

Biosorption of Methylene Blue by Activated Carbon from Sugarcane Waste (ACSW)

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ABSTRACT

This study was aimed to produce and characterized activated carbon from sugarcane bagasse by physical and chemical activation. Physical activation was performed by carbonation process in temperatures 450°C and 650°C. While chemical activation used H₃PO₄ 10%, FeCl₃ 10% and KMnO₄ 10% as activator. The results showed that total yield (%) 49.8396 - 80.635; pH 4.0-7.9; ash content (g) 0.3338-0.8820; adsorption capacity of iod (%) 93.92-99.20. Morphological structure, functional group and Crystal structure was studied by using SEM analysis, FT-IR and XRD diffractogram respectively. Adsorption capacity (%) of methylene blue 1.5 ppm and 2.5 ppm using UV-VIS Spectrophotometer produces; for H₃PO₄ activator at 450°C = 99.24 and ND; at 600°C = ND and 99.24. FeCl₃ activator at 450°C = 93.8 and 28.68; At 600°C = ND and 99.24. KMnO₄ activator at 450°C = 61.24 and 65.12; At 600°C = 39.4 and 53.79.

Keywords: activated carbon, bagasse, methylene blue

INTRODUCTION

Biomass as an alternative to renewable and sustainable raw materials in the production of renewable energy [1]. The development of agricultural waste-based adsorbents is one of the main goals of green chemistry, besides being economical, regenerative, does not produce toxic and effective products for adsorbing metals and dyes [2][3], as well as catalysts and electrodes for supercapacitor material [4].

Lignocellulosic biomass consists of cellulose, hemicellulose and lignin with covalent bonds between molecules and van der Waals bonds forming complex structures that are resistant to enzymatic hydrolysis [5]. Lignocellulose has active C-O, NH and OH groups which can be modified to form pore structures and high surface area to increase bioadsorbent capability [6]. The abundance and availability of lignocellulosic waste for the production of activated carbon (KA) at a low cost, so it is widely applied in various studies, namely water purification, heavy metal adsorption, dyes, organic/inorganic compounds, as a catalyst and the basic material for making capacitors and batteries [7-9].

KA is mostly in the form of amorphous solids resembling granular charcoal, widely used as an adsorbent in wastewater treatment that is difficult to remove by process (WWTP). Biomass precursors of lignocellulosic waste as a source of active carbon production are useful in multidisciplinary technologies such as adsorption, separation and catalytic processes. In applications, the adsorption capacity produced is high [10]. Surface activated carbon (KA) is charged (+), so to increase the capability of bioadsorbent can be modified through active groups of CO, NH and OH to form pore structures and high surface area [8], as well as through the

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formation of bonds with O, N, S atoms [9] in applications can be modified through processing methods and conditions such as heating rate, temperature, time, activating media and degree of activation. Activated carbon (KA) produced is stable in high temperatures, has reactivity, surface area $\pm 3000 \text{ m}^2/\text{g}$, porosity and high carbon content [11-12].

Sugarcane bagasse as one of the lignocellulosic agroindustrial residues is a source of activated carbon precursors [13][14] has a high surface reactivity [15]. The activation process will affect the nature of lignocellulose and porosity of raw materials. Various physical and chemical activation methods have been studied in the presence of bases, acids, organic salts and hydrothermal carbonization [12]. Surface area, pore size and carbon distribution are strongly influenced by activation temperature [8]. The method of physical activation involves the reaction of carbonization of organic substances into charcoal through heating followed by the activation process using oxidizing gases, O_2 and CO_2 at high temperatures [16][17], using Ar/N gas at temperatures of 600°C - 1200°C to produce activated carbon pulp sugar cane with a fine pore structure [1]. In the process of bio-oil pyrolysis and pellet making carbonation temperature of 800°C has a surface area of $300\text{-}410 \text{ m}^2 \cdot \text{g}^{-1}$ and $255.909 \text{ m}^2 \cdot \text{g}^{-1}$ [13]. At pyrolysis temperature of 680°C and 900°C of steam gasification for 2 hours with a heating rate of $10^\circ\text{C}/\text{min}$ having a surface area of $995 \text{ m}^2/\text{g}$, 50% adsorption capacity for iodine dye 994 mg/g and methylene blue 256 mg/g [12]. The two-stage pyrolysis process shows the surface area of mesoporous stages I and II are $48.1 \text{ m}^2/\text{g}$ and $50.3 \text{ m}^2/\text{g}$ with an adsorption capacity of Cd 107.5 mgCd/g for stage I 32.8 mg Cd/g [19].

