Study on adsorption performance of pine needle biochar on rhodamine B

Wenbing Li¹,², Tie chen³*, Zheng Zhang¹,², Changjun Du² and Guanghua Wang¹,²

¹Research Center for Green and Intelligent Coal Chemical Engineering, Wuhan University of science and technology, Wuhan, Hubei Province, 430081, China
²Institute of Chemistry and Chemical, Wuhan University of science and technology, Wuhan, Hubei Province, 430081, China
*Corresponding author’s e-mail: 1070789057@qq.com

Abstract. Biochar is regarded as a kind of high-efficiency, environmentally friendly and economical new adsorbent because of its low preparation cost, large specific surface area, developed pore structure and rich surface functional groups. It has broad application prospects in the field of sewage treatment. Using pine massoniana as raw material, the pine needle charcoal was obtained by pyrolysis at 300 °C, and the material was characterized by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The dyeing wastewater was simulated with rhodamine B to study the pine needle. The adsorption performance of biochar showed that the adsorption kinetics of rhodamine B and the pseudo-second-order kinetic equation were higher, indicating that the adsorption rate was controlled by liquid membrane diffusion and intraparticle diffusion. The liquid membrane diffusion was main control step.

1. Introduction
Dyes are widely used in textile, leather, printing and dyeing, cosmetics and other industries. The environmental impact caused by dye wastewater generated in the production process is also increasingly serious. The dye wastewater has a large amount of COD, high chroma, deep color, high toxicity and complex composition. It has great harm to the water environment and human health. Therefore, there is an urgent need to find an efficient and low-cost dye wastewater treatment method[1]. The adsorption method is widely used in dye wastewater treatment research because of its simple operation, high efficiency, abundant source of adsorbed materials and low cost[2]. Biochar is a solid carbon-rich product produced by high temperature pyrolysis of bioorganic materials under anoxic conditions. The raw materials for the preparation of biochar are mainly biomass waste, and the utilization of waste resources can effectively alleviate environmental pollution[3]. The preparation methods of biochar mainly include thermal cracking, hydrothermal carbonization, gasification, etc. Different bioorganic materials, pyrolysis temperature, modification methods and other factors will have an impact on the performance of biochar. Existing biochar research has focused on areas such as soil performance regulation, global climate change, and renewable biofuels. In recent years, the application of biochar in the field of sewage treatment has gradually become a research hotspot[4]. At present, biochar adsorption technology is gradually applied in the field of sewage treatment. It has been shown that biochar has a good adsorption effect on typical pollutants such as heavy metals, nitrogen and phosphorus, which are widely present in aquaculture wastewater[5]. After being treated by magnetization, the biochar has good magnetic properties and is easily separated from the aqueous phase[6]. Compared with commercial activated
carbon products, it is easier to apply to sewage treatment. At the same time, because biochar has good adsorption capacity for nitrogen and phosphorus, it can be used as a slow-release fertilizer after adsorption, and has agricultural environmental friendliness[7]. In this paper, the biochar was made from Pine massoniana and the dye wastewater was simulated with rhodamine B. The adsorption process of pine needle biochar on rhodamine B was studied.

2. Materials and methods

2.1. Materials and instruments
Materials: Wild horsetail pine needles in Jingmen, Hubei; Rhodamine B; Analysis of pure KOH. Instruments: SK2-4-10 tube type resistance furnace; Ultra-violet and visible spectrophotometer; Drying oven.

2.2. Preparation of pine needle biochar
Selection of Hubei jingmen wild pine massoniana, water to wash away the dust on the pine needles, dry and cut into small pieces, put in the oven baked 2 h under 80 ℃ atmosphere, remove the pine needles in the crucible, put in tube furnace, the crucible modulation tube furnace at 300 ℃ and 10 ℃ / min up to the insulation 2 h, cooling them, remove the biochar milling grinding into powder, washed with distilled water, into the dryer after drying, sieving, weighing and set aside[8].

