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The Comparison of Surface Modification Methods of the Heavy Metals Adsorption of Activated Carbon from Rice Husk

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Abstract Surface modification of activated carbon (AC) could be done through different methods in order to modify their specific physical and chemical properties to facilitate metals removal from wastewater. Three methods were used to modify the rice husk AC (RHAC) including the use of (1) HNO_3, (2) dithizone and (3) the combination of HNO_3 with dithizone. These modification agents were increased its affinity towards the desired pollutant. The modification methods demonstrated the effective process for the metal ions adsorption capability and the removal of them from water. For Ni^{2+} and Cd^{2+} adsorption, RHAC was modified by HNO_3 giving the best adsorption capacity in comparison with using dithizone or the combination of HNO_3 with dithizone. That adsorption was reached 17.23 mg/g for Ni^{2+} and 29.61 mg/g for Cd^{2+}. Additionally, the surface area, which was characterized by BET (Brunauer–Emmett–Teller) of RHAC, was 710.8 m^2/g and DA micropore volume was 0.447 (cm^3/g). Especially, the only modified RHACs had the peak of N-H functional group by using Fourier transform infrared spectrum (FTIR). Besides, the only RHAC modification by HNO_3 had peak of C=O. That significantly contributed to increase the metal ions adsorption capacity of RHAC.

Introduction

Rice is a common food and it plays an important role in every meal for 3.5 billion people in the world. The produce of rice was reached 749.1 million tones in 2015 according to Food and Agriculture Organization of the United Nations (FAO), and it will increase year by year. According to statistics, rice husk (RH) was about 20% of total produce after milling process. Thus, the total RH on the world was estimated around 150 million tons. Moreover, RH was approximately 8.94 million tons in Vixet Nam (2015) corresponding to 5.96 % of the world's RH. Currently, the RH is still underused for many appications such as water treatment, metal ion adsorption. In developing countries including Vietnam, most RH was burned or directly dumped into canals leading to environmental pollution. Additionally, we know that AC with a large adsorption capacity is the carbonaceous material highly needed for various industrial purifications and wastewater treatments [1]. However, AC is not so cheap due to their fabrication process and their original material such as wood, coal and coconut husk. So, it is so important to find out some other source of materials or modification process for AC to reduce its price and having wide applications.

Generally, ACs were made by carbonization of the raw materials such as coal or coconut husk via steam activation. Based on this carbonization process, AC products were contained a large of porosity in the char. The porosity structure was then improved by activation process to obtain final produce [2]. In the other hand, heavy metal was played an important role in environmental pollution due to their toxicity. There are some methods, which was used to remove the metal ions in solution such as precipitation method or reverse osmosis. However, both of them have some inherent

drawbacks including the metal discharge standards and expensive. Nowadays, many researches have been focused on innovative technologies because of its cost-effective and high possibility to remove heavy metal ions. To enhance the specific adsorption properties of ACs, ACs should be modified through some different processes. For different pollutant types, ACs should be accordingly modified. For instant, removing ion from river or lab wastewater, pH and reaction time or initial concentration of solution to enhance adsorption capacity need to be controlled [3-5]. Among different modification methods, acid treatment is a promising method for surface modification of ACs due to their easy to control and cost-effective method.

In this paper, we present the effect of the different surface modification methods for RHAC to find the appropriate conditions for increasing the adsorption capacity of Ni^{2+} and Cd^{2+}. The properties of RHAC such as pore diameter, micropore volume, the surface area and the morphology are characterized by BET, Scanning Electron Microscope (SEM). The adsorption capacity of RHAC without and with different surface modification is determined by using Ni^{2+} and Cd^{2+} solution. The results obtained offer the potential applications to produce ACs for the treatment of heavy metals.

Materials and Methods

Materials. RH from the rice mill in Tra Vinh province was used as raw material to produce AC. First, RH was washed thoroughly with distilled water to remove soil and dust. Then, that was dried at 105 ^{o}C in an oven for 24 hours.

Methods.

Methods of analysis. Ni^{2+} adsorption capacity is determined by 1-(2 Pyridylazo)-2-Napthol (PAN) method. The method to determine the Cd^{2+} adsorption capacity was described by Lopez Garcia *et al*., 1998 [6]. The Ni^{2+} and Cd^{2+} adsorption capacity was calculated equation:

$$The\ adsorption\ capacity\left(\frac{mg}{g}\right) = \frac{w_i - w_t}{w_M} \quad (1)$$

where, w_i is the initial mass of Ni^{2+} or Cd^{2+} before adsorption process and w_t is the mass of Ni^{2+} or Cd^{2+} after adsorption process (mg), w_M is the mass of sample (g). All of determinations were performed in triplicate.

