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EXPERIMENTAL RESULTS OF ADSORPTION OF Ni (II) FROM WASTEWATER USING COFFEE HUSK BASED ACTIVATED CARBON

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ABSTRACT

In recent years, the studies on finding the low cost methods to remove metal ions have been increased. Use of agricultural wastes such as coffee husk, coffee residue, coconut fiber, rice husk, peanut shells, cob, etc. as adsorbents to remove heavy metals, pollutants in wastewater has been of great concern in Viet Nam and regional countries. The results showed that the material from coffee husk had superior adsorption. In this study, the coffee husk was heated in Ar gas at temperatures of 300 ^{o}C, 400 ^{o}C, 500 ^{o}C, 600 ^{o}C for 30 minutes, 60 minutes and 90 minutes, then was denatured by impregnation with HNO_3 at different concentrations (1M, 3M, 5M). The adsorbent products from the above process from coffee husk were tested to find the best technical solution by studying the influences of pH (2 ÷ 9), contact time (10 ÷ 100 min), adsorbent dose (0.2 ÷ 10 g/L) and initial concentration Ni(II) (10 ÷ 60 mg/L). The research results showed that while the activated carbon samples treated at 400 ^{o}C in 30 minutes had Ni (II) adsorption capacity of 1.97 mg/g, the activated carbon by HNO_3 had Ni (II) adsorption higher capacity, maximum adsorption capacity is 21.14 mg/g (more than 10 times in comparison with the non-denatured or non-modified coal).

Keywords: activated carbon, heavy metals, adsorption, coffee husk.

1. INTRODUCTION

Wastes from many industries such as paint and dye production, mineral exploitation, metal plating, metallurgy, etc. contain heavy pollutants such as Pb, Cd, Cr, Ni, Zn, Cu and Fe. These heavy metals in non-biodegradable wastewater and their existence in rivers, lakes and streams cause biological accumulation in the living organism, leading to many health problems in animals, plants and humans such as cancer, metabolic acidosis, mouth ulcers, kidney failure, and rodent trauma [1].

Charcoal and activated carbon are often selected as an adsorbent in the treatment of polluted water by adsorption due to their large surface area, which is highly adsorbed [2]. Activated carbon is produced from cellulosic materials such as coffee husk, coconut shell, palm kernel, doum seed, rice husk, lotus stem, core corn, etc.

The coffee husk is a cellulosic lignin material capable of splitting heavy metals dissolved in water by the porous structure and high cellulose content. In this study, coffee husk in Dak Lak province were selected for the production of activated carbon at different temperatures and times. The adsorption capacity of coffee husk based activated carbon was evaluated. The activated carbon functionalized by HNO_3, which showed the highest adsorption capacity, was chosen to study the ability to adsorb Ni (II) in water under the effect of different parameters.

2. MATERIALS AND METHOD

2.1. Materials and chemicals

The coffee husk were washed, boiled to remove color and impurities, then dried at 110^oC for 12 hours. Before being dried, coffee husks were milled into powder and collected through a 250-mesh sieve. The $NiSO_4.6H_2O$, NH_3 solutions, saturated bromine solution, dimethylglyoxime, distilled water, concentration of 1 M, 3 M, 5 M HNO_3 were used in the study. These chemicals were of analytical grade of Merck. Experimental equipment: Dryer; Nabertherm furnace in Ar gas; The Ni (II) adsorption process was performed on stirring machine from the heat, concentrations of Ni (II) were determined on a ShimaDzu UV-Vis1800 colorimeter, pH was determined by a pH meter.

2.2. Experimental section

Synthesis of charcoal preparation: 20 g of crushed material was heated at 300 ^oC, 400 ^oC, 500 ^oC C, 600 ^oC for 30, 60, 90 minutes. The procedure was described [3]. Then the efficiency of Ni (II) adsorption at pH = 4, 10 g/L charcoal, adsorption time of 60 minutes with different Ni (II) initial concentrations was evaluated [4]. Each experiment was repeated three times. The evaluation was based on the average value. After that, the best coalification conditions was chosen for subsequent treatments.

*Synthesis of activated materials:*10g of charcoal mixed with HNO_3 (concentration 1M, 3M, 5M) by ratio of 1:10, then boiled and stirred for 4 hours. The solution for solids was removed and washed by distilled water to pH = 7, then dried at 110 ^oC for 4 hours [3]. Ni (II) adsorption capacity of activated carbon was determined to be equal to 10 g/L, with the initial concentration was equal to 25 mg/L. Each experiment was repeated three times. The best coalification conditions were obtained from the evaluation based on the average values.