Chemical activation methods have also been reported with activators KOH , NaOH , HCl , ZnCl_2 , MgCO_3 [20]. ZnCl_2 , H_2SO_4 , H_3PO_4 produce sugarcane bagasse activated carbon having a high surface area of $1502.1 \text{ m}^2/\text{g}$, carbon atoms 40.0-45.7% and adsorption capacity of 45.7% at calcination temperature of 500°C [16][17][25]. An increase in carbonization temperature of 300°C - 600°C on H_3PO_4 activation reduces porosity and surface area by 1100 and $780 \text{ m}^2/\text{g}$ [21]. Activation in organic solvents has been carried out such as formaldehyde in H_2SO_4 as methyl red bioadsorbent [22], propionic acid as methylene blue and orange II bioadsorbent have adsorption capacity of 59.5% and 25.5% [3]. Data from Freundlich and Langmuir isotherms at a concentration of 100 ppm-450 ppm adsorb methylene blue of 108.67 mg/g [23]. The use of H_2SO_4 activator at calcination temperature of 600°C with mesoporous structure in the area of $838 \text{ m}^2/\text{g}$ as bioadsorbent methylene blue dye [24]. XRD diffraction at $2\theta = 25^\circ$ 45° illustrates the amorphous nature and crystallinity with activation of H_3PO_4 - KOH [25]. In addition, the activation was carried out by heating microwaves, bagasse activated carbon capable of adsorbing ammoniac nitrogen and orthophosphate respectively 138.46 mg/g and 12.81 mg/g . The adsorption performance of the Langmuir Isotherm shows the monolayer adsorption [26].

EXPERIMENT

Chemicals and instrumentation

Raw material came from bagasse waste of PT.Tolangohula Sugar Factory, Paguyaman, Gorontalo Regency. The Reagents were H_3PO_4 10%, FeCl_3 10%, KMnO_4 10% and aquadest. The research was performed in the Chemistry Laboratory of FMIPA UNG, Organic Chemistry Laboratory of Brawijaya University, and Geology Laboratory in Bandung. Instrument were digital mesh particle size 80 mesh, analytical balance, furnace, glassware and oven. Fourier Transform-Infra Red (FT-IR), JEOL JSM-6360LA X-Ray Diffraction, SEM-EDS and UV-VIS Spectrophotometer.

Procedure of Analysis

Chemical Activation of Sugarcane Waste

Modification procedure [Amit Bhatnagar, et al 2015]. Sugarcane waste samples with 80 mesh particle size are activated in 10% H_3PO_4 solution, 10% $FeCl_3$, 10% $KMnO_4$, (ratio 1:10) for 2 hours at $80^\circ C$ then filtered and dried in an oven at $100^\circ C$ for 24 hours. Furthermore, the physical carbonization process, heating temperatures $450^\circ C$ and $600^\circ C$. KAAT products are stored in an excavator for further analysis.