Experiment procedures. *Preparation of ACRH:* The dried rice husk was impregnated with NaOH 2M in the ratio of RH:NaOH = 1:8 and stirred 1 hour at 100 ^{o}C. Then, the RH was washed with distilled water until pH of neutral water, the clean RH 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. For removing of oxygen, the whole system was then purged by nitrogen gas. Next, the reactor containing the dried rice husks was placed into furnace with flowing of nitrogen gas and heated to 500 ^{o}C with a heating rate of 10 ^{o}C/min during 1 hour. When temperature was reached to 800 ^{o}C, the gas was switched off and steam was sprayed in the system. This condition was then maintained for 30 min to active the char. After that, it was cooled under flowing of nitrogen until reached room temperature.

Modification of ACRH by HNO_3: 0.5 g of RHAC was mixed with HNO_3 of 3 M (volume of 25 ml). Then, this mixed solution was stirred for 4 hours at 100 ^{o}C. The mixture was then filtered to obtain RHAC and then the RHAC was washed with distilled water until the filtrate was neutral. Then, the obtained RHAC was dried at 100 ^{o}C for 6 hours. The adsortion capacity of RHAC was evaluated by the reducing concentration of Ni^{2+} and Cd^{2+} solutions based on UV/Vis spectrophotometer.

Modification of ACRH by dithizone: 0.6 g of RHAC was added with 50 ml of dithizone 0.02 M in erlen 100 ml. Then the erlen was stirred at 60 ^{o}C for 24 hours in a water bath. The mixture was filtered and washed with DMF solution and ethanol/diethyl ether mixture. Then, it was dried at 70 ^{o}C for 8 hours.

Modification of ACRH by the combination of HNO_3 and dithizone: At first, the RHAC was modified by HNO_3 3M, then it was modified by dithizone 0.02M as the individual modification methods above.

Data analysis. The comparison of mean values was performed by one-way ANOVA (analysis of variance) followed by Tukey's test (*p-value* < 0.05).

Results and Discussion

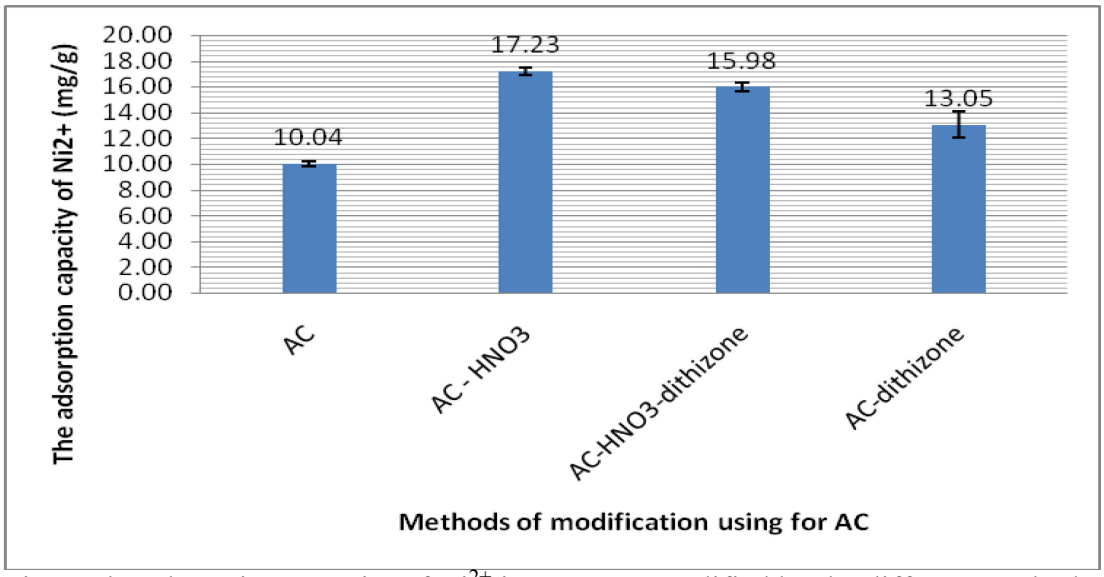


Fig. 1 The adsorption capacity of Ni^{2+} into RHAC modified by the different methods.

