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Preparation, Characterization and Adsorption Performance of Reed Biochar

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In this article, basic physical and chemical properties and apparent performance of the reed biochar prepared under different temperature conditions are studied, and the change of the adsorption time with the change of time, initial solution pH value, initial solution Pb2+ concentration for three kinds of biochar have been studied. The main study results are given below, in the preparation of these three kinds of biochar, with the rise of temperature, the biochar productivity decreases, ash content increases and pH value increases. With the rise of pyrolysis temperature, the percentage of the C and N elements of reed biochar increases, while the percentage of O and H elements decreases. BET specific surface area, Langmuir specific surface area, T-plot microporous specific surface area, and BJH adsorption accumulative specific surface area have manifested L500>L700>L300. There is the law of L500>L700>L300 for the quantity of nitrogen adsorption by biochar. The adsorption experiment has shown the best adsorption effect of biochar L500 being prepared at 500°C, the optimal adsorption condition is pH6, the adsorption time is 150min, and adsorption temperature is 25°C.

1. Introduction

Biochar is prepared through pyrolysis and carbonization of biomass in part or total lack of oxygen, has high carbon content and developed gap structure, capable of maintaining the nutrient and water content, and is an ideal soil conditioner (Lehmann et al., 2006; Liang et al., 2006) Biochar has very high anticorrosion stability, superhigh nutrient retaining capability, and has played a huge role in alleviating the greenhouse gas effect, soil improvement, environmental pollution alleviation, and resource utilization of solid wastes (Deng, 2012). The raw materials for the preparation of biochar come from various sources, and based on the consideration of environment-friendly and waste resource recycling and reutilization, the raw materials are mostly taken from the waste biomasses, such as wood cuttings, shell, cow dung and the organic wastes generated in the industrial and urban life. Such biochar prepared with the waste biomass is used for biological adsorption of the environmental recovery due to its excellent performance, so it has attracted more and more emphasis and attention (Sohi, 2009). Biochar has the unique surface properties for being the excellent adsorption material. From the microstructure, it may be seen that biochar is characterized by being loose and porous and large specific surface area, and the functional groups on the surface of biochar include carboxyl group, phenolic hydroxyl group and acid anhydride groups. These make biochar have good adsorption characteristics, and can influence and change the migration, transformation and ecological effect of the pollutants in the environment, and reduce the environmental risks (Jiang et al., 2013).
The basic nature of biochar is mainly influenced by the factors, such as raw materials, preparation temperature and preparation time. Due to the difference in raw materials, technical process and pyrolysis conditions, biochar has manifested very wide diversity in the physical and chemical properties, such as structural composition, pH, ash content, water content and specific surface area. Different biomass materials contain different specific gravity of cellulose, semi-cellulose and lignin, have different tissue structures and the porous structures of the carbides vary very significantly (Lehmann, 2007). At present, it is universally held in the academic field that the raw materials and pyrolysis temperature of biochar have the largest impact on the carbon physical and chemical properties and environmental functions, and the biochar precursor raw material constituents are the basis for deciding the biochar composition and nature, while the impact of biochar

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pyrolysis temperature on its environment application characteristics is always the hot point in study (Xie, 2011).

Reed is the typical wetland plant, and as a gramineous tall and perennial emergent aquatic and herbaceous plant, it has very wide adaptability and very strong stress resistance, and it is characterized by long growth season, quick growth and high production. Reed has very large aboveground biomass, and in Baiyangdian Reed Wetland, the aboveground dry mass of the reed is 6,000~7,500kg/hm^2. But, due to lack of economically efficiency resource utilization technology, the reed in the wetland system cannot be removed in a timely manner, and in case of natural decay and decomposition, the pollutants and nutrients will be released into the wetland system, resulting in the secondary pollution. Since reed is characterized by fast growth and large biomass, being suitable for acquisition and having low cost, it is the plant resource suitable for being processed into the biochar.

In this study, reed is prepared by using the raw materials through pyrolysis in different temperatures for the preparation of biochar, thus revealing the rules between biochar characteristics and preparation conditions, such as pyrolysis temperature and pyrolysis time, through the representation of the biochar characteristics, thus providing the basic evidence for the quotation and promotion of biochar. Besides, in this study, the adsorption performance and principle of biochar to Pb are also analyzed, and in this article, the new materials are provided for the environmental repair. At the same time, the adsorption performance and law of biochar to Pb has been analyzed. This article has developed the new technology of resource utilization for the wetland plant, and provided new information for the environmental recovery.

