A Review of Production, Properties and Application in Scavenging of Dyes of Biochar

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ABSTRACT
Biochar is a charcoal that produce from biomass feedstock and act as promising agent for many application such as wastewater treatment, energy production, soil amendment and gas storage. This review summarizes recent research development on production, properties and application of biochar. This review summarize production technology of biochar with different biomass feedstock. Besides, this review summarizes the properties such as microstructure and elemental content of biochar. Also, this review focus on the application of biochar in removal of dyes contains in wastewater. This review focus on biochar due to its large surface area and high adsorption capacity which are main factors in the removal of dyes. The adsorption performance of biochar with different biomass feedstock in removal of different dyes are summarized. This review also discusses the future research on production of biochar and its application in different field. As a conclusion, biochar technology is a low cost, high energy efficient, environmental friendly and new solution with great prospect in removal of dyes.

Keywords: Biochar, production technology, properties, removal of dyes

1. INTRODUCTION
Research on biochar is rapidly growth over past ten years which covers in both scientific and engineering field. The term “biochar” is refer to those porous carbonaceous material generated by thermal decomposition under low oxygen or no oxygen environment from different biomass feedstock. Biomass feedstock is refer to those organic waste that comes from animals and plants such as woods, forest residue, food crops, manures, sewage plants and municipal solid waste. There are several methods for thermal decomposition to produce biochar which are slow pyrolysis, fast pyrolysis, microwave-assisted pyrolysis, torrefaction and hydrothermal carbonization. There are many advantages or benefits of biochar which lead to an increasing in research on biochar over past ten years. For instant, biochar is high energy efficient, low cost and environmental friendly as an adsorbent that used in wastewater treatment due to its large surface area and high adsorption capacity [1]. Properties of biochar is depending on the biomass feedstock used and condition of production such as temperature, residence time and heating rate. In general, carbon content in biochar is around 70% - 80% except those derived from sewage plants, manures and woods due to the carbon content in these biomass feedstock is low. Besides that, biochar also contain oxygen, nitrogen, hydrogen and other metal elements such as sodium, magnesium, calcium and iron. Biochar can be stored for hundred of years due to its stable form which is alkyl and aromatic compounds [2]. There are many application of biochar, for instant, wastewater treatment which is act as an adsorbent to adsorb contaminants from wastewater, clean energy production with great prospect to replace fossil fuels, soil amendment which can improve soil fertility and promote the growth of crops and reduce greenhouse gases emission by applied to pollutants. This review is only focus on removal of dyes due to there is only few review articles have discussed the relationship between production technologies and properties of biochar and the effect of production technologies on removal of dyes [3].

The objective of this article is to present a review on the production technologies of biochar and its application on removal of dyes. First, production technologies of biochar with different biomass feedstock are summarized. Next, the properties of biochar is elucidated in this review. Also, this review discusses the future perspective and research of biochar on removal of dyes.

2. PRODUCTION TECHNOLOGIES
The process of production of biochar from biomass feedstock is called thermal carbonization. There are some examples of thermal carbonization such as slow pyrolysis,
fast pyrolysis, microwave-assisted pyrolysis, torrefaction and hydrothermal carbonization. All of these production technologies is summarized in Table 1.

A process called pyrolysis is a process of thermal decomposition of biomass feedstock into biochar without the presence of oxygen. Generally, pyrolysis can divided into two categories which are slow pyrolysis and fast pyrolysis. The differences between slow pyrolysis and fast pyrolysis are depends on heating rate and the final temperature reached. Slow pyrolysis is a process to decomposed biomass feedstock at low temperature (300 - 500°C) and slow heating rate for a long residence time. The moisture content in biomass feedstock does not affect slow pyrolysis process [4]. For fast pyrolysis process, biomass feedstock is heated at high temperature (500 - 700°C) with high heating rate for a short residence time (i.e. less than 2s). Both slow pyrolysis and fast pyrolysis is carry out under a condition of without presence of oxygen [5]. The thermal energy applied to both slow and fast pyrolysis process is used to break down the long polymeric chains of cellulose, hemicellulose and lignin.