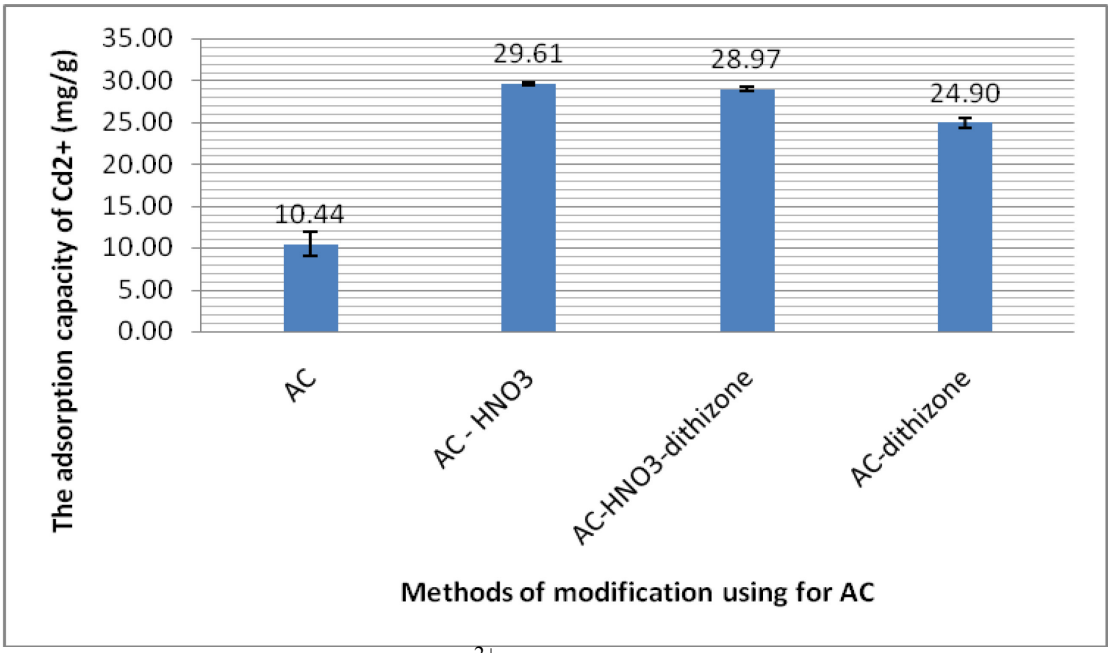
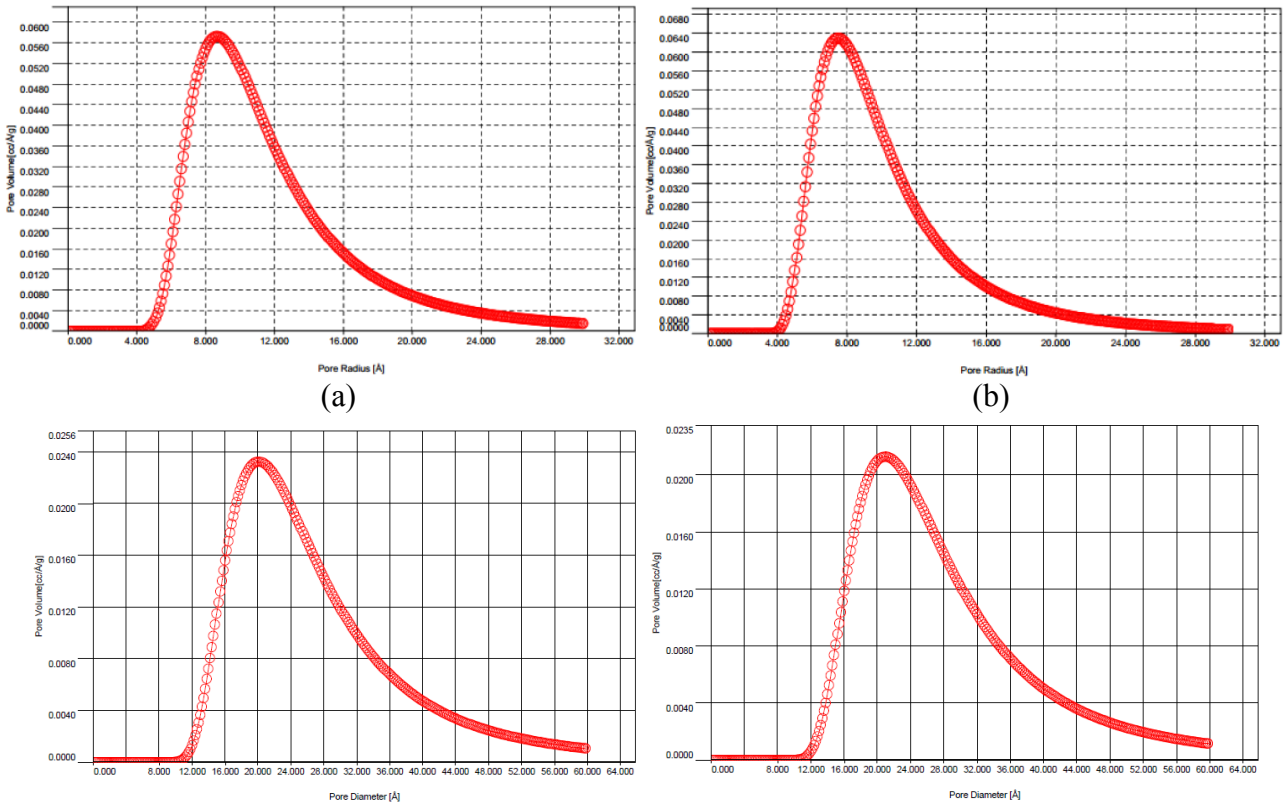


