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Research on preparation and organic wastewater treatment of pomelo peel biomass adsorbent

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Abstract. This paper uses grapefruit peel as raw material, carbonized at 300°C, 400°C, 500°C, and 600°C, respectively, to prepare biochar at the corresponding temperature, and select the optimal carbonization temperature through adsorption degradation experiments. Then the biomass charcoal prepared at the optimal carbonization temperature was modified by 1 mol/L hydrochloric acid and 2.5 mol/L sodium hydroxide solution, and the modified grapefruit skin biomass was mainly studied by hydrochloric acid modified biomass charcoal. The optimum adsorption conditions of carbon for organic wastewater were studied. The methylene blue and phenol-containing wastewater were selected respectively. The adsorption and adsorption laws of grapefruit skin biochar on two organic wastewaters were tested.

1. Introduction

Biomass materials are new materials with superior performance and greater value prepared by using natural materials such as woody plants and their processing residues as raw materials, using various high-tech methods such as physical chemistry and biology. In the south of China, grapefruit is a very common fruit. The method of modifying biomass raw materials is mainly pretreatment by chemical agents, and there are many methods for modifying carbonized carbon. Compared with unmodified biochar, the modified biochar has improved performance in terms of specific surface area, surface oxygen-containing functional groups, adsorption sites, etc. Therefore, the adsorption and fixation ability of biochar to pollutants is also enhanced. In this study, grapefruit peel was used as the basic raw material, and the methylene blue simulated wastewater and phenol-containing wastewater were adsorbed by hydrochloric acid modification.

2. Selection of two modified biomass carbons and organic dyes

Three kinds of dyes, methylene blue, acid magenta and methyl orange, were selected to explore the adsorption effects of the two modified biochars on the three dyes, so as to select the method and health of the modified biochar. The best adsorption dye for material charcoal.

Three kinds of organic dyes of methylene blue, acid fuchsin and methyl orange were prepared at a concentration of 10 mg/L. The same volume of three organic dye wastewaters were taken in a beaker, and the same quality modified biochar was added to the middle. Each group of experiments was controlled under the same conditions to explore the adsorption kinetics of different dyes in different groups of biomass carbon.

Tables 1 and 2 list the raw record data for the removal rates of the three dyes by acid-modified biomass carbon and alkali-modified biomass carbon.

Table 1. Original record of removal rate of three dyes by acid-modified biomass carbon

Time /min	2	4	8	12	20	40	60	90	120
Methylene blue removal rate /%	76.8	70.4	76.8	77.6	80.8	84	88	96	97.6
Acid fuchs removal rate /%	56.52	58.39	62.73	62.73	67.08	70.19	73.91	69.57	77.02
Methyl orange removal rate /%	14.04	24.56	21.05	17.57	17.54	17.57	19.3	14.04	21.05

Table 2. Original record of removal rate of three dyes by alkali-modified biomass carbon

Time /min	2	4	8	12	20	40	60	90	120
Methylene blue removal rate /%	90.22	95.44	97.46	97.62	98.27	98.56	98.78	98.99	99.01
Acid fuchs removal rate /%	63.29	63.92	66.46	66.46	67.72	70.25	72.15	79.11	79.75
Methyl orange removal rate /%	31.58	31.58	38.6	33.33	42.11	42.11	49.12	49.12	47.37

The removal rate of three simulated wastewaters of methylene blue, acid fuchsin and methyl orange by acid-modified biomass carbon can reach 98%, 79% and 49%, respectively; alkali-modified biomass carbon to methylene blue, acid fuchsin and methyl The removal rates of three simulated wastewaters in orange can reach 97%, 77%, and 21%, respectively. Thus, it can be found that the removal of methylene blue by both modified biomass carbons is obvious, and for acid magenta and methyl orange, it is difficult for biomass carbon to adsorb the two dye wastewaters. Therefore, in the process of influencing the factors affecting the adsorption performance of modified biomass carbon, the methylene blue wastewater was selected as the substrate for adsorption experiments.

