Experimental study on biochar modified characteristics

Yan-Ru Ma, Li-Ming Wang†, Wen-Yang Sun, Kang Feng and Yang Lv
College of Engineering, Heilongjiang Bayi Agricultural University
Daqing, China
E-mail:1114179963@qq.com

With agricultural waste corn cob, corn straw and sawdust as raw material, utilizing limited oxygen pyrolysis (400,500,600,700°C) of biochar. By NaOH and microwave modification, respectively by element analysis, Boehm titration method and scanning electron microscopy (sem) characterization of the composition and structure of biochar. The results showed that the corn cob, corn straw and sawdust three biochar, the content of each element of microwave modification and pH were higher than in NaOH modification of biochar. Biochar by NaOH modification in the indexes of yield, aperture and alkaline groups compared with the unmodified biochar are promoted. 700 °C after microwave modified corn stover biochar than other biochar has a larger specific surface area (131.57 m2 / g) and the smallest aperture (2.08 nm). After modified with NaOH, biochar basic reactive than other method to get a total of 103.51%-418.37% improvement, lactone base number were similar, carboxyl amount 30.27% - 133.73% of the decline, reduce 1.77% - 35.56% of the total acid group.

Keywords: Biochar; Modified; Specific Surface Area; Aperture; Functional Groups.

1. Introduction

Along with the rapid development of our country industry, more and more industrial wastewater containing heavy metal ion emission is not up to standard, caused serious pollution to soil and water. The adsorption is a important method in wastewater treatment process, has a wide range of applications. The main adsorbent with biochar, zeolite and bentonite, etc. Biochar because of its porous structure and huge specific surface area showed good adsorption performance. However, biochar is much by coconut shell, wood raw materials, such as preparation, the cost is higher, restricts its widespread application [1]. Therefore, development of efficient, low-cost adsorbent becomes the focus of current research. Biochar is to point to by a variety of biological materials by high temperature cracking by-product, namely the biological material in the case of lack of oxygen or less oxygen, after pyrolysis and charring effect and the solid matter [2]. Research suggests that biological carbon is added to the soil to improve soil nutrient elements intercept, encouraged the growth of beneficial

microorganisms and improve soil water, and promote the growth of crops [3]. Biological carbon prepared from waste biomass has strong adsorption ability, for organic pollutants and heavy metals have good adsorption effect (4-8). Biochar modification and application is the focus of the present study.

Based on waste corn cob, corn straw and sawdust as raw material with limited oxygen decomposition of biochar, prepared by using microwave method and NaOH reagent on the surface modification, respectively before and after the modification by Boehm titration method of characterizing the biochar, the research content of oxygen containing functional groups on the surface of biochar.

2. Materials and Methods

2.1 *Test materials and equipments*

Raw materials come from Heilongjiang daqing region surrounding farmland abandoned corn straw, corn cob and sawdust, NaNO3 (analysis), NaOH (analysis),HNO_3(analysis).

The instrument adopts element analyzer(Vario EI Elemental Analyzer, Germany),Specific surface area analyzer(NOVA4200e,United State),Infrared spectrometer(Nexus 670 FTIR, United State),and Scanning electron microscopy (SEM, EVO 18, Germany).Boehm titration method is used to quantitative analysis of the changes of surface oxygen containing functional groups of biochar.

2.2 *Test methods*

This experiment chooses the biochar adopt limited oxygen pyrolysis method, three kinds of biochar raw material of corn straw, corn cob and sawdust respectively. Natural materials will be dried to break into 5-10 cm of small pieces; all raw materials wash three times with tap water. Preparation of raw material called biochar take sifted 20g in a crucible, compaction, cover, and put into a muffle furnace carbonization, pyrolysis temperature set for 400,500,600,700°C , reached the final temperature after continued carbonation 0.5h, to be cooled to room temperature muffle taken out, polished, 100-mesh sieve to prepare a powder sample biochar.

(1) NaOH Modified

At room temperature, the solution preparation 5mol/LNaoH were taken biochar NaOH solution and 150mL pretreated 50g after mixing, stirring every 20 minutes, after soaking 8h, washed with deionized water until the filtrate was neutral by after drying oven 120°C , and different biological modifiers modified

carbon numbered. Weigh 0.5 g of different biological carbon tile in the bottom of the crucible placed in a muffle furnace open at 400°C ashing 2h, to obtain biological carbon ash, ash content calculated according to the mass balance.

