

SURFACE MODIFICATION OF ACTIVATED CARBON FROM RICE HUSK FOR ENHANCING THE NICKEL(Ni^{2+}) AND CADMIUM (Cd^{2+}) ADSORPTION CAPACITY

Hoa Thai Ma^{1,2}, Van Thi Thanh Ho³, Hung Cam Ly³, Nguyen Bao Pham², Tuan Dinh Phan^{3*}

¹*Vietnam National University, Hochiminh City University of Technology, 268 Ly Thuong Kiet street, Ward 14, District 10, HCMC, Vietnam*

²*Tra Vinh University, 126 Nguyen Thien Thanh street, Ward 5, Tra Vinh city, Vietnam*

³*Hochiminh City of University of Natural Resources and Environment Vietnam, 236 Le Van Sy street, District Tan Binh, HCMC, Vietnam*

*Email: pdtuan@hcmunre.edu.vn

Received: 15th August 2016 / Accepted for publication: 10th November 2016

ABSTRACT

Activated carbon (AC) has been proven to be an effective adsorbent for the removal of a variety of pollutants. AC is extensively used for adsorption because its high surface area is well-developed internal micro porosity. The objective of this study is to determine the optimal condition of the surface modification process of activated carbon from rice husk (ACRH) using HNO_3 . That increase the functional group, and improve affinity towards certain contaminants of ACRH for increasing the adsorption capacity of Ni^{2+} and Cd^{2+} . Two factors were taken into account as: the concentration of HNO_3 (1, 3, and 5 M), reaction time (1, 2, 3, 4 and 5 hours). The results showed that the optimal condition of the surface modification process was derived at the equilibrium concentration of $\text{HNO}_3 = 3$ M and the equilibrium reaction time = 4 hour. Interestingly, in comparison with the control sample (ACRH not modified), the adsorption capacity of Ni^{2+} and Cd^{2+} increased from 10.0 to 17.2 mg/g and 10.4 to 29.6 mg/g, respectively. This adsorption capacity of modified ACRH shows the increase significantly.

Keywords: surface modification, HNO_3 , activated carbon, rice husk.

1. INTRODUCTION

Activated carbon (AC) has been proven to be effective for removal of a wide variety of inorganic and organic pollutants [1, 2, 3]. The demand of using ACs is increasing rapidly with enhanced awareness about environment protection. However, the price of ACs 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 growing interest in the production of ACs using cheap agricultural and industrial wastes [4, 5, 6]. Several wastes including coffee husks, rice husks, cotton stalks, coconut husks, herb residues, and corn cobs have been investigated as precursors to produce activated carbon. The precursors are still receiving renewed attention because of their cheap prices and abundant resources. Many of the waste-based ACs also enabled comparable or even better performance than the commercial ACs in many applications. Consequently, the conversion of cheap biomass wastes into value-added ACs 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 [7].

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), the yield of paddy in 2015 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 [8]. Thus, The annual generated RH on the world is about 150 million tons. In Vietnam, it is about approximately 8.94 million tonnes, 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.

RH on burning gives 14–20 % ash which contains 80–95 % silica in the crystalline form and minor amounts of metallic elements [9]. RH is little commercial value and not useful to feed either humans or animals because it contains high content of silicon dioxide [10] which is dissolved in hot concentrated alkali [11].

The presence of heavy metals in the environment is a major problem due to their toxicity to many life forms. The treatment of metals using precipitation is not always able to meet the metal discharge standards. Technologies such as reverse osmosis, able to meet the standards, are expensive. The innovative technologies that are cost-effective and able to reduce heavy metal concentration to low levels is important [12, 13].

Surface modification of activated carbon, in order to modify their specific physical and chemical properties to facilitate metals removal from waste water, can be done through different methods. Based on the type and nature of the pollutant to be removed, surface modification in activated carbon has been carried out to increase its affinity towards the desired pollutant. The modification method has been proved effective for metal ions adsorption capability and the removal of them from water [14, 15, 16]. Acid treatment method have been studied to develop the surface modification of activated carbon which is considered as a promising and attractive way toward new applications of activated carbon in many fields.

The aim of this study is to determine the interactive effect of the concentration of HNO_3 and time on the adsorption capacity of Ni^{2+} and Cd^{2+} in the modification process of ACRH. That is highly significant and bring new information for the research. Because the actual adsorption process takes place simultaneously with the interaction of the elements without the individual effect. The efficiency of the modification showed improvement in the sorption of Ni^{2+} and Cd^{2+} .

