Jzurnal Presipitasi
Media Komunikasi dan Pengembangan Teknik Lingkungan
e-ISSN: 2550-0023

Vol 19, No 3, 2022, 553-565
Article available at homepage presipitasi

Review Article

Methylene Blue Adsorption by Activated Carbon and Nano–Activated Carbon from Biomass Waste: A Review

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Abstract
Dyes are becoming increasingly prevalent in wastewater, and their presence caused serious threats to the environment. One of the most widely used dyes is methylene blue which has been used in the textile industry to dye cotton, wool, and silk. As a solution to this problem, using biomass (usually considered agricultural or plantation waste) as activated carbon is an important issue. Because based on previous studies, these materials are not only abundant and affordable but also have high efficiency in removing dye. Therefore, this paper will provide a further review of the latest research on the use of activated carbon from biomass as an adsorbent for methylene blue, which includes the conversion process of biomass into activated carbon, the mechanism of methylene blue adsorption, the factors that influence adsorption process, and the characteristics of activated carbon. In addition, it also reviewed the implementation of nanotechnology on activated carbon from biomass to adsorb with methylene blue.

Keywords: Biomass; activated carbon; methylene blue; nano-activated carbon

1. Introduction

The dyeing process is one of the most important processes in the textile industry. In this process, dyes and other chemicals such as metals, salts, surfactants, organic adjuvants, sulfides, and formaldehyde are added to enhance the color adsorption process by textile materials (Velusamy et al., 2021; Yaseen & Scholz, 2019). In a dyeing process, some dye is not bound to the fiber, so it is carried away by the flow of wastewater. The percentage of this unbounded dye varies from 1–50% depending on the type of dye used (R Ananthashankar, 2013). The textile industry's most commonly used dyes are azo dyes, reaching 60–70% of the total dye produced (Balapure et al., 2015). This is because azo dyes are stable dyes and have various color variations but have low prices. The release of wastewater containing azo dyes into the environment can reduce sunlight's ability to penetrate water bodies which later can reduce the photosynthesis process of aquatic plants, reducing the concentration of dissolved oxygen and reducing water quality. In addition, azo dyes also have an acute toxic effect, carcinogenic and mutagenic for living things (Saratale et al., 2011). One example of an azo dye is methylene blue (Fatkhasari et al., 2019).

Removal of dyes/color in wastewater can be done in several ways, namely physically, chemically, and biologically. One example of chemical processing is AOP (advanced oxidation process) and ozonation. However, both processes are expensive because they require large quantities of

chemicals and energy. The membrane filtration process has also improved dye removal by about 90%. However, this process is susceptible to pore blockage. Color can be removed biologically through batch reactor sequencing and moving bed biofilm reactors. However, this process takes a long time and produces sludge which must be managed further. As an alternative to these processes, adsorption is the most promising technique to remove dye (Shelke et al., 2022). The adsorption process is fast, affordable, and simple. Moreover, this process does not produce sludge, has high efficiency, is stable, and can be recycled (Dutta et al., 2021).

Activated carbon is the most widely used adsorbent in dye adsorption (Bedmohata MA et al., 2015). The identification of the potential use of biomass as raw material for activated carbon has been carried out by previous researchers (Shelke et al., 2022). Biomass is the main material for activated carbon because of its effectiveness in removing dyes, low prices, and abundant availability (Tuli et al., 2020). In addition, using biomass as carbon raw material is also an effort to overcome the waste problem because biomass is generally waste from agricultural or plantation processes that have no economic value (Sulyman et al., 2017). Some examples of biomass that are used as raw material for activated carbon to remove dyes, especially methylene blue, include corn cobs (Hien Tran et al., 2022; Medhat et al., 2021), dragon fruit skins (Jawad et al., 2021), walnut shells (Li et al., 2020), rice husks (Shrestha et al., 2019), orange peels (Rani & Chaudhary, 2022), empty oil palm bunches (Baloo et al., 2021), banana stem (Misran et al., 2022), palm shell (Muniyandi et al., 2021), grass (Abdulhameed et al., 2021), and mangosteen's rind (Zhang et al., 2021).

