Research on adsorption performance of magnetic bio-char for tetracycline in water

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Abstract. In this paper, waste coconut shells are used as raw materials to prepare the corresponding bio-char (BC), and further prepare magnetically modified magnetic bio-char (MBC), and explore the adsorption of BC and MBC on the amount of adsorbent, adsorption time and pH. The recyclability of BC and MBC were contrasted. The results of the study found that compared to BC, the magnetically modified MBC has a larger specific surface area and richer functional groups, which provides more adsorption sites for the adsorption and removal of tetracycline. It can be used in different adsorbent dosages and adsorption times. Under the conditions of pH and pH, it shows better adsorption performance. In addition, MBC has better recycling properties than BC, which has higher application prospects. This research provides a theoretical basis for the utilization of waste resources and the removal of antibiotics in wastewater.

1 Introduction

In recent years, with the abuse of antibiotics, a large number of antibiotics have entered the water environment. Tetracycline antibiotics (TCs) are one of the most commonly used antibiotics in human health care and animal feed additives^[1]. However, only a very small part of antibiotics can be digested and absorbed by the stomach and intestines of humans and animals^[2]. Most antibiotics are excreted into the body through feces in the form of parent compounds. Because antibiotics are not easily biodegradable, they will remain and accumulate in the environment, causing serious environmental problems Pollution. Residual antibiotics in the environment have aroused everyone's attention because they pose a potential long-term adverse threat to human health and natural ecosystems^[3-4]. Therefore, how to efficiently and quickly remove residual TCs and other antibiotic pollutants in the environment has become an environmental problem that needs to be solved urgently.

At present, the main methods of treating antibiotic wastewater are: membrane separation, biodegradation, photocatalytic degradation, chemical oxidation, adsorption^[5-10]. Among them, the adsorption method is recognized as one of the most promising methods due to its high removal efficiency, simple operation and low cost^[11-13]. However, for any adsorption method to treat wastewater, its adsorption efficiency depends on the choice of a suitable adsorbent^[14]. Therefore, the development of high-efficiency and low-cost adsorption materials is the key to promoting its practical application. Bio-char is a kind of porous carbon material formed by high temperature pyrolysis of biomass under anaerobic or anaerobic conditions. It not only has high specific surface area, porosity and abundant functional groups,

but also has a wide range of sources and simple preparation process. It has been successfully used in the treatment of wastewater, and creating great possibilities for the resource utilization of waste biomass. Nevertheless, it is difficult to separate the bio-char in the system after adsorption, and there is a risk of secondary pollution.

Therefore, this study intends to combine bio-char and magnetic materials to make a magnetic bio-char composite material, to investigate its adsorption capacity for antibiotics under different conditions, and to provide theoretical basis and technical support for the removal of antibiotics.

2 Materials and methods

2.1. Material

First, the coconut husk is cleaned, dried and ground in an oven, and then passed through a 100-mesh sieve. Then the coconut shell powder was placed in an alumina porcelain boat and calcined in a tube furnace, heated to 800°C at a rate of 5°C/min under the protection of nitrogen, maintained for 5 hours, and cooled to room temperature to obtain black BC powder.

Slowly add aqueous FeCl₃ (3 g/25 mL) to FeSO₄ • 7H₂O (6.15 g/250 mL), and stir thoroughly (200 rpm) at 60-70°C for about 5 min. The solution was added to the aqueous ultrasonic dispersion BC at room temperature and stirred slowly for 30 min. The pH value of the Fe²⁺/Fe³⁺/BC suspension was adjusted to ~10.5 by adding 10MNaOH dropwise and stirring by the following method, and then aged at room temperature for 24 hours. Iron oxide nucleates and precipitates on the

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surface of biochar during the aging process. The product is filtered (Whatman No. 1 filter paper), rinsed with distilled water, and then the obtained MBC is filtered with ethanol, and then dried overnight in a drying oven at 50°C and 1 atm.

