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Research article

Nanoporous Carbon from Water Hyacinth via Hydrothermal Carbonization assisted Chemical Activation for Dye adsorption

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Abstract

Keywords

nanoporous carbon;

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methylene blue adsorption;

Freundlich Isotherm

Nanoporous carbon was successfully prepared by hydrothermal carbonization with chemical activation using water hyacinth as a raw material. The porous carbon was produced for the adsorption of methylene blue (MB), which is an organic pollutant in wastewater from several industries. The effect of various parameters such as pH, dye concentration and adsorption period time on dye removal were studied. The highest removal efficiency of MB obtained using WH nanoporous carbon was approximately 96.8-99.9% within an adsorption time between 10 and 30 min. The dye removal capacity increased with increasing of period time during the adsorption test. Moreover, the adsorption kinetics of MB during adsorption process was explained by the Langmuir and Freundlich adsorption isotherms.

1. Introduction

A number of water resources have been contaminated by industrial dyes that were produced from several industries. The dye had a relatively high pH, and their release into bodies of water proved toxic

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for aquatic life. Colored particles can block the transmission of light into water. As a result, aquatic plants and algae cannot photosynthesize, causing the water to lack oxygen, a condition which in turn affects the surrounding environment of the water. Furthermore, the color of the dye effluent itself changes the color of the water, making the water source offensive looking to the public. There are many ways to treat dye polluted water resources but one way that is cheap and effective is the use of nanoporous carbon sorbent derived from biomass [1]

Water hyacinth (WH) is one of the most common weed species found in Thailand. WH can reproduce easily. In most water resources, slow water flow facilitates the growth of large quantities of water hyacinths. In drainage area, WH can grow and reproduce rapidly, clogging the system and causing drainage system failure. Water hyacinth, under some conditions, can assist water purification as it can absorb (excess) nutrients, and its use in water purification has been studied. However, when WH grows in large quantities, it affects living things in the surrounding environment because it causes a lack of dissolved oxygen (DO) to occur. The use of WH is beneficial and can reduce these pollution problems and increase value of water hyacinth plants. One of the alternative pathways for water hyacinth application is nanoporous carbon sorbent derived from plant biomass [2, 3].

Traditionally, the reaction to transform biomass into carbonaceous materials such as biochar or porous carbon is thermochemical conversion, in this case, hydrothermal carbonization with activation. In hydrothermal treatment, there are 4 reactions involved: hydrolysis, dehydration, polymerization and carbonization. These reactions play an important role in the decomposition of cellulose, hemicellulose and lignin components in the chemical structure of lignocellulosic materials leading to an increase in carbon content. In addition, the development of porosity is also obtained by hydrothermal treatment [4-6].

In this study, hydrothermal carbonization was used as a pretreatment process to develop nanoporous carbon from water hyacinth feedstock at mild operating conditions (temperature <300°C). This process produced a high yield [7]. The purpose of this work was to transform water hyacinth into nanoporous carbon to utilize as an adsorbent. Hydrothermal carbonization and chemical activation were utilized in the nanoporous carbon production. For the dye adsorption test, methylene blue was selected as the adsorbate. The different activating agents such as K_2CO_3, KOH, NaOH, and Na_2CO_3 at different concentrations for the production of WH porous carbons were studied and their effects on the physicochemical properties of the WH-based nanoporous carbon were observed. Moreover, the dry adsorption capacity was measured by the UV-VIS spectroscopy.

2. Materials and Methods

2.1 Water hyacinth derived nanoporous carbon

In this study, the raw material for producing porous carbon was WH residual biomass which included leaves, stalks, and roots obtained from the Ladkrabang canal, Ladkrabang, Bangkok, Thailand. The collected WH residues was pretreated in a sun-drying process for 7 days, followed by crushing in a ball milling machine and sieving into sizes between 350-500 µm. Moreover, high purity-grade (99.99%) nitrogen was used in all experimental studies. In the experiment, the hydrothermal of water hyacinth residues was conducted in a Teflon chamber with a steel autoclave system using a ratio of raw material to water carrier at 1/3 (g/ml). The hydrothermal process was relatively carried out at temperatures of 160, 180, and 200°C, with treatment times between 4 and 24 h for each condition. The hydrochar samples were then dried in an oven at 105°C overnight. After that, the WH nanoporous carbon was successfully produced by activation at 900°C using different chemicals including KOH, NaOH, K_2CO_3, and Na_2CO_3 at different activating concentrations of 2, 4 and 6 M and with a heating rate of 5°C/min for 2 h under N_2 atmosphere. Then, all samples were washed with deionized water until reaching neutral pH, and finally dried. They were then ready for the dye adsorption test.