One way to alter the adsorption properties of activated carbon, such as its adsorption capacity, is by reducing its size to the nanoscale. Nano-activated carbon has a higher efficiency than conventional activated carbon (Naser et al., 2021). As the activated carbon particle size decreased, the surface area of activated carbon increased, thereby increasing the adsorption capacity and surface reactivity (Pandey et al., 2017). In addition, nano adsorbents can also remove pollutants with various hydrophobicity, charge, and size (Neha et al., 2021). Although not too many studies have been carried out on the use of nano-activated carbon to remove dyestuffs, several researchers have used biomass derived from garlic peel (Pathania et al., 2022), orange peel (Khalil et al., 2022), powder saw (Huang et al., 2022), and lignin (Seto et al., 2021). In this review, the efficiency of activated carbon from various biomass in removing methylene blue dye and increasing the adsorption capacity of activated carbon due to the implementation of nanotechnology was discussed further.

2. Methylene Blue Adsorption Mechanism

The mechanism for movement of contaminant molecules to the adsorbent's surfaces occurs through several mechanisms. The main mechanisms of the process are electrostatic interactions, π–π interactions, Van der Waals forces, hydrogen bonds, acid-base reactions, hydrophobic interactions, and the formation of surface complexes. Each contaminant undergoes a different adsorption mechanism. For ions, electrostatic interactions and ion exchanges are the dominant mechanisms. In contrast, in organic molecules (pesticides, dyes, etc.), the hydrophobic interactions and the π–π interactions are dominant in the adsorption process. In each adsorption process, various mechanisms can occur simultaneously. The adsorbed particles can adhere to the adsorbent's surface or in the adsorbent's pores (Dutta et al., 2021; Sahoo & Plot, 2020).

In the methylene blue (MB) adsorption process using activated carbon from dragon fruit peel heated at a temperature of 700^{o}C for 1 hour and contacted with KOH at an impregnation ratio of 2, the adsorption mechanisms that play a role are electrostatic interactions, hydrogen bond formation, and the π–π interactions. The electrostatic interactions are caused by functional groups containing oxygen, such as hydroxyl (–OH), negatively charged on the activated carbon surface. This negatively charged functional group can bind to a positively charged methylene blue molecule. Hydrogen bonds can occur between the hydrogen atoms on the surface of the activated carbon and the nitrogen atoms in the methylene blue molecule. Hydrogen bonds can also occur between functional groups containing

oxygen, such as hydroxyl (–OH) and carbonyl (–C=O), with organic compounds. Meanwhile, π–π interaction between the hexagonal bonds of activated carbon and aromatic bonds in the methylene blue molecule. This interaction is commonly found in the adsorption process of this cationic dye (methylene blue) with activated carbon from biomass (Jawad et al., 2021). The same adsorption mechanism also occurs in the adsorption process of methylene blue with activated carbon derived from grass heated at a temperature of 700°C for 1 hour and contacted with K_2CO_3 at an impregnation ratio of 2 (Abdulhameed et al., 2021). Meanwhile, in the adsorption process of methylene blue with activated carbon derived from acacia wood, the dominant mechanism is Van der Waals forces and electrostatic interactions (Yusop et al., 2021).

Different functional groups, such as carbonyl, carboxyl, and phenol, on the surface of activated carbon, facilitate the adsorption process of pollutants contained in the solution. Activated carbon is an effective adsorbent in the adsorption of various pollutants. The amount of pollutant adsorbed mostly depends on the interaction between the adsorbate and the functional group of the adsorbent. Functional groups are generally affiliated with heteroatoms on the activated carbon surface and are classified into functional groups containing oxygen, sulfur, or nitrogen. The type of functional group on the activated carbon surface is determined based on the treatment to modify the surface properties. These treatments can be grouped into physical, chemical, and biological. Physical processes generally involve heating the adsorbent, and the chemical process involves using acid or base in the activation process. In contrast, the biological process uses microbes to promote biodegradation of the adsorbate on the surface of the adsorbent (Sultana et al., 2022). For example, in activated carbon from corn cobs that are activated with KOH, there is the formation of functional groups containing oxygen such as –OH (hydroxyl), C–H (methyl), C=C (aromatic), C–O–C (ether, ester, or phenol), and C=O (Hien Tran et al., 2022). While H_3PO_4 activates the activated carbon from corn cobs, the functional groups formed on the surface of the activated carbon are –OH (hydroxyl), C=O (ketone, aldehyde, lactone, or carboxyl), and C–O–C (alcohol, ether, or phenol) (Farnan et al., 2018).