Fig. 2 The adsorption capacity of Cd^{2+} into RHAC modified by the different methods.

The surface modification in AC has been carried out by three methods with using HNO_3, dithizone and the combination of HNO_3 and dithizone. The relationship between the modifications and the adsorption capacity were identified. The result in Fig. 1 and Fig. 2 showed that the various modified agents effected significantly to the adsorption capacity both Ni^{2+} (~0.5 time) and Cd^{2+} (3 times) compared to AC without modification. Significantly, when RHAC was modified by HNO_3, the adsorption capacity of Ni^{2+} and Cd^{2+} reached the highest value (17.23 and 29.61 mg/g, respectively). While RHAC was modified by dithizone or HNO_3-dithizone, the adsorption capacity of Ni^{2+} reached to the values of 15.98 and 13.05 respectively, the adsorption capacity of Cd^{2+}reached the values of 28.97 and 24.9 mg/g respectively. These results indicated that the method

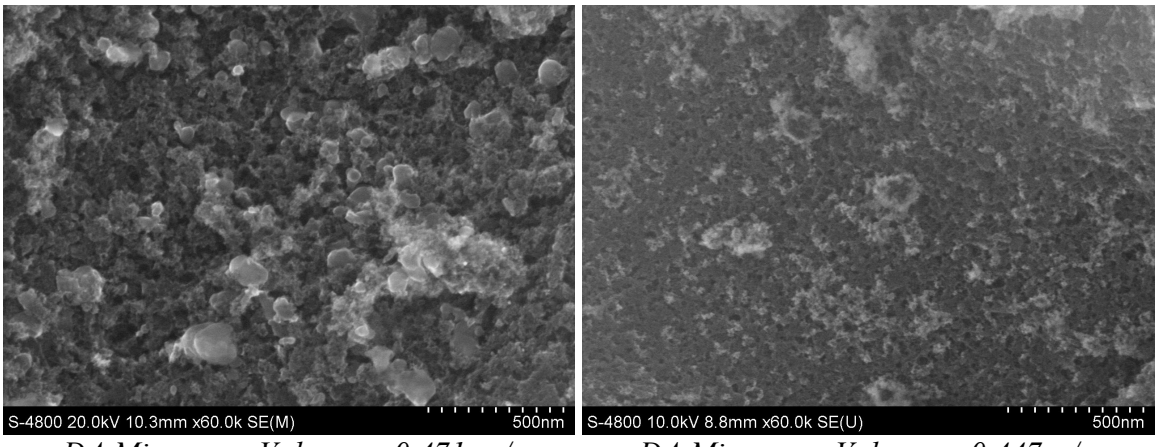
of modification RHAC by HNO_3 had effective adsorption capacity of Ni^{2+} and Cd^{2+}. That could be explained that the treatment by HNO_3 could increase the amount of total acidity resulting in the increase of surface oxide groups such as carboxyl, lactone and phenol. The increase of the total acidity changed the point of zero charge of ACRH and led to an increasing of the adsorption capacity for metal ions. These results were corresponding with the previous report by Bento *et al.* 2003 [7].



