Sorption Of Methylene Blue In Aqueous Solutions By Adsorption Material From Bagasse

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***Abstract*—This report presents the results of research on the adsorbents are made from bagasse by different methods: Bagasse was cut into small pieces, repeatedly washed by water to remove sugar, boiled at 100^0C within 50 minutes and dried to have raw bagasse (VL1). The raw materials (VL1) will be continuously manufactured by virtue of anaerobic heat at 300^0C (VL2) and 700^0C (VL3) and activated by condensed sulfuric acid 98% within 48 hours (VL4). The characterization of the product was performed by Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD), energy dispersive analysis of X-rays (EDX), scanning electron microscopy (SEM). The investigation reveals that bagasse thermalized at 700^0C (VL3) may highly absorbent capacity for methylene blue, about 132.98 mg/g. That material have high activity nearly compare with commercial activated carbon (VL5). This materials can used to treatment organic compounds in wastewater**

Keywords—Bagasse, adsorption, organic compounds, treatment, wastewater

I. INTRODUCTION

At present, the problem of water pollution due to organic matters is quite serious, especially textile dyes. These pollutants can infiltrate in our body through the respiratory, oral, percutaneous ... If the content of organic compounds exceeds the allowable limits will cause physiological dysfunction of the living body, causing cancer, nerve… Therefore, researching on removing them from the environment is very important [1-7].

There are many methods of water pollution treatment were applied: biological methods, chemical methods, physicochemical methods [8-14]. Adsorption method which is one of physicochemical methods has so far been considered as a way to effectively treat these contaminants [15-34].

Agriculture residues is known for high carbon contents in this structure, is a potential source for making biochar. There are many research has been made the adsorption materials form agricultural residues, from sources as: Tea waste, rice straw, bamboo hydrochar, vegetable residues, oil extraction from almond peanut, corncob… [16, 19-25, 29-31]. Agricultural residues available in large quantities are bagasse-the fibrous byproduct resulting from the milling of sugarcane. Sugarcane bagasse accounts for 25-30% of the weight of sugarcane. The annual global production of 800 million tonnes of sugarcane results in 240 million tonnes of bagasse [34]. Bagasse has many special applications: Be pressed and used as a fuel to replace firewood; an important source of raw materials for paper pulp, plywood, ceiling; be used as bedding for livestock pens; make natural water filter material, absorb heavy metals, absorb organic compounds; be a substitute for straw, grass; fermentation as fertilizer and potting media for growing mushrooms. In this study, we made biochar from bagasse by different methods: by heat, concentrated sulfuric acid to increase the adsorption capacity of the material, and the first study the adsorption of methylene blue in the laboratory

II. MATERIAL AND METHODS

Bagasse was obtained from GiaLam in HaNoi, VietNam. Bagasse was cut into small pieces, repeatedly washed by water to remove sugar, boiled at 100^0C within 50 minutes and dried in an oven at 110^0C for 6h (VL1)

A. Synthesis of biochar from bagasse

Raw material (VL1) was heated in a muffle at 300^0C in 2h obtained VL2. Raw material (VL1) was heated in a muffle at 700^0C in 2h obtained VL3. The raw material VL1 was immersed in H_2SO_4 98% with ratio VL1: H_2SO_4 = 1g:1.5ml within 48h, washed several times with distilled water, then soaked in $NaHCO_3$ 5% in 24h. Filter and retrieve materials. Wash several times to neutral pH and then dried at 150^0C in 6h to obtain VL4. And VL5 - activated carbon, was a commercial product, which was used to compare with the synthetic materials

B. Characteristic structure of the materials

The physico-chemical structure of materials was analyzed by thermogravimetric analysis was measured on 4.000 Mettler TA TGA machine at a temperature range of 0-1000^0C with heating speed of 10^0C/min. X-ray diffraction (XRD) technique using a Bruker B8 Advance X-ray powder diffractometer. The elemental composition was determined by Energy dispersive analysis of X-rays (EDX, Varian Vista Ax). The size and morphology of materials was examined using scanning electron microscopy (SEM, Hitachi S-4800FEG). The surface area and pore distributions of the material sample was determined by a Beckman Coulter SA3100 surface area analyzer based on the nitrogen adsorption-desorption isotherm at the temperature of liquid nitrogen (-196°C).