Microwave-assisted pyrolysis is a promising method in production of biochar due to its easy accessibility and short processing time. This method is used widely in most of the processing industry. Microwave is an electromagnetic wave with a wavelength range does not affect pyrolysis process [4]. For fast pyrolysis process, biomass feedstock is heated at high temperature (500 - 700°C) with high heating rate for a short residence time (i.e. less than 2s). Both slow pyrolysis and fast pyrolysis is carry out under a condition of without presence of oxygen [5]. The thermal energy applied to both slow and fast pyrolysis process is used to break down the long polymeric chains of cellulose, hemicellulose and lignin.

Microwave-assisted pyrolysis is a promising method in production of biochar due to its easy accessibility and short processing time. This method is used widely in most of the processing industry. Microwave is an electromagnetic wave with a wavelength range between 0.001 m to 1 m which also equivalent to frequencies of 300 GHz to 300 MHz [6]. The frequencies of microwave is lies between frequencies of radio and infrared. Microwave-assisted pyrolysis is starts from the internal to the external part of the substances through molecular interaction with electromagnetic field [7]. However, the conventional heating begins from the external into the internal part of the substances.

Hydrothermal carbonization is a process of conversion of biomass feedstock with water at a temperature range of 180 - 300°C and pressure above 1 MPa into biochar. The residence time of this process is between 1 to 4 hours. The amount of salts and minerals contain in biochar is reduced due to the presence of water. This is because water promotes the decomposition process by hydrolysis. Temperature plays an important role in hydrothermal carbonization process. The higher the temperature, the more the acidic functional groups contains on the surface of biochar which can increase the adsorption capacity [8].

Torrefaction is firstly performed by Bourgeois and Dot in 1980s. Torrefaction is a dry thermal conversion process of biomass feedstock in a confined system with inert environment up to a temperature range between 200°C to 300°C and ambient pressure into biochar. Biomass feedstock with low moisture content is suitable for torrefaction process. The major product of torrefaction is solid torrefied materials known as biochar, oily liquid known as bio-oil and gases [9].

The microscopic structure of biochar is shown in Figure 1(a) and the microscopic structure of the biomass feedstock is illustrated in Figure 1(b). In this two figure, the difference between biochar and its biomass feedstock is observed which is the pore size of biochar is smaller than the pore size of banana pseudo stem. This is because there are some volatile organic compounds generated during the thermal decomposition process and hence influence the pore size of biochar. The pore size is an important factor that influence the specific surface area and adsorption capacity of the biochar [10]. Small pore size provide large specific surface area and hence increase the adsorption capacity of the biochar. Also, reaction temperature influence the structure of biochar. High temperature turns biochar into more ordered shape due to the decrease of micropores and increase in macropores.

Generally, the element contains in biochar are carbon (C), oxygen (O), hydrogen (H), nitrogen (N), sulphur (S) and other trace elements. The elemental composition of different biomass feedstock based biochar is summarized in Table 2. From Table 2, the carbon content of all types of biochar is the highest among the elemental composition. The carbon content of palm kernel shell based biochar is 30% - 35% higher than other biomass feedstock based biochar. Also, the sulphur content of all types of biochar is the lowest among the elemental composition which is less than 0.2 wt%. The oxygen content of all types of biochar is reaches a maximum content of 53.47 wt%. The nitrogen content of all types of biochar is less than 3 wt% whereas the hydrogen content is less than 7 wt%. The remaining fraction is ash and other mineral materials. Generally, the element contains in biochar are carbon (C), oxygen (O), hydrogen (H), nitrogen (N), sulphur (S) and other trace elements. The elemental composition of different biomass feedstock based biochar is summarized in Table 2. From Table 2, the carbon content of all types of biochar is the highest among the elemental composition. The carbon content of palm kernel shell based biochar is 30% - 35% higher than other biomass feedstock based biochar. Also, the sulphur content of all types of biochar is the lowest among the elemental composition which is less than 0.2 wt%. The oxygen content of all types of biochar is reaches a maximum content of 53.47 wt%. The nitrogen content of all types of biochar is less than 3 wt% whereas the hydrogen content is less than 7 wt%. The remaining fraction is ash and other mineral materials.

