Research on the Transformation of Nitrogen during Hydrothermal Carbonization of Sludge

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Abstract. The nitrogen in the sludge mainly exists in the form of inorganic nitrogen and organic nitrogen. In this paper, the transformation of nitrogen during the hydrothermal carbonization of sludge was studied. The results showed that during the hydrothermal carbonization of the sludge, both the total nitrogen and the inorganic nitrogen in hydrochar decrease with the increase of the carbonization temperature. The reason is that part of the inorganic nitrogen compounds in the sludge undergoes thermal decomposition to release NH_3, and some organic nitrogen will be hydrolyzed to produce ammonia nitrogen into the liquid phase.

1 INTRODUCTION

The sludge produced by sewage treatment plants has soared worldwide in recent years. At present, sludge production in China is estimated to reach 6 million dry tons every year [1]. Sludge is rich in nutrients (nitrogen, phosphorus, potassium, etc.) and available organics (such as protein, sugar, fat, etc.). The nitrogen in the sludge mainly exists in the organic and inorganic forms. The organic nitrogen is mainly nitrogen-containing functional groups, such as protein nitrogen, pyridine nitrogen, pyrrole nitrogen, etc, while the inorganic nitrogen is mainly ammonium nitrogen, nitrate nitrogen and nitrite nitrogen[2].

Hydrothermal carbonization is a thermochemical treatment method that converts solid biomass to carbon-enriched solid carbon materials at a temperature of 180 °C to 350 °C and a pressure of 2-10 MPa in the presence of liquid water [3]. After the sludge is hydrothermally carbonized, the produced hydrochar may have many kinds of applications. In particular, the sludge is rich in nitrogen elements, which can be transformed to form inorganic nitrogen or redox functional groups after hydrothermal carbonization. The conversion of the nitrogen elements has an important influence on subsequent reuse. For example, sludge hydrochar can be used as a soil conditioner due to that inorganic nitrogen, such as ammonium nitrogen and nitrate nitrogen, is available for plant absorption and utilization. In addition, the sludge hydrochar also has a good application in adsorption, and some of its surface nitrogen, oxygen and sulfur functional groups can be used to adsorb heavy metals in water [4]. The sludge hydrochar can also be used as fuel. When the sludge is hydrothermally carbonized, its calorific value will increase [5]. However, nitrogen in the combustion process may form some NOx when the sludge hydrochar is used as fuel, which is a problem to be considered during thus application. In summary, the changes of nitrogen content and form have an important influence on the application of sludge hydrochar. It is of great significance to study the transformation of nitrogen during sludge hydrothermal carbonization. In this paper, the changes of nitrogen content and form in solid phases were determined after hydrothermal carbonization of sludge under different conditions, and the possible conversion pathways of nitrogen were proposed.

2 METHODS

2.1 Sludge samples

The dewatered sludge samples used in this study were taken from a sewage treatment plant in Shanghai. After the sludge samples were collected, they were baked in an oven at 105 °C for two days, then ground through 100 mesh screens and sealed.

2.2 Experimental method

Weigh 10 g of original sludge sample into a beaker, add 60 ml of deionized water, stir it with a magnetic stirrer for 1 h. Then pour it into a hydrothermal dish, pass nitrogen gas at a flow rate of 100 ml/min for 15 min to exhaust the oxygen in the system, and then quickly cap and place it in a high-pressure reactor for completely sealed. Then put it in a constant temperature drying oven and the temperature is raised at a certain rate. When the temperature reaches a certain degree, the temperature is fixed for a period of time.

After reaching the carbonization time, remove the

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autoclave and cool it to room temperature, then pour it into a 100 ml centrifuge tube and centrifuge it in a centrifuge at 3000 r/min for 10 min. The liquid phase product is transferred to a centrifuge tube and stored in a refrigerator. At the same time, the solid product was dried in a thermostatic drying oven at 105 °C to a constant weight. After that, the resulting solid product was ground through a 100 mesh sieve and stored for future use.

The total nitrogen content in hydrochar was determined by alkaline potassium persulfate oxidation-ultraviolet spectrophotometry. The hydrochar sample was digested by high pressure in the presence of potassium persulfate to convert nitrite, ammonium, and organic nitrogen into nitrate. The absorbance was measured at 220 nm and 275 nm on an ultraviolet spectrophotometer, and the total nitrogen of the sample was calculated. The ammonium nitrogen content in hydrochar was determined by the method of nessler's reagent. The basic solution of mercury iodide and potassium iodide reacts with ammonia to produce a light yellow-brown colloidal compound. Its color intensity is proportional to the ammonia nitrogen content, and the absorbance is usually measured at a wavelength of 410 nm-425 nm to calculate the content of ammonium nitrogen in hydrochar.