2. Materials and method

2.1 Preparation of biochar

The reed, as the test plant, is taken from Red Beach National Natural Reserve in Dawa County, Panjin City, Liaoning Province, and the sampling place is situated in the wetland of Erjiegou Town. Clean the plant, and then air-dry it for 72h. Then crush it, and place it into the electric heating oven for 1h drying. When it is cooled down to the room temperature, a proper amount of precursor raw material is weighed with the electric balance (accurate to 0.01g) into the combustion boat (self-produced) and then transferred into tube-type vacuum furnace for pyrolysis. Set different carbonization temperature (300°C, 500°C, 700°C) for carbonization, with the temperature increment of 5°C/min, and keep the temperature for 2h for each increment. Fill the high-purity nitrogen at the flow rate of 0.7L⁄min in the whole process. Let it cool down, and grind the sample, let it pass the 100-mesh sieve, thus obtain the biochar finished product, and place it into the sealed bag for storage. Mark them as the reed biochar (L300, L500, L700) respectively.

2.2 Method of characterization for the characteristics of biochar

Determine productivity of biochar: weigh the biochar before and after the treatment. Th ratio of the sample mass after the carbonization to the dry weight of raw material is the productivity;

Determine ash content of biochar: weigh about 1.0g biochar sample passing 100-mesh (accurate to 0.01mg), lay it flatly in the bottom of the porcelain crucible, place the open side into the muffle furnace, for ashing at 800°C for 4h, let it cool down to the room temperature, take it out and weigh it.

Calculate the ash content with the formula: $A=((G_2-G_1)/G)x100\%$

Where, A is the percentage of ash content in the sample, %; G is the content of biochar before the ignition, g; G1 is the mass of the empty crucible, g; G2 is the ash content and crucible mass, g.

Determine the pH value of biochar: refer to the method in Masulili (2010) for the determination method of biochar pH, that is, dilute biochar sample with the deionized water, for the preparation of 1% biochar suspension. Heat it to 90°C and fully stir it for 20min, so that the soluble constituents in biochar can be dissolved in the aqueous solution, finally let it cool down to the room temperature, and determine the corresponding pH value with pH meter. Determine the content percentage of C, H, N and O elements in reed biochar with vario Micro cube element analyzer (Elementar (Germany), model: vario Micro cube). According to BET method, determine the specific surface area and pore size distribution of reed biochar with the specific surface area and pore size distribution analyzers under the conditions of liquid nitrogen temperature (77K). Add the biochar passing the 100-mesh sieve into water, then add certain quantity of sodium oxalate to dissolve it, separate and suspend it in CNC ultrasonic cleaner, and take the suspension for the determination of the potential with ZETA potentiometric analyzer (brand: MALVERN, model: Nano-Z). Make the gold plating on a small amount of biochar samples, and attach them on the sample table, then observe the shape and surface characteristics of the sample with the scanning electron microscope (SEM). Determine the infrared spectrum of biochar with Fourier transformation infrared spectrometer.

2.3 Biochar adsorption capability and law

(1) Adsorption dynamic test
Weigh 0.1000g biochar sample into 150mL triangular flask, add 50 mL 20 mg·L^{-1} Pb^{2+} ion solution, where the concentration of background electrolyte $NaNO_3$ is 0.01mol·L^{-1}. Regulate the pH value of the solution to 5.5 by using the diluted HNO_3 and NaOH, vibrate it at constant temperature (25°C, 200 r·min^{-1}), determine the adsorption quantity of Pb^{2+} for the sampling at 5, 10, 15, 20, 30, 40 min, and 1, 2, 8, 16, 24, 30, 48 h, taking that without addition of biochar as the positive control, and the deionized water as the negative control.
(2) The influence of initial pH value of the solution on the adsorption rate
Weigh 0.1000g biochar sample into 150 mL triangular flask, where the concentration of background electrolyte $NaNO_3$ is 0.01 mol·L^{-1}, the initial mass concentration is 20 mg·L^{-1} Pb^{2+} solution 50mL. Regulate pH value to 2, 3, 4, 5, 6, 7, vibrate it at constant temperature (25°C, 200 r·min^{-1}) for 24h, filter it, and determine the final pH of the suspension, regulate the filtrate pH<2, determine the concentration of Pb^{2+}, taking that without addition of biochar as the positive control, and the deionized water as the negative control.
(3) Isothermal adsorption
Weigh 0.1000g biochar sample into 150 mL triangular flask. Where the initial pH value of the solution is 5.5, and the concentration of background electrolyte $NaNO_3$ is 0.01 mol·L^{-1}. Regulate Pb^{2+} mass concentration as 2.0, 5.0, 10.0, 20.0, 40.0, 80.0 mg·L^{-1} respectively, vibrate it at constant temperature for 24 h (200 r·min^{-1}), and determine the isothermal adsorption of biochar to Pb^{2+} at 25°C. Take the sample, filter it, regulate the filtrate pH<2, determine the concentration of Pb^{2+}. Take that without addition of biochar as the positive control, and the deionized water as the negative control. Calculate the adsorption of biochar to Pb^{2+} according to initial concentration and balance concentration of Pb^{2+}. Repeat the above tests for twice.
(4) Orthogonal test
According to the optimal single-factor test results, draft the three-factor and three-level orthogonal test, and survey the optimal adsorption conditions of the biochar.

