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Production of activated carbon from HNO_3-treated sawdust for methylene blue adsorption in solution

Chau Quang Minh[1,2]; Nguyen Thi Hong Phuong[2,*]

[1] *Institute for Technology of Radioactive and Rare Elements, Vietnam Atomic Energy Institute, 48 Lang Ha Road, Hanoi, Vietnam.*
[2] *School of Chemistry and Life Sciences, Hanoi University of Science and Technology, 1 Dai Co Viet Road, Hanoi, Vietnam.*
**Email: phuong.nguyenthihong@hust.edu.vn*

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ABSTRACT

The report presents the process of preparing activated carbon (AC) from sawdust treated with HNO_3 and evaluating the adsorption capacity of methylene blue (MB) of the material in solution. AC was synthesized under suitable conditions: carbonization at 600°C, then activated with HNO_3 2M for 3 hours and further treated with NaOH. The structure and properties of the material were determined by modern methods such as XRD, SEM and FTIR. Analysis of the nitrogen adsorption – desorption process gave the specific surface area (BET) of 440.5433 m^2/g. Investigation of the adsorption of activated carbon in the methylene blue concentration range from 5 - 35 ppm showed that 0.02g AC gave high adsorption efficiency when the MB concentration was below 20 ppm (H > 90%). Langmuir and Freundlich models were used to investigate the adsorption capacity, in which MB adsorption according to Langmuir isotherm model is more suitable than Frendlich model.

Introduction

Dyes are an important commodity used in many fields such as paper, textiles, leather, plastics, food or pharmaceuticals - cosmetics. The uncontrolled consumption of dyes in industry causes significant impacts on the environment and living organisms. One of them is the textile dyeing industry, with companies, factories and thousands of small establishments in traditional craft villages. Wastewater from the dyeing process contains many types of toxic organic color compounds. On a small scale, this wastewater is almost not treated but discharged directly into the sewer system, directly into rivers and lakes, causing serious water pollution [1]. Their toxicity to the environment and humans is very high, and can cause cancer in people exposed to a long time.

Methylene blue (MB) is a widely used cationic dye, but its effects on human health have also been documented in practice. In some cases, MB can cause burns or eye damage, meningitis, neurodegeneration, increased heart rate and nausea [2]. Treatment of MB-contaminated wastewater is necessary to reduce the concentration before discharging into the environment to minimize the impact on the ecosystem and human health.

There are many different methods that can remove toxic substances from solutions such as chemical precipitation, oxidation, ion exchange, membrane filtration, reverse osmosis... in which adsorption is the

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simplest and most cost-effective method [2]. Activated carbon (AC) is chosen as a popular adsorbent material, due to its large specific surface area, high mechanical strength and regeneration ability. In particular, the AC surface can be appropriately modified through the activation process to change the structure to suit special applications [3].

HNO_3 is an effective inorganic oxidant to transform materials, increasing the acid groups on the surface of activated carbon, especially carboxyl, lactone (ester) and phenol (hydroxyl) groups, thereby significantly increasing the amount of dye adsorbed [4] [5] [6]. Xing Rong's study [4] showed that after activated carbon was further treated with HNO_3, the specific surface area increased significantly, from 905.72 m^2/g to 1,140.40 m^2/g. In addition, carbonization using a furnace in an oxygen-deficient condition is also highly economical when there is no need to blow inert gas.

In this report, we mention the research results on the fabrication of activated carbon adsorbent materials treated with HNO_3 and adsorbing methylene blue in solution.

Experimental

After collection, pine sawdust is washed, dried and chopped to a size of d < 2.2 mm. The chemicals used are practical grade (PA), originating from Xilong and Shanghai Zhanyun, China.

Synthesis of AC from sawdust

Sawdust was calcined at 400 – 800°C in anoxic conditions for 1.5 hours. The resulting carbon was further activated with 0.1 – 6M HNO_3 at a ratio of biochar/HNO_3 = 1:5 (g/mL) for 0.5 – 7 hours. The sample was then washed with water to pH = 5, then continued to be soaked in 0.3M NaOH solution at a solid/liquid ratio of 1:20 (g/mL) for 2 hours. The final activated carbon was filtered, washed to pH 7, dried and stored.

