Adsorption performance of biochars from agricultural and forestry wastes

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Abstract. Four types of biochars were prepared by using sawdust, corn straw, peanut hull and fallen leaves as materials, respectively. The characteristics of four types of biochars were analyzed by SEM, FTIR and BET, the SBET of SDC, PHC, CSC and FLC were 1168.45, 846.95, 825.51 and 401.26 m²·g⁻¹. The adsorption conformed to the pseudo-second-order model and the Langmuir isotherm.

Keywords: Agricultural and forestry wastes; preparation; biochar; dye; adsorption.

1. Introduction
Dyes are widely applied in papermaking, textile, food, plastic, leather and many other industries. However, during manufacturing and processing operations, some dyes inevitably entering the industrial wastewaters will damage environment if they are not being disposed properly [1]. These effluents are difficult to degrade due to its high biochemical oxygen demand, metals, high chrome and suspended solids. There are various methods for removing dyes, such as biodegradation, coagulation and flocculation, filtration, advanced oxidation, photocatalysis, adsorption and so on. Among these methods, the adsorption has attracted many experts’ attentions due to its high removal efficiency and simple operations. Activated carbon has been mostly used. In order to reduce cost and achieve greater economic and social benefit, it is necessary to develop low-cost adsorbents [2,3]. Many agricultural and forestry wastes can be reused as inexpensive materials for adsorbents, such as wheat straw, rice straw, soybean hulls, corn straw, rambutan peel, Agricultural peels, Iranian milk vetch, pine cone, peanut shell, Albizia lebbeck seed pods, walnut and poplar woods, Korean cabbage waste and so on.

This study aimed to assess the performance of four types of biochars from corn straw (CSC), sawdust (SDC), peanut hull (PHC) and fallen leaves (FLC). The characteristics of four types of biochars were analyzed and the adsorption mechanisms of azo dye (Orange G) onto CSC, PHC, SDC and FLC were investigated, such as adsorption kinetics, adsorption equilibrium and adsorption thermodynamics, and the parameters were also obtained.

2. Experimental

2.1. Preparation of biochar
In this work, four different agricultural and forestry wastes (corn straw, sawdust, peanut hull and fallen leaves) were selected to prepare the biochar for dye adsorption. Corn straw was taken from a farm in the
suburb of Taiyuan, China. Sawdust was collected from a woodworking factory nearby, peanut hull and fallen leaves were obtained from campus. The samples were firstly air-dried, and then ground by multifunction pulverizer (JP-150A, China) to pass through a 0.425mm standard screen. The powders were fully mixed with ZnCl₂ according to a certain mass ratio. The mixture was carbonized at 500°C in a box-type resistance furnace (BSX2-2.5-12TP, China) for 120 minutes under oxygen deficit condition. The carbides were immersed in 3mol.L⁻¹ of hydrochloric acid solution for 30 minutes to remove impurities. The final samples were washed with deionized water until the samples were close to neutral, and dried at 105±5°C in an electrothermal drier (DHG-9070, China) to reach the constant weight, then ground to pass through a 0.150mm standard screen for further experiments.

2.2. Dye solutions
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2.3. Adsorption experiments
Adsorption equilibrium experiments were conducted with varying initial OG concentration (60~300 mg·L⁻¹) at 298, 308 and 318K for 720 minutes, respectively.

Adsorption capacity of dye was obtained by equation (1).

\[ q_t = \frac{(c_0 - c_t) \times V}{m} \]  \hspace{1cm} (1)

Equilibrium adsorption capacity was obtained by the following equation (2).

\[ q_e = \frac{(c_0 - c_e) \times V}{m} \]  \hspace{1cm} (2)

Where, \( c_0 \) is the initial concentration of dye solution (mg·L⁻¹); \( c_t \) is the concentration of dye solution at t moment; \( c_e \) is the concentration of dye solution at adsorption equilibrium state (mg·L⁻¹); \( q_t \) is adsorption capacities at t moment; \( q_e \) is adsorption capacities and adsorption equilibrium state (mg·g⁻¹); \( V \) is the volume of dye solution in contact with the adsorbent (L); and \( m \) is the weight of the biochar (g) [4].

3. Results and discussion

3.1. Characteristics of biochar
A Four types of biochar from corn straw (CSC), sawdust (SDC), peanut hull (PHC) and fallen leaves (FLC) were characterized by the SEM (FEI Nova NanoSEM 430, American) to gain insight to the surface morphology and structure.