3. Results and analysis

3.1 Reed biochar apparent performance and physical and chemical property analysis

(1) Productivity, ash content and pH value of reed biochar
The productivity, ash content and pH value of biochar at different pyrolysis temperature are shown in Table 1. With the rise of temperature, the biochar productivity decreases, ash content increases, and pH value rises. With respect to productivity, there is L300>L500>L700; with respect to ash content, there is L300<L500<L700; and with respect to pH value, there is L300<L500<L700. It indicates that with the rise of pyrolysis temperature, the material pyrolysis increases, the biochar productivity decreases, and ash content is gradually accumulated. At low temperature, high productivity of biochar is obtained because of low concentration of the fatty hydrocarbon substances in the raw material, and small escape of CH_4, H_2 and CO (Yang, 2007). At 300°C, biochar productivity is 26.24%, and when temperature rises to 700°C, the productivity decreases to 18.96%, with the decrease rate of about 28%. The biochar of the material has significant mass loss at 500°C~700°C, while has small mass loss at 300°C~500°C, so it may be inferred that, 500°C~700°C is the key interval for the mass loss of raw materials. With the rise of the pyrolysis temperature, pH value increases from 6.44 to 8.98, with the increase rate of 39%. As the soil conditioner, biochar can improve the pH value of the soil, and the increase of pH value in soil can inhibit the release of some greenhouse gases. Therefore, it is possible to alleviate the global warming trend by adding biochar into the soil.

Table 1: Productivity, ash content and pH value of biochar

Reed biochar	Productivity (%)	Ash content (%)	pH value
L300	26.24	6.10	6.44
L500	25.10	11.24	7.72
L700	18.96	11.43	8.98

(2) Biochar element composition analysis
The element composition and atomic ratio of reed raw material and biochar are shown in Table 2. With the rise of pyrolysis temperature, the percentage content of C and N elements of reed biochar increases, while the percentage content of O and H elements decreases. After pyrolysis of the raw material, the percentage content of C and N elements increases by comparison with that in the raw material, and the percentage content of O and H elements decreases by comparison with that in the raw material. By comparison with that at 300°C, that at 700°C has the percentage content of C element increased by 46%, percentage content of N element increased by 44%, percentage content of O element decreased by 85%, and percentage content of H

element decreased by 73%. The main reason is that a large amount of O element and H element has been lost due to the dehydration reaction, decarboxylic reaction and dehydroxylation reaction of cellulose, semi-cellulose and lignin in the reed raw material during the pyrolysis. A large amount of CO_2 has been produced during the pyrolysis of biomass, with the volatilization of some micromolecular organisms, and with the loss of some C element. But in general, more O element and H element has been lost, and the general trend is that percentage content of C element will increase with the rise of pyrolysis temperature. Kuhlbusch et al. defined H/C≤0.2 for black carbon (Graetz, 2003) and Graetz et al. thought that the biochar formed in high temperature had H/C≤0.5 (Schmidt and Noack, 2000). In this study, the biochar H/C is lower than 0.2 at all of these three temperatures, and with the rise of the pyrolysis temperature, H/C and O/C will decrease, indicating that the reed biochar products have high aromaticity and degree of curing, and good characteristics.

