a} *Lack of fit*, ^{b} *Pure error*, ^{s} *Significant at p < 0.05*, ^{n} *Not significant at p > 0.05.*

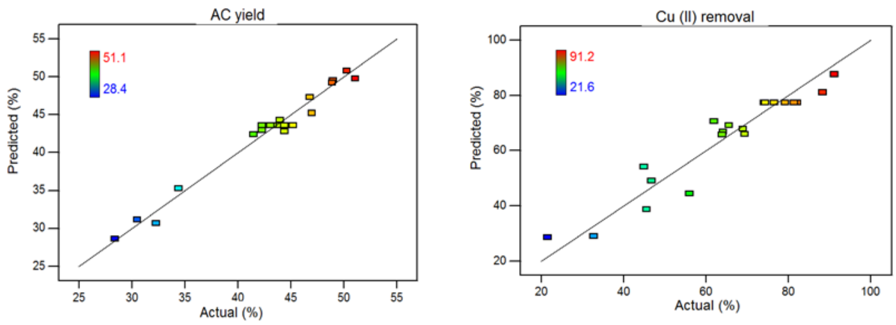

Figure 1. Comparison of actual values with predicted values of (left) AC yield and (right) Cu (II) removal.

In detail, values of P < 0.05 implied the model terms were significant. For example, both AC yield model and Cu (II) ion removal model were significant because of P < 0.0001 and P = 0.0005, respectively. In contrast, values P > 0.05 indicated that the model terms were not significant. For example, impregnation ratio was not significant for AC yield variable (P = 0.0844) but significant for Cu (II) ion removal variable (P < 0.0001). Besides, one of the important parameters of compatible model evaluation is difference between observed values and predicted values. A perfect correlation model describes a negligible variation of such results. It is obvious that suitable correlations between the actual and predicted values of AC yield and Cu (II) ion adsorption capacity are shown in Figure 1. Finally, consideration of normal probability and comparison of observed values and predicted values consolidated significant compatibility of quadratic regression model for RSM.

3.3. Optimization of independent variables for maximized responses

Three–dimensional optimization plots consisting of one response and two independent variables describe the effect of experimental parameters on optimal outputs (Figure 2). Activation temperature strongly influences both AC productivity (%) and Cu (II) ion uptake capacity (%). Especially, maximum AC yield and Cu (II) ion removal at temperature 673 K were achieved with approximately 49 % and 88 %, respectively in Figure 2 (A1) and (B1). Clearly, the more temperature increased, the more AC yield and Cu (II) ion uptake decreased. One of the causes for this circumstance is quicker carbonaceous material combustion and larger releasing volatiles at higher temperature [9].

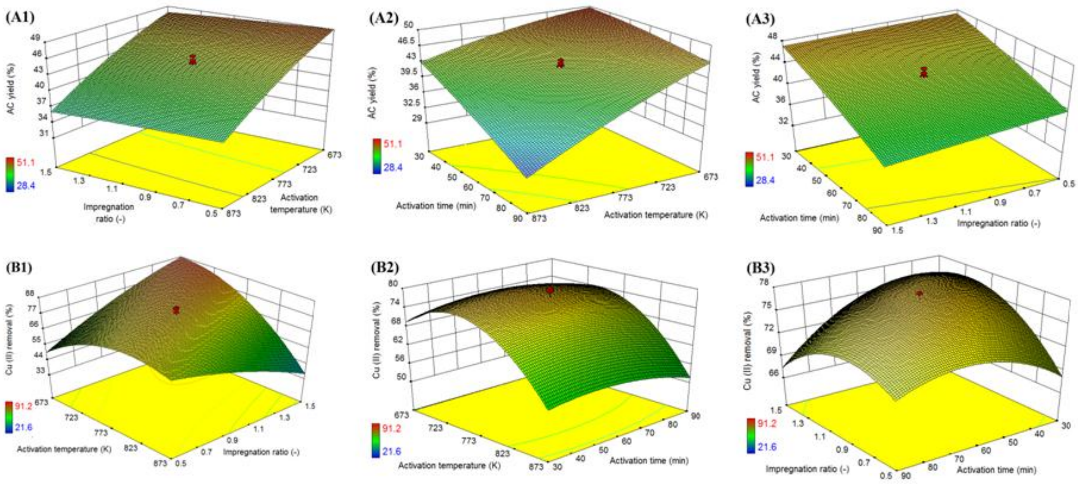

Figure 2. Three dimensional plots of surface response for (A1 – A3) AC yield and (B1 – B3) Cu (II) removal.