3. Comparison of phenol removal by alkali-modified biomass carbon and acid-modified biomass carbon

Figure 1 and Figure 2 show the effect of acid-modified and alkali-modified grapefruit biochar on the removal of phenol. The analysis shows that the removal of phenol by acid-modified biomass carbon is better than that of alkali-modified biomass carbon. The removal effect is better, so the subsequent research on the factors affecting the adsorption of phenol by modified biomass carbon selects acid-modified biomass charcoal as the research object.

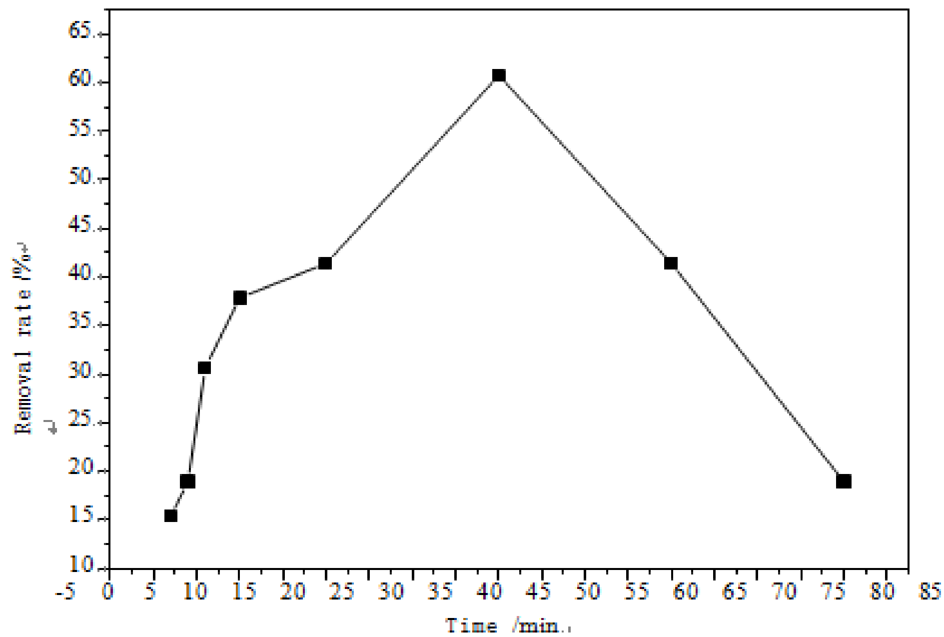

Figure 1. Removal of phenol by acid-modified biomass carbon

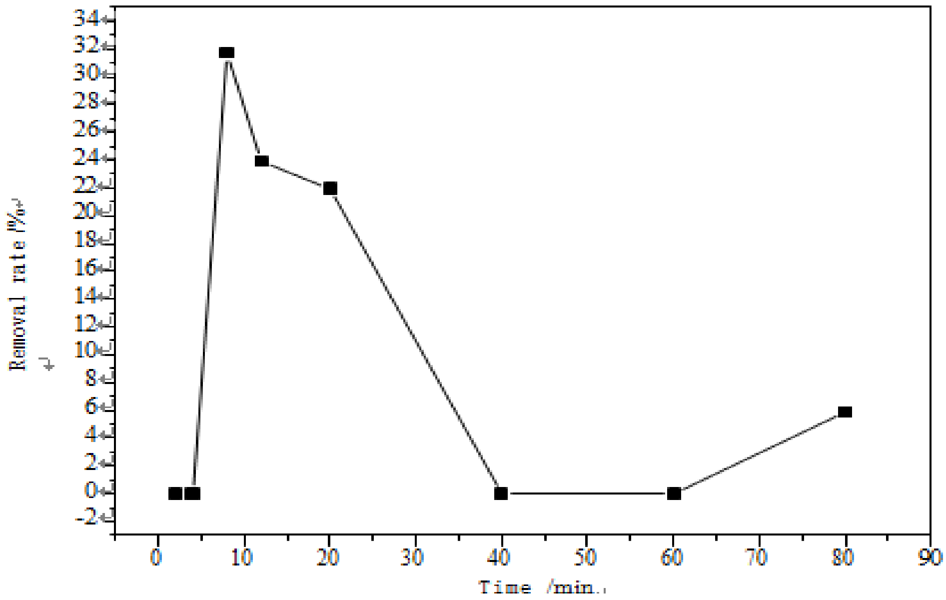

Figure 2. Removal effect of alkali modified biomass carbon on phenol

4. Characterization of biochar

According to the previous experiments, acid-modified biomass charcoal was selected for characterization. The prepared acid-modified biomass carbon was characterized and analyzed by specific surface area, scanning electron microscopy and converted infrared spectroscopy. In the experiment, the specific surface area of the biomass carbon material was determined by the BET-N2 method. The BET-N2 method is based on the property of N2 adsorption and desorption on the surface of a solid substance to determine the surface area of the biomass carbon.

The apparent structure analysis of biomass carbon materials was carried out using Zeiss SUPRA-55 field emission scanning electron microscope. Scanning electron microscopy has the following applications: a). under any environmental conditions, scanning electron microscopy can perform non-destructive analysis on the composition and morphology of various substances; b). It can characterize specific target substances during the experiment. Quantitative analysis, elemental composition and distribution analysis. The experimental samples were sent to the Analytical Testing Center of the Food College of the School of Petrochemical Engineering of Changzhou University for testing. The transform spectrum was measured by */TENSOR 27 type conversion spectroscopy. The sample was scanned by KBr tableting method, and a certain amount of sample was mixed with KBr in a ratio of 1:100.

5. Characterization and analysis of modified grapefruit skin biochar

The grapefruit skin is a white floc layer. The carbonaceous adsorbent prepared by carbonization has a porous structure and a large specific surface area. The specific surface area is 21.83 m^2/g. As shown in Figure 3, the surface topography of the acid-modified biomass carbon is shown. The surface of the biomass charcoal is in the form of a sheet and a block structure, and the surface has many pores and irregularities. This may be due to the collapse of the surface pores during the process of biomass carbon preparation and drying. Part of the micropores on the surface is due to the reaction of hydrochloric acid with the inorganic minerals on the surface after the acid carbon is acid-modified, so that the inorganic minerals on the surface of the biomass carbon are removed, exposing more pore structure. Such a structure facilitates the progress of the biomass carbon adsorption process.