Table 2: Element composition and atomic ratio of reed biochar at different temperatures

Reed biochar	C(%)	H(%)	N(%)	O(%)	H/C	N/C	O/C
Raw material	44.80	6.20	0.41	43.25	0.14	0.01	0.97
L300	55.81	5.40	0.52	30.23	0.10	0.01	0.54
L500	74.46	3.12	0.68	9.09	0.04	0.01	0.12
L700	81.38	1.45	0.75	4.61	0.02	0.01	0.06

(3) Reed biochar specific surface area, microporous volume and pore size distribution

Refer to Table 3 for the specific surface area and average pore size of reed biochar under different preparation temperatures. The study has shown, BET specific surface area, Langmuir specific surface area, T-plot microporous specific surface area, and BJH adsorption accumulative specific surface area have been L500>L700>L300, and BET average pore size is L700>L300>L500. This has shown that at 500°C, the prepared biochar has large specific surface area, and strong adsorption potential.

Table 3: Reed biochar specific surface area and average pore size

	BET specific surface area (m^2/g)	Langmuir specific surface area (m^2/g)	T-plot microporous specific surface area (m^2/g)	BET Average pore size (nm)	BJH Adsorption accumulative specific surface area (m^2/g)
L300	1.2293	1.7923	0.0217	5.9316	0.420
L500	2.4487	3.5441	2.3531	5.1236	1.074
L700	1.4810	1.9811	0.0383	6.2375	0.534

(4) Adsorption and desorption of reed biochar to nitrogen under different pressures

The adsorption and desorption of the reed biochar prepared at different temperatures to nitrogen under different pressures have the similar laws, with the details shown in Fig. 1-Fig. 3. From the adsorption of biochar to nitrogen, it may be seen that, L500>L700>L300, which shows that at 500°C, the prepared biochar has good adsorption performance.

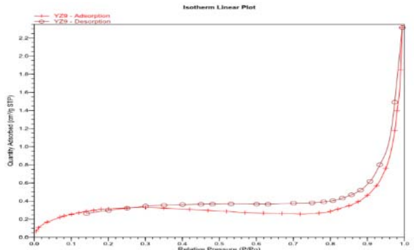

Figure 1: Adsorption and desorption of L300 to nitrogen at different pressures

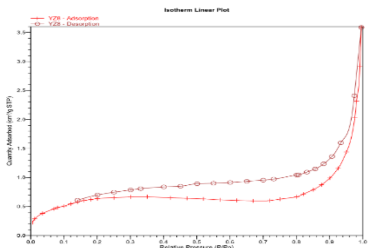

Figure 2: Adsorption and desorption of L500 to nitrogen at different pressures

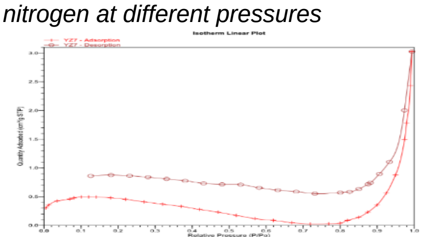

Figure 3: Adsorption and desorption of L700 to nitrogen at different pressures

(5) Potentiometric analysis
From Table 4, it may be seen that, there is the negative charge on the surface of three kinds of biochar, L500 has the biggest charge, and L700 has the smallest charge. The positive/negative and size of the charge on the surface of the biochar has decided the electric neutralization effect. So these three kinds of biochar have the capability of adsorbing positive charges, where L500 might have the highest adsorption capability.

Table 4: Potential of reed biochar

	Zata potential (mV)	Mob (μmcm/Vs)	Conductivity(mS/cm)
L300	-34.9	-2.735	-0.0559
L500	-35.4	-2.777	-0.0715
L700	-34.5	-2.702	-0.0354

3.2 Reed biochar adsorption performance analysis

(1) Influence of time, initial pH value of the solution and Pb^{2+} concentration on the biochar adsorption capability
Figure. 4-Figure. 6 have displayed the law for the change of adsorption rate of reed biochar prepared under different temperatures with the reaction time, initial solution pH value and Pb^{2+} concentration. From Fig. 4, it may be seen that, with the change of time, the adsorption rate of these three kinds of biochar is L500>L300>L700. With the extension of the time, the adsorption rate gradually increases, and after two hours, it basically tends to be stable. The maximum adsorption rate of the biochar to Pb^{2+} is up to 48%. From Fig. 5, it may be seen that, due to the difference of pH values of the initial solution, these three kinds of biochar have the adsorption rate L500>L700>L300. With the increase of pH value of the initial solution, the adsorption rate gradually increases, and when pH value reaches 6~7, the adsorption rate reaches the maximum level. The maximum adsorption rate of biochar to Pb^{2+} is up to 49%. From Fig. 6, it may be seen that, with the increase of Pb^{2+} concentration in initial solution, the adsorption rate increases, and these three kinds of biochar have the adsorption rate L500>L700>L300. When the Pb^{2+} concentration reaches 20mgL^{-1}, the adsorption rate reaches the maximum level, and then slightly decreases. The maximum adsorption rate of biochar to Pb^{2+} is up to 46%.