Material properties

The synthesized materials were studied by chemical measurements according to ASTM D – 4607 standards and modern physical methods such as: X-ray diffraction (XRD) recorded on a Bruker D8 Advance diffractometer and Fourier transform infrared spectrum (FTIR) from a Fourier mid-IR InfraLUM FT – 08 to determine the phase composition and chemical nature of the materials; the product morphology was observed by a HITACHI S – 4800 scanning electron microscope (SEM). The specific surface area was determined by nitrogen adsorption-desorption isotherm using a Micromeritics Tristar II Plus. All measurements were performed at the Vietnam Academy of Science and Technology.

Investigation of MB adsorption capacity of AC

The factors affecting the MB adsorption process were investigated as initial MB concentration and MB adsorption time. To ensure accuracy, each experiment was performed at least 3 times and the results obtained were the average of the experiments.

Effect of time:

Weigh 0.02 g of activated carbon for adsorption with 40 mL of 12 ppm MB solution, stir continuously for 1 - 10 minutes.

Effect of initial MB concentration:

Add 20 mL of MB solution with different concentrations from 5 - 35 ppm into a 100 mL glass beaker containing 0.02 g of AC material. The adsorption process was carried out under the same conditions (retention time of 20 minutes at room temperature).

The MB concentration of the filtrate before and after adsorption was determined by UV-vis absorption spectroscopy on a HALO DB-20 UV-vis Double Beam Spectrophotometer at wavelength λ = 664.5 nm. At the concentration range of 0 – 15ppm MB, the standard curve equation is y = 0.1873x + 0.0336.

Results and discussion

Investigation of suitable conditions for AC fabrication

The factors: calcination temperature, HNO_3 concentration and activation time with HNO_3 were studied to synthesize materials with high adsorption capacity. Iodine index was used to evaluate the adsorption capacity of the obtained AC material.

The iodine index of the material increases gradually when the carbonization temperature increases to 600°C. This may be because at low temperatures, organic substances in the raw material have not been completely decomposed, forming few capillaries. Continuing to increase the temperature, the iodine index decreases because a part of the biochar burns into ash, becomes inert and difficult to activate. Therefore, the carbonization temperature T = 600°C is chosen for further research.

Table 1 also shows that 2M HNO_3 is the suitable concentration to activate the formed biochar. When the concentration of HNO_3 increases, the iodine index decreases or the adsorption capacity of AC decreases.

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This is explained that: at high concentrations with long retention times, carbon has reacted significantly, reducing the specific surface area, leading to a decrease in the adsorption capacity of activated carbon.

Table 1: Iodine index of AC at survey conditions

carbonization and activation with 2M HNO_3 for 3 hours					
Temperature, °C	400	500	600	700	800
Iodine index, mg/g	139,7	254,0	588,4	533,4	501,7
carbonization at 600°C and activation with HNO_3 for 3h					
C_{HNO3}, M	0,5	1	2	4	6
Iodine index, mg/g	406,4	457,2	588,4	469,0	427,2
carbonization at 600°C and activation with 2M HNO_3					
Activation time, h	0,5	1	3	5	7
Iodine index, mg/g	412,8	419,1	588,4	482,6	431,8

Under the same carbonization and activation conditions with 2M HNO_3, the iodine index of AC increased and reached a maximum after 3 hours of activation, and then tended to decrease. When the incubation time with HNO_3 was short, the heavy metal reaction was not complete; the pores generated on the surface were few, leading to the formation of few capillaries. If the activation time was too long, under the action of acid, part of the carbon chain was converted into ash, reducing the surface area of the material. Therefore, the adsorption capacity of AC decreased. In summary, an activation time of 3 hours was chosen to produce activated carbon (m-AC).

