ADSORPTION OF METHYLENE BLUE BY DIFFERENT TYPES OF STRAW BIOCHAR WITH PERFORMANCE COMPARISON

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Abstract. In order to study the adsorption property of straw biochar of methylene blue dye, five kinds of biochar (rice straw, corn straw, wheat straw, peanut straw and reed straw) were prepared at 500°C through the method of oxygen limiting and temperature control. The microstructure, functional group and elemental composition of biochar were characterized with a scanning electron microscope, Fourier transform infrared spectroscopy and X-ray diffraction. The adsorption experiments of the methylene blue solution by five kinds of straw biochar were carried out, and the properties of the biochars after the adsorption of the methylene blue solution were compared and analyzed. The result revealed that S500, X500 and L500 have round hole microporous structure, and Y500 and H500 have parallel wall microporous structure. The FTIR spectra of five kinds of straw biochar contained polar groups and aromatic structures. Their adsorptive capacities were as follows: X500 > S500 > L500 > Y500 > H500. Among the five kinds of straw biological charcoals, X500 had good surface characteristics and the ability to adsorb methylene blue. It is the preferred material for adsorbing organic contaminants. Moreover, the surface characteristics of the five kinds of straw biological charcoal also affected their ability to adsorb the methylene blue solution.

Keywords: charcoal, surface features, adsorb-ability

Introduction

Biochar is a carbon rich material (Warnock et al., 2007) cracking under both the presence of oxygen and oxygen free conditions, has rich surface functional groups, high carbon content and developed pore structure, and can be used as a new adsorbent of organic pollutants (Yang and Sheng, 2003). Methylene blue (C₁₆H₁₈ClN₃S) is widely used in the field of chemical indicators, dyes, biological dyestuffs, drugs and so on (Zhou, 2010). In the printing and dyeing industry, a large amount of organic dye wastewater is produced, which holds great environmental risks. Using a low-cost material to control environmental pollution has become a popular topic of researches (Yang et al., 2006; Warnock et al., 2007). A new technology of biomass carbonization and a resource for agricultural products has been gradually conceived (Jian et al., 2016). Therefore, biochar plays an important role in industrial waste treatment and the remediation of environmental pollution.

Through studying three kinds of improved corn straws, Ci and Chen (2016) discovered that the improved corn straw adsorption capacity of methylene blue increased. Huang et al. (2018) found that the adsorption of methylene blue on activated carbon from rice straw was mainly affected by pore size. Fragiskos et al. (2008) found that the untreated wheat straw had strong ability to adsorb methylene blue and could be used as a low-cost adsorbent. Hammes et al. (2008) explored the changes in the elemental composition of black carbon after pyrolysis, indicating that the hydrogen and oxygen elements in biochar continued to remove hydrophobicity with increasing temperature. Chen and Chen (2009) studied the surface functional groups of wood biochar and found that they were adsorbed by π-π conjugated structure and filled with pores. Lu et al. (2013) compared rice straw biochar and corn straw biomass, found that corn straw biochar degree of aromatization was higher, thus
enhancing organic solution adsorption. Zhang et al. (2016) studies showed that the biochar adsorption capacity of reed straw pyrolyzed at 500°C was the strongest. Ji et al. (2016) found that the adsorption of methylene blue on cationic dyes by rice straw biochar was mainly mediated by ion exchange. From the above, the surface morphology, functional groups and chemical composition of straw biochar have great influence on the adsorption properties of methylene blue organic solution. The biological charcoal of different straw has different structures and components. It is of great significance to study the physicochemical characteristics and adsorb-ability of straw biological charcoal for the treatment of organic dyes.

In this paper, five kinds of straw biomass were selected at 500°C for slow oxygen slow thermal cracking and carbonization, the structure characterization of five kinds of biological charcoal and the adsorption experiment on methylene blue solution. The physical and chemical properties of five kinds of biological charcoal were characterized by electron microscope scanning, Fourier transform infrared spectrum analysis and modern analysis of X-ray diffraction. The physicochemical properties of five kinds of biological charcoal were compared.

Materials and Methods

Preparation of biological carbon from straw

Five kinds of straw biomass were selected as the raw materials for preparing biochar. Rice straw and corn straw were collected from farm field in Pu Kou District of Nanjing, China. Wheat straw and peanut straw were collected from a farm field in Yang Zhou, and reed straw was collected from Nanjing Bagua. Each straw was collected at 1 kg. The straw was washed, dried, cut in 1-2 cm pieces, put into a grinding machine, smashed in 60 mesh, and stored in 90°C drying oven.