However, preparation of AC at such moderate temperature could reduce the energy cost and experimental complication. According to Figure 2 (A1) and (B1), AC yield was not almost improved for wide range of impregnation ratio (IR), while Cu (II) ion removal efficiency strongly depended on IR. When IR was enhanced with rate of 0.5 to 1.5, copper uptake capacity raised 50 – 90 (%). Ucar and his group recognized that different concentrations of $ZnCl_2$ developed the various porosity [10]. As a result, porous space containing inside adsorptive sites as special functional groups are imposed to adsorb metal ions in aqueous solution. Impregnation ratio accounts for metal uptake capacity of AC. However, amount of $ZnCl_2$ could be minimized to avoid environmental pollution and to preserve livings. According to Figure 2 (A2) and (B2), both activation time and temperature time closely concerned about AC yield and Cu (II) ion removal. In additional, it is evident that AC yield would be insignificant at the high temperate and time level. In contrast, facilities of carbonaceous material formation are at 673 K for 30 min and maximum yield value reaches nearly 50 %. In Figure 2 (B2), optimized Cu (II) ion adsorption percentage was identified at central position of experimental design. As a result, temperature of 773 K, impregnation ratio of 1.0 and time of 60 min were suitable conditions with 77.3 % of removal.

According to Figure 2(A3) and (B3), the impregnation ratio also did not have any association with production yield significantly. The AC yield was approximately stable at a fixed activation time point regardless of increasing impregnation ratio from 0.5 to 1.5. Furthermore, fluctuation range of AC yield was 39 – 47 (%). Both the other variables had close correlation with Cu (II) ion removal capacity with 77.3 % maximum. Activation temperature simultaneously influenced both outputs. Impregnation ratio was insignificant for AC synthesis while it strongly affected Cu (II) ion elimination. And activation time has a moderate domination for outputs. The results indicated that ZnC_2–impregnated sugarcane bagasse using optimized conditions could improve Cu (II) ion removal efficiency and AC yield (Table 4). As a result, maximized Cu (II) ion elimination and AC yield using $ZnCl_2$–impregnated sugarcane bagasse precursor with optimized conditions including activation temperature of 673 K, impregnation ratio of 1.5 and activation time of 35.2 minutes were also shown with AC yield of 48.8 % (–1.01 % error) and Cu (II) ion elimination of 92.3 % (+4.87 % error). Consequently, those values indicated that RSM with quadratic regression model obeys actual results.

Table 4. Optimization of the preparation of AC and elimination of Cu (II) ion: Model assessment.

Optimal conditions			AC yield			Cu (II) ion elimination		
x_1 (K)	x_2 (-)	x_3 (min)	Predict (%)	Test (%)	Error (%)	Predict (%)	Test (%)	Error (%)
673	1.5	35.2	49.3	48.8	–1.01	88.0	92.3	+4.87

4. CONCLUSIONS

In this study, it is recognized that chemical $ZnCl_2$ was the most efficient activation agent for sugar bagasse treatment in comparison with activation agents including $ZnSO_4$, KOH, $ZnSO_4$, H_3PO_4 and H_2SO_4. Results of ANOVA indicated that quadratic regression models were significant with $P < 0.05$. Optimization of AC yield and Cu (II) ion removal using RSM were investigated with remarked results, 48.8 % and 92.3 %, respectively. Activation temperature strongly affected both two responses including AC yield and Cu (II) ion removal with optimized temperature 673 ^{o}K. Effect of impregnation ratio on AC yield was negligible while effect of impregnation ratio on Cu (II) ion removal were significant with optimized impregnation ratio 1.5. Effect of activation time on AC yield and Cu (II) ion removal was also shown with optimized condition was 35.2 minutes.

Acknowledgements. This research was funded by Ministry of Industry and Trade under grant number 31.15.ĐTKHCN/HĐ-KHCN.