We conducted experiments with each individual metal because each type of waste water contain a different metals content. In fact, depending on the demand for treatment of each metal in wastewater, we will choice the most appropriate condition for the metal. That promises to leverage agricultural by-product to produce modified ACRH using for metal ions treatment.

2. EXPERIMENTAL

Preparation of ACRH

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

The dried rice husk was impregnated with 2 M NaOH solution with the ratio of rice husk per NaOH = 1:8 and stirred at least 1 hour at 100 °C [7].

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

40 g of the dried rice husks were placed in a quartz reactor of the vertical electric heating furnace. The whole system was purged nitrogen gas to remove the oxygen. Then the reactor was heated at 500 °C in the presence of nitrogen flow with a heating rate of 10 °C/min. and was held at this temperature for 1 hour. Thereafter the temperature was raised to 800 °C. After the activation temperature was reached, the gas was switched to steam and sample was kept under this condition for 30 min. before it was finally cooled in nitrogen flow.

Experimental

Modification of ACRH by HNO₃

0.5 g of each adsorbent was added with 25 ml of HNO₃ concentrations (1 to 5 M) in erlen 50 ml. The erlen was stirred at 100 °C for 1 to 5 hours for each experimental concentration of HNO₃ as shown in Table 1. The mixtures were filtered and washed with distilled water until the filtrate was neutral. Then the mixtures were dried at 100 °C for 6 hours. The sample was used to measure the adsorption capacity of Ni²⁺ and Cd²⁺ using atomic absorption spectrophotometry.

Table 1. Experimental design with the interactive effect of the concentration of HNO₃ and time for the modification of ACRH.

		Reaction time (hour)				
		B ₁ (1 hour)	B ₂ (2 hours)	B ₃ (3 hours)	B ₄ (4 hours)	B ₅ (5 hours)
Concentration of HNO ₃ (M)	A ₁ (1 M)	A ₁ B ₁	A ₁ B ₂	A ₁ B ₃	A ₁ B ₄	A ₁ B ₅
	A ₂ (3 M)	A ₂ B ₁	A ₂ B ₂	A ₂ B ₃	A ₂ B ₄	A ₂ B ₅
	A ₃ (5 M)	A ₃ B ₁	A ₃ B ₂	A ₃ B ₃	A ₃ B ₄	A ₃ B ₅

Determination of Ni²⁺ adsorption capacity using 1-(2 Pyridylazo)-2-Naphthol (PAN) method

The method to determine the Cd²⁺ adsorption capacity was described by Lopez Garcia et al. [17].

The Ni²⁺ and Cd²⁺ adsorption capacity was calculated equation [18]:

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

where w_i is the initial mass of Ni²⁺ or Cd²⁺ before adsorption process and w_f is the mass of Ni²⁺ or Cd²⁺ after adsorption process (mg), w_M is the mass of sample (g).

All of determinations were performed in triplicate.

3. RESULTS AND DISCUSSION

The effect of HNO_3 concentration and reaction time on the Ni^{2+} adsorption capacity

Table 2. The Ni^{2+} adsorption capacity at different conditions of the concentration of HNO_3 and the reaction time.

	The concentration of HNO_3 (M)			Average	ACRH is not modified
	1	3	5		10.04±0.2
Time (h)	1	11.2	11.9	13.0	12.0±0.1 ^d
	2	12.6	13.4	14.2	13.4±0.3 ^c
	3	13.5	15.5	15.7	14.9±0.3 ^b
	4	14.5	17.2	17.3	16.3±0.1 ^a
	5	14.6	17.0	17.4	16.3±0.2 ^a
Average	13.3±0.1 ^b	15.0±0.3 ^a	15.5±0.1 ^a		

Note: ^a highest value denotes a statistically significant difference; ^{b, c, d} lower values

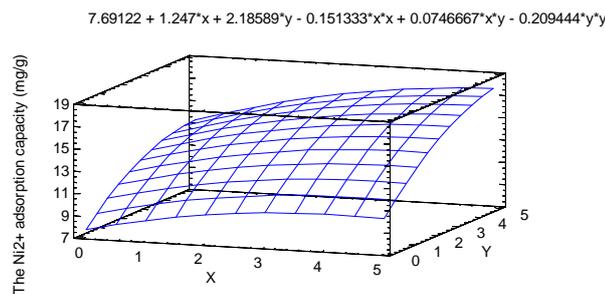


Figure 1. The effect of the concentration of HNO_3 and time on the Ni^{2+} adsorption capacity.