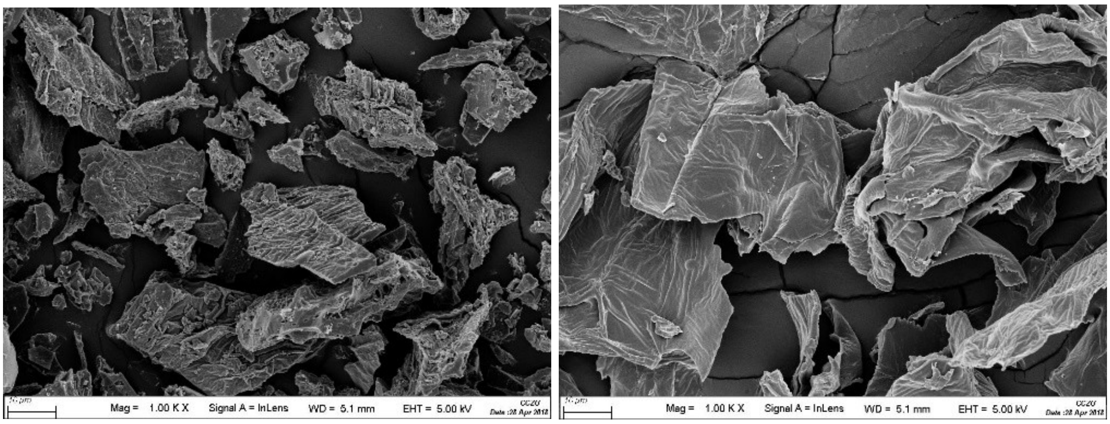

Figure 3. SEM image of biochar

6. The effect of different pH of the solution

Weigh 0.16 g of modified grapefruit skin biochar and add it to 20 mL of phenol solution to adjust the pH of the solution to 2, 3, 4, 5, 6, 7, 8, 9, 10, and 11 at constant temperature. After shaking for 45 min in the apparatus, the concentration of phenol in the solution after adsorption was measured after passing through the microfiltration membrane.

The pH in the solution not only affects the solubility and morphology of the phenol, but also plays a decisive role in the activity of the surface adsorption site of the biomass carbon in the aqueous solution and its physicochemical properties. According to the literature, the pH control can increase the adsorption amount of biomass carbon to pollutants within a certain range. Table 3 lists the original records of the removal rate and adsorption capacity of phenol on biomass carbon under different pH conditions. The removal rate is at a higher level under acidic conditions, and the removal rate is gradually decreased when the pH is acidic. This is due to the protonation of the negatively charged functional groups on the surface of the biomass carbon under acidic conditions. The active site of adsorbing phenol is increased, and the removal rate is high. Since the pKa of phenol is 9.59, such as the relationship between the ionization intensity of phenol and pH, as the pH increases, the power intensity of phenol increases, so the solution The ionized phenol concentration in the medium increases, and since the ionized phenol and the electrons on the surface of the biomass carbon generate repulsive force, the biomass carbon is less likely to adsorb phenol, so the removal rate is lowered.

Table 3. Raw data record of phenol removal rate under different pH conditions

pH	3	4	5	6	7	8	9	10	11
Removal rate /%	56.62	23.35	22.42	21.04	18.23	19.42	14.31	12.25	12.01
Adsorption capacity /mg/g	1.95	1.38	1.37	1.34	1.29	1.31	1.23	1.19	1.19

7. Effect of dosage of modified grapefruit peel biochar

Different quality modified grapefruit peel biochars were weighed separately (0.02 g/20 mL, 0.04 g/20 mL, 0.06 g/20 mL, 0.1 g/20 mL, 0.16 g/20 mL, 0.2). g/20 mL, 0.4 g/20 mL) Add 20 mL of 20 mg / L phenol solution to the Erlenmeyer flask. Do not adjust the pH of the solution, shake for 45 min in the shaker, and measure the absorbance after adsorption. , thereby calculating the removal rate. Table 4 lists the raw record data of the removal efficiency and adsorption capacity of phenol for different dosages of modified biomass carbon. When the biomass carbon dosage increased from 0.02 g/20 mL to 0.16 g/20 mL, the adsorption decreased from 10.35 mg/g to 3.06 mg/g, and the removal rate increased from 17.96% to 60.4%. This is because as the amount of biomass carbon increases, the number of adsorption sites for adsorbing phenol on the surface of the biomass carbon is increasing, so that the removal rate of phenol is gradually increased; and then the dosage of biomass carbon is increased. The larger the adsorption point of biomass carbon in the process of biomass carbon adsorption, the more and more the saturation

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site cannot be saturated, and the interaction between biomass carbon particles such as agglomeration increases the diffusion path and reduces the growth. The total specific surface area of the material char, resulting in a decrease in the amount of biomass carbon adsorbed. When the dosage increased from 0.16 g/20 mL to 0.2 g/20 mL, the removal rate of phenol decreased, which may be due to the possibility of desorption, which resulted in a decrease in the removal rate of biomass carbon. Taken together, the dosage in the subsequent experiments was 0.16 g/20 mL.