3. Use of Biomass as Activated Carbon to Remove Methylene Blue

Currently, 60% of the total activated carbon comes from coal. However, the high price is a limiting factor for using coal-based activated carbon in water/wastewater treatment. Biomass is an alternative raw material for activated carbon because of its abundant availability and is generally considered waste from agricultural processes. In addition, biomass generally contains polysaccharides from hemicellulose, cellulose, and lignin as the main constituents of cells. Biomass can be converted into activated carbon through an activation process consisting of pyrolysis to increase the porosity of the material and the process of pore widening (Sulyman et al., 2017).

Zhang et al. (2021) used mangosteen rind waste as a precursor material for activated carbon. Mangosteen rind was crushed and sieved using an 80mesh (177µm) sieve. The crushed mangosteen's rind was then soaked in H_3PO_4 solution for 12 hours with an impregnation ratio of 1:1; 1:1.5; 1:2; 1:2.5; 1:3. The mangosteen rind was then dried at a temperature of 1050C for 24 hours and carbonized at various temperatures of 350, 400, 450, 500, and 550°C for 30 minutes to 2 hours. The activated carbon was then rinsed with distilled water to pH 7, dried, and crushed to a sieve of 120mesh (125µm). The effect of variables such as pH and temperature was further analyzed with a batch system to determine the optimum adsorption conditions. In addition, the kinetics, isotherm, and thermodynamic analysis of the adsorption process were also carried out. Based on the analysis, the impregnation ratio, carbonization time, and optimum carbonization temperature were 1:3, 60 minutes, and 450°C. The greater the impregnation ratio, the greater the adsorption capacity of methylene blue at equilibrium (Qe) due to the availability of more reagents. Meanwhile, when the carbonization time and temperature are too large, there will be a decrease in Qe which can be caused by damage to the active surface of the adsorbent. Using SEM and BET analysis, it is known that activated carbon from mangosteen's peel has a dense pore structure with a surface area and a total pore volume of 1832 m^2/g and 1046 cm^3/g,

respectively. FTIR analysis shows that the functional groups on the surface of the activated carbon are C=C aromatic bonds and P=O bonds. The adsorption process was optimum at pH 10 and temperature 298K. The adsorption process followed the pseudo-second-order kinetic model, Liu's isotherm model, and the adsorption process was spontaneous and exothermic.

Ahmad et al. (2021) used pomegranate peel as a raw material for the manufacture of activated carbon. The skin of the pomegranate was washed with distilled water and dried in an oven at a temperature of 105°C for 24 hours. The dried pomegranate peel was then carbonized at a temperature of 500°C for 1 hour. The resulting carbon is contacted with KOH and placed in the microwave for the activation process. Carbon activated with KOH is heated again to a temperature of 500°C. The activated carbon was washed using hot distilled water and HCl until the pH reached 6–7 and dried again. Variables analyzed in this study include adsorbate concentration, contact time, and batch temperature. In addition, the isotherm, kinetics, and thermodynamics analysis of the adsorption process were also carried out. Based on the analysis, the adsorption capacity of 1.0g adsorbent at a temperature of 303K with a contact time of 24 hours increased from 24.06 to 218.16mg/g when the concentration of methylene blue was changed from 25 to 300mg/g. The highest adsorption rate occurred in the first 3 hours. After 3 hours, the adsorption rate decreased and reached the equilibrium point after 6 hours. Meanwhile, in the temperature variable, the higher the solution temperature, the lower the adsorption capacity. The adsorption capacity was reduced from 218 to 197.45mg/g when the temperature changed from 303 to 333K, indicating that the adsorption process is exothermic.