C. Sorption experiments

Adsorption of methylene blue (MB) onto different adsorbents was studies in batch experiments. A fixed amount of each dry adsorption (0.5g) and 50ml methylene blue solution were carried out in 250ml glass beakers and shaken at 150rpm at room temperature. Then, the adsorbed samples were filtered. The methylene blue concentration in the solution after adsorption was determined by UV-VIS Spectro 2550 spectrophotometer at its maximum absorbance wavelength of 660nm. To ensure the reproducibility of data, each experiment was conducted in triplicate and average of the three measurements was reported. The adsorbed amounts of substances were calculated from the mass balance equation:

$$Q_e = (C_0 - C_e).V/m$$

Investigate the effect of reaction time and methylene blue concentration on the adsorption capacity of the materials

Table 1. Experimental steps and conditions

No.	Experiment	Conditions		
		C_{MB} (mg/L)	Time (min)	$m_{Adsorption}$ (g)
1	Effect of reaction time	100	0-150	0.5
2	Effect of MB concentration	50-2500	60	0.5

III. RESULTS AND DISCUSSION

A. Structure characteristics of materials

- *The thermal gravimetric analysis diagram of bagasse*

The bagasse was used in this study are the local materials, was taken from Gia Lam, Ha Noi, Viet Nam. Thermal gravimetric analysis (TGA) is a method of thermal analysis in which the mass of a sample is measured over time as the temperature changes. This measurement provides information about physical phenomena, such as phase transitions, absorption and desorption; as well as chemical phenomena including chemisorptions, thermal decomposition, and solid-gas reactions

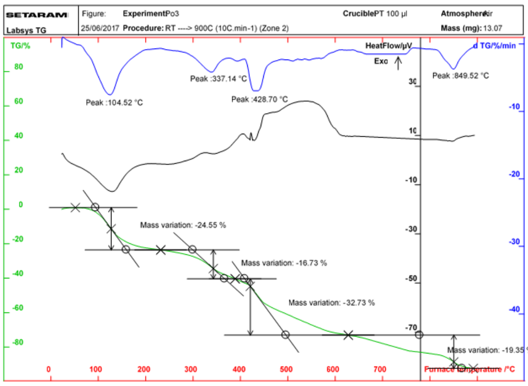


Fig 1. Thermal gravimetric analysis (TGA) of bagasse

Thermoanalytical techniques such as TGA have been widely used to study the thermal behavior of agricultural by-products such as bagasse. Therefore, it is possible that thermal analysis would make an important contribution to knowledge of the thermal behavior of biomass. The TGA showed that four steps of weight loss occur at the heating rate of 10°C/min, from the TGA curve. From the start of the experiment until the temperature of 104.52°C, the amount of weight loss recorded 24.55%. That was the endothermic process, was due to the loss of moisture present in the sample and the external water bound by surface tension. The second weight loss step occurred at 104.52– 337.14°C. This step was due to the removal of volatile matter which corresponded to the decomposition of the three major bagasse components, cellulose, hemicellulose and lignin, the weight loss 16.73%. The maximum rate of weight loss occurred at rapid decomposition of the sample and was observed between 200 and 337.14°C. The next broad weight loss step that occurs above 428°C, that is the exothermic process, is due to carbonization process which may be attributed to cellulose, hemicellulose and lignin intermediates being transformed to gaseous materials and tars with the weight loss 32.73%. At the end of the combustion is the combustion of multi-ring organic compounds, that have a stable structure at about 849°C, with the weight loss 19.35%

Based on the evolution of the decomposition temperature of bagasse. We carried out bagasse at temperature about 300°C and 700°C that was the temperature range is occrring the decomposition structure of bagasse

- *The results of elements analysis in the samples*

The EDX method allows to determine the composition of the chemical elements present in the material. The carbon content of the initial material is about 44%. This is mainly a cellulose component with the structure of β-D-Glucoside linking together to form long chains.