The biological carbon was prepared by the slow speed hot cracking method. The straw treated with powder was placed in a quartz boat and placed in a muffle furnace and passed into nitrogen for 10 min to discharge the air in the tube. The heating rate was set at 5°C /min, and the temperature was raised to 300°C for 1 h. Then the temperature was kept at the highest temperature of 500°C for 2 h, and then cooled to room temperature after the pyrolysis was completed, and the biological charcoal was dried. The biochar samples of rice straw, wheat straw, corn straw, peanut straw and reed straw were signed as S500, X500, Y500, H500 and L500.

Properties and characterization of biological carbon

Carbon yield

The quality of five kinds of straw before and after pyrolysis was weighed. The carbon yield of biological charcoal was referred to "Wood Charcoal and Charcoal Test Method (GB/T17664 - 1999)" (Wood charcoal and test method of wood charcoal), and the mass ratio of straw before and after was the carbon yield. The carbon yield of different straw biochar was calculated according to Formula (1).

\[ \eta = \frac{m_2}{m_1} \times 100\% \]  

(Eq.1)

where \( \eta \) is carbon yield and \( m_1 \) and \( m_2 \) represent the mass /g before and after carbonization.
Microstructure of biological carbon from straw

Field emission scanning electron microscopy (SEM) (US FEI Inspect F50) was used to observe the microstructure of the straw bio carbon. The instrument voltage of the scanning electron microscope was 20 KV, and the magnification was 1000 and 3000, and their SEM images were recorded.

Fourier transform infrared spectroscopy

Five kinds of biological charcoal were called each 0.002 g, and the KBr particles of 0.2 g were mixed (1:100), lapped, pressed (Lu et al., 2013) via using Nicolet 380 Fourier Transform Microscopic infrared spectrometer, and the sample was scanned on the spectrometer sample frame.

X-ray diffraction

The crystal structure characteristics of biochar were analyzed by Brook D8 ADVANCE. 1.5 g biochar samples were collected and placed on the sample stage for equipment diffraction. CuK was used as the transmitter source, and the tube voltage and tube current were 40 kV and 30 mA, respectively. The scanning angle was 10-60°, the step length was 0.02°, and the scanning speed was 7°/min (Kim et al., 2012).

Adsorption test of methylene blue by biological carbon

Five kinds of biochar 0.8 g were added and standard methylene blue solution with 20 mL of 100 mg · L⁻¹ (BZ) was added. Then it was put in constant temperature cradle for shocking at 25 °C and 150 r·min⁻¹ for 2 h, then is was placed statically for 24 h. The adsorbed methylene blue solution was filtered through the 0.45 μm polyethersulfone filter membrane through a needle filter, and the color image of the filtrate was recorded. The filtrate was used to measure the absorbance of the solution at 665 nm with the UV visible spectrophotometer, and compared with the 5 g/LCuSO₄ solution (CuSO₄).

The absorbance and concentration of methylene blue solution after adsorption were measured by ultraviolet visible spectrophotometer after absorption of methylene blue standard solution by five kinds of biochar. The adsorption rate of 5g/LCuSO₄ solution for standard methylene blue solution is 100%, and the setting value is 100, and the standard methylene blue solution corresponds to the standard methylene blue adsorption rate of 0% and the setting value of 0.

Results and discussion

Analysis of carbon yield

Five kinds of straw biochar were calculated by Formula (1). Figure 1 was pyrolytic carbon yield of five kinds of straw materials at 500°C. From the Figure, 1, the yield of H500 is 46.96% and the yield of Y500 is 37.01%. The yields of S500 and X500 are 38.83% and 38.93%, respectively, and their yields are similar. The yield of L500 is 39.93%. The decomposition of cellulose, hemicellulose and lignin in the straw component at 500°C shows that the carbon yield will decrease slowly with the increase of pyrolysis temperature, so the biochar has a good thermal stability (Yang et al., 2017). The carbon yield of H500 is high. On the one hand, the ash content of H500 is high and the component of pyrolysis is not easily affected by high temperature. At 500°C, the heat stabilization
ability of H500 is stronger than other straw. On the other hand, the lignin content in H500 is higher than that of other straw. Lignin is a kind of high aromatic substance. The temperature range of the molecular compound is broad and the thermal stability is strong. The yield of S500 is similar X500 (Yang et al., 2017; Wei, 2017). It is found that the composition of metal salts in Y500 is low, and the composition of metal salts can catalyze the pyrolysis of biomass (Raveendran et al., 1995), resulting in low carbon yield of Y500.