Figure 1. SEM images of biochar (a) CSC, (b) SDC, (c) PHC and (d) FLC.
As can be seen from Fig.1, they are rough and porous on the surfaces of four types of biochars. There are many holes in the surface of biochars, especially on the biochar from sawdust (SDC). When the dye adsorption occurs, the dye molecules will enter into these holes through diffusion.

BET surface area and pore features of four types of biochars were analyzed by a Surface Area & Pore Size Analyzer (TriStar 3000, USA). Characteristics of four types of biochars are shown in table 1.

### Table 1. Characteristics of biochar (a) CSC, (b) SDC, (c) PHC and (d) FLC.

| Samples | BET surface area m²·g⁻¹ | Langmuir surface area m²·g⁻¹ | Pore volume cm³·g⁻¹ | Pore size nm |
|---------|-------------------------|-----------------------------|---------------------|--------------|
| CSC     | 825.51                  | 1303.59                     | 0.4979              | 2.41         |
| SDC     | 1186.45                 | 1923.48                     | 0.6993              | 2.36         |
| PHC     | 846.95                  | 1336.01                     | 0.4900              | 2.31         |
| FLC     | 401.26                  | 575.08                      | 0.2510              | 2.50         |

As can be seen from table 1, the \( S_{\text{BET}} \) of SDC is 1186.45 m²·g⁻¹, higher than the \( S_{\text{BET}} \) of PHC (846.95 m²·g⁻¹) and CSC (825.51 m²·g⁻¹), and the \( S_{\text{BET}} \) of FLC is the lowest (401.26 m²·g⁻¹).

Surface functional groups were detected by a Perkin Elmer spectrum 100 FTIR spectrometer. Figure 2 shows the FTIR spectra.

**Figure 2.** FTIR spectra of four types of biochars

The flat and broad band in the wavelength range 3375~3357 cm⁻¹ can be recognized as the stretching of O-H groups, and the weak band at 2980~2924 cm⁻¹ can be the C-H symmetric and asymmetric stretching vibration bands of methyl groups. The band at about 1583~1575 cm⁻¹ can be attracted to the C=C vibration in aromatic rings, and the band at about 1160 cm⁻¹ can be ascribed to the C–O stretching of cellulose and hemicelluloses [5, 6].

### 3.2. Adsorption kinetics

Effects of contact time on the adsorption capacity of OG were showed in the Figure 3.

**Figure 3.** Effects of contact time on the adsorption capacity of OG
The adsorption curves rose sharply as the increase of contact time at the first 60 minutes and then slowed down to equilibrium. This behavior might be due to the fact that there were many vacant sites and the concentration gradient of OG was high at the beginning. When more and more dye molecules were adsorbed, the number of vacant sites decreased gradually.

The adsorption kinetics of OG dye on the biochar was analyzed using different kinetic models [7, 8] and their linear forms are presented in table 2.

| Items             | Kinetic model                                      | Rate constant          |
|-------------------|---------------------------------------------------|------------------------|
| Pseudo-first-order| $\ln(q_e - q_t) = \ln q_e - k_1 t$                | $k_1$: min$^{-1}$      |
| Pseudo-second-order| $t/q_t = 1/k_2 q_t^2 + t/q_e$                      | $k_2$: g·mg$^{-1}$·min$^{-1}$ |
| Intra-particle     | $q_t = k_3 \sqrt{t} + C$                          | $k_3$: mg·g$^{-1}$·min$^{-0.5}$ |

The experimental data were fitted by using above mentioned three kinetic models, Table 3 showed the fitting parameters.

| Samples | $q_{e,exp}$ mg·g$^{-1}$ | $q_{e,cal}$ mg·g$^{-1}$ | $k_1$ min$^{-1}$ | $R^2$ | $q_{e,cal}$ mg·g$^{-1}$ | $k_2$ g·mg$^{-1}$·min$^{-1}$ | $R^2$ | $k_p$ | C | R$^2$ |
|---------|------------------------|-------------------------|------------------|-------|------------------------|-----------------------------|-------|-------|---|------|
| SDC     | 82.31                  | 83.33                   | 0.001424         | 0.9995| 0.9715                 | 63.84                       | 0.9357 |
| CSC     | 48.18                  | 47.62                   | 0.002295         | 0.9989| 0.5414                 | 36.64                       | 0.9407 |
| PHC     | 46.77                  | 43.29                   | 0.000953         | 0.9912| 0.9024                 | 23.99                       | 0.9565 |
| FLC     | 29.02                  | 29.24                   | 0.001759         | 0.9982| 0.6988                 | 15.35                       | 0.9051 |

As can be seen from Table 3, the best-fitting model was the pseudo-second-order equation. The $R^2$ (0.9912–0.9995) was higher than those for pseudo-first-order equation (0.9460–0.9702) and intra-particle equation ($R^2$: 0.9357–0.9565). The values of $q_{e,cal}$ ($q_e$ from calculation) were closer to $q_{e,exp}$ ($q_e$ from experiment). Thus, the OG dye adsorption on four types of biochars could be explained by pseudo-second order kinetics, the adsorption might be chemisorption. $C\neq0$ indicated that there could be many rate-limiting steps besides intra-particle diffusion, such as liquid film diffusion, solid-liquid interface diffusion, boundary layer control and so on.