Table 2. Results of elemental analysis of materials from bagasse

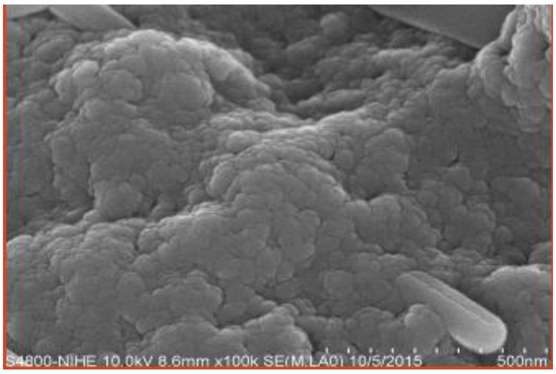
Materials	Elements (%)											
	C	O	Si	N	P	K	Zn	Cu	Mg	Fe	Ca	Al
VL1	44.75	46.28	1.94	1.27	0.3	4.58	0.05	0.09	0.05	0.14	0.09	0.46
VL2	54.20	24.74	13.7	-	-	5.03	0.08	0.1	1.02	0.09	0.25	0.79
VL3	60.61	10.93	16.03	-	-	6.01	0.25	0.46	2.06	1.13	0.51	2.01
VL4	60.55	34.37	5.08	-	-	-	-	-	-	-	-	-
VL5	95.18	4.59	0.19	-	-	0.01	-	-	-	0.02	0.01	-

Bagasse has high cellulose content, the carbon content is about 44.75%, under the treatment by high temperature and acid H_2SO_4 concentration, the dehydrate reactions and hydrolysis reactions will occur and the callulose chain will be cut off to formed the shorter chain and the results will increase the –COOH functional groups, increase the specific surface area and that leading increase adsorption and exchange capacity of the samples

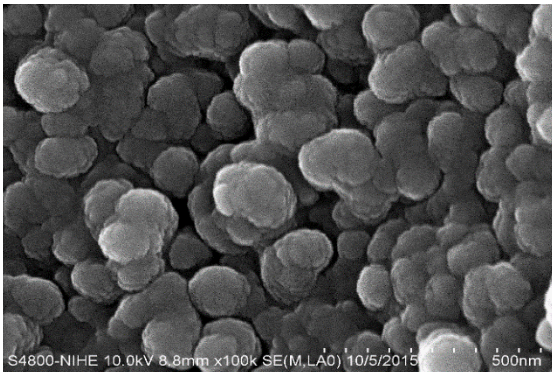
In anaerobic digestion, the composition of oxygen is significantly altered. Under the effect of high temperetures, the organic matter was decomposed, the water was strongly evaporated. There fore, the material have low oxygen content. In VL2 has 24.74% and in VL3 has 10.93% of oxygen. In acid modification, under the very strong oxydizing agents. All of the metals in the samples were dissolve. Thus, after formation, the sample only have C, O and Si elements

- *The SEM images of material samples*

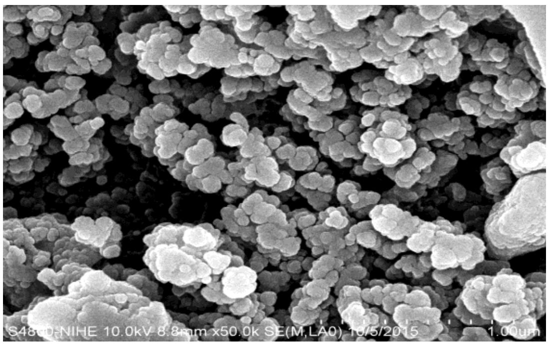
SEM images allow to determine the surface and particle size of the material. The results of the SEM analysis are shown in figure 2