Morphology analysis

Figure 2 is a scanning electron microscope (SEM) of five kinds of straw biomass at 500°C carbonization. Figure 2 shows, there are pore structures on the surface of five kinds of straw biochar.

The pore shape of S500, X500 and L500 show a circular pore shape, with smooth surface and different pore structure and specific shape. The pore distribution of S500 is uniform, the pore size is the same, the pore distribution of X500 is uneven, the pore size is gradually reduced, and the pore size of L500 is smaller. The space is large and the hole is evenly distributed. The pore shape of Y500 and H500 appear as parallel wall type, the surface is rough, the arrangement of pore structure and specific shape are different.
Compared with the first three kinds of pore size, the maize straw bio carbon hole arrangement is dense, H500 arrangement is compact, the pore distribution is uneven, and the aperture is not shaped. Under the same amplification conditions, the number of holes in S500, X500 and L500 is more than that in Y500 and H500. Although there is obvious pore structure on the surface of S500 and H500, there is no lamination structure of X500, L500 and Y500, which may be related to the temperature and time of carbonization, the structure breaking of pore structure as well as the surface structure of its own straw. The volatile components in biomass can be precipitated in large quantities and thus gradually form porous structures. The number of pores and pore size pores will affect the adsorption capacity of biological carbon. The pore structure of the straw bio carbon is rich in pore structure and the pore size is obvious. It can be used as an efficient adsorbent to remove methylene blue from the waste-water (Xu et al., 2012).

**FTIR analysis**

*Figure 3* is a Fourier transform infrared spectrum analysis of straw biochar. The changes in the functional groups of the five kinds of biological carbon are basically the same.

There is a peak of phenol hydroxyl absorption at 3440 cm\(^{-1}\), and a higher methylene absorption peak of the aliphatic (C-H) is found at 2920 cm\(^{-1}\) (Zhang et al., 2016). Because of the bending vibration of aromatic ring C=O, the absorption peak appears between 1730~1520 cm\(^{-1}\). 1080 cm\(^{-1}\) appeared C-O-C antisymmetric stretching vibration in Six-element dioxygen ring ether (Yang et al., 2010). The absorption peak at 1522 cm\(^{-1}\) and 1430 cm\(^{-1}\) is aromatic ring C=C, and there are many aromatic (C-H) flexural vibration peaks between 650~788 cm\(^{-1}\). It shows that straw biochar contains hydroxyl, carboxyl, carbonyl, ester, aldehyde groups and other oxygen-containing functional groups. Therefore, five kinds of biochar mainly exist hydroxyl and other polar groups, and they
have aromatic structure at the same time. It shows that the adsorption of methyl blue on methylene blue solution is due to the effect of polar group, and the aromatic structure of biological carbon and aromatic methylene blue can form $\pi$-$\pi$ conjugated structure, and there is a kind of $\pi$-$\pi$ interaction (Ji et al., 2016).

The content of surface functional groups on the surface of biochar affects its adsorption capacity. From Figure 3, in the vicinity of 1520~1730 cm$^{-1}$ it can be seen that the expansion vibration intensity of aromatic ring functional groups on the surface of S500, X500 and L500 is greater than that of H500 and Y500, among which H500 is used. The vibration intensity of straw biochar is the weakest. It can be concluded that the content of $\pi$-$\pi$ conjugated structure of H500 is the lowest in the process of adsorbing methylene blue.

XRD analysis

Figure 4 is a X-ray diffraction pattern of five kinds of straw biochar. It can be seen from Figure 4 that the main peaks of S500, X500 and Y500 appear in 2θ=23.5°, L500 has a wide peak of 22.5°, and H500 has no obvious main peak. This kind of peak corresponds to the diffraction peak of the amorphous structure. The diffraction peak of the amorphous structure on the surface is mainly related to the crystalline structure of cellulose in biomass (Keiluweit et al., 2010; Kim et al., 2012).

The main peak is not found in H500. Most of the cellulose is completely pyrolyzed at 500°C. The other four kinds of biological carbon cellulose diffraction peak still exist at 500°C, which may have the good thermal stability of these crystalline cellulose. Without complete pyrolysis, it can be concluded that the crystallisation of H500 is not high, the high crystal stability is good, and the adsorption effect is good (Lin et al., 2016). In this experiment, there are potash mineral components in S500 and X500. The mineral diffraction peak of SiO$_2$, CaCO$_3$ is found in Y500 and H500. It is found that L500 has an amorphous structure but no mineral diffraction peak, but it is L500. The content of the components of the mineral salt is very small, and the content of K is only 0.22%, and the content of P is 0.16%. Compared with the C element with the content of 46.8%, the
content is not obvious (Meng et al., 2015). On the other hand, it might be related to the source of L500 and the content of local environmental elements, which has a low impact.