(2) Microwave Modified

Select the same conditions carbonized charcoal biological sample, 20g of biochar charged into a quartz reactor and a vertical resonator, high purity N_2 sweep is turned 30min, the air in the reactor is discharged. Thereafter, the high-purity N_2 (flow rate of 500 mL / min) for the protection of gas was treated at 2min 800w microwave power. It cooled to room temperature under N_2 atmosphere, stored in a desiccator filled with N_2 standby.

3. Results and Analysis

3.1 *Analysis method*

Biological carbon surface characteristics analysis: The content of carbon, nitrogen and hydrogen in the biological carbon was measured by the element analyzer (Vario EI Elemental Analyzer, Germany. The content of oxygen element is calculated after deducting ash. Determination of specific surface area of biomass (BET-N_2 method) by specific surface area analyzer (NOVA4200e, United State). Under the liquid nitrogen temperature (77 K), the adsorption of the adsorbent on the high purity liquid nitrogen was determined, and the sample was 200 h under the condition of 24h before the analysis. Calculation of specific surface area by multi point BET method. Using infrared spectrometer (Nexus 670 FTIR, United State) Determination of biological carbon infrared spectra, scanning range from 400 to 4000cm^{-1}, resolution 4.0cm^{-1}. The surface morphology of bio carbon was observed by scanning electron microscope (SEM, EVO 18, and Germany). The surface acidity was determined by Boehm titration method.

3.2 *Basic physical and chemical properties of biological carbon*

Table 1 Comparison of the elements content, pH and EC in different preparation methods. Select 700°C prepared by pyrolysis of corn cob, corn straw and sawdust biochar was modified. The results showed that the modified biological carbon element content, pH, EC and raw materials, different modified biochar pH and EC have varying degrees of increase, microwave modification of biological carbon elements content and pH were higher than that of NaOH instead of biochar.

Table 1. The content, pH and EC of the biocarbon elements obtained by different preparation

Biocarbon	treatment	C%	H%	N%	S%	pH	EC ms/cm
	No Modificated	71.12	2.3	0.75	0.3	9.13	0.94
Corn cob Biocarbon	NaOH Modificated	63.53	2.62	0.77	0.09	9.80	——
	Microwave Modificated	73.69	1.8	0.75	0.11	10.54	1.22
	No Modificated	56.57	3.11	0.56	0.81	10.13	2.18
Corn straw biocarbon	NaOH Modificated	54.12	2.37	0.48	0.37	10.35	——
	Microwave Modificated	67.32	3.03	0.51	0.42	10.77	2.87
	No Modificated	79.36	1.77	1.23	0.14	9.53	0.27
Sawdust biocarbon	NaOH Modificated	72.69	2.61	0.64	0.07	9.85	——
	Microwave Modificated	85.61	1.73	0.85	0.1	10.04	0.3

3.3 *The structural characteristics of biochar*

The physical and chemical properties of different raw materials and different preparation conditions are different. As shown in Figure 1 and Figure 2, by sodium hydroxide modified biological carbon in the yield, aperture, basic groups and other indicators compared to unmodified biochar has been on the rise, due to the NaOH particle attached on the surface of biological carbon, resulting in decreased specific surface area. The pore size, specific surface area and unmodified biomass of the modified biological carbon were not different. With the increase of pyrolysis temperature, the specific surface area of the char is increasing, and the pore size is decreasing. Compared with other biological activated carbon, the corn stalks of 700 degrees C after microwave modification had larger specific surface area (131.57m^2/g) and the smallest pore size (2.08nm).

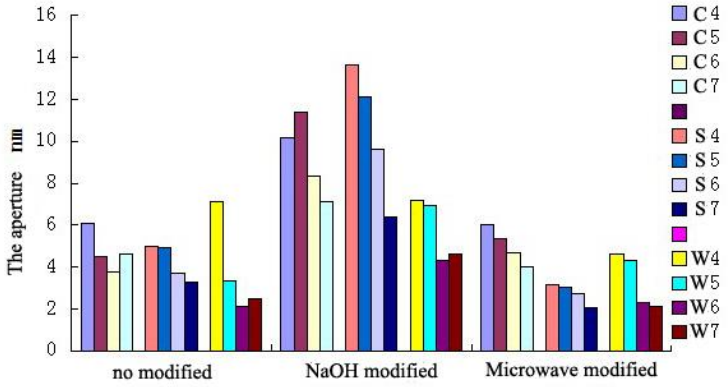

Fig. 1. Different kinds of biocarbon.