(x is the concentration of HNO_3 (1 to 5M), y is modification time (1 to 5 hours)).

$$\text{The } Ni^{2+} \text{ adsorption capacity} = 7.69122 + 1.247*x + 2.18589*y - 0.151333*x*x + 0.0746667*x*y - 0.209444*y*y \quad (1)$$

The equation (1) shows that the Ni^{2+} adsorption capacity of ACRH depends on the concentration of HNO_3 and the modification time by quadratic of x and y. This relationship has high statistical significance due to $P\text{-Value} < 0.01$ as shown in Table 3.

Table 3. Analysis of Variance.

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Model	168.259	5	33.6518	192.31	0.0000
Residual	6.82447	39	0.174986		
Total (Corr.)	175.083	44			

The concentration of HNO_3 (1 to 5 M) and the reaction time (1 to 5 hour) using for the surface modification of ACRH have a significant impact on the Ni^{2+} adsorption capacity. The result in Table 2. shows that at the equilibrium the concentration of HNO_3 from 3 to 5 M, the Ni^{2+} adsorption capacity is highest and there is no significant difference between them. At 3M of HNO_3 , the Ni^{2+} adsorption capacity reaches 15 mg/g and at 5 M, the Ni^{2+} adsorption capacity is 15.52 mg/g. While the Ni^{2+} adsorption capacity may be reached lower in the lower concentration condition. Besides, reaction time still plays a role in increasing the Ni^{2+} adsorption capacity. At equilibrium reaction time of 4 and 5 hours, the Ni^{2+} adsorption capacity is highest and reaches 16.33 and 16.31 mg/g, respectively. The results have statistically significant difference in comparison with the Ni^{2+} adsorption capacity at the shorter reaction time. The effect of variables to the Ni^{2+} adsorption capacity can be seen on the response surface as shown in Fig.1. This Ni^{2+} adsorption capacity of this study is higher than the results previously reported by Lakherwal, (2016) (7.6569 mg/g of granular AC) and Nabarlantz, (2012) (7.65 mg/g of activated carbon based on a native lignocellulosic precursor) [19,20]. But it is slightly lower than the result of Rahman, (2014) (19.61 mg/g of palm shell AC) [21].

The effect of the concentration of HNO_3 and the reaction time on the Cd^{2+} adsorption capacity

Table 4. The Cd^{2+} adsorption capacity at different conditions of the concentration of HNO_3 and the reaction time.

	The concentration of HNO_3 (M)			Average	AC is not modified 10.44±0.1
	1	3	5		
Time (hour)	1	10.2	18.4	19.7	16.1±0.2 ^d
	2	13.7	21.6	24.8	20.0±0.1 ^c
	3	15.5	26.1	32.4	24.7±0.2 ^b
	4	16.6	29.6	34.1	26.8±0.3 ^a
	5	24.8	33.6	33.6	30.7±0.2 ^a
Average	16.1±0.2 ^b	25.9±0.2 ^a	28.9±0.1 ^a		

Note: ^a highest value denotes a statistically significant difference; ^{b, c, d} lower values

The conditons of the modification affect not only the Ni^{2+} absorption capacity but also the Cd^{2+} adsorption capacity as shown in Table 4. The experimental factors achieving the highest adsorption capacity of Cd^{2+} (25.86 mg/g) can be determined as the equilibrium concentration of HNO_3 of 3 M and this value has not significant difference as HNO_3 concentration increases to 5M (28.91 mg/g). The results have statistically significant difference in comparison with the Cd^{2+} adsorption capacity at the concentration of HNO_3 and that values are sill higher the control sample. This can be ascribed to the enhancement of the ions migration to the absorbent surface by the increased concentration [14]. Besides, reaction time still plays a role in increasing the Cd^{2+} adsorption capacity as of Ni^{2+} . At the equilibrium reaction time of 4 and 5 hours, the Cd^{2+} adsorption capacity is highest, that reaches 16.33 and 16.31 mg/g respectively. While the Cd^{2+} adsorption capacity may be reached lower values in the shoter reaction time. The results have statistically significant difference. The effect of variables to the Cd^{2+} adsorption capacity can be seen on the response surface as shown in Fig. 2. This Cd^{2+} adsorption capacity of this study is

higher than the results previously reported by Alslaibi [22] (11.72mg/g of microwaved olive stone AC), Tounsadi [23] (0.85 mg/g of AC from *Glebionis coronaria L.*) and Wang [24] (8.08 mg/g of granular AC supported magnesium hydroxide) [22 - 24]. But it is lower than the result of Tounsadi [25] (31.6 mg/g of AC from *Diplotaxis Harra* biomass).