### 3. PROPERTIES OF BIOCHAR

The properties of biochar such as surface area, elemental composition and microstructure are depends on the types of biomass feedstock and condition of production process.
Table 1: Summary of production technologies of biochar

| Production technologies | Conditions (Temperature and Residence time) | Advantages | Disadvantages | References |
|-------------------------|--------------------------------------------|------------|---------------|------------|
| Slow pyrolysis          | 300 - 500°C 1 - 3 hours                    | Low temperature required, high yield, low cost | Low heating rate | [11]       |
| Fast pyrolysis          | 500 - 700°C < 2s                           | Short residence time, high heating rate | High cost, Low yield | [12]       |
| Microwave-assisted pyrolysis | 500 - 800W 20 - 30 mins                | High heating efficient, low cost, short processing time | High power consumption | [6]        |
| Hydrothermal carbonization | 180 - 300°C 1 - 4 hours              | Suitable for high moisture content biomass feedstock | High cost | [13]       |
| Torrefaction            | 200 - 300°C 6 - 8 hours                    | Easy to operate, efficient heating | Low yield, long residence time | [14]       |

Fig. 1. (a) SEM image of biochar (b) SEM image of banana pseudo stem

Table 2: Elemental composition of different biomass feedstock based biochar

| Biomass feedstock | C/wt% | O/wt% | H/wt% | N/wt% | S/wt% | Reference |
|-------------------|-------|-------|-------|-------|-------|-----------|
| Banana pseudo stem| 42.58 | 42.24 | 6.31  | 0.97  | 0.05  | [15]      |
| Banana pseudo stem| 40.40 | 53.47 | 6.02  | 0.11  | -     | [16]      |
| Palm kernel shell  | 70.0  | 26.0  | 3.0   | 1.0   | 0     | [17]      |
| Palm kernel shell  | 49.50 | 42.30 | 5.90  | 0.47  | 0.03  | [18]      |
| Palm kernel shell  | 48.60 | 38.77 | 5.64  | 0.22  | -     | [19]      |
| Palm kernel shell  | 81.40 | -     | 1.6   | 1.8   | 0.16  | [20]      |
| Palm kernel shell  | 43.6  | 51.0  | 4.9   | 0.5   | -     | [21]      |
| Palm kernel shell  | 78.8  | 11.4  | 2.4   | 0.9   | -     | [22]      |
| Palm kernel shell  | 64.0  | 30.0  | 5.0   | 1.0   | -     | [23]      |
| Palm kernel shell  | 48.31 | 45.28 | 6.04  | 0.37  | -     | [24]      |
| Pineapple peel - 350°C | 62.54 | 23.59 | 4.12  | 1.83  | -     | [25]      |
| Pineapple peel - 650°C | 73.55 | 10.01 | 2.11  | 2.26  | -     | [25]      |
| Pineapple peel      | 61.53 | -     | 4.13  | 1.51  | -     | [26]      |
| Pineapple peel - 300°C | 68.57 | 19.7  | 4.25  | 0.90  | -     | [27]      |
| Pineapple peel - 600°C | 78.84 | 8.51  | 1.59  | 1.01  | -     | [27]      |
| Potato peel          | 18.1  | 3.37  | 0.48  | 0.6   | 0.05  | [28]      |
| Potato peel          | 77.07 | 19.68 | 1.08  | 2.17  | 0.00  | [29]      |
| Potato stem          | 75.81 | 19.30 | -     | -     | -     | [30]      |
| Biomass feedstock | Dyes used | BET surface area (m²/g) | Initial concentration (mg/L) | Contact time and temperature | Adsorption capacity (mg/g) | Ref. |
|-------------------|-----------|-------------------------|------------------------------|-----------------------------|--------------------------|-----|
| Banana trunk waste | Methylene blue | 1173.16 | 250 | 0.3 h, 25°C | 166.51 | [36] |
| Banana pseudo stem | Methylene blue | 3.741 | 20 | 24 h, 25°C | 146.23 | [15] |
| Banana peels | Malachite green | 388.0 | 20 | 2 h, 25°C | 38.92 | [37] |
| Banana peels | Methylene blue | 25 - 500 | 50 | 12 h, 20°C | 862.0 | [38] |
| Rice husk | Congo red | - | 100 | 96 h | 15.81 | [39] |
| Cow dung | Congo red | - | 100 | 96 h | 12.46 | [39] |
| Rice husk | Methylene blue | - | 100 | 25°C | 17.97 | [40] |
| Cow dung | Methylene blue | - | 100 | 25°C | 17.50 | [40] |
| Sugarcane bagasse | Methylene blue | 322.96 | 50 | 3 h, 30°C | 93.16 | [34] |
| Ashe juniper | Methylene blue | 511.0 | 100 - 500 | 72 h, 25°C | 421.18 | [41] |
| Litchi peels | Congo red | 1006.0 | 300 2000 | 12 h, 35°C | 404.4 2468.0 | [42] |
| Empty fruit bunch | Cibacron blue | 362.84 | 100 | 0.75 h, 70°C | 99.0 | [43] |
| Pine trees | Rhodamine B Methyl orange | 139.02 | 10 10 | 0.5 h | - | [44] |
| Crab shell | Malachite green Congo red | - | 4000 6000 | 6 h, 25°C | 12501.98 20317.0 | [45] |
| Chicken bone | Rhodamine B | 328.06 | 100 | 24 h, 26°C | 113.31 | [46] |
| Algae | Congo red | - | 90 | 2 h, 30°C | 51.29 | [47] |
| Peanut shell | Methylene blue Acid orange 7 | 220.0 | 500 | 48 h, 25°C | 120.0 | [48] |
| Date palm petiole | Crystal violet | 640.0 | 500 | 24 h, 30°C | 24.0 | [49] |
| Weeds | Methylene blue | 5.138 | 400 | 8 h, 50°C | 49.05 | [50] |
| Switchgrass | Methylene blue Methyl orange Congo red | 25.98 | 200 100 100 | 24 h, 25°C | 196.1 38.2 22.6 | [51] |
| Frass of mealworms | Malachite green Crystal violet Congo red | 62.14 | 500 200 100 | 15 h, 25°C | 1738.6 175.6 86.9 | [52] |
| Korean cabbage | Congo red Crystal violet | 33.89 | 500 500 | 24 h, 30°C | 95.81 1304.0 | [53] |
4. ADSORPTION PERFORMANCE OF BIOCHAR IN REMOVAL OF DYES