**Experimental analysis of adsorption of methylene blue standard solution by biochar**

The absorbance and concentration of methylene blue solution after adsorption were measured by ultraviolet visible spectrophotometer after the adsorption of methylene blue standard solution by five kinds of biochar. The adsorption rate of 5 g/LCuSO₄ solution for standard methylene blue solution is 100%, and the set value is 100, and the standard methylene blue solution corresponds to the standard methylene blue adsorption rate of 0% and the set value of 0. Absorbance and adsorption rate of biochar after adsorption of standard methylene blue solution are in Figure 5. The lower the absorbance value, the higher the transmittance of the solution (is) and the better its adsorption effect. With the absorbance 0.1068Abs of 5 g/LCuSO₄ solution as the transparent index of solution, the absorbance of X500 is lowest 0.0571Abs, less than the absorbance of CuSO₄ solution. It is considered that the adsorption rate reaches the maximum value of this experiment, which is 100% adsorption, and the absorbance of S500 is 0.1091Abs, its adsorption rate is 97.4%. The absorbance of L500 is 0.3356Abs, its adsorption rate is 94.6%. The absorbance of Y500 is 0.6865Abs, its adsorption rate is 83.9%, and the adsorption rate of H500 is 2.1945Abs, and its adsorption rate is 51.5%. The biological charcoal with higher adsorption rate than 90% believes that the adsorption effect is good, and the adsorption efficiency is less than 50%. The adsorption effect of S500, X500 and L500 on methylene blue solution is better, the adsorption rate of H500 is near 50%, and the adsorption effect of H500 is not good (Fu et al., 2012).

![Figure 5. Absorbance and adsorption rate of five kinds of straw biochar adsorption solution, methylene blue standard solution and 5g/LCuSO₄ solution](image)

Figure 6 is the effect of five kinds of biological carbon adsorbed on the standard methylene blue solution. The effect of the adsorbed solution is: X500 > S500 > L500 > Y500 > H500. Compared with the effect of five kinds of adsorbed methylene blue solution and standard methylene blue solution, the adsorption solution of X500 becomes transparent and clear due to the pore shape of the microstructure of X500. Besides that, it is also because the number of pores is more, the texture structure is obvious, the polar and aromatic structure content of X500 is more than that of X500, and it has an amorphous structure. The pore size of S500 and L500 is different, and the content of functional group is less than that of X500, so the adsorption effect of methylene blue solution is second only to that of X500, which can be determined as the main factor affecting the adsorption
capacity of methylene blue solution. The pore shape of H500 microstructure is parallel wall shape. The pore structure is damaged by high temperature, large pore size, less pore number and is has no obvious bedding structure. Most of the cellulose pyrolysis after the carbonization of H500 has a large number of SiO₂, CaCO₃, and the peak expansion vibration peak of polar group is weak, and the number of aromatic structure is obviously less. In other biochar, the adsorption capacity of ion exchange and π-π interaction are weakened, which is the reason why the adsorption effect of H500 is not good. The biological charcoal of Y500 also has the shape of parallel wall, and its polar and aromatic structure content is less, it contains more SiO₂, CaCO₃ mineral diffraction peak, and the adsorption effect of Y500 to methylene blue solution is not good.

**Figure 6.** Comparison of adsorption effect between five kinds of biochar and standard methylene blue solution (a. S500; b. X500; c. L500; d. Y500; e. H500)

**Conclusion**

The microstructure, elements and functional groups of five kinds of straw biochar, also the adsorption properties of methylene blue solution were analyzed. The conclusions are as follows:

1) The pore shape of S500, X500 and L500 is round, and the hole shape of Y500 and H500 is parallel wall shape, and the number of pore number is more than that of the latter. Pore shape, pore number and pore size affect the adsorption capability of biochar to methylene.

2) There are mainly hydroxyl group and aromatic structure in the straw biological carbon. Additionally, the higher content of the polar and aromatic structural functional groups of the straw bio carbon, the better effect of the adsorption of methylene blue.

3) The adsorption capacity of five biochar to methylene blue: X500 > S500 > L500 > Y500 > H500. The adsorption rate of X500 reaches 100%. The results show that X500 has the best adsorption capacity for methylene blue and it is suitable for the application of organic dye pollution control.

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**REFERENCES**