2.3. Adsorption test of rhodamine B
The Put 0.1g biochar in a 250ml conical flask, add 100ml diluted 100mg /L rhodamine B solution into it, put it in a constant temperature water bath, stir it with magnetic force at the rotating speed of 400r/min, take samples at intervals, and take the supernatant to determine the concentration of rhodamine B. According to equation (1), the adsorption amount of biochar was calculated, and the mean value of all experiments was taken three times in parallel.

\[
q = \frac{(C_0 - C_t)V}{M}
\]

In the equation  
q- adsorbing capacity, mg/g;  
C0-Initial concentration of rhodamine B, mg/L;  
Ct-Residual concentration in solution, mg/L;  
V- The volume of rhodamine B solution, L;  
M-The quality of the adsorbent, g.

3. Results and discussion

3.1. Characteristics of pine needle biochar
The chemical composition of biochar is shown in table 1. Compared with traditional peat, pine needle charcoal has higher carbon and hydrogen content and lower ash content. The strong adsorption ability of pine needle carbon is mainly due to its larger surface area and micropore volume. Although its polarity is better than that of traditional peat, which is not conducive to its adsorption of non-polar compounds, its surface area and micropore still play a dominant role[9].

The organic structure of biochar consists of two parts: a stacked graphene layer and an aromatic structure randomly dotted with a graphene layer, which promotes the biochar with a large specific surface area and a rich void structure. The larger specific surface area enhances the physical adsorption capacity of the biochar, and the rich void structure helps to adsorb organic matter of comparable molecular weight. The pine needle charcoal prepared by Pinus massoniana has a very rich void structure, and the mesoporous structure accounts for nearly 90% of the total void structure. The adsorption of rhodamine B mainly occurs in the mesoporous structure.
### Table 1. Properties of pine needle charcoal and peat.

|                        | Pine needle carbon | Peat  |
|------------------------|--------------------|------|
| **Elemental analysis** (wt.%) |                    |      |
| Carbon                 | 65.1               | 60.5 |
| Hydrogen               | 4.3                | 3.9  |
| Nitrogen               | 1.8                | 3.3  |
| Ash content            | 9.8                | 18.7 |
| Oxygen (by difference) | 34.46              | 24.01|
| **Surface properties** |                    |      |
| BET surface area (m$^2$·g$^{-1}$) | 389.4              | 285.6|

Peat after time is greater than 0.5 h, adsorption quantity increases slowly, gradually into balance, in order to assure the so equilibrium time of adsorption can be fully for 5 h, homemade pine needles biochar adsorption quantity increases with the increase of the time, when the time is more than 5 h, the trend of increase gradually slow, gradually into balance, in order to assure the so equilibrium time of adsorption can be fully for 70 h.

Through comparison, it can be seen that the adsorption time of purchased peat to reach equilibrium is shorter than that of homemade pine needle biochar. The reason for this phenomenon may be that the pore diameter and surface area of peat are smaller, and part of the physical impurities inherent in the pine needle adsorbed on the fired activated carbon during the firing process[10].

3.2. Adsorption kinetics

When the initial concentration of rhodamine B solution was 100 mg/L, the amount of adsorbent was 50 mg/L, the pH was 7.0, and the temperature was 25 °C, the effects of different adsorption times on rhodamine B were studied. The results were shown in the figure 3 below. The reaction was rapid within 2.0 h, and slow after 2.0 h. The initial rapid reaction was due to the high affinity sites on the surface of the adsorbent, and rhodamine B could occupy these sites quickly[11]. Later, the sites were reduced, and the internal diffusion of the particles was dominant, with a slow adsorption rate, which reached the adsorption equilibrium at 4.0h. The experimental data were fitted with the quasi-first-order kinetic equation, quasi-second-order kinetic equation and particle diffusion equation.

\[
\ln(Q_e - Q_t) = \ln Q_e - k_1 t
\]

\[
\frac{1}{Q_t} = \frac{k_2 Q_e}{1 + \frac{1}{Q_e t}}
\]

\[
Q_t = k_3 t^{1/2} + C
\]

Kinetic parameters obtained by linear fitting, including correlation coefficients (R2), $Q_e$, $k_1$, $k_2$, $k_3$, and $C$. It can be concluded from the table that the linearity of the quasi-secondary fit is higher than the
quasi-first-order fit. It indicated that the adsorption mechanism of pine needle charcoal on rhodamine B may be chemical adsorption. In the intraparticle diffusion equation, if C = 0, it indicates that internal diffusion is the only factor affecting the adsorption process. However, as can be seen from the table, C>0. Therefore, internal diffusion is not the only control step affecting the adsorption of pine needle carbon on rhodamine B, and its adsorption process is affected by many factors[12].