Absorption evaluation: Ni(II) adsorption capacity of activated carbon under different conditions such as pH, time, contents of adsorbent and concentration of Ni (II) solutions was investigated. The initial Ni (II) concentration was 25 mg/L. The adsorption experiments were performed in a beaker with magnetic stirrer of 120 rpm stirring speed and room temperature. After adsorption, settling, filtration and determination of Ni (II) at wavelength of 550 nm, the line regression equation was obtained. By using the equation, adsorption capacity "q" (mg/g) of the activated carbon was obtained and compared with that of charcoal. Each experiments were repeated three times, then the average value was obtained for evaluation.

Adsorption capacity of the materials is calculated according to the formula:

$$q_e = \frac{C_0 - C_e\ V}{m} \quad (1)$$

Adsorption efficiency of materials with heavy metals is evaluated according to the formula:

$$H = \frac{C_0 - C_e}{C_0} \times 100\% \quad (2)$$

where: q_e: adsorption capacity of the material (mg/g); C_o: initial metal concentration (mg/L); C_e: residual metal concentration in the test solution (mg/L); V:volume of solution (L); m: mass of material (g).

3. RESULTS AND DISCUSSION

3.1. Evaluation of the Ni (II) adsorption capacity of charcoal

The results show that the coffee husk charcoalised at 400 ^oC in Ar gas environment had the highest Ni (II) adsorption capacity, while those charcoalised at 300 ^oC, 500 ^oC and 600 ^oC Ni (II) had lower adsorption capacity (Figure 1a). This can be explained in a manner that at low temperatures, carbonization occurs slowly and charcoal was not burned completely so the porosity of charcoal was low so the adsorption capacity was not high. As the coalization temperature increased to 500 ^oC, 600 ^oC, the decomposition of carbon was stronger, carbon content in charcoal and adsorbents active groups decreased due to oxidation and denaturation [3] so the adsorption capacity decreased compare with charcoalised at 400 ^oC. Figure 1b showed that the coffee husk charcoalised at 400 ^oC and had a high Ni (II) adsorption capacity (adsorption capacity reached 1.7 mg/g) and the highest adsorption capacity when 30 minutes was q = 1.97 mg/g. So we chose sample charcoalised at 400 ^oC for 30 minutes for subsequent studies.

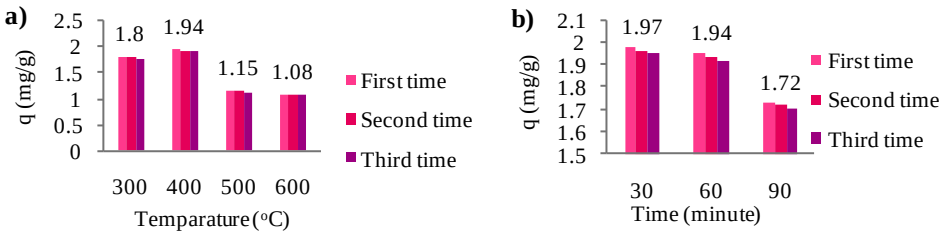

Figure 1. Effect of temperature (a) and heating time (b) on Ni (II) adsorption capacity.

3.2. Evaluation of the surface structure of the material

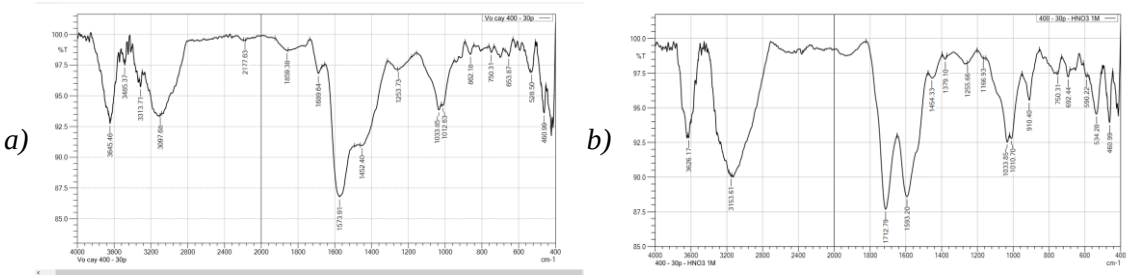

Figure 2. The results of analysis the non- modified coal material (a) and the modified coal material (b) on IR spectra.