3 RESULTS AND DISCUSSION

3.1 The proportion of different forms of nitrogen in sludge samples

Table 1. The proportion of each form of nitrogen in sludge samples.

	Sludge samples
Total nitrogen (%)	100%
Inorganic nitrogen	12.00%
Organic nitrogen	88%

It can be seen from Table 1 that the forms of nitrogen in sludge mainly include inorganic nitrogen (mainly ammonium nitrogen and nitrate nitrogen) and organic nitrogen (mainly protein nitrogen, pyrrolic nitrogen, and pyridine nitrogen). The content of organic nitrogen accounts for 88 % of the total nitrogen in the sludge. This is because organic nitrogen mainly contains protein nitrogen, pyrrole-N and pyridine-N. The sludge contains a lot of microorganisms, and the microbial cells themselves contain a lot of protein where the protein nitrogen is derived. Inorganic nitrogen accounted for 12.00% of the total nitrogen in the sludge. Among them, pyrrole nitrogen and pyridine nitrogen are derived from the decomposition products of nucleic acids during the carbonization of sludge.

3.2 Analysis of nitrogen in sludge hydrothermal product

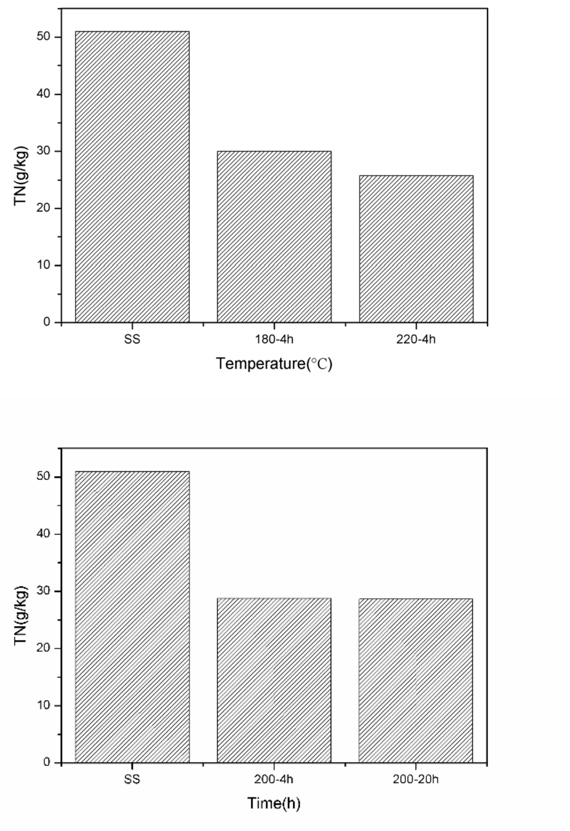
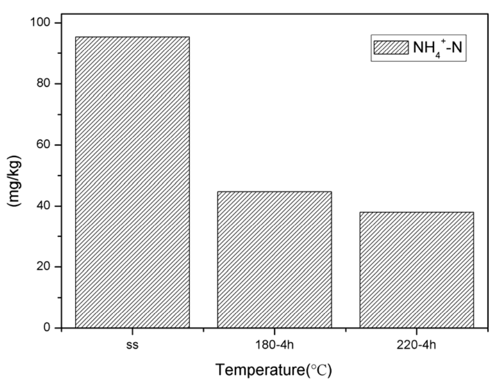


Figure 1. Total nitrogen content in raw sludge and its hydrochar under different carbonization conditions.

As shown in figure 1, the total nitrogen content in the raw sludge was 50.98 g/kg. After hydrothermal carbonization, the total nitrogen content decreased. With the carbonization temperature rising from 180 °C to 220 °C, the total nitrogen content in the hydrochar was decreased from 30.00 g/kg to 25.74 g/kg. With the increase of the carbonization time from 4 h to 20 h, the total nitrogen content is basically unchanged. The reason is that in the process of hydrothermal carbonization, the inorganic nitrogen in the sludge undergoes thermal decomposition to release NH_3, and the organic nitrogen in the sludge is decomposed into ammonia nitrogen and enters to the liquid phase. With the increase of carbonization temperature, more inorganic nitrogen is decomposed due to the increase of its gas yield. Therefore the total nitrogen content is decreasing.