Table 4. Raw record data of phenol removal efficiency and adsorption amount of different dosages of modified biochar

Dosing amount /g	0.02	0.04	0.06	0.1	0.16	0.2
Removal rate /%	17.96	20.62	31.04	56.77	60.4	39.2
Adsorption capacity /mg/g	10.35152	5.48419	4.06737	3.05728	1.98791	1.34358

8. Biomass carbon recovery

In this study, biomass charcoal was recycled after adsorption experiments. The recovery method is directly washed three times with a large-capacity centrifuge, washed once with ethanol, and dried in a vacuum drying oven at a temperature of 80 ° C overnight, and the amount of modified biomass carbon added before adsorption is 0.56 g. The recovered modified biomass carbon was 0.2063 g, and the recovery rate was 36.83%. After that, the removal rate of methylene blue after recovery and the removal rate of methylene blue from the modified biomass carbon raw material were investigated, and the following comparison was made. As can be seen from Fig. 4, the recovered modified biomass carbon to methylene blue was observed. The removal rate is longer than the removal rate of methylene blue by the modified biomass carbon raw material. The former tends to be the maximum value for a long time, and the former has a lower maximum value, but the removal rate of methylene blue by both materials can reach 96% or more. Therefore, the recovery of acid-modified grapefruit skin biochar is practical in practical application, which further proves that the adsorption of methylene blue by acid-modified biomass carbon is mainly physical adsorption.

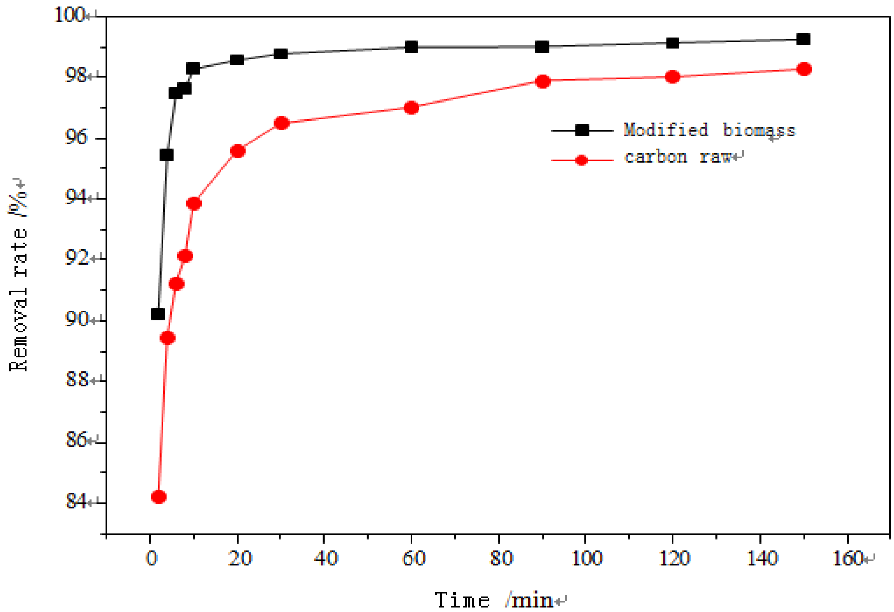

Figure 4. Change of removal rate of methylene blue with modified biomass carbon raw materials and recovered biomass carbon over time

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9. Summary

The hydrochloric acid-modified grapefruit skin biochar has better removal effect on methylene blue and phenol than the alkali-modified grapefruit skin biomass carbon. The hydrochloric acid modification can increase the acidic functional groups on the surface of the biomass carbon, and the alkali modification can increase the basic groups on the surface of the biomass carbon. Methylene blue is a basic dye. The dye solution is colored as a cation. The surface of the acid-modified biomass carbon contains more acidic groups. The surface is negatively charged, and it is easier to adsorb methylene blue ions. Therefore, hydrochloric acid-modified biomass Carbon has better removal effect on methylene blue and phenol than alkali modified biomass carbon.

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