Figure 1. Flow diagram of Activated Carbon from Sugarcane Waste (ACSW)

Table 1. Activator and Carbonation Conditions

Sample Code	Sample No	Activation Conditions	Carbonation ($^\circ C$)
ACSW/ H_3PO_4 10%/450 $^\circ C$	1	H_3PO_4 10% wt.ratio 1 : 10	450
ACSW / H_3PO_4 10%/600	2	H_3PO_4 10% wt.ratio 1: 10	600
ACSW / $FeCl_3$ 10%/450	3	$FeCl_3$ 10% wt.ratio 1 : 10	450
ACSW / $FeCl_3$ 10%/600	4	$FeCl_3$ 10% wt.ratio 1 : 10	600
ACSW / $KMnO_4$ 10% /450	5	$KMnO_4$ 10% wt.ratio 1 : 10	450
ACSW / $KMnO_4$ 10% /600	6	$KMnO_4$ 10% wt.ratio 1 : 10	600

2.3 Characterization of activated carbon from sugarcane waste

2.3.1 Calculation of Total Yield

The total yield of activated carbon from sugarcane waste products is calculated using the formula :

$$\text{Yield (wt\%)} = \frac{\text{weigh to f activated carbon}}{\text{weigh to f waste raw material}} \times 100(1)$$

2.3.2 Ash Contents

Porcelain dishes were washed and dried in oven at $100^\circ C$ for 30 minutes, then cooled in an desicator for 30 minutes and weighed to a constant weight. 1 gam of activated charcoal was placed in a known weightpetri dish, then put it in the furnace at $450^\circ C$ for 4-6 hours then placed in an oven at $100^\circ C$ for 30 minutes, cooled in desicator then weighed. Weighing wasperformed several times to obtain a constant weight.

2.3.3 Water Content

Petri dishes were washed, dried in an oven at 100°C for 30 minutes, then cooled in desiccator for 30 minutes and weighed until a constant weight is obtained. 1 gram activated charcoal to be placed in a Petri dish that has known weight. Petri dishes containing activated charcoal are then dried in an oven at 100°C for 24 hours and cooled in desiccator then weighed, to a constant

2.3.4 pH Measurement

pH measurements using the ASTM D 3838-80 standard test (ASTM, 1996). 0.1 g of carbon is heated in 100 mL of water for 15 minutes. The solution is filtered and measured pH at 50°C.

2.3.5. Calculation of Adsorption Capacity of Iodine Number Method [Gara R, 2012].

To determine the amount of iodine, 25 mL of iodine solution (0.05 N) was taken using a volumetric pipette. Iodine solution was put into a flask with a sample (± 0.1 g) centrifuged for 3 minutes. 10 mL of solution was titrated with sodium thiosulfate (0.04 N).

2.3.6 Fourier Transform Infrared (FTIR) Analysis

FT-IR Analysis (Shimadzu IR-Prestige21, Laboratory of Instruments, Brawijaya University, Malang). To determine the functional groups in the 4000 to 500 cm^{-1} region.

2.3.7 X-ray Diffraction (XRD) Analysis

Crystal structure analysis using XRD diffractometer (PANalytical, X'Pert HighScore, at Geologi Laboratories, Bandung).

2.3.8 Morphological Characteristic Analysis using SEM

SEM is used for microscopic structure analysis and surface morphology of active carbon SEM-EDS JEOL JSM-6360LA, Japan, at Geologi Laboratories, Bandung.

2.4 Stage of Application of ACSW to Methylene Blue Dyes

Preparation of a standard solution of methylene blue 1 ppm, 5 ppm, 10 ppm, 15 ppm and 20 ppm. Standard solution was measured to make a standard curve with the mechanism of adsorption of 0.1 g adsorbent in 50 mL of methylene blue solution with a concentration of 5 ppm, 7 ppm, 9 ppm using magnetic stirrer for 1 hour. Then let stand for 5-10 minutes and filtered. UV-VIS Spectrophotometer readings are performed at certain wavelengths.

2.4.1 Data Analysis Technique

The amount of methylene blue adsorbed by the adsorbent was calculated using the formula:

$$\% \text{ adsorption} = \frac{(C_o - C_s)}{C_o} \times 100 \%$$

where: C_o = concentration of methylene blue (MB) before adsorbed (mg/L) and C_s = concentration of methylene blue (MB) after adsorbed (mg/L). Adsorption capacity of methylene blue (MB) dyes can be calculated using the formula:

$$Q = \frac{V(C_0 - C_a)}{m}$$

where: Q = adsorption capacity per adsorbent weight (mg / g), V = volume of solution (L), C₀ = initial concentration of solution (mg/L), C_a = final concentration of solution (mg/L), m = mass of adsorbent (g).