3.3. Adsorption isotherms

The equilibrium isotherms can illuminate the adsorption mechanisms and the heterogeneity of the adsorbent surface. Three common isotherms are shown in table 4 [7].

| Items | Isotherm | Parameter |
|-------|----------|-----------|
| Langmuir | $\frac{c_e}{q_e} = \frac{c_n}{q_m} + \frac{1}{K_s q_m}$ | $k_s$: L·mg$^{-1}$ |
| Freundlich | $\ln q_e = \ln k_F + \frac{1}{n} \ln c_s$ | $k_F$ |
The fitting parameters in Table 5 were obtained from Langmuir isotherm and Freundlich isotherm, respectively.

**Table 5.** Fitting parameters of different isotherms.

| Samples | $T/K$ | $q_m$ mg·g$^{-1}$ | $k_L$ L·mg$^{-1}$ | $R_L$ | $R^2$ | $k_F$ (mg·g$^{-1}$)(L·mg$^{-1}$)$^{1/n}$ | $n$ | $R^2$ |
|---------|-------|-------------------|-------------------|-------|-------|---------------------------------|-----|-------|
| SDC     | 298   | 158.73            | 0.2158            | 0.049–0.015 | 0.9954 | 52.13                          | 3.88 | 0.9351 |
|         | 308   | 163.93            | 0.3245            | 0.033–0.010 | 0.9946 | 60.13                          | 3.69 | 0.9156 |
|         | 318   | 181.82            | 0.5140            | 0.021–0.006 | 0.9984 | 71.25                          | 3.37 | 0.8491 |
|         | 298   | 123.46            | 0.1142            | 0.089–0.028 | 0.9930 | 31.48                          | 3.27 | 0.9814 |
| CSC     | 308   | 125.00            | 0.2446            | 0.043–0.013 | 0.9903 | 47.08                          | 4.32 | 0.9524 |
|         | 318   | 129.87            | 0.4118            | 0.026–0.008 | 0.9957 | 543.3                          | 4.25 | 0.9125 |
|         | 298   | 128.21            | 0.0740            | 0.131–0.043 | 0.9926 | 24.94                          | 2.85 | 0.9926 |
| PHC     | 308   | 129.87            | 0.1208            | 0.073–0.023 | 0.9902 | 34.65                          | 3.22 | 0.9623 |
|         | 318   | 131.58            | 0.2890            | 0.037–0.011 | 0.9905 | 49.40                          | 3.99 | 0.9938 |
|         | 298   | 82.64             | 0.0609            | 0.154–0.052 | 0.9925 | 13.34                          | 2.58 | 0.9917 |
| FLC     | 308   | 86.21             | 0.0852            | 0.115–0.038 | 0.9914 | 16.10                          | 2.62 | 0.9853 |
|         | 318   | 96.15             | 0.2396            | 0.044–0.014 | 0.9904 | 27.34                          | 2.78 | 0.9559 |

Most of $R^2$ values for Langmuir model (0.9902–0.9984) were higher than those for Freundlich (0.9125–0.9938). This fact indicated Langmuir model could well describe the adsorption of OG onto SDC, CSC, PHC and FLC. The adsorption might be monolayer coverage at homogeneous sites. As observed, the values of $R_L$ were all between 0 and 1, and increased with the decrease of initial dye concentration, suggesting that the adsorptions of OG onto four types of biochars were all favorable. The maximum adsorption capacities of OG for SDC, CSC, PHC and FLC were 181.82, 129.87, 131.58, 96.15 mg·g$^{-1}$ at 318K, respectively.

4. Conclusion

In this study, forestry and agricultural residues (sawdust, corn straw, peanut hull and fallen leaves) were used as materials to prepare prospective biochars for dye adsorption. The characteristics of four types of biochars were analyzed by electron microscope, Infrared spectrometer and surface area analyzer. The biochar with the maximum BET specific areas were SDC, CSC, PHC and FLC. The adsorption of OG onto four types of biochars could be considered to be well fitted to pseudo-second order kinetics model, and the adsorption isotherm could be conformed to Langmuir model.

Acknowledgments

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