2.2 Dye adsorption test

Methylene blue at initial concentration of 100 ppm and at pH = 7.0 was used as the adsorbate in the dye adsorption tests. For each sample, WH nanoporous carbon was added to a 100 ml methylene blue solution, and the adsorption test was conducted in an electrical shaker at interval times of 10, 20, and 30 min. The adsorption performance of MB was determined by UV-visible spectrophotometer model T92+ over the wavelengths of 200-800 nm. The adsorption efficient was determined via equation (1), and the adsorption kinetics investigations were described by equations (2) and (3).

$$q_t = \frac{(C_0 - C_t)}{W} \times V \tag{1}$$

Where, C_0 (ppm) is the initial concentration of dyes, C_t (ppm) is the dye concentration at time t, W(g) is the mass of WH porous carbon, and V is the dye solution volume.

$$\ln(q_e - q_t) = ln(K_1 q_e) - K_1 t \tag{2}$$

$$log q_e = log K_F + \frac{1}{n} log C_e \tag{3}$$

Where, q_e is adsorption capacity at equilibrium (mg/g), q_t is maximum adsorption capacity at each period time (mg/g), K is adsorption constant (l/mg), and C_e is constant related to heat of sorption (J/mol).

2.3 Characterization

The physical and chemical properties of the WH porous carbon samples were comprehensively characterized. Surface morphology was studied using scanning electron microscope (Zeiss EVO MA10). The chemical functional groups on the surface were analyzed using Fourier Transform Infrared Spectroscopy (FT-IR, Perkin Elmer Spectrum Two). The chemical structures of the WH porous carbon samples were measure using Raman spectroscopy. The adsorption isotherms were determined using an N_2 adsorption analyzer (Quantachrome Autosorp iQ-MP-XR).

3. Results and Discussion

3.1 Effects of chemical activation on WH porous carbon

The effects of chemical activation on porous carbon morphology are represented in Figure 1. The SEM micrographs of (a) non-activated carbon reveal a fiber structure with large particle size between 10 and 70 µm. In the case of alkaline activation as shown in Figure 1(b-e), the activation produced a significantly greater porous structure than WH biochar. Activation with KOH solution (Figure 1b) produced the highest surface area and porosity of carbon. During the carbon-KOH reaction, evaporation of water vapor during the activation process with steam resulted in carbon that had a structure with high numbers of pores. It resembled a sponge and the pores were connected in three dimensions. Moreover, Figure 2 shows the mixed characteristics of the adsorption isotherms between Type 1 and Type 4 according to IUPAC classification. At lower relative pressure, the sorption was assigned to the Type I isotherm, which revealed a monolayer adsorption on micropores. Also, the isotherm has a hysteresis loop at high relative pressure revealing the appearance of mesopores (Type 4) [7, 8]. It can be concluded that in the sample which was activated with KOH at 4 M concentration was mesoporous on the surface [1, 9].

Table 1 illustrated the pore characteristics of WH porous carbons. The results showed that the sample obtained by KOH activation at 4 M concentration had the highest surface area of 948.818 m^2g^{-1}, pore volume 0.686 cm^3g^{-1}. Figure 2 represented the adsorption isotherm Type 4, which was found in most porous materials, mainly of mesoporous structure.