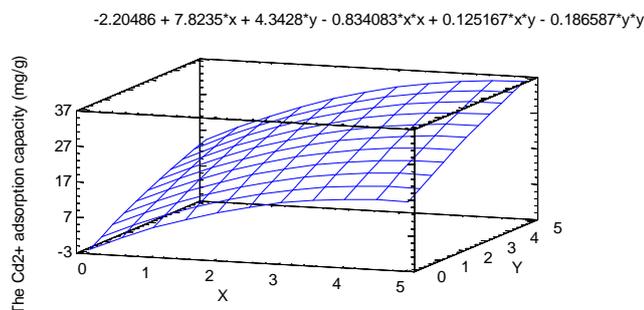


Figure 2. The effect of the concentration of HNO₃ and time on the Cd²⁺ adsorption capacity. (x is the concentration of HNO₃ (1 to 5 M), y is modification time (1 to 5 hours)).

Table 5. Analysis of Variance.

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Model	2509.65	5	501.929	162.92	0.0000
Residual	120.153	39	3.08084		
Total (Corr.)	2629.8	44			

$$\text{The Cd}^{2+} \text{ adsorption capacity} = -2.20486 + 7.8235*x + 4.3428*y - 0.834083*x*x + 0.125167*x*y - 0.186587*y*y \quad (2)$$

The equation (2) shows that the Cd²⁺ adsorption capacity of ACRH depends on the concentration of HNO₃ and the modification time by quadratic of x and y. This relationship has high statistical significance due to *P-Value* < 0.01 as shown in Table 5.

The Ni²⁺ and adsorption capacity increase when the concentration of HNO₃ increases from 3 to 5 M and the reaction time increases from 4 to 5 hours. That can be explained so that the oxidation treatment by HNO₃ gives rise to a large increase in the amount of total acidity resulting from the increase of surface oxide groups such as, carboxyl, lactone and phenol. The increase of the total acidity changed the point of zero charge of ACRH and led to an increase of adsorption capacity for metal ions [16]. Besides, the increase of the Ni²⁺ and Cd²⁺ adsorption capacity mainly attributes to the abundant vacant sites on activated carbon surface. The high adsorption capacity of Ni²⁺ and Cd²⁺ by the modified RHAC confirms that the adsorption process is related to the concentration of HNO₃ and reaction time.

The concentration of HNO₃ of 3 M for 4 hours was selected for the modification process of ACRH sample regarding the cost of the process.

4. CONCLUSION

The effect of the fixed conditions of ACRH modification on the Ni²⁺ and Cd²⁺ adsorption capacity investigated. The results showed that concentration of HNO₃ and reaction time of the

modification process effect significantly to the Ni²⁺ and Cd²⁺ adsorption capacity. Based on the experimental data, the best conditions were identified to be the equilibrium concentration of HNO₃ of 3 M and the equilibrium reaction time of 4 hours. At this condition, the adsorption capacity of Ni²⁺ and Cd²⁺ were highest and there is no significant difference in comparison with the concentration of HNO₃ of 5 M for the reaction time of 5 hours.

Acknowledgement. This work was supported by the Ministry of Natural Resources and Environment (Monre), grant no. 2015.04.19. We acknowledge positive contributions from team members: Dat Chi Nguyen, Lien Tu Lam, Thoa Tu Lu, Thinh Truong Pham, Thuong Thi Hong Mai for this work.