3. RESULTS AND DISCUSSION

3.1 Characteristics of activated carbon from sugarcane waste

The activation process and biomass activating agent will affect the lignocellulosic properties and porosity of raw materials. In this research, a chemical activation process has been carried out with a variety of activators in the same concentration of 10% H₃PO₄, 10% FeCl₃/10% KMnO₄, with variations in the activation temperature of 450°C and 600°C, shown in Figure 2.

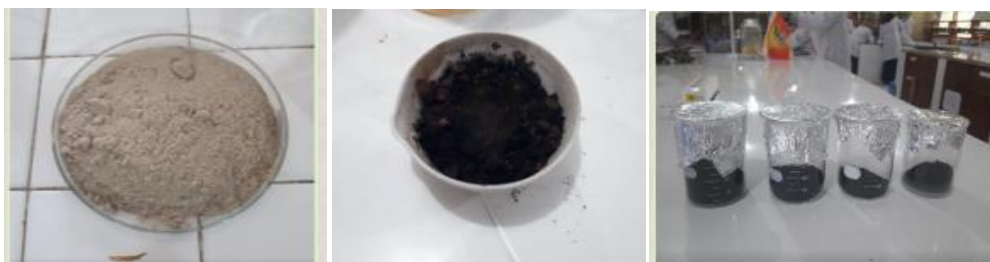


Figure 2. Bagasse activated carbon (KAAT) products

The activating agent plays an important role in the physicochemical properties of biocarbons. The increase in adsorption capacity performance is caused by sufficient free space in the micropore structure, thus effectively increasing the interaction between carbon surfaces and electrolytes. Likewise, the activation temperature greatly influences the specific surface area, pore size and porous carbon distribution [27][8].

3.1.1 Total yield, carbon weight, ash content and pH

Data on total yield, carbon weight, ash content and pH of activated carbon of sugarcane bagasse with various chemical activations at temperature variations are shown in Table 1:

Table 2. Total yield, carbon weight, ash content and pH of activated carbon

Code sample / Carbonation Temperature	(°C)	Activation Conditions	Initial weight (g)	Carbon Weight (g)	Total Yield (%)	Ash Content (g)	pH
ACSW/H ₃ PO ₄ 10%/450	450	H ₃ PO ₄ 10% wt.ratio 1:10	25	20.1588	80.6352	0,8820	4.0
ACSW/H ₃ PO ₄ 10%/600	600	H ₃ PO ₄ 10% wt.ratio 1:10	25	13.1915	52.7660	0,8326	3.4
ACSW/FeCl ₃ 10%/450	450	FeCl ₃ 10% wt.ratio 1:10	25	12.8506	51.4024	0,6960	5.0
ACSW/FeCl ₃ 10%/600	600	FeCl ₃ 10% wt.ratio 1:10	25	14.0227	56.0908	0,7648	4.0
ACSW/KMnO ₄ 10% /450	450	KMnO ₄ 10% wt.ratio 1:10	25	13.1773	52.7092	0,4084	6.
ACSW /KMnO ₄ 10% /600	600	KMnO ₄ 10% wt.ratio 1:10	25	12.5499	49.8396	0,3338	6

Based on Table 2. that activated carbon ACSW/H₃PO₄ 10%/450⁰C has the highest total yield of 80.6352% with a carbon weight of 20.1588 g. While ACSW/FeCl₃ 10%/600 and ACSW/H₃PO₄10%/600 have the lowest total yield and carbon weight i.e 56.0908 g and 52.7660%. Carbonization at different temperatures, the lignocellulosic precursors namely hemicellulose, cellulose and lignin decompose based on the thermal transformation reactivity of each component. Physically activated activated carbon provides better adsorption capacity than chemically activated KA [28]. An increase in temperature causes an increase in pore size, converts lignocellulosic substances into biocarbon residues and liberates most of the non-carbon elements especially gases so that only the aromatic carbon solids remain [27].