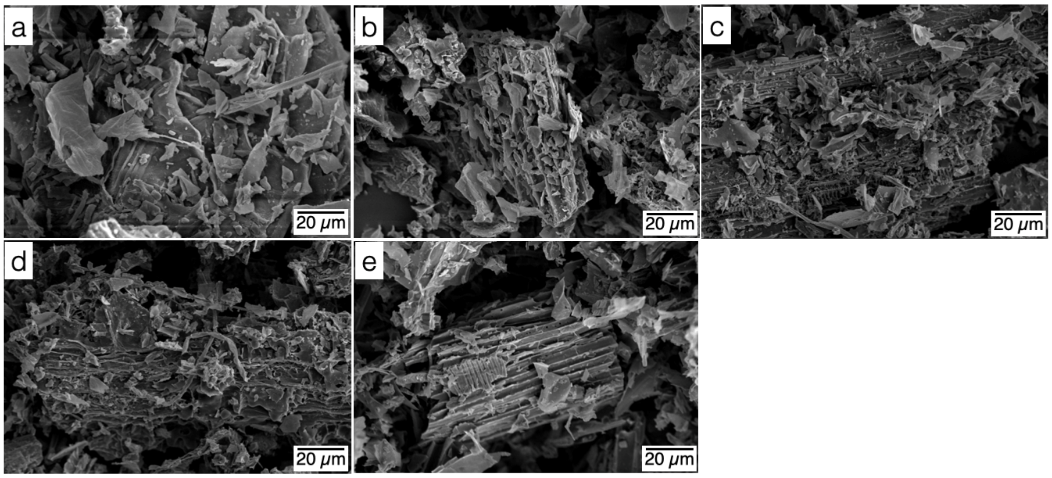

Figure 1. SEM (500x magnification) image of (a) non-activated carbon, and alkaline activation by (b) KOH (c) NaOH (d) K_2CO_3 (e) Na_2CO_3 using a relative concentration of 4 M at 900°C for 2 h

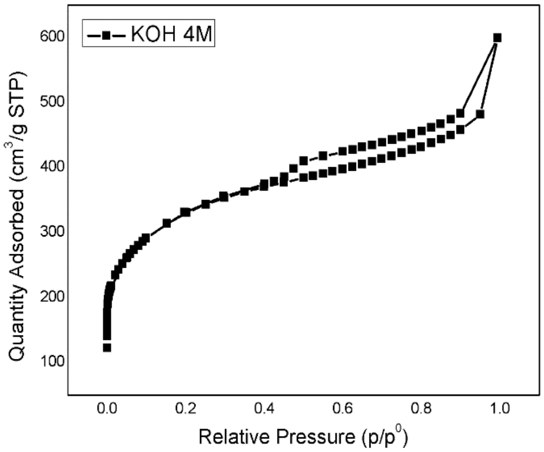

Figure 2. Adsorption/Desorption isotherm of WH porous carbon obtained using 4 M KOH

Table 1. Pore characteristics of WH porous carbon samples obtained using 4 M KOH

Parameter	S_{BET} (m^2g^{-1})	Pore volume (cm^3g^{-1})	Pore size (nm)
KOH	948.818	0.686	2.7
NaOH	902.394	0.563	2.5
K_2CO_3	843.036	0.481	2.2
Na_2CO_3	814.862	0.475	2.3

Figure 3a showed the Raman shift patterns of WH porous carbon. According to the I_D/I_G ratio, the band at 1350 cm^{-1} was assigned to the D band, which corresponds to a graphitic lattice vibration mode with A1g symmetry, which is typical for carbon materials, and it is detected around 1300-1380 cm^{-1}. The G band typically at 1560-1585 cm^{-1} arises from the stretching of the C-C bond in graphitic materials, and it is common for all sp_2 carbon systems [5, 10]. Moreover, the FTIR spectra of WH porous carbon are displayed in Figure 3b. The peaks between 3680-3000 cm^{-1} and 1421 cm^{-1} are assigned to the C-H deformation of lignin. Moreover, the peak at 1700 cm^{-1} corresponds to the C=O stretching of cellulose. The intense band centered at 2882 cm^{-1} significantly refers to lignin compositions, and the peak intensity between 700-950 cm^{-1} also refers to C-H stretching of cellulosic compounds [11, 12].