The obtained infrared spectra in Fig. 2b showed that activated charcoal modified with HNO_3 exhibits the bonds -OH (3626.17 cm^{-1}, 910.40 cm^{-1}), C-O-H (3153.61 cm^{-1}), C=C (1593.20 cm^{-1}), C=O (1712.79 cm^{-1}), -C-H (750.31 cm^{-1}), and C-O (1033.85 cm^{-1}). The material after denaturation showed oscillation wavelength changed and indicated a presence of the group carboxyl. No NO_3^- group reflected on the spectrum revealed that during the charcoal washing it completely eliminated the excess acid after denaturation.

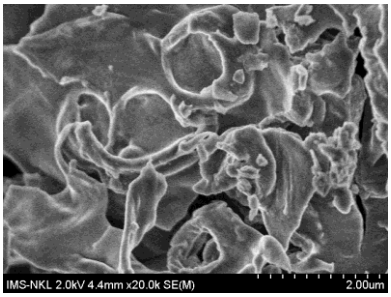

Figure 3. Charcoal.

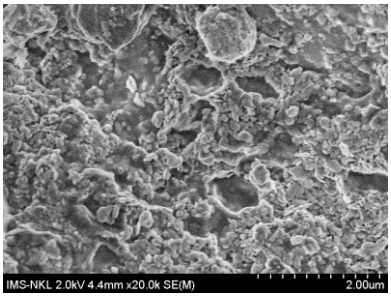

Figure 4. Activated carbon modified by HNO_3.

The SEM images in Figures 3 and 4, for charcoal and activated carbon modified by HNO_3, showed that surface morphology of charcoal material varies considerably when denatured by HNO_3. At a magnificant of 20000, the charcoal denaturedby HNO_3 sample showed a clear crystal structure, while the untreated charcoal was inert and reflective. Activation of charcoal by HNO_3 with small holes formation made charcoal more adsorbable (The BET results showed that the material surface area after denaturation with HNO_3 was 7.06 m^2/g, increased 1.5 times while the unmodified material surface area was 4.85 m^2 /g) and kept the impurities much better than the unmodified charcoal, so the charcoal denatured by HNO_3 can adsorb the ions metal easier.

3.3. Evaluation of Ni (II) adsorption capacity of modified charcoal

The results in Fig. 5 showed that the Ni(II) adsorption capacityof modified charcoal samples increased up to 1.2 times, whereas with unmodified charcoal and the maximum adsorption capacity was 2.5 (mg/g) when the HNO_3 concentration was 1M. This proves that the denaturation process by HNO_3 had made the number of acidic functional groups such as carboxylic (-COOH) group, which was functional groups that can participate in the cation exchange process in the water increased significantly compared with the number of acidic clusters on the original coal surface [3].

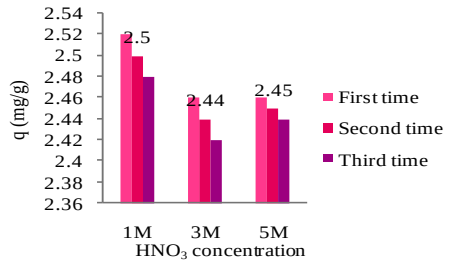

Figure 5. Effect of HNO_3concentration on adsorption capacity of Ni (II).

Ni (II) adsorption capacity was mitigated when HNO_3 concentration increased to 3 M and 5 M. Therefore, in this study the adsorbent for subsequent experiment was retrieved through heating at 400 ^oC for 30 minutes and modified with HNO_3 1M.

3.4. Factors affecting on adsorption capacity of Ni (II) of modified charcoal

3.4.1. Effect of pH on adsorption capacity of Ni (II)

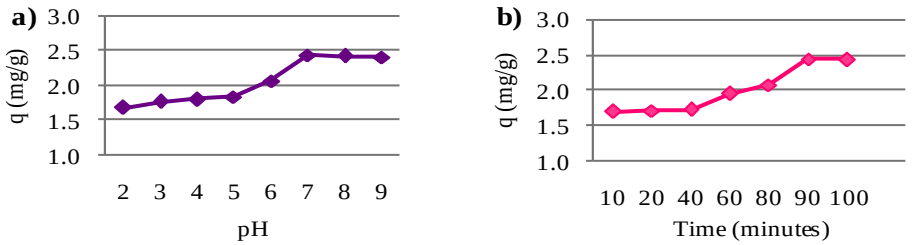

Figure 6. Effect of pH (a) and effect of time (b) on adsorption capacity of Ni (II).