2.2. Material characterization

The Merlin ultra-high resolution field emission scanning electron microscope of Zeiss, Germany was used for SEM analysis to determine the surface morphology characteristics of biochar. X-ray diffraction (XRD) analysis was performed using the D8 ADVANCEX-ray diffractometer (Cu target, $K\alpha$ as radiation source, Lynx Exe array detector, wavelength 0.15418 nm) from Bruker, Germany, scanning speed $10^\circ \cdot \text{min}^{-1}$, scanning The range is $5 \sim 80^\circ$, the working voltage is 40 kV, the current is 40 mA, and the working temperature is room temperature. Use Perkin Elmer's 1725X infrared spectrometer to perform Fourier transform infrared spectroscopy (FT-IR), the scanning range is $4000 \sim 400 \text{ cm}^{-1}$, the resolution of the instrument is 4 cm^{-1} , the number of scanning is 64 times, and the test temperature is 25°C , using potassium bromide tablet method for sample preparation. BET analysis uses American Kantar Autosorb iQ to analyze the specific surface area and micropores of the material. The test conditions are: helium is used as the carrier gas, degassed at 80°C for 12 h, and the specific surface area of the adsorbent is measured by the N_2 adsorption method. The t-plot method measures the surface area and volume of the micropores, and the DFT method calculates the average micropore diameter. For elemental analysis, an elemental analyzer (Vario EL cube, Elementar, Germany) was used to determine the C, H, N, and S content of biochar, and the O content was obtained by subtraction.

2.3 Tetracycline determination

Weigh 1g of tetracycline hydrochloride and dissolve it in 1L of deionized water to prepare TC stock solution. Dilute an appropriate amount of stock solution into a series of concentration gradient standard solutions. An ultraviolet-visible spectrophotometer was used to measure the absorbance of the standard solution at 355 nm, and a standard curve was drawn from the absorbance and the mass concentration of TC.

2.4 Batch adsorption experiments

Weigh 1.0 g of tetracycline hydrochloride, dry it at 105°C for 2 hours, add deionized water to make the volume to 1 000 mL, and configure it as a 1000 mg/L TC standard stock solution. The TC solution used in the experiment was obtained by diluting the above-mentioned standard stock solution. At 25°C , shake with 130 min^{-1} .

2.4.1 The effect of adsorbent dosage on adsorption

Add a certain amount of biomass charcoal and magnetic biomass charcoal to the TC solution, set the dosage of the adsorbent to 0.2-1.2g/L, set the temperature at 25°C , and oscillate for 36h to calculate the removal rate and adsorption capacity.

2.4.2 The effect of adsorption time on adsorption

Add 0.4 g/L of BC and MBC to a series of conical flasks containing 50 mL and 50 mg/L TC dye solution, respectively, and shake in a constant temperature water bath shaker. Take out the Erlenmeyer flask at different time intervals of 0~300 min, measure the absorbance of TC in the supernatant at a wavelength of 355 nm, calculate the dye removal rate, and analyze the effect of adsorption time on the TC adsorption effect;

$$q = (c_0 - c) V / m \quad (1)$$

$$\eta = (c_0 - c) / c_0 \times 100\% \quad (2)$$

q is the adsorption capacity of BC and MBC, mg/g; c_0 is the concentration of the TC solution before adsorption, mg/L; c is the concentration of the remaining TC solution after adsorption, mg/L; V is the volume of the CR solution, L; m is the quality of BC and MBC, g.

2.4.3 The effect of initial pH on adsorption

Adjust the pH (4~11) of the TC solution with 0.5 mol/L HCl and 1 mol/L NaOH solution, add 0.4 g/L adsorbent to the 50 mg/L TC dye solution, and shake to balance the adsorption After centrifugation, the supernatant was taken to measure the absorbance of TC, the removal rate was calculated, and the effect of initial pH on the adsorption was studied.

2.5 Recyclability experiment

Add 0.06g of BC and MBC to 150 mL, 100 mg/L of TC solution respectively. After the adsorption is saturated, place them in a H_2O_2 solution with a concentration of 0.003 mmol/L for desorption for 1 hour. After washing with deionized water several times Centrifuge, and then dry in a constant temperature drying oven at 60°C for 6 h. The dried samples were repeated four times in accordance with the above steps for recyclability experiments.