(a) (b)

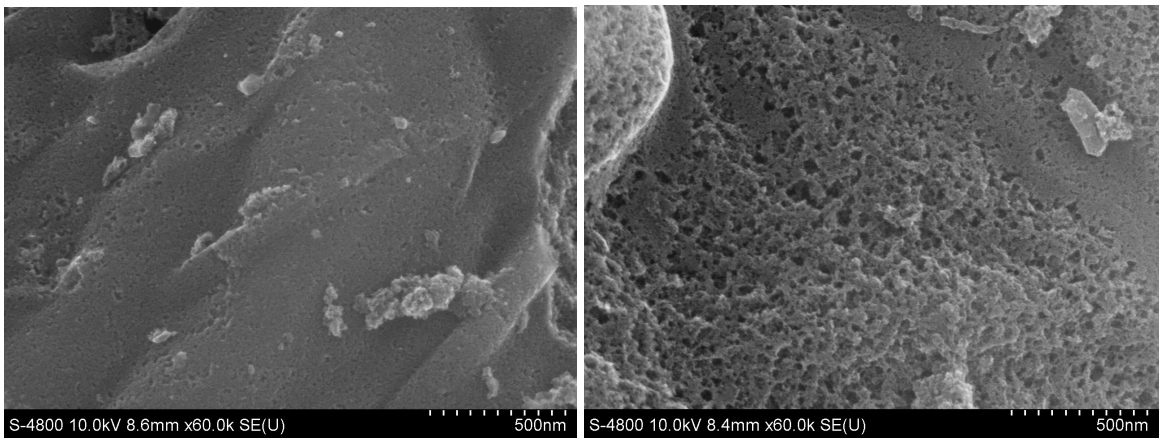
(c) (d)

Fig. 3 Pore diameter and DA micropore volume of the modification methods (a): RHAC without modification, (b) RHAC modified by HNO_3, (c) RHAC modified by dithizone, (d) RHAC modified by HNO_3 and dithizone.



DA Micropore Volume = 0.471 cc/g
Pore Radius (mode)= 8.700e+00 Å
(a)

DA Micropore Volume = 0.447cc/g
Pore Radius (mode) = 5.500e+00Å
(b)



DA micropore volume = 0.443 cc/g
Pore radius (mode)= 2.020e+01 Å
(c)

DA micropore volume = 0.423 cc/g
Pore radius (mode)= 2.100e+01 Å
(d)

Fig. 4 SEM images of the surface morphology of RHAC modified by different methods (a): RHAC without modification, (b) RHAC modified by HNO_3, (c) RHAC modified by dithizone, (d) RHAC modified by HNO_3 and dithizone.

Table 1 BET surface area and micropores volume of RHAC modified by the different methods.

Sample	BET (m^2/g)	DA micropore volume (cm^3/g)
RHAC	710.777	0.471
RHAC-HNO_3	775.615	0.447
RHAC-HNO_3-dithizone	504.016	0.423
RHAC-dithizone	554.938	0.443

The result from Table 1 showed when RHAC was modified by HNO_3, the result obtained highest BET surface area of 775.6 m^2/g. This result was consistent with the appearance of uniform small pores. Besides, it had a few large pores as shown in Fig. 4. For the case of RHAC without modification, BET only got 710.8 m^2/g. While RHAC was modified by dithizone or the combination of HNO_3 and dithizone, BET surface areas were lower. This could due to dithizone breaking some of the pore structure having a small size or combining them into larger pores (the case of RHAC was modified by the combination of HNO_3-dithizone). Besides, when RHAC was modified by dithizone, it could lead to the destruction of a part of the porous surface causing of the smoother surface as shown in Fig. 4, that decreased the pore volumes. The use of HNO_3 modified the functional groups and reduced the amount of ash on the surface [8]. That could be the cause increasing the Ni^{2+} and Cd^{2+} adsorption capacity.