The pH of the solution is an important factor for the removing of Ni (II) by activated carbon [5]. The results in Fig. 6a showed that the adsorption capacity of Ni (II) increased in pH range from 2 to 7 and stabilized at pH from 7 to 9. This result is consistent with the results reported by K. Druirvelu and coworkers. [5] The adsorption capacity of Ni (II) of activated carbon increased at pH ≥ 7 due to partial hydrolysis of metal ions leading to MOH^+ and $M(OH)_2$ formation [5]. $M(OH)_2$ was adsorbed to a greater extent than MOH^+ on activated carbon. The low resolution of hydrolysis metal ion may be another cause for maximum absorption in the pH range of 7 ÷ 9. In the pH range of 2 ÷ 6, the metal ions exist mainly M^{2+}. The competitive adsorption between H^+ and Mn^{2+} at the ion exchanging sites of charcoal lowers the Mn^{2+} adsorption capacity as reported previously [5].

3.4.2. Effect of time on adsorption capacity of Ni (II)

According to the theory of isothermal adsorption, molecules adsorbed on the surface of the adsorbent can move backward, involving the time factor of contact between the adsorbent and the adsorbed. The results in Fig. 6b showed that in the first 10 ÷ 90 minutes, the adsorption capacity of Ni(II) increased relatively fast (from 1.7 ÷ 2.44 mg/g) and gradually stabilized in the period of 90 ÷ 100 minutes with the adsorption capacity was ≈ 2.44 mg/g. Thus, the 90-minute exposure time was chosen for further experiment.

3.4.3. The effect of the modified charcoal content on the adsorption efficiency

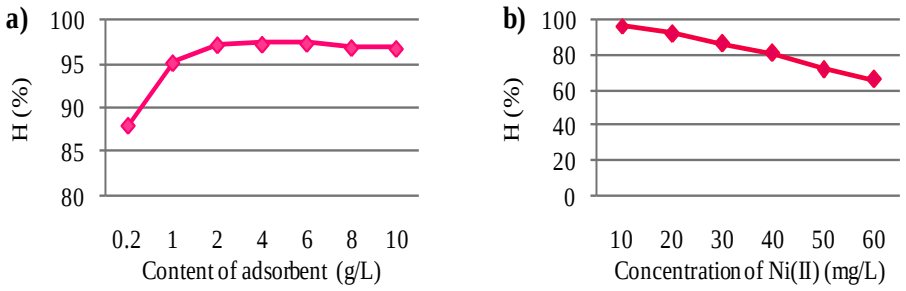

Figure 7. Effect of the modified charcoal content (a) and effect of Ni (II) concentrations (b) on the adsorption efficiency ofNi (II).

The increase of adsorption efficiency of adsorbents for Ni (II) was due to an increase in the number of adsorption sites. However, to a certain extent, the adsorption efficiency was maximized, the increase of the content adsorbentis not significant [5]. The results in Figure 7a showed that in the content range of 0.2 ÷ 2 (g/L), the adsorption efficiency of Ni (II) increases and gradually stabilizes in the content range of 2 ÷ 6 (g/L). So we chose the content of modified charcoal 2 g/L for further experiments.

3.4.4. Effect of initial concentration of Ni (II) on adsorption efficiency

The higher the concentration, the lower the amount of absorbed Ni (II) (Figure 7b). At a concentration of 10 mg/L, the treatment efficiency was high and it decreases as the initial concentration of Ni(II) increases from 20÷60 mg/L.It can be explained as follows: When initial concentrations of Ni (II) was low, the active centers on the surface of the adsorbents was not filled by Ni (II) so adsorption capacity was high. However, at some point, when the centers are covered by Ni (II), the adsorption capacity of the material decreases rapidly, the adsorbent surface becomes saturated by Ni (II).

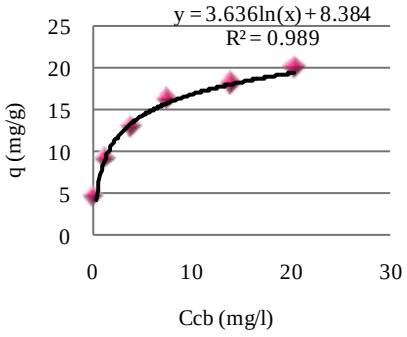

Figure 8. Langmuir Isothermal adsorption of adsorbent for Ni (II).

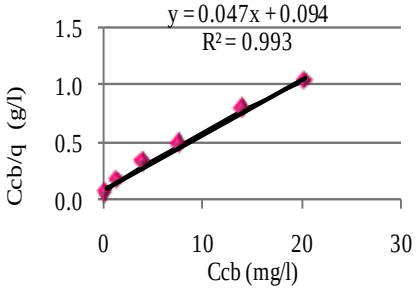

Figure 9. C_{cb}/q dependence on C_{cb} for Ni(II).

Isothermal adsorption is a math ematical model that describes the distribution of Ni (II) content in water, based on the homogeneous / non-homogeneous assumptions of the adsorbent. Experimental results showed that Ni (II) adsorption of the material follows the Langmuir isothermal adsorption model:

$$\frac{C_{cb}}{q} = \frac{1 \times C_{cb}}{q_m} + \frac{1}{q_m \times b} \quad (3)$$

as shown in Fig. 8. Where: C_{cb}: residual metal concentration in the test solution (mg/L); q: adsorption capacity of the material (mg/g); q_m: maximum adsorption capacity of the material (mg/g); b: Langmuir constant. The adsorption process takes place in water, so Langmuir is the most commonly used model [6], with higher accuracy.

From Fig. 9 we can calculate the maximum absorption capacity of Ni (II) through the slope: $q_m = \frac{1}{\tan\alpha} = \frac{1}{0.0473}$ = 21.14 (mg/g). The results showed that the maximum adsorption capacity of Ni (II) of adsorbent was 21.14 mg/g and the Langmuir constant was 0.5.

Compared with similar activated carbon samples, our samples had a higher adsorption capacity of Ni (II) than with other adsorbent such as charcoal made from rice husk [3], lotus [4], doum seed coat [7], banana peels [8], sheep waste [9], the content of adsorbent was less than other materials, processing and fabrication charcoal was simple, not take much time. This result opened aprospect of applying biochar from coffee husks in the field of water treatment of heavy metals.

4. CONCLUSION

Charcoalised coffee husk at different temperatures and time conditions in Ar gas environment then adsorbed Ni (II) at pH = 4; 10 g/L charcoal, 60 minutes adsorption time, initial concentration of Ni (II) was concerned in this study. The results showed that the adsorption capacity of Ni (II) of charcoal was quite good (1.9 mg/g). Study on the denitrification of charcoal by activating with HNO_3 concentrations of 1 M, 3 M, 5 M impregnated ratio of 1:10, the results showed that the ability of adsorbed Ni (II) of the modified charcoal has increased compared with charcoal samples and the highest adsorption capacity reached 2.5 mg/g. Study on the adsorption capacity of Ni (II) of selected adsorbent under optimum conditions: pH = 7, adsorption time of 90 minutes, content adsorbent of 2 g/L showed maximum adsorption capacity of Ni (II) of adsorbent was 21.14 mg/g.

REFERENCES

1. Mehmet E. A., Sukru D., Celalettin O. and Mustafa K. - Heavy metal adsorption by modified oak sawdust, Journal of Hazardous Materials **141** (2007) 77–85).
2. Ramakrishna Gottipati, Dr. Susmita Mishra - Preparation and Characterization of Microporous Activated Carbon from Biomass and its Application in the Removal of Chromium (VI) from Aqueous Phase, Thesis of Doctor of Philosophy in Chemical Engineering. National Institute of Technology Rourkela, Odisha, 2012.
3. Phan Dinh Tuan - Research on technology to process some wastewater from activated carbon produced from rice husk, University of Natural Resources and Environment Ho Chi Minh City: report synthesizing scientific and technological results, 2016 (in Vietnamese).
4. Vu Thi Hau, Trinh Thu Nguyen - Research on adsorption capacity of Ni (II), Cr (VI) of coal produced from lotus, Journal of Chemical Analysis, Physics and Biology **22** (4) (2017) 81-88.
5. Kadirvelu K., Senthilkumar P., Thamaraiselvi K., Subburam V. - Activated carbon prepared from biomass as adsorbent: elimination of Ni(II) from aqueous solution, Bioresource Technology **8l** (2002) 87–90.
6. Lan Huong Nguyen, Thi Mai Vu, Thi Trinh Le, Van Tuyen Trinh, Thi Pha Tran & Huu Tap Van – Ammonium removal from aqueous solutions by fixed-bed column using corncob-based modified biochar, Enviromental Technology (2017)1-10. DOI: 10.1080/09593330.2017.1404134
7. Manal El-Sadaawy, Ola Abdelwahab - Adsorptive removal of nickel from aqueous solutions by activated carbons from doum seed (Hyphaenethebaica) coat, Alexandria Engineering Journal **53** (2014) 399-408.
8. Annadurai G., Juang R. S., Lee D. J. - Adsorption of heavy metals from water using banana and orange peels, Water Sci. Technol. **47** (2002) 185-190.
9. Bansal M., Singh D., Garg V. K., Rose P. - Use of agricultural waste for the removal of nickel ions from aqueous solution: equilibrium and kinetics studies, Int. J. Civil Environ. Eng. **1** (2) (2009) 108-114.