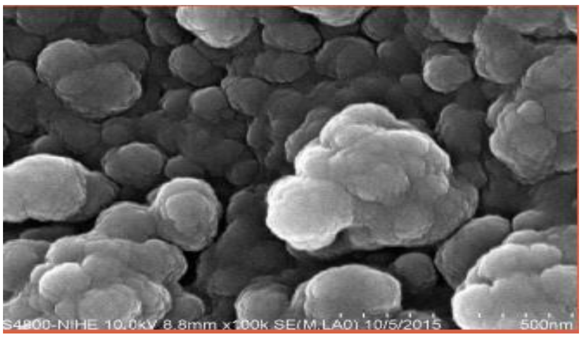
VL1



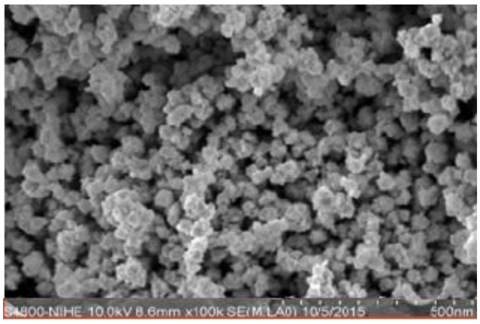
VL2



VL3



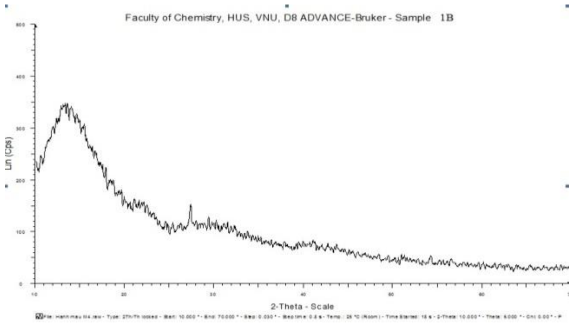
VL4



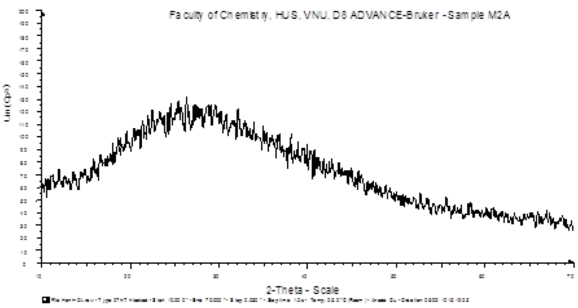
VL5

Fig 2. The SEM analysis of materials

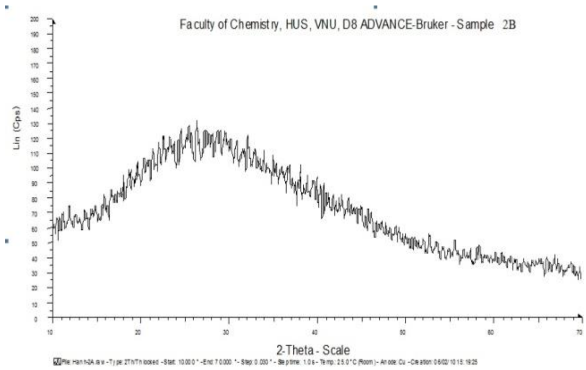
Bagasse has a stable structure, created by β-D-glucose monomers that link each other by β-1,4-glucoside. The products obtained under treatment by temperature and acid have a small grain structure, about 50-100nm



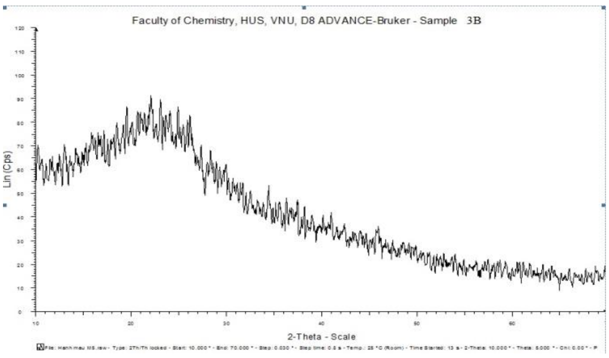
VL1



VL2



VL3



VL4

Fig 3. The XRD diffraction of materials

- *The XRD diffraction diagram*

XRD diffraction allows to determine the structure of the material, the results of the XRD diffraction analysis of the materials are shown in figure 3.