3.1.2 Calculation of Adsorption Capacity by the Iodine Number Method

Tabel 3. Adsorption capacity of iod

No	Activator	Temperature (°C)	Titran Voleme (mL)	Initial iodine concentration (M)	Adsorbed Iod Concentration (M)	Adsorbed iod (%)
1	H ₃ PO ₄	450	1	0,05	0,04960	99,20
		600	2,2	0,05	0,04912	98,24
2	FeCl ₃	450	5,3	0,05	0,04788	95,76
		600	5,3	0,05	0,04788	95,76
3	KMnO ₄	450	7,6	0,05	0,04696	93,92
		600	7,4	0,05	0,04704	94,08

Based on Table 3. carbonation temperature geatly affects the adsorption capacity of an activated carbon. The carbonation temperatures of 450⁰C and 600⁰C with activating substances H₃PO₄10%, FeCl₃10%, and 10% KMnO₄ have an adsorption capacity of iod 93.92% - 99.20%. H₃PO₄10% temperature of 450⁰C has the highest adsorption capacity of 99.20%. The activation process and biomass activating agent will affect the lignocellulosic nature and porosity of the raw material and the adsorption capacity [28].

3.1.3 Interpretation of FT-IR Result

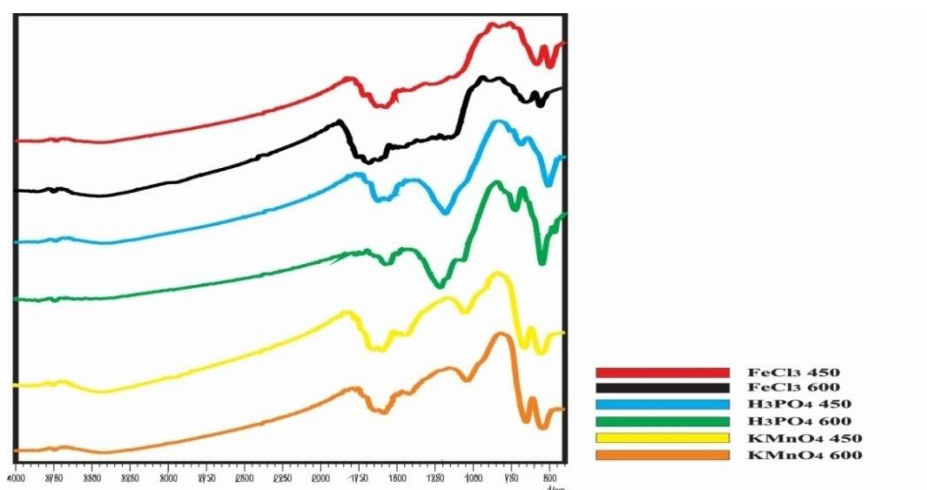


Figure 3. FT-IR Spectra of ACSW by H₃PO₄10%, FeCl₃10%, KMnO₄ 10%

Based on the data in Figure 3, each activator shows a strong band at 1750-1500 cm⁻¹ due to C-C vibrations in the aromatic ring of activated carbon [16] due to the decomposition of C-H bonds to form C=C aromatic bonds which are more stable at the activation temperature which is higher [26]. This peak may also be caused by the C=O group conjugated with an aromatic ring [27] and the formation of the C-O group during carbonation [28]. Strengthening the shoulder peaks of 1500 cm⁻¹ and 1400 cm⁻¹ is associated with the carboxyl-carbonate structure [21]. Broad band characteristics at 1000-1250 cm⁻¹ are shown to be strongly absorbed by activated carbon compounds with phosphoric acid activator H₃PO₄10% carbonation temperature 450⁰C-600⁰C.