The use of fruit peels as a precursor material for activated carbon was also done by Gupta et al. (2022). The orange peel was washed, dried, crushed, and sieved through a 60mesh (250µm) sieve. The orange peel powder was then carbonized at a temperature of 200°C for 2 hours. The resulting carbon was then activated using H_3PO_4 at a temperature of 450°C for 60 minutes. The activated carbon was then washed with distilled water and dried. Analysis of the effect of batch adsorption was carried out to determine the adsorbent dosage, adsorbate concentration, pH, contact time, and temperature. Based on the characterization of the adsorbent, the surface area of the adsorbent was 316.2m^2/g. In the analysis of the effect of adsorbate concentration, there was a decrease in the efficiency of methylene blue removal from 96.80 to 81.79% when the concentration was changed from 100 to 400mg/L. Meanwhile, the removal efficiency of 100mg/L methylene blue increased from 41.60 to 96.02% when the adsorbent dose was increased from 0.2 to 1.0g/L. Increasing the pH and temperature also increased the removal efficiency of methylene blue. The removal efficiency increased from 59.46 to 96.44% when the pH was increased from 3 to 11, and the efficiency increased from 64.44 to 96.69% when the temperature was increased from 40 to 60°C. Based on testing the effect of adsorbate concentration, it was found that the adsorption process is consistent with the Langmuir isotherm model.

In addition to fruit peels, the analysis of other biomass, such as leaves, seeds, and branches of plants, as raw material for activated carbon has also been carried out by previous researchers. One of the uses of leaves as raw material for activated carbon was carried out by Do et al. (2020) using Moringa leaves. Moringa leaves were washed and carbonized at a temperature of 350°C for 2 hours. The carbon was then washed to pH 7 and dried at 105°C. The dried carbon was then crushed to 1mm and contacted with 0.1M NaOH for 24 hours. The activated carbon powder was then rinsed with distilled water until the pH was neutral and dried. The effect of variables that affect the adsorption process, such as pH, adsorbent dose, temperature, and contact time, were analyzed to determine the optimum value in a batch system. In addition, the isotherm, kinetics, and thermodynamics analysis of the adsorption process were also carried out. Characteristic analysis of activated carbon showed that activated carbon had a surface area of 1.688 m^2/g and an iodine index of 1016, with the dominant functional groups on the activated carbon surface consisting of carboxylate, phenol, hydroxyl, and aromatic oxyl groups. Based on the variables' influence analysis, the adsorption process was optimum at pH 7, contact time of 90 minutes, an adsorbent dose of 0.05g, and low temperature because efficiency decreases when the temperature increases. The maximum adsorption capacity of methylene blue is 136.99 mg/g. The

adsorption process follows the second-order kinetics model, the Langmuir isotherm model, and the adsorption process takes place spontaneously and is exothermic.

Dao et al. (2021) utilized Litsea glutinosa plant seeds as raw material for activated carbon. Clean and dry Litsea glutinosa seeds were soaked in $NaHCO_3$ solution at a temperature of 50°C for 24 hours. The concentration of $NaHCO_3$ was varied to 5–15%. After that, Litsea glutinosa seeds were carbonized at a temperature of 300–500°C for 15 to 75 minutes to determine the optimal activation conditions. The activated carbon was then washed with 0.1% HCl to remove the ash content and rinsed with distilled water until the pH was neutral. In the adsorption experiment, an analysis of the variables affecting the adsorption process was carried out, namely the adsorbent dose, adsorbate concentration, pH, and temperature in a batch system. Kinetics, isotherms, thermodynamics, and adsorbent regeneration were also analyzed further. Based on the analysis, the most optimal temperature, time, and activation concentration occurred at 450°C, 60 minutes, and 5%. The activated carbon produced has an average size of 5mm with a porous surface. These pores are 10–15µm connected to the activated carbon core. Based on the FTIR test, the functional groups on the activated carbon surface consist of phenol, alcohol, carboxyl, hydroxyl, and aromatic groups. The measurement of surface area and total pore volume using the BET method shows that activated carbon has a surface area of 33.16m^2/g and a pore volume of 0.028cm^3/g. The adsorption process for methylene blue occurs through four adsorption phases. At a contact time of 0–45 minutes, the adsorption efficiency reached 46.5% and increased slowly to an efficiency of 50.6% at a contact time of 45–90 minutes. The adsorption rate then increased again with an adsorption efficiency of 87.2% at a contact time of 90–300 minutes. The adsorption rate then slowed to an efficiency of 96.3% at a contact time of 300–540 minutes and reached equilibrium at 600 minutes. The adsorption efficiency increased when the pH was changed to alkaline, with an optimum pH value of 9. While for the variable dose of adsorbent and adsorbate concentration, the optimum doses were 6g/L and 25mg/L. The efficiency of the adsorption process also increased when the temperature was changed from 25 to 40°C. However, at temperatures higher than 40°C, the adsorption capacity was reduced. The maximum adsorption capacity reached 29.03mg/g. Based on the analysis, it is known that the adsorption process follows the Langmuir isotherm model, a pseudo-second-order kinetics model. The adsorption process is spontaneous and endothermic. The results of the regeneration test showed that the activated carbon did not experience a significant reduction in adsorption capacity. The efficiency of the adsorption process ranged from 73.4 to 92.1% when the activated carbon was regenerated 5 to 8 times.