![Fig 3. Effect of adsorption time on adsorption of rhodamine B by pine needle charcoal](image)

4. Conclusion
The adsorption performance of biological carbon of pine needles is better than that of grass carbon on the market, and the self-made biological carbon of pine needles is a good adsorbent of dye, which has the characteristics of easy access to materials, simple production, low cost, fast adsorption efficiency, environmentally friendly, etc. It is a new adsorption material that can be vigorously promoted. The adsorption rate of pine needle charcoal to high and low concentration dye solution was faster. The dye adsorption process is mainly concentrated in the first 1 h, low concentration of dye solution. The adsorption can reach the equilibrium faster, the stabilization time is short, the diffusion speed of high concentration dye solution dye to the pores inside the adsorbent is slow, the duration is longer, the adsorption rate of the diffusion phase within the particles has an important influence on the adsorption rate of the whole process.

References
[1] Duan S, Xu X, Liu X, et al. (2018) Highly enhanced adsorption performance of U(VI) by non-thermal plasma modified magnetic Fe3O4 nanoparticles. Journal of Colloid and Interface Science, 513: 92 – 103.
[2] Karthick K, Namasivayam C, Pragasan L A. (2017) Kinetics and isotherm studies on acid dye adsorption using thermal and chemical activated Jatropha husk carbons . Environmental Progress & Sustainable Energy, 37(2):719 – 732.
[3] Reddy D H K, Yun Y-S. (2016) Spinel ferrite magnetic adsorbents: Alternative future materials for water purification? Coordination Chemistry Reviews, 315: 90 – 111.
[4] Warner C L, Chouyyok W, Mackie K E, et al. (2016) Manganese Doping of Magnetic Iron Oxide Nanoparticles: Tailoring Surface Reactivity for a Regenerable Heavy Metal Sorbent . Langmuir, 28(8): 3931 – 3937.
[5] Gao S, Zhang W-W, Zhou H-P, et al. (2018) Magnetic composite Fe3O4/ CeO2 for adsorption of azo dye. Journal of Rare Earths, 986-993.
[6] Li X-Y, Wang X, Song S, et al. (2012) Selectively Deposited Noble Metal Nanoparticles on Fe3O4/Graphene Composites: Stable, Recyclable, and Magnetically Separable Catalysts. Chemistry - A European Journal, 18(24): 7601–7607.
[7] Cheng S, Zhang L, Ma A, et al. (2018) Comparison of activated carbon and iron/cerium modified
activated carbon to remove methylene blue from wastewater. Journal of Environmental Sciences, 65:92 - 102.

[8] Roberts K, Gloy B, and Joseph S, et al. (2010) Life cycle assessment of biochar systems: Estimating the energetic, economic and climate change potential. Environ Sci Technol, 44 (2) : 827-833.

[9] Xiao X, Chen B, Zhu L. (2014) Transformation, morphology, and dissolution of silicon and carbon in rice straw-derived biochars under different pyrolytic temperatures. Environmental Science & Technology, 48(6):3411-3419.

[10] Fidel R B, Laird D A, Thompson M L, et al. (2017) Characterization and quantification of biochar alkalinity. Chemosphere, 167:367-373.

[11] Wang X J, Wang Y, Wang X, et al. (2011) Microwave-assisted preparation of bamboo charcoal-based iron-containing adsorbents for Cr(VI) removal. Chemical Engineering Journal, 174(1):326-332.

[12] Gan C, Liu Y, Tan X, et al. (2015) Effect of porous zinc-biochar nanocomposites on Cr(VI) adsorption from aqueous solution. Rsc Advances, 5(44):35107-35115.