Generally, biochar can be used as an adsorbent to remove various contaminants in wastewater. This section mainly discusses the use of biochar for removal of dyes. Dyes are usually used widely in textile industry and food industry for the purpose of colouring the products. There are more than one hundred thousands of commercially dyes and over seventy thousands tonnes of dyes pollutants produced annually. Due to its complex aromatic molecular structures, dyes are very stable and hard to biodegrade [54]. One of the most harmful and hazardous pollution is water pollution which is also a biggest challenge for Malaysia today. One of the cause of formation of water pollution is the discharge of waste water containing dyes from textile, paper, heavy metal and cosmetic industry to the environment [55].

Adsorption is one of the most effective processes to remove dyes from the polluted water. The types of dyes normally used by the researchers are methylene blue, malachite green, congo red, cibacron blue, rhodamine blue, acid orange 7, methyl orange and crystal violet. Biochars are the most frequently used material as dyes adsorbents. The adsorption performance of different biomass feedstock based biochar are summarized in Table 3. From Table 3, the adsorption capacity of biochar based on their microscopic structure and elemental composition. The application of biochar in wastewater treatment is due to its high energy efficient, low cost and short processing time. (2) The pore size of biochar is smaller than the pore size of its raw biomass feedstock. The main elements content of biochar are carbon, oxygen, hydrogen, nitrogen and sulphur which compose more than 70% of biochar, followed by ash and other mineral materials. Biochar is more suitable than its raw biomass feedstock for wastewater treatment is due to it have larger surface area which provide higher adsorption capacity.

Biomass feedstock based biochar is suitable for removal of dyes and the potential of biochar for removal of dyes from wastewater has been well demonstrated in laboratory. Banana waste have high potential to convert into biochar for the removal of methylene blue. There are still knowledge gaps that need to filled even though there are some researches have been done on the production technologies, properties and application of biochar for removal of dyes. Additional studies are need to develop a new and low cost production technology of biochar. Also, the adsorption capacity of biochar on dyes can be improved by further research. Last but not least, the practical application of biochar for removal of dyes can be increased.

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