Characterization results

The XRD pattern of the activated carbon sample (m-AC) is shown in Figure 1a. The XRD results show that the carbon sample exhibits two broad reflection bands (peaks) corresponding to 2θ = 23° and 43.5° corresponding to the (002) and (101) planes, which are assigned to the lattice plane of amorphous carbon. On the other hand, a broad and large, asymmetric diffraction peak at around 2θ = 15 – 30° is observed in the XRD patterns of this sample, possibly due to the expansion of the distance between the graphite layers. In particular, the obtained XRD pattern only has typical diffraction peaks of activated carbon, no signs of impurities are observed. [2]

The chemical nature of the surface of the prepared AC was investigated by FTIR, and the results are shown in Figure 1b.

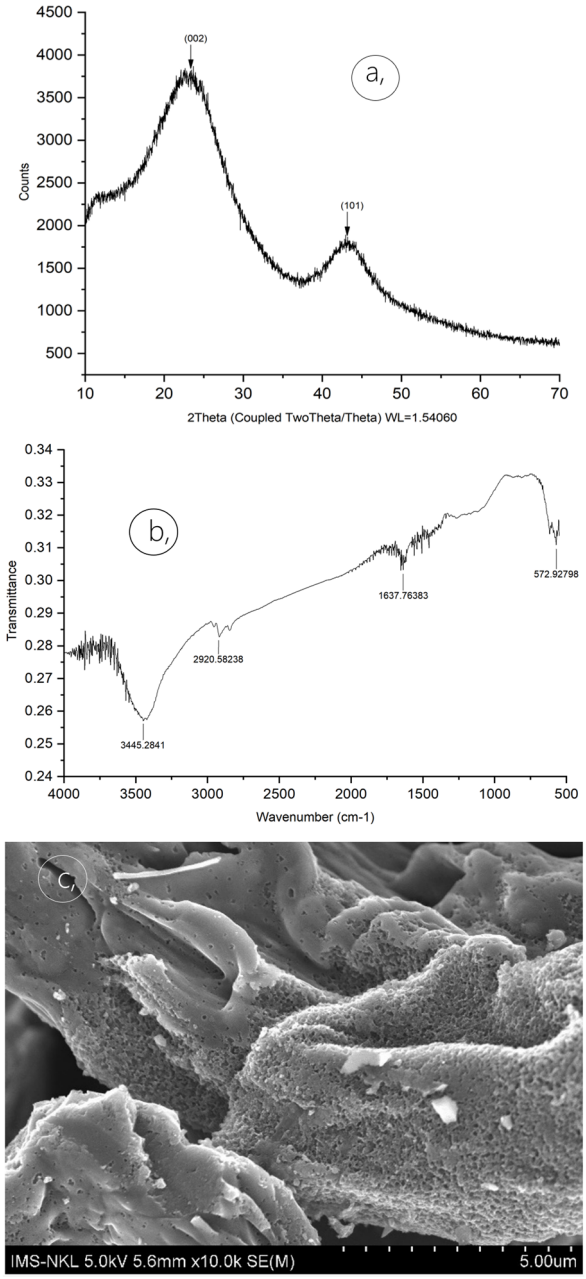

Figure 1: Results of m-AC sample analysis using the methods: (a) XRD; (b) FTIR; (c) SEM

In the FTIR spectrum of the prepared AC sample, a band at 3445.28 cm^{-1} appeared, which can be attributed to the stretching vibration of the hydroxyl functional group –OH on the surface of the activated carbon. This appearance is due to the –OH bond in the carboxyl group after treatment with HNO_3 and from the adsorbed water in the activated carbon structure. A new peak appeared at 2920.58 cm^{-1} in the spectrum, which may be due to the saturated C–H group of the straight-

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chain carbon or may be due to the deformation of CH_2 or CH_3 [7]. The band at about 1637.76 cm^{-1} is characteristic of the C=O bond in the lactone group, carboxyl group and anhydride [8]; The peak at 572.93 cm-1 is assigned to the C-H bond [9]. These results indicate that the activated carbon prepared from sawdust contains functional groups, suitable for the adsorption of organic compounds, including toxic dyes.