3.1.4 Interpretation of SEM Result

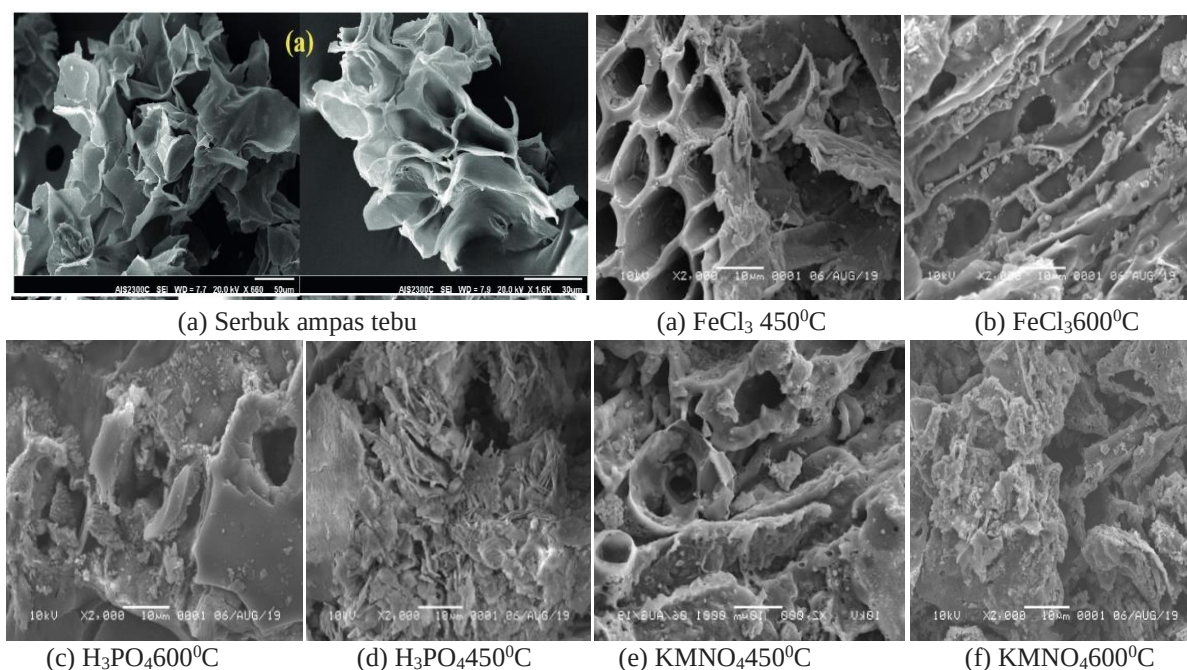
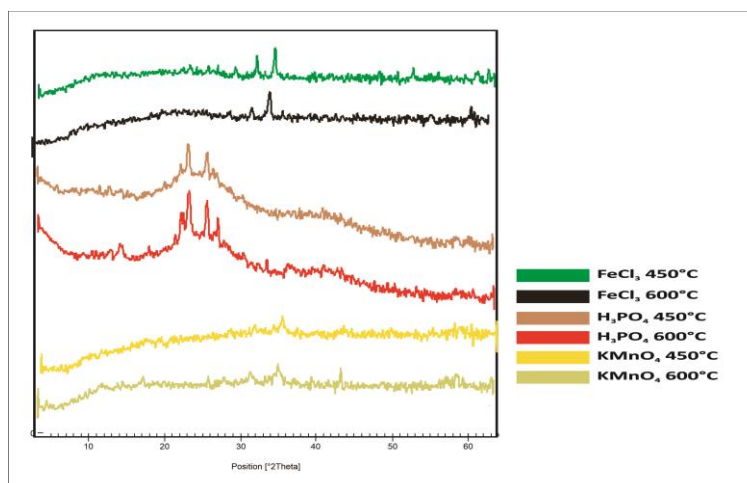


Figure 4. SEM photo data (a) raw material for activated carbon with an activating agent H_3PO_4 10%, FeCl_3 10%, KMnO_4 10% magnification 2000x