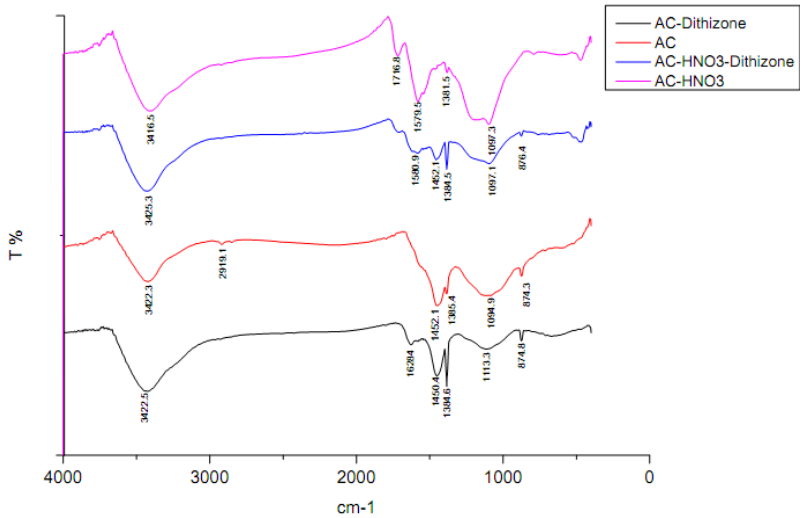


Fig. 5 FTIR Spectrum of RHAC and modified RHACs by different modification methods.

Fig. 5 showed FTIR Spectrum of RHAC without modification and modified RHACs all had O-H bonds with the peaks at 3400 cm^{-1}. The band at 1450 cm^{-1} corresponded to vibration in -C-H. The absorption band about 1380cm^{-1} could be attributed to the stretching vibrations of N-O. The absorbance peak about 1150 – 1050 cm^{-1} was due to the bending vibration of C-O bonds. And at 874cm-1 was a band related to the =C-H bond [9]. However, RHAC without modification had the peak of C-H at 2919.1 cm^{-1}, whereas modified RHACs would have the peak of N-H around 1630 - 1579 cm^{-1} [10]. Besides, only RHAC modified by HNO_3 had peak of C=O bond at 1716.8cm^{-1}. Carbonyl or hydroxyl groups formation was due to the breakdown of the acid function groups on RHAC surface.

Conclusions

The different surface modification methods significant effected to the Ni^{2+} and Cd^{2+} adsorption capacity of RHAC. When using HNO_3 to modify RHAC, the Ni^{2+} and Cd^{2+} adsorption capacity were given the highest in comparison with the modification by dithizone or combination of HNO_3 and dithizone. With this modification condition, the BET surface area was the largest. Besides, only the modified RHACs had the peak of N-H functional group and only RHAC modified by HNO_3 had peak of C=O. That could be the reason for the increase in the adsorption capacity of RHAC. The RHAC modification method by HNO_3 is considered as a promising way toward to new applications of AC in the removal of heavy metal in the wastewater.

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References

[1] A. Dabrowski, P. Podkoscielny, Z. Hubicki, M. Barczak. Adsorption of Phenolic Compounds by Activated Carbon, A Critical Rev. Chemosp. 58 (2005) 1049-1070.

[2] W. M. A. W. Daud, W. S. W. Ali, M. Z. Sulaiman. The effects of carbonization temperature on pore development in palm-shell-based activated carbon. Carbon. 38 (2000) 1925–1932.

[3] S. Yao, et al. Removal of Pb(II) from water by the activated carbon modified by nitric acid under microwave heating. J. Colloid Interf. Sci. 463 (2015) 118-127.

[4] G. Jin, Y. Eom, T. G. Lee. Removal of Hg(II) from Aquatic Environments using Activated Carbon Impregnated with Humic Acid. J. Ind. Eng. Chem. 42 (2016) 46-52.

[5] J. W. Shim, S. J. Park, S. K. Ryu. Effect of modification with HNO and NaOH on metal adsorption by pitch-based activated carbon fibers. Carbon. 39 (2001) 1635–1642.

[6] I. Lopez Garcia, P. Navarro and M. Hernandez Cordoba. Manual and fia methods for the determination of cadmium with malachite green and iodide. Talanta. 35 (1998) 885-889.

[7] V. Bento, C. L. Donnici, R. M. Lago. Tailoring Activated Carbon by Surface Chemical Modification with O, S, and N Containing Molecules. Mater. Res. 6 (2003) 129-135.

[8] J. Zhang, et al. Study On The Preparation Of Activated Carbon For Direct Carbon Fuel Cell With Oak Sawdust. Wiley Online Library. 90 (2012) 762-768.

[9] Y. C. Sharma and Uma, Optimization of Parameters for Adsorption of MB on a Low-cost Activated Carbon, J. Chem. Eng. Data, 55 (2010) 435-439.

[10] S. Han, D. Shin, H. Choi, S. Lee, Molecular determinants of the interaction between Doa1 and Hse1 involved in endosomal sorting, Biochem. Biophys. Res. Commun. 446 (2014) 352-357.