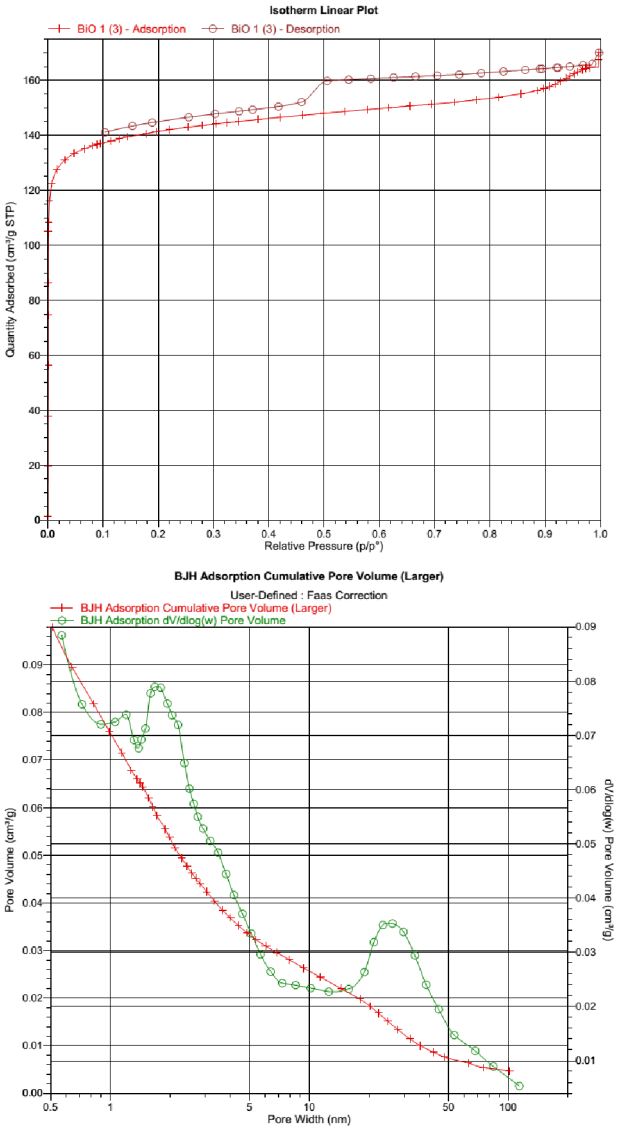

Figure 2: BET measurement results of fabricated AC

From the SEM image, it can be seen that the activated carbon has a porous structure with many pores, however the size of the capillary pores is mainly medium and large.

BET measurement results show that the synthesized AC has a specific surface area S_{BET} = 440.5433 m^2/g. The capillary has an average volume of 0.254928 cm^3/g and an average diameter of 2.31467 nm. With this result, the molecules that need to be adsorbed will go deeper into the capillary pores, adsorbing more molecules or in other words, the synthesized AC has a relatively good adsorption capacity.

MB adsorption capacity on AC material

Survey of time to reach equilibrium

Table 2 shows the results of AC adsorption survey over time. As the stirring time increases, the adsorption efficiency increases. After 7 minutes, the concentration reaches equilibrium, the efficiency is about 55.5%. This is a short retention time, however, the efficiency is quite low, possibly because the capillaries are full, no longer able to adsorb more. Thus, it is possible to consider increasing the amount of adsorbent to improve the efficiency.

Table 2: Dependence of adsorption efficiency on time

Time (min)	MB concentration after adsorption (ppm)	Efficiency H (%)
1	6.90	42.53
2	6.83	43.07
3	6.63	44.72
4	6.19	48.42
5	6.06	49.53
6	5.79	51.71
7	5.32	55.70
8	5.36	55.33
9	5.34	55.49
10	5.36	55.32

Effect of MB concentration

The results from Table 3 show that the MB adsorption efficiency gradually decreases with increasing MB concentration. Specifically, from a concentration of 5 to 20 ppm, the MB adsorption efficiency of AC in a constant time (20 minutes) tends to decrease gradually (from about 99.31% to 90.87%). In particular, the efficiency drops sharply to 64.16% when the concentration increases from 20 to 30 ppm. Thus, with a small amount of AC, the adsorption efficiency obtained is high when the MB concentration is less than 20 ppm. This result is suitable for practical application. With higher MB concentrations, it is necessary to add more AC or adjust to increase the S_{BET} of AC.