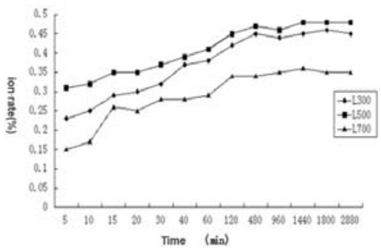

Figure 4: Influence of the time change on on the reed biochar adsorption rate

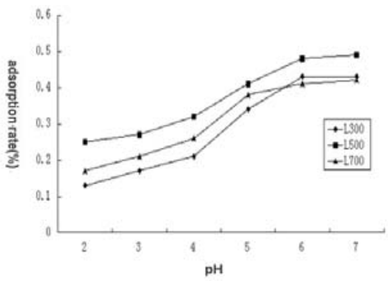

Figure 5: Influence of the change of initial solution pH value the reed biochar adsorption rate

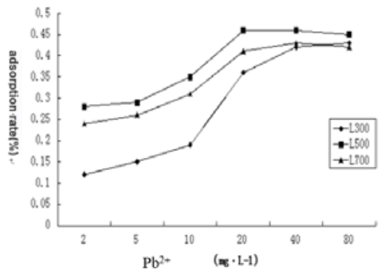

Figure 6: Influence of the Pb^{2+} concentration change on reed biochar adsorption rate

(2) Orthogonal test result analysis
This experiment is the three-factor and three-level orthogonal test for three kinds of biochar, where the three factors are temperature, time and pH value, and three levels are the optimal levels selected from the single factor experiments. The final experiment results have shown that biochar L500 prepared at 500°C has the best adsorption effect, and the optimal adsorption condition is pH6, adsorption time is 150min, and adsorption temperature is 25°C.

4. Conclusion and discussion

Biomass is mainly composed of cellulose, semi-cellulose, lignin and a small amount of organic extract and inorganic minerals. These constituents vary due to the types of biomass, and in addition, for specific biomass, the component proportion is highly influenced by the soil type, climatic conditions and collection time. the decomposition temperature of semi-cellulose is 200~260°C, the decomposition temperature of cellulose is 240~350°C, and the decomposition temperature of lignin is 280~500°C (Hamelinck, 2005). Therefore, the percentage of these constituents in the raw material influences the biochar activity and the structural change in the pyrolysis. For the given raw material, the factors influencing the biochar include heating rate, maximum pyrolysis temperature, maximum pyrolysis temperature retention time, pretreatment and device to be used, where the critical factor is the maximum pyrolysis temperature, because the release of the volatile and the forming and volatilization of the intermediate melt is closely related to the temperature. In this study, when the temperature rises to 500°C, the pyrolysis of the lignin structure has resulted in the sharp decrease of the biochar productivity to about 25.1%. Thus, when the characteristics of biochar meet its use, it shall be possible to realize the maximization of the productivity. While in the maximization of the productivity, it is required to determine the optimal pyrolysis temperature according to the type of the raw material. The adsorption rate of the biochar will change with the external conditions, and it is required to explore the external conditions for biochar adsorption rate to reach the maximum level.

The final experiment results in this study are given below: in the preparation of these three kinds of biochar, with the rise of temperature, the biochar productivity decreases, ash content increases and pH value increases. With the rise of pyrolysis temperature, the percentage of the C and N elements of reed biochar increases, while the percentage of O and H elements decreases. BET specific surface area, Langmuir specific surface area, T-plot microporous specific surface area, and BJH adsorption accumulative specific surface area have manifested L500>L700>L300. There is the law of L500>L700>L300 for the quantity of nitrogen adsorption by biochar. The adsorption experiment has shown the best adsorption effect of biochar L500 being prepared at 500°C, the optimal adsorption condition is the optimal adsorption condition is pH6, the adsorption time is 150min, and adsorption temperature is 25°C.

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