REFERENCES

1. Pak S. H., Jeon M. J., Jeon J., W. -Study of sulfuric acid treatment of activated carbon used to enhance mixed VOC removal. *International Biodeterioration & Biodegradation* **113** (2016) 1-6
2. Gokce Y., Aktas Z. - Nitric Acid Modification of Activated Carbon Produced from Waste Tea and Adsorption of Methylene Blue and Phenol. *Applied Surface Science* **313** (2014) 352-359.
3. Korotta-Gamage S. M., Sathasivan A. - A review: Potential and challenges of biologically activated carbon to remove natural organic matter in drinking water purification process. *Chemosphere* **167** (2017) 120-138.
4. Suhas, Carrott P.J., Ribeiro Carrott M. M. - From Natural Adsorbent to Activated Carbon: A Review. *Bioresour. Technol.* **98** (2007) 12.
5. Paraskeva P., Kalderis D., Diamadopoulos E. - Production of Activated Carbon from Agricultural by Products. *J.Chem.Technol. Biotechnol* **83** (2008) 581-592.
6. Dias J., Alvim-Ferraz M., Almeida M., Rivera-Utrilla J., Sanchez-Polo M. - Waste Materials for Activated Carbon Preparation and Its Use in Aqueous-phase Treatment: A review. *J.Environ. Manage.* **85** (2007) 833-846.
7. Yang J., Yu J., WeiZhao, Li Q., Wang J. and Xu G. - Upgrading Ash-Rich Activated Carbon from Distilled Spirit Lees. *Industrial & Engineering Chemistry Reseach* **51** (2012) 6037–6043
8. Daifullah A. A. M. Girgis B. S., Gad H. M. H. - Utilization of agro residues (rice husk) in small waste water treatment plans. *Materials Letters* **57** (2003)1723–1731.
9. Liou T. H. - Preparation and characterization of nano-structured silica from rice husk. *Mat Sci Eng A* **364** (2004) 313-323.
10. Hassan A.F. - Preparation and characterization of microporous NaOH-activated carbons from hydrofluoric acid leached rice husk and its application for lead(II) adsorption. *Carbon Letters.* **15** (2014) 57-66.
11. Greenwood N. N., Earnshaw A. - *Chemistry of the Elements.* Oxford: Pergamon Press (2005) 393–399. ISBN 0-08-022057-6.
12. Abdo M.H. - Environmental studies on Rosetta branch and some chemical applications at the area extends from El-Kanater-Khyria to Kafr El-Zyat City” Ain Shams University. Cairo, Egypt (2002) 464 pp.

13. Masoud M. S. et al. - Rice husk and activated carbon for waste water treatment of El-Mex Bay, Alexandria Coast, Egypt. *Arabian Journal of Chemistry* (2012).
14. Yao S., Zhang J., Shen D., Xiao R., Gu S., Zhao M., Liang J. - Removal of Pb(II) from water by the activated carbon modified by nitric acid under microwave heating, *Journal of Colloid and Interface Science* **463** (2015) 118-127.
15. Jin G., Eom Y., Lee T. G. - Removal of Hg(II) from Aquatic Environments using Activated Carbon Impregnated with Humic Acid, *Journal of Industrial and Engineering Chemistry* **42** (2016) 46-52.
16. Shim J. W., Park S. J., Ryu S. K. - Effect of modification with HNO and NaOH on metal adsorption by pitch-based activated carbon fibers. *Carbon* **39** (2001) 1635-1642
17. Lopez Garcia I., Navarro P. and Hernandez Cordoba M. - Manual and fia methods for the determination of cadmium with malachite green and iodide. *Talanta* **35** (1998) 885-889
18. Chen Y., RuZhai S., Liu N., Song Y., An Q., Song X. - Dyeremoval of activated carbons prepared from NaOH-pretreated rice husks by low-temperature solution-processed carbonization and H₃PO₄ activation. *BioresourceTechnology* **144** (2013) 401-409
19. Lakherwal D., Rattan V.K., Singh, H.P. Studies on Adsorption of Nickel by Activated Carbon in a Liquid Fluidised Bed Reactor. *Canadian Chemical Transactions*. **4** (2016) 121-132.
20. Nabarlantz D., Celis J., Bonelli P., Cukierman A.L. - Batch and dynamic sorption of Ni(II) ions by activated carbon based on a native lignocellulosic precursor. *Journal of Environmental Management*. **97** (2012) 109-115.
21. Rahman M.M., Adil M., Yusof A.M., Kamaruzzaman Y.B. and Ansary R.H. - Removal of Heavy Metal Ions with Acid Activated Carbons Derived from Oil Palm and Coconut Shells. *Materials*. **7** (2014) 3634-3650.
22. Alslaibi T.M., Abustan I., Ahmad M.A., Foul A.A. - Cadmium removal from aqueous solution using microwaved olive stone activated carbon. *Journal of Environmental Chemical Engineering*. **1** (2013) 589-599.
23. Tounsadi H. *et al.* - Highly efficient activated carbon from *Glebionis coronaria L.* biomass: Optimization of preparation conditions and heavy metals removal using experimental design approach. *Journal of Environmental Chemical Engineering*. **4** (2016) 4549-4564.
24. Wang K., Zhao J., Li H., Zhang X., Shi H. - Removal of cadmium (II) from aqueous solution by granular activated carbon supported magnesium hydroxide. *Journal of the Taiwan Institute of Chemical Engineers*. **61** (2016) 287-291.
25. Tounsadi H., Khalidi A., Abdennouri M., Barka N. - Activated carbon from *Diplotaxis Harrabi* biomass: Optimization of preparation conditions and heavy metal removal. *Journal of the Taiwan Institute of Chemical Engineers* **59** (2015) 1-11.