REFERENCES

1. Leyval C., Turnau K., Haselwandter K. - Effect of heavy metal pollution on mycorrhizal colonization and function: physiological, ecological and applied aspects, Mycorrhiza **7** (1997) 139-153
2. Bouhamed F., Elouear Z., Bouzid J. - Adsorptive removal of copper(II) from aqueous solutions on activated carbon prepared from Tunisian date stones: Equilibrium, kinetics and thermodynamics, J. Taiwan Inst. Chem. Eng. **43** (2012) 741–749
3. Ahmadpour A. and Do D. - Preparation of activated carbon from macadamia nutshell by chemical activation, Carbon **35** (1997) 1723 – 1727.
4. Junior O., Cazetta A., Gomesa R., Barizão É., Isis P.A.F. Souza, Martinsa A., Asefa T., Almeida V. - Synthesis of $ZnCl_2$-activated carbon from macadamia nut endocarp (Macadamia integrifolia) by microwave-assisted pyrolysis: Optimization using RSM and methylene blue adsorption , J. Anal. Appl. Pyroly. **105** (2014) 166 – 176.

5. Asfaram A., Ghaedi M., Hajati S., Rezaeinejad M., Goudarzi Al., Purkait M. - Rapid removal of Auramine-O and Methylene blue by ZnS/Cu nanoparticles loaded on activated carbon: A response surface methodology approach, J. Taiwan Inst. Chem. Eng. **53** (2015) 80–91
6. Donald J., Ohtsuka Y., Xu C. – Effects of activation agents and intrinsic minerals on pore development in activated carbons derived from a Canadian peat, Mater. Lett. **65** (2011) 744–747.
7. Sahu J., Acharya J., Meikap B. - Response surface modeling and optimization of chromium (VI) removal from aqueous solution using Tamarind wood activated carbon in batch process, J. Hazard. Mater. **172** (2009) 818–825
8. Tan I., Ahmad A., Hameed B. - Optimization of preparation conditions for activated carbons from coconut husk using response surface methodology, Chem. Eng. J. **137** (2008) 462-470.
9. Asadullah M., Rahman M., Motin M., Sultan M. - Adsorption studies on activated carbon derived from steam activation of jute stick char, J. Surf. Sci. Tech. **23** (2007) 73–80.
10. Ucar S., Erdem M., Tay T., Karagoz S. - Preparation and characterization of activated carbon produced from pomegranate seeds by $ZnCl_2$ activation, Appl. Surf. Sci. **255** (2009) 8890–8896.

TÓM TẮT

ỨNG DỤNG PHƯƠNG PHÁP ĐÁP ỨNG BỀ MẶT (RSM) ĐỂ TỔNG HỢP CARBON HOẠT TÍNH TỪ BÃ MÍA BẰNG TÁC NHÂN $ZnCl_2$ LÀM VẬT LIỆU LOẠI BỎ ION Cu (II) TRONG NƯỚC

Văn Thuận Trần, Bùi Thị Phương Quỳnh, Phùng Thanh Khoa, Giang Ngọc Hà, Nguyễn Thị Thương, và Long Giang Bạch*

Viện Kĩ thuật Công nghệ cao NTT, Đại học Nguyễn Tất Thành, 300A Nguyễn Tất Thành, P.13, Q.4, TP.Hồ Chí Minh, Việt Nam

*Email: *blgiangntt@gmail.com*

Nghiên cứu này trình bày quá trình tổng hợp carbon hoạt tính từ nguồn nguyên liệu chi phí thấp (bã mía) sử dụng tác chất hoạt hóa $ZnCl_2$ và đánh giá ảnh hưởng của các điều kiện tổng hợp thông qua phương pháp đáp ứng bề mặt (RSM) để làm vật liệu hấp phụ loại bỏ Cu (II) trong nước. Bài báo đã tiến hành khảo sát các yếu tố ảnh hưởng: nhiệt độ hoạt hóa, tỉ lệ ngâm hóa chất và thời gian hoạt hóa dựa trên kết quả phân tích phương sai (ANOVA). Điều kiện tối ưu cho quá trình than hóa bã mía dựa trên hiệu suất tạo thành carbon hoạt tính và khả năng loại bỏ Cu (II) sử dụng phần mềm Design – Expert 9 được xác định ở nhiệt độ hoạt hóa 673 K, tỉ lệ ngâm hóa chất $ZnCl_2$ 1,5 và thời gian hoạt hóa 35,2 phút. Kết quả ở điều kiện tối ưu cho hiệu suất chế tạo carbon hoạt tính là 48,8 % và khả năng hấp phụ Cu (II) trong nước là 92,3 %

Từ khóa: bã mía, carbon hoạt tính, phương pháp đáp ứng bề mặt (RSM).