The XRD scheme of pure cellulose shows the peaks at angles of 2θ = 14.5; 16.3; 22.6^0. In modified material, under the treatment of temperature and acid, the cellulose chain would be broken down, make the peaks in the 2θ corners more fluid the the original. Specifically, all four samples of modified material are no longer retain peak peak pic at 2θ = 14.5^o. Thus, X-ray diffraction pattern (XRD) shows that the structure of the denatured material has been broken and changed a lot compared to the original material. These characteristics will determine the absorption capacity of the viral load.

- *Specific surface area of these samples*

The surface area and pore distributions of the material sample was determined by a Beckman Coulter SA3100 surface area analyzer based on the nitrogen adsorption-desorption isotherm at the temperature of liquid nitrogen (-196^{o}C).

Table 3. The results determine the specific surface area of the materials

Samples	VL1	VL2	VL3	VL4	VL5
S_{BET} (m^2/g)	14.82	280.35	487.61	389.12	327.86

The raw material has a small surface area about 14.82 m^2/g. Modified materials under the reactions of temperature, acid… The hydrate reactions would be occur and they made the change on the structure of materials, significantly increase the surface area. The highest surface area of VL3 reached 487.61m^2/g when treated at temperature of 700^{0}C

B. *Investigate the absorption capacity of Methylene blue solution*

- *The effect of time on the adsorption capacity of the materials on the MB solution*

Preparetion of methylene blue with concentration at 100 mg/l, shaking for a period of 0 to 150 minutes at 150 rpm. The results of the adsorption capacity of these materials for the methylene blue solution are shown in the fig 4

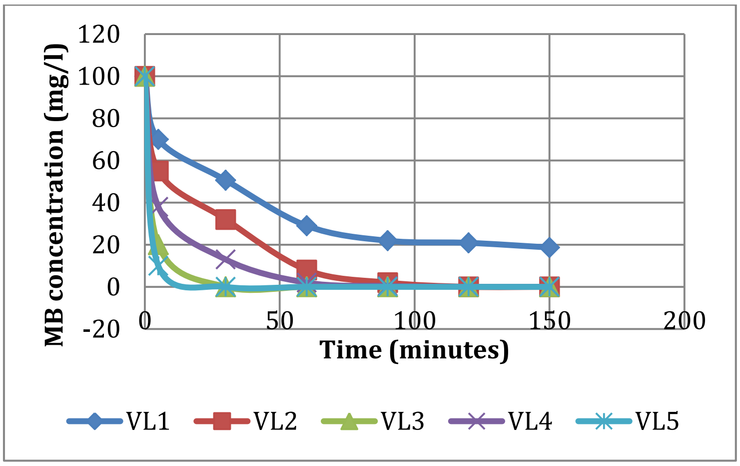


Fig 4. The effect of time on the adsorption capacity of the material on the MB solution

The results showed that, during the period from 0 - 150 minutes, when increasing the shaking time, the absorption capacity of materials increased. Raw material adsorption(VL1) slow occurred, after 60 minutes adsorption efficiency is about 71%, then the concentraition was slow down. These materials are capable of high absorption, VL3, VL5 completely absorbed MB solution after 30 minutes. VL2, VL4 adsorption was about 92.3% and 98.7% respectively. The further experiments will be conducted at 60 minutes

- *The effect of MB concentration on the adsorption capacity of the materials*

Carry out adsorption with different initial concentrations of MB solutions (50 - 1500 mg/l), adsorption time 60 minutes, the speed 150 rpm (especially with VL3 and VL5 would be experimented with higher concentrations until 2000 and 2500mg/l). The adsorption capacity of these materias for methylene blue were calculated and the results were shown in fig 5.