3 Results and discussion

3.1 Effect of adsorbent dosage

Add different masses of BC and MBC to a 100 mg/L tetracycline solution, and you can see the effect of BC and MBC dosage on TC adsorption as shown in the figure. It can be found that the unit adsorption amount of TC decreases with the increase of BC and MBC dosage. When the dosage increases from 0.1 g/L to 1.2 g/L, the unit adsorption capacity of BC and MBC on TC decreases from 149.8 mg/g and 201.2 mg/g to 29.3 mg/g

and 76.3 mg/g, respectively. The main reason is that under the condition of constant tetracycline concentration, although with the increase of the adsorbent dosage, its surface area and effective adsorption sites increase, but the increase of dosage will cause the utilization rate of BC and MBC to gradually decrease, and the unit adsorption The amount is then reduced. The adsorption effect of MBC on TC is much higher than that of BC. This may be because the magnetically modified MBC has a larger specific surface area and can provide more adsorption sites.

Fig. 1. Effect of adsorbent dosages on TC adsorption of BC and MBC.

3.2 Effect of contact time

The adsorption under different contact times and the subsequent time to reach adsorption equilibrium is an important parameter of the adsorption process. The influence of contact time on the adsorption effect of tetracycline is shown in the figure. At the initial stage of adsorption, the adsorption speeds of BC and MBC to TC are both faster. This is mainly due to the sufficient active sites on the surface of the initial adsorbent. As time goes by, the adsorbed material gradually fills the active sites of the adsorbent, and adsorption becomes more and more difficult, and the upward trend of adsorption slows down. Finally, BC and MBC reach adsorption equilibrium at 240 min and 90 min, respectively. They are 89.9 mg/g and 155.2 mg/g respectively. The magnetically modified MBC has a higher specific surface area and can provide more active sites for the adsorption of tetracycline. Therefore, MBC can not only reach the adsorption equilibrium faster, but also the adsorption equilibrium amount is much higher than that of BC.

Fig. 2. Effect of contact time on TC adsorption of BC and MBC.

3.3 Effect of pH

Solution pH plays a vital role in the adsorption process, because pH can change the existence of TC in the aqueous solution and affect the surface charge of the material, which in turn affects the adsorption behavior. Figure 3 shows the effect of pH on the adsorption capacity of BC and MBC. The results show that the adsorption capacity of BC and MBC both have a great influence. For BC and MBC, the adsorption capacity showed a gradual decrease as the pH value increased. When the pH value was 11.0, the adsorption capacity of BC and MBC were 35.3 mg/g and 82.1 mg/g, respectively. However, the adsorption capacity of MBC has always been higher than that of BC. This is mainly because the pore structure of MBC is richer, the aromaticity is enhanced, and the hydrophilicity and polarity are also increased, the surface functional groups are more abundant, and the oxygen-containing functional groups are increased.

Fig. 3. Effect of pH on TC adsorption of BC and MBC.

3.4 Recycling

The reusable performance of the adsorbent is an important indicator for evaluating whether the adsorbent has practical application value. As shown in the figure, the unit adsorption capacity of MBC and BC after 5 adsorption and desorption has decreased to varying degrees. This may be Because there are still some

adsorption sites in MBC and BC that are not completely desorbed, in addition, there will be a certain loss of MBC and BC during the separation process. It is worth mentioning that the unit adsorption capacity of MBC decreased from 97.8 mg/g to 29.1 mg/g after 5 times of adsorption and desorption. However, the unit adsorption capacity of NMBC decreased from 159.8 mg/g to 105.5 mg/g after 5 times of adsorption and desorption, and the unit adsorption capacity was still 141.2 mg/g after three times of adsorption and desorption. It can be seen that MBC has more advantages over BC in terms of reusability, MBC has good stability and reusability in 3 cycles, and MBC can be reused 3 times.

Fig. 4. the recyclability of BC and MBC

4 conclusion

(1) The dosage of adsorbent, adsorption time and pH have a great influence on the unit adsorption capacity of BC and MBC, and MBC shows more excellent adsorption performance, this is mainly because the pore structure of MBC is richer, the aromaticity is enhanced, and the hydrophilicity and polarity are also increased, the surface functional groups are more abundant, and the oxygen-containing functional groups are increased.

(2) The recyclability of magnetically modified MBC is better than that of BC, and it has higher application prospects.

Acknowledgements

This work was supported by the Science and Technology Project of Zhejiang Water Resources Department (NO. RC1830) and “the Fundamental Research Funds for the Colleges” (NO. FRF2019005).

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