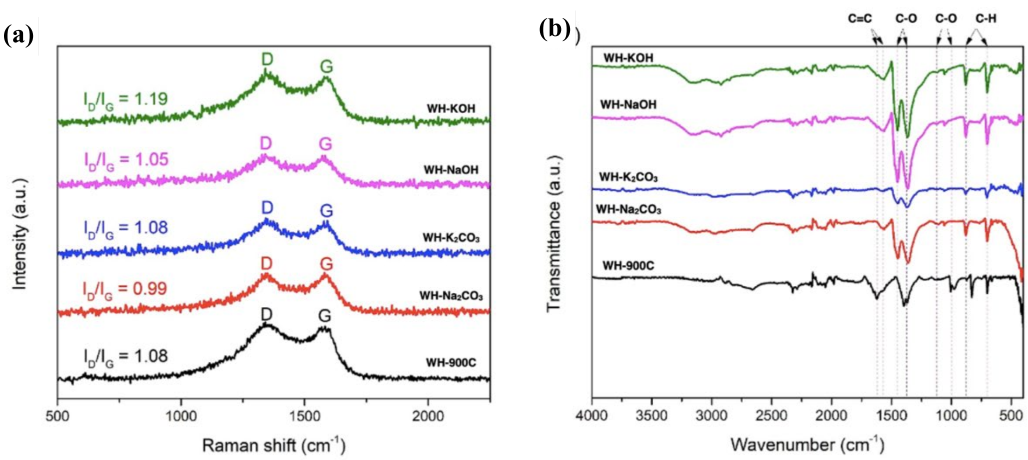

Figure 3. Raman shift (a) and FTIR spectra (b) of non-activated WH porous carbon and WH porous carbon obtained from alkaline activations (KOH, NaOH, K_2CO_3, Na_2CO_3) using a relative concentration of 4 M at 900°C for 2 h

3.2 Methylene blue adsorption test

Figure 4 shows the appearance of solution after the adsorption test using 100 ppm methylene blue solution of 100 ml with 0.1 g WHC obtained from different activation conditions, as seen in Figures 4 a, b, and c. The adsorption test by WHC obtained from KOH activation significantly showed a superior adsorption capacity when compared to the others with the colorless of methylene blue solution. According to the effects of NaOH, K_2CO_3, and Na_2CO_3 in the synthesis of WH porous carbon, the results similarly showed a good adsorption performance consistent with the WH porous carbon obtained by KOH.

However, Figure 4a showed higher adsorption capacity than the appearance results displayed in Figure 4b. By increasing the concentration of chemical activation to 4 M, the result showed that only the WH porous carbon obtained from KOH activation exhibited colorless solution after the adsorption test. In contrast, a colorless solution results from using WH porous carbon obtained from the other alkaline catalysts at 6 M. Then, the adsorption percentage obtained at different adsorption times using corresponding WH porous carbon are displayed in Table 2 and Figure 5, which shows that increase in absorption time of the dye increased the adsorption capacity until adsorption equilibrium was reached. Carbon that was processed by hydrothermal carbonization and chemical stimulation by KOH exhibited a higher adsorption of dye than hydrochar samples obtained without any chemical activation. Moreover, the WH porous carbon obtained by chemical activation reached high adsorption capacity, and the adsorption capacity was increased by increasing the activating agent concentration. This showed that the alkaline activation extremely enhanced the porosity and surface area of WH porous carbon. However, porosity and adsorption performance can be developed by adjusting the valuables in the chemical activation process such as type of activating agent, activation time, and concentration of activating agent.