The utilization of waste from eucalyptus trees in the form of branches as raw material for the activated carbon was carried out by Han et al. (2020). Eucalyptus tree branches that have been crushed to a size of 60–80mesh (177–250µm) were washed and dried. The eucalyptus branch powder was then contacted with 40% H_3PO_4 for 12 hours with a ratio of 1; 1.5; 2; 2.5; and 3 (H_3PO_4 to powdered branches). This mixture was then dried at 80°C for 8 hours and carbonized at a temperature of 300, 400, 500, and 600°C for 3 hours. The activated carbon was then washed with distilled water and dried. The adsorption test was carried out with a batch system to determine the optimum conditions for variable adsorbate concentration, contact time, pH, and temperature. Based on the characteristic test of the adsorbent, the surface area of the adsorbent ranged from 995.52 to 1545.44m^2/g, with the optimum area occurring at a heating temperature of 4000C and an H_3PO_4 ratio of 2.5. The pore volume at the optimum condition reached 1.7cm^3/g with a mesoporous to an overall pore ratio of 97.6%. The functional groups on the activated carbon surface consist of hydroxyl groups, carboxyl groups, C=C aromatic bonds, P=O hydrogen bonds, P–O–C aromatic bonds, P=OOH bonds, and phosphate esters. The adsorption process was optimum at pH 10, with the adsorption capacity at equilibrium conditions reaching 1.112mg/g and the equilibrium point reaching a contact time of 400 minutes. Based on the analysis, it is also known that the adsorption capacity increases at the higher adsorbate concentration. However, at higher temperatures, the adsorption capacity decreased. Kinetic, isotherm, and thermodynamic analysis showed that the adsorption process followed the pseudo-second-order kinetic

model, the Langmuir isotherm, and the adsorption process took place spontaneously and was exothermal. The adsorption process is dominated by physical processes, as indicated by the enthalpy value <40kJ/mol and the high efficiency of adsorbent regeneration (85.5–95.7%).

Identification of the potential use of biomass as raw material for activated carbon is also carried out in a continuous system. One such study was conducted by Mariana et al. (2021) using a nutmeg shell as raw material for activated carbon to adsorb methylene blue. Nutmeg shells that have been cleaned with distilled water, crushed to a particle size of <150µm, and dried at a temperature of 110°C for 24 hours. The nutmeg shell powder was then contacted with KOH solution at an impregnation ratio of 1:0.25; 1:0.5; and 1:1. The mixture was then dried at a temperature of 120°C for 4 hours and activated at a temperature of 700°C for 30 minutes using a muffle furnace. The activated carbon was then washed with 0.1M HCl solution at a temperature of 85°C and rinsed with distilled water until the pH was neutral. The clean activated carbon was then dried at a temperature of 110°C for 24 hours. The performance of activated carbon was analyzed in a continuous system with feed rates of 5, 10, and 15mL/min at concentrations of methylene blue 100, 200, and 300mg/L and pH 7.0. As much as 1g of activated carbon was put into a fixed bed column in a reactor with a height of 6cm and a diameter of 1cm. Based on the analysis, the optimum KOH impregnation ratio for activated carbon activation is 1:0.5, with the largest surface area and pore volume reaching 1462m^2/g and 0.873cm^3/g. Activated carbon with a KOH impregnation ratio of 1:0.5 has a dominant pore structure in the form of micropores, with a ratio of micropores to mesopores reaching 88.9%. Based on FTIR analysis, it is known that the functional groups on the surface of the activated carbon consist of hydroxyl groups (–OH), alkynes, carbonyls (C=O), alkoxy (C–O), and methylene and methyl (C–H). Based on feed discharge and dye concentration analysis, a faster breakthrough time is achieved at higher discharge and concentration. The adsorption process followed the Thomas kinetic model with a maximum adsorption capacity of 346.85mg/g.