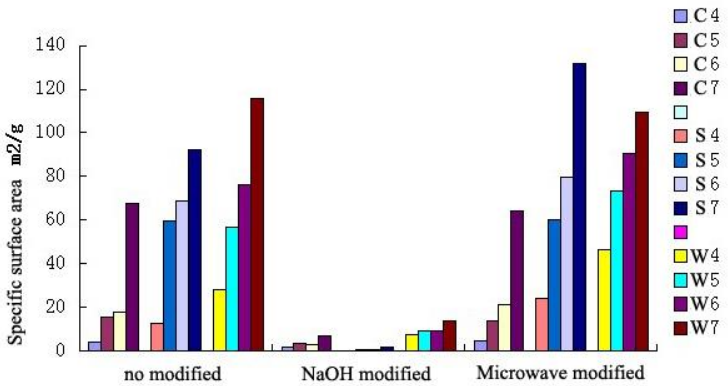

Fig. 2. Specific surface area of different types of biocarbon.

3.4 *Analysis of surface functional groups of different kinds of biological carbon*

The number of basic groups increased with the increase of pyrolysis temperature, and the number of acidic groups such as carboxyl group and carboxyl group decreased. Compared with unmodified and modified NaOH, the number of basic groups, carboxyl groups and carboxyl groups were significantly different from those of modified activated carbon. After NaOH modified, biochar, the total number of basic groups than other methods have 103.51 - 418.37% ascension, lactone number is vary little. 133.73% 30.27% decline in the number of carboxyl and total acidic group is 1.77% 35.56% reduction.

4. Conclusion

(1) Corn cob, corn straw and sawdust three biological activated carbon, microwave modification of the element content and pH value were higher than that of NaOH modified biological carbon.

(2) After NaOH modification of biological carbon in yield, pore size, alkaline groups and other indicators compared to unmodified biological carbon have increased. Compared with other biological activated carbon, the corn stalks of 700 degrees C after microwave modification had larger specific surface area (131.57m2/g) and the smallest pore size (2.08nm).

(3) After NaOH modified, biochar, the total number of basic groups than other methods have 103.51 - 418.37% ascension, lactone number is vary little. 133.73% 30.27% decline in the number of carboxyl and total acidic group is 1.77% 35.56% reduction.

References

1. Zhang Yang,Zi fu Li, Zhang Lin, and so on. The modified cotn cobs biological carbon adsorption characteristics of ammonia nitrogen[J].Journal Of Chemical Industry, 2014.
2. Li Jihui, modified biochar nitrate and phosphate adsorption study [D]. The Chinese Academy Of Agricultural Sciences, 2012
3. Ennis Christopher J, Evans A Garry, Islam Meez, et al. Biochar: carbon sequestration, land remediation, and impacts on soil microbiology [J]. Crit. Rev. Env. Sci. Tec., 2011, 42(22): 2311-2364
4. Chen Xincai, Chen Guangcun, Chen Linggui, et al. Adsorption of copper and zinc by biochars produced from pyrolysis of hardwood and corn straw in aqueous solution [J]. Bioresource Technol., 2011, 102(19): 8877- 8884
5. Chen Baoliang, Zhou Dandan, Zhu Lizhong. Transitional adsorption and partition of nonpolar and polar aromatic contaminants by biochars of pine needles with different pyrolytic temperatures [J]. Environ. Sci. Technol., 2008, 42(14): 5137-5143
6. Chun Yuan, Sheng Guangyao, Chiou Cary T, et al. Compositions and sorptive properties of crop residue-derived chars [J]. Environ. Sci. Technol., 2004, 38(17): 4649-4655
7. Wang Hailong, Lin Kunde, Hou Zhenan, et al. Sorption of the herbicide terbuthylazine in two New Zealand forest soils amended with biosolids and biochars [J]. Journal of Soils and Sediments, 2010, 10(2): 283-289
8. Yang Yaning, Sheng Guangyao. Enhanced pesticide sorption by soils containing particulate matter from crop residue burns [J]. Environ. Sci. Technol., 2003, 37(16): 3635-363