Based on the data in Fig. 4, (ACSW) with activator H_3PO_4 10%, FeCl_3 10%, KMnO_4 10% at carbonation temperatures of 450°C and 600°C have cracks, cracks and pores as a result of the separation of organic groups in the structure of macromolecules [Küçük İ, Önal Y., 2019]. The formation of cavities on carbon surfaces resulted from the evaporation of the activating agent during carbonization. activation with H_3PO_4 occurs through dehydration and decomposition of organic matter which reduces particle dimensions. The presence of activators in the particle structure inhibits reduction to some extent. This can be done by forming bridges such as phosphate esters and polyphosphates connecting biopolymers]. The small size of the molecule affects the formation of the area and pore size. Examples under the same conditions FeCl_3 has a smaller surface area and pores with a uniform surface morphological structure compared to H_3PO_4 . This is related to the small size of the hydrate ZnCl_2 molecule that penetrates inside the precursor structure. While H_3PO_4 forms mesoporous activated carbon with a variety of surface morphological structures. This might be the presence of other molecules with dimensions that vary from small H_3PO_4 and $\text{H}_4\text{P}_2\text{O}_5$ to large $\text{H}_{13}\text{P}_{11}\text{O}_{34.3}$ [29]

3.1.5 Interpretation of XRD Result

The XRD (ACSW) diffractogram data at carbonation temperatures of 400°C and 600°C with variations in the activating agent H_3PO_4 10%, FeCl_3 10%, KMnO_4 10%, are shown in Figure 5 below:



Picture. 5. XRD data with activator H_3PO_4 10%, FeCl_3 10%, KMnO_4 10%

The XRD results of (ACSW) diaphragm data with an activation agent H_3PO_4 10%, FeCl_3 10%, KMnO_4 10%. show varying crystallinity. The average pore size distribution of some samples is in a relatively narrow range and most of the molecular sieve size is in nano pore size.

3.2 Stage of Application

H_3PO_4 adsorption levels in Methylene Blue

No	Temperature (°C)	Concentration MB	Absorption after	Absorption before	% adsorption
1	450°C	1,5 ppm	0,129	-0,005	ND
2	600°C	1,5 ppm	0,129	-0,004	ND
3	450°C	2,5 ppm	0,132	-0.001	ND
4	600°C	2,5 ppm	0.100	0.001	99,24%

FeCl_3 adsorption levels in Methylene Blue

No	Temperature (°C)	Concentration MB	Absorption after	Absorption before	% adsorption
1	450°C	1,5 ppm	0,129	0,008	93,8
2	600°C	1,5 ppm	0.100	0.092	28,68
3	450°C	2,5 ppm	0,132	0,005	96,21
4	600°C	2,5 ppm	0.100	0.081	38,61

KMnO_4 adsorption levels in Methylene Blue

No	Temperature (°C)	Concentration MB	Absorption after	Absorption before	% adsorption
1	450°C	1,5 ppm	0,129	0,05	61,24
2	600°C	1,5 ppm	0.100	0.045	65,12
3	450°C	2,5 ppm	0,132	0,08	39,4
4	600°C	2,5 ppm	0.100	0.061	53,79

CONCLUSION

Activated carbon with carbonation temperatures 450°C and 600°C using activator H₃PO₄ 10%, FeCl₃ 10%, KMnO₄ 10% have adsorption capacity of iod (%) 93.92-99.20. KAAT / H₃PO₄ 10% at carbonation temperatures of 450°C and 600°C have the highest adsorption capacity (%) 99.20 and 98.24. Each activator shows a strong band at 1750-1500 cm⁻¹ due to C-C vibrations of the aromatic ring. SEM pictures of 2000x magnification showed that external surface of activated carbon particles has cracks and several crystals of various sizes in small holes. XRD diffractogram shows crystallinity in each activator. Activated carbon has an adsorption capacity of 99.24% methylene blue in an H₃PO₄ activator at carbonation temperature of 600°C.

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