Table 1. Use of Biomass as Raw Material for Activated Carbon to Adsorb Methylene Blue

Biomass	**Activation Temp. (°C)**	**Activator**	**Particle Size (µm)**	**Surface Area (m^2/g)**	**Adsorption Capacity (mg/g)**	**Sources**
Mangosteen rind	450	H_3PO_4	<125	1832	871.49	Zhang et al., 2021
Pomegranate skin	500	KOH	–	845.96	250	Ahmad et al., 2021
Orange peel	450	H_3PO_4	<250	316.2	142.86	Gupta et al., 2022
Moringa leaves	350	NaOH	–	1688	136.99	Do et al., 2020
Litsea glutinosa seed	450	$NaHCO_3$	5000	33.16	29.03	Dao et al., 2021
Eucalyptus branch	400	H_3PO_4	177–250	1545.44	1112	Han et al., 2020
Corbcob	800	KOH	<500	965.03	498.4	Hien Tran et al., 2022
Dragon fruit skin	700	KOH	<250	756.3	195.2	Jawad et al., 2021
Acacia wood	550	KOH	5000–10000	425.41	338.29	Yusop et al.,

Biomass	**Activation Temp. (°C)**	**Activator**	**Particle Size (µm)**	**Surface Area (m^2/g)**	**Adsorption Capacity (mg/g)**	**Sources**
						2021
Ashitaba leaves and walnut shell	800 (ashitaba leaves) 900 (walnut shell)	$ZnCl_2$	<250	1228.53 1626.96	381.88 400.11	Li et al., 2020
Orange peel	600	H_2SO_4	150–300	–	1149.42	Rani and Chaudhary, 2022
Ashitaba waste	900	$ZnCl_2$	<250	1505.37	323.54	Xue et al., 2022
Empty fruit bunches and mesocarp fiber	500	HCl	75	35.63 (empty fruit bunches) 552.72 (mesocarp fiber)	24.00 (empty fruit bunches) 18.76 (mesocarp fiber)	Baloo et al., 2021
Palm shell	500	HNO_3	90	–	21.7	Muniyandi et al., 2021
Corn stigmata fiber	500	H_3PO_4	≤250	820	330.5	Mbarki et al., 2022
Grass	700	K_2CO_3	≤250	1245.6	364.2	Abdulhameed et al., 2021
Coriander (stem, root, leaves)	300	H_3PO_4	297	193	94.9	de Souza et al., 2022
Peanut shell	800	NaOH	–	868.75	555.60	Ahmad et al., 2020
Ackee apple pods	400 500	$ZnCl_2$	<88	321.01 812.79	46.95 47.17	Bello et al., 2021
Banana stem	400	H_3PO_4	<500	837.45	101.01	Misran et al., 2022
Mangrove	300 400 500	H_3PO_4	500–1000	1011.8 835.7 821.3	72.3 67 62.8	Zakaria et al., 2021
Corncob	700	KOH $(NH_4)_2SO_4$	125–250	492 113	333 147	Medhat et al., 2021
Rice husk	900	KOH	<200	2342	608	Shrestha et al.,

Biomass	Activation Temp. (°C)	Activator	Particle Size (µm)	Surface Area (m^2/g)	Adsorption Capacity (mg/g)	Sources
						2019
Cane bagasse	600	Steam	<297	592.4	21.01	Rahmawati et al., 2021
Nutmeg shell	700	KOH	<150	1462	346.85	Mariana et al., 2021