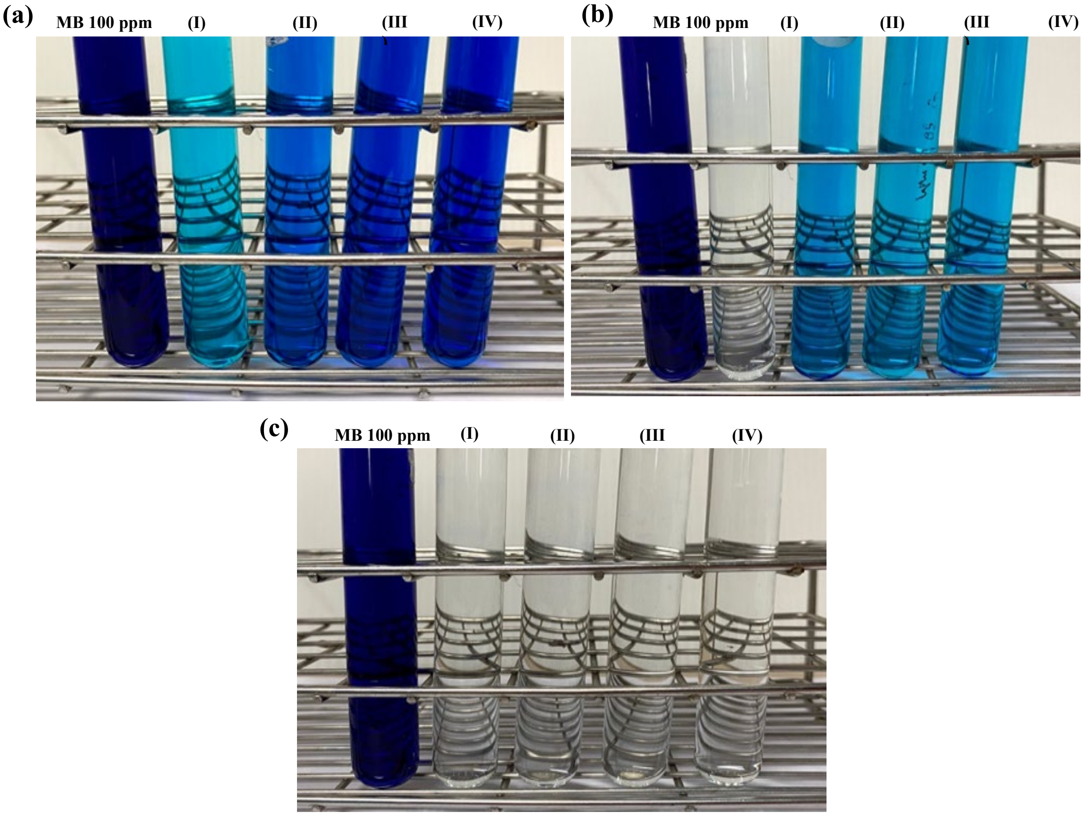

Figure 4. Adsorption test of 100 ppm methylene blue concentration of 100 ml using 0.1 g WHC obtained by chemical activation by different chemicals at activating agent concentration of (a) 2 M (b) 4 M, and (c) 6 M; where, (I) KOH (II) NaOH, (III) K_2CO_3, and (IV) Na_2CO_3

Table 2. Adsorption test of 100 ppm methylene blue concentration of 100 ml using 0.1 g WH carbon obtained by chemical activation by different chemicals as activating agent at adsorption period time of 10 min

Chemicals	Adsorption time (min)	Adsorption capacity (%)					
		2M	pH	4M	pH	6M	pH
KOH	10	92.459	6.9	99.807	7.0	99.903	7.0
NaOH		91.678	7.0	97.016	7.1	99.895	7.1
K_2CO_3		89.533	7.1	91.075	7.0	99.860	6.9
Na_2CO_3		87.864	7.1	89.590	7.2	99.865	7.1
KOH	20	93.015	7.0	99.817	6.9	99.882	7.0
NaOH		86.032	7.2	88.638	7.0	99.672	7.1
K_2CO_3		94.321	7.1	98.200	7.1	99.904	7.1
Na_2CO_3		88.467	7.1	93.098	7.1	99.795	7.0
KOH	30	96.763	7.4	99.965	7.0	99.764	7.2
NaOH		96.252	7.1	97.348	7.1	99.847	7.3
K_2CO_3		97.794	7.1	99.834	7.2	99.908	7.0
Na_2CO_3		97.676	7.2	97.755	7.1	99.908	7.1