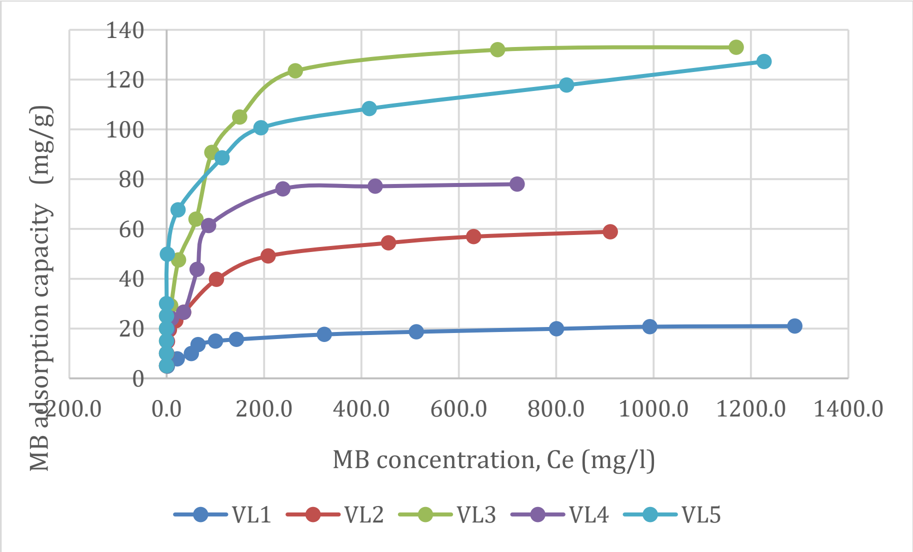


Fig 5. The effect of MB concentration on the adsorption capacity of the material

The adsorbents made from bagasse have a good capacity to absorb MB, as the concentration increases, the adsorption capacity increases. The adsorption capacity will increase to a limit value, called the maximum adsorption capacity of the material (qmax). From Fig 2, the maximum adsorption capacity of the following materials can be seen:

Qmax VL1 = 20.96mg/g;

Qmax VL2 = 58.86 mg/g;

Qmax VL3 = 132.98 mg/g;

Qmax VL4 = 77.98mg/g;

Qmax VL5 = 127.27mg/g

The results show that these materials have highly absorbable to MB solution. Modified materials, which have higher adsorption capacity than the original bagasse from 2.81 times (VL2) to 6.34 times (VL3). VL3 has as good adsorption capacity as commercial activated carbon

Table 4. Reported MB adsorption capacities of various carbon-based sorbents

No	Materials	Treatment methods	S_{BET} (m^2/g)	Qmax (mg/g)	Reference
1	Sugarcane bagasse	300^0C, 2h 700^0C, 2h H_2SO_4 98%	280.35 487.61 389.12	58.86 132.98 77.98	This work
2	Sugarcane bagasse	300^0C, 1.5h 450^0C, 1.5h 600^0C, 1.5h	- - 359	169 300 260	[18]
3	Bamboo	300^0C, 1.5h 450^0C, 1.5h 600^0C, 1.5h	- - -	202 250 225	[18]
4	Hickory chips wood	300^0C, 1.5h 450^0C, 1.5h 600^0C, 1.5h	- - 222	114 250 240	[18]
5	Foumanat tea waste	NaOH 0,05M, 4h	45	461	[19]
6	Rice husk	H_3PO_4 85%	571	88.65	[20]
7	Rice husk	oxalic acid 1.2M	-	29.15	[21]
8	Bamboo	NaOH 0.25M	26.249 31.602	655.76 268.93	[22]
9	Prickly pear peel	H_3PO_4 85%	1025	416.7	[23]
10	Corncob	saline conditions.	-	163.93	[24]
11	Maize silk	Grind to powder	-	71.6	[25]

IV. CONCLUSIONS

From this study, the modified materials has demonstrated its capability in removing methylene blue from aqueous solutions. The sorption of methylene blue on bagasse and modified materials was studied as a function of various parameter such as: contact time, concentration of MB in solutions. The rates of sorption for MB dye at various initial concentrations were rapid at the beginning, followed by a more gradual process and equilibrium was attained within 60 minutes. The maximum adsorption capacity of these materials was 132.98 mg/g (VL3) and this adsorbent can served as a good low cost adsorbent to replace costly adsorbents in dye removal.

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