4. Use of Biomass as Nano-Activated Carbon to Remove Methylene Blue

Nano adsorbents are nano-sized particles (1–100nm) derived from organic or inorganic materials that have a high affinity for the adsorption of a substance. Nano adsorbents have advantages over conventional adsorbents, namely being able to adsorbate with various hydrophobicity, sizes, and charge, having large porosity, surface area, surface reactivity, and high adsorption capacity (Neha et al., 2021; Shokry et al., 2019). In general, there are two approaches to synthesizing nano adsorbents: the top-down and bottom-up approaches. In the top-down method, materials with large sizes are reduced to nano size by several methods, such as erosion, reactive milling, sputtering, high-energy ball milling, and mechanical alloying. While in the bottom-up method, the components are combined into a larger size by physical and chemical processes. Some bottom-up processes include molecular self–assembly, supercritical fluid, sol-gel, and physical and chemical vapor deposition (Nik–Abdul–Ghani et al., 2021).

Identification of the use of biomass as a raw material for nano–activated carbon has been carried out by several previous authors. Nazem et al. (2020) synthesized nano-activated carbon from green almond, almond, and walnut shells using a ball mill with water vapor. This nano-activated carbon has a particle size of 50–100nm with a surface area of 1196–1261m^2/g. Meanwhile, the use of activated carbon nano from biomass to remove methylene blue dye has been carried out by several authors, such as Khalil et al. (2022), Huang et al. (2022), and Seto et al. (2021).

Khalil et al. (2022) utilized orange peel waste as raw material for the manufacture of nano-activated carbon. Orange peels that had been chopped, washed, and dried were soaked in 85% H3PO4 solution (a ratio of H3PO4: orange peel = 1:2; 1:1; 2:1). The mixture was then dried at a temperature of 1100C for 24 hours and thermally activated using a furnace to temperatures of 400, 500, 600, and 800°C for 60 minutes. The activated carbon was then washed using distilled water until the pH was 6.5 and dried at a temperature of 120°C for one night. Factors affecting the adsorption process, namely the adsorbent dose, adsorbate concentration, pH, and temperature, were analyzed in batches. Based on the adsorbent characterization test, it was found that the particle size ranged from 2–3nm with a surface area of 1706m^2/g and a total pore volume of 1.536cm^3/g. On the surface of activated carbon, there are functional groups dominated by carboxyl groups, aromatic rings, phenol, ethers, esters, P–O bonds, and P–O–C aromatic bonds. The adsorbent with a maximum adsorption capacity of 452mg/g was obtained from the activation process with a ratio of H3PO4: orange peel = 2:1 and a temperature of 800°C. Based on the adsorption analysis, the adsorption capacity decreases at higher pH and temperature. The test results on the effect of adsorbent dose and adsorbate concentration showed that the adsorption process adhered to the Langmuir isotherm and pseudo-second-order kinetics. In addition, based on testing the effect of temperature, it was found that the adsorption process was dominated by physisorption.

Huang et al. carried out the utilization of Firmiana simplex sawdust waste to make nano-activated carbon (2022). The sawdust was washed thoroughly, dried, and crushed to a size of 40–80 mesh (177–400µm). Then, various treatments for sawdust were carried out to become:

- 4g sawdust mixed with 30mL H_3PO_4 in a 1:4 ratio. The mixture was then heated in an autoclave at 200°C for 12 hours. Then the sawdust was dried at a temperature of 200°C for 24 hours. These products are marked with the PHTC notation.

- PHTC–W is PHTC which is washed with distilled water until the washing water is neutral and dried.
- 4g of sawdust and 30 mL of water were heated using an autoclave at a temperature of 200°C for 12 hours. After cooling, sawdust is mixed with H_3PO_4 in a ratio of 1:4. This mixture was then dried at 200°C for 24 hours. This sample is called HPTC.
- 4g of sawdust was mixed with 30mL of H_3PO_4 in a ratio of 1:4. The mixture was stirred for 12 hours and then dried at 200°C for 24 hours. The sample is referred to as PIC.