** Adsorption capacity of WH carbon (without treatment) is 22.145%

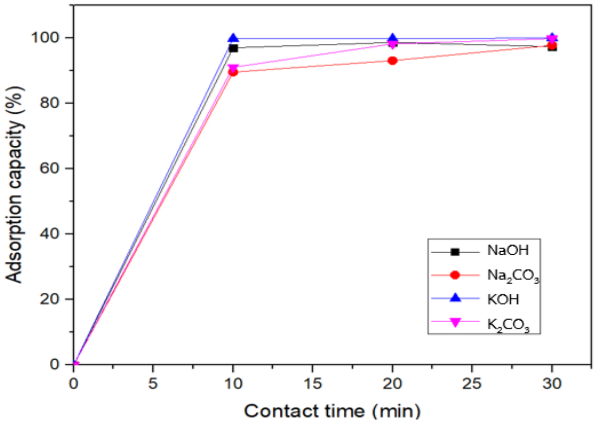

Figure 5. Effects of contact time on the capacity of adsorption of methylene blue dye using WH porous carbon

3.3 Effects of contact time on the capacity of adsorption

The effects of adsorption time on the adsorption of 100 mg/l (ppm) methylene blue dye at a concentration of 100 mg/l (ppm), with a pH 7.0 with carbon at 10, 20, and 30 min were investigated (Table 3). The findings revealed that the adsorption capacity of the methylene blue dye increased when the contact time between adsorbate and adsorbent was increased, and the adsorption capacity increased from 0 to 99.921% in 10 min of adsorption time. Adsorption of methylene blue dye with carbon was equivalent in 10 min. From the results of the experiment, the relationship of the linear equations of Langmuir and Freundlich showed the adsorption isotherm of methylene blue dye using the synthesized nanoporous carbon. When using the Langmuir and Freundlich equations, as shown in Table 3, the accuracy of the adsorption isothermal was determined by the highest coefficient of determination (R^2). It was found that most coefficient values were more consistent with the Freundlich equation than the Langmuir equation indicating that the adsorption occurred by gravity. However, the adsorption of methylene blue can be explained by the continuous absorption process in which methylene blue was continuously adsorbed by the pores of carbon.

Table 3. Adsorption isotherm of methylene blue dye with WH porous carbon obtained by hydrothermal carbonization assisted chemical activation

	Langmuir isotherm			**Freundlich isotherm**		
Adsorbent	**Q_m(mg/g)**	**K_L(l/mg)**	**R^2**	**K_F(mg/g)(l/mg)**	**1/n**	**R^2**
NaOH	76.923	-0.663	0.998	124.595	-0.140	0.999
Na_2CO_3	59.054	-0.346	0.805	185.097	-0.307	0.934
KOH	99.632	-0.621	0.945	99.426	-0.261	0.926
K_2CO_3	71.942	-0.523	0.912	141.297	-0.115	0.961

4. Conclusions

Water hyacinth based nanoporous carbon was successfully produced by hydrothermal treatment at 200° C for 12 h, with carbonization process at 900°C for 2 h combined with the KOH activation. The condition of 4 M KOH activation resulted in the highest surface area of 942.818 m^2g^{-1} and the appearance of mesopores. Furthermore, dye adsorption tests were successfully accomplished at various adsorption conditions using WH nanoporous carbon of 0.1 g for adsorption times of 10, 20 and 30 min using 100 ml of 100 ppm methylene blue dye solution. The adsorption capacity reached 94-99% in 10 min adsorption period time. Moreover, when the adsorption time was increased, the adsorption capacity of the dye also increased until adsorption equilibrium was reached. Thus, the obtained WH nanoporous carbon displayed an excellent adsorption performance compared to hydrochar samples. The adsorption capacity of methylene blue dye increased rapidly and reached equilibrium in 10 min, and then the adsorption capacity slightly increased when the adsorption time reached 30 min. After that, the experimental results were simulated on the adsorption isotherm of methylene blue dye adsorption using nanoporous carbon. In terms of the Langmuir and Freundlich equations, it was found that most coefficient values of determination (R^2) were more consistent with the Freundlich equation than the Langmuir equation, which suggested that adsorption behavior occurred by gravity, and chemical interaction was not reversed.

5. Acknowledgements

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