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Table 3: Effect of MB concentration on MB adsorption process of AC

Initial MB concentration (ppm)	MB concentration after adsorption (ppm)	Efficiency H (%)
5	0.03	99.31
10	0.40	96.02
15	0.78	94.80
20	1.83	90.87
25	4.73	81.09
30	10.75	64.16
35	14.09	59.74

From the results of table 3, the adsorption process of MB by AC was investigated according to the Langmuir and Freundlich adsorption isostatic model, and the results were shown in Figure 3.

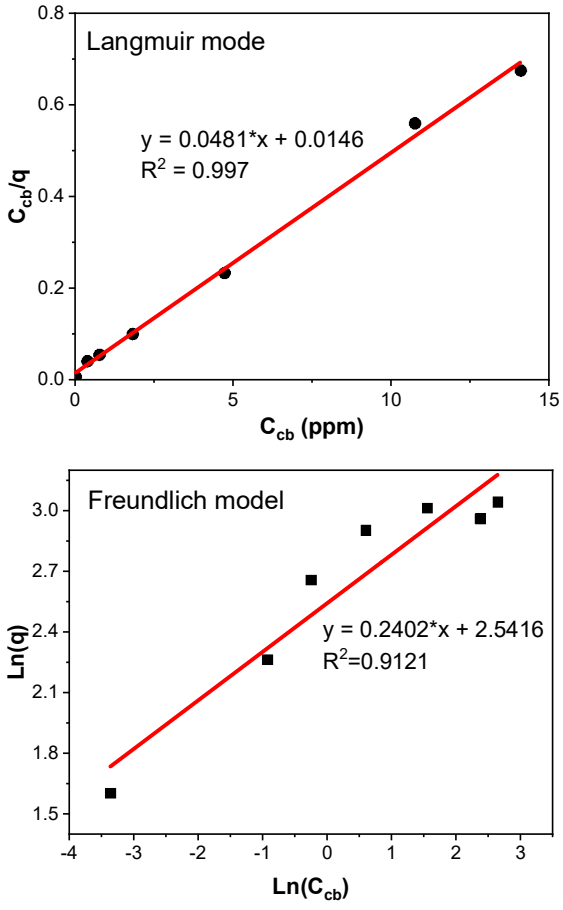

Figure 3: MB adsorption isotherm graph of AC

We see that the two isotherm adsorption models Langmuir and Freundlich describe relatively accurately the MB adsorption process of the fabricated AC. The coefficient n = 4.163 (1 < n < 10) is favorable for the adsorption process. R^2 (Freundlich) = 0.9121 is much lower than R^2 (Langmuir) = 0.997. This shows that the Langmuir model describes the MB adsorption process more appropriately than the Freundlich model. Thus, the adsorption of MB by the fabricated activated carbon is a monolayer adsorption, controlled by a homogeneous and similar process at all locations with a maximum adsorption capacity of 20.79 mg/g.

Conclusion

The synthesis of activated carbon from sawdust and treatment with HNO_3 is feasible. The obtained product has a porous structure, amorphous structure with a little graphite, containing mainly medium-sized capillaries, specific surface area S_{BET} = 440.5433 m^2/g. The functional groups on the surface of activated carbon from sawdust include C=C, OH and C–H, showing good organic matter adsorption capacity.

The investigation of the influence of time and MB concentration on the absorption capacity of AC has determined the maximum adsorption capacity of the material for the MB adsorption process is qmax = 20.790 mg/g. The Langmuir isotherm model is suitable for this process.

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