All samples were then converted into activated carbon by heating at a temperature of 450°C for 2.8 minutes. The activated carbon formed was then washed with distilled water until the remaining washing water was neutral and dried at a temperature of 105°C for 24 hours. This activated carbon is called PHAC (from PHTC), HPAC (from HPTC), PHAC–W (from PHTC–W), and PIAC (from PIC). All samples were used for methylene blue adsorption analysis. A total of 0.01g of activated carbon and 50mL of methylene blue solution with a concentration of 100mg/L were contacted at 25°C and stirred for 24 hours. After that, the solution was filtered with filter paper, and its permeate was measured with a spectrophotometer. Based on the BET test, the PHAC–W surface area is 48m²/g. The surface area increases in the sample mixed with H3PO4 before heating. PHAC has a surface area of 1980m²/g, HPAC has a surface area of 1791m²/g, and PIAC has a surface area of 1490m²/g. The adsorption capacities of PHAC, HPAC, PIAC, PHAC–W on methylene blue dye were 422mg/g, 384mg/g, 331mg/g, and 73mg/g. Because PHAC has the largest adsorption capacity, a kinetic analysis of the process was carried out, and it was found that the adsorption process followed a pseudo-second-order.

Seto et al. (2021) utilize lignin, waste from the pulp and paper industry, as raw material for nano-activated carbon. The dealkaline lignin powder dried at 105°C for one night. Then, 2.5g of lignin was dissolved in 50mL of water and sonicated for 2 hours to produce nanoparticles. The solution of nano lignin particles is then freeze-dried to become nano-based freeze–dried lignin (NFLN). After that, lignin and NFLN underwent a pyrolysis process at temperatures of 600, 750, 900, and 1050°C for 6 hours. NFLN, which has undergone a pyrolysis process, was further refined using ball milling and used for methylene blue adsorption analysis at pH 3.7 and 10. Based on the analysis, activated carbon derived from NFLN has a larger surface area than activated carbon derived from lignin. The higher the pyrolysis temperature used, the greater the surface area. The maximum surface area (T = 1050°C) of activated carbon (NFLN) is 72.47m²/g, while that of activated carbon (lignin) is 8m²/g. The maximum adsorption capacity of activated carbon (NFLN) reaches 109.77mg/g, with the most optimal adsorption process occurring at pH 10.

Table 2. Use of Biomass as Raw Material for Nano–Activated Carbon to Adsorb Methylene Blue

Biomass	**Activation Temp. (°C)**	**Activator**	**Particle Size (nm)**	**Surface Area (m²/g)**	**Adsorption Capacity (mg/g)**	**Sources**
Orange peel	800	H_3PO_4	2–3	1204	452	Khalil et al., 2022
Firmiana simpleks sawdust	450	H_3PO_4	200–400	1980	422	Huang et al., 2022
Lignin	1050	–	20–220	72.47	109.77	Seto et al., 2021
Orange peel	220	–	6–19	–	35.014	Adedokun et al., 2017
Wakame	800	KOH	–	744.15	479.49	Yao et al., 2020
Glucose	400	$ZnCl_2$	–	2902.5	3152	Chang et al.,

Biomass	Activation Temp. (°C)	Activator	Particle Size (nm)	Surface Area (m^2/g)	Adsorption Capacity (mg/g)	Sources
						2013
Glucose	160	NaOH	400	12.7	682	Song et al., 2012
Banana peel	550	NaOH	–	1071.7	76.7	al Jebur and Alwan, 2022

5. Conclusions

Based on the results of a review from previous studies, activated carbon produced from biomass effectively removes methylene blue, which is generally used in the dyeing process in the textile industry. Converting biomass into activated carbon generally consists of washing, drying, crushing, carbonization, and chemical activation. Some commonly used activators include KOH, H3PO4, ZnCl2, HCl, and NaOH. The adsorption process of methylene blue dye with activated carbon from biomass is influenced by several factors, such as pH, contact time, adsorbent dose, adsorbate concentration, and temperature.

The conversion of activated carbon into nano size showed an increase in activated carbon's adsorption capacity and surface area. This can increase the wastewater treatment process's efficiency and the adsorption process's reliability. However, all studies on the utilization of nano-activated carbon were carried out in a batch system, so further research is needed to determine the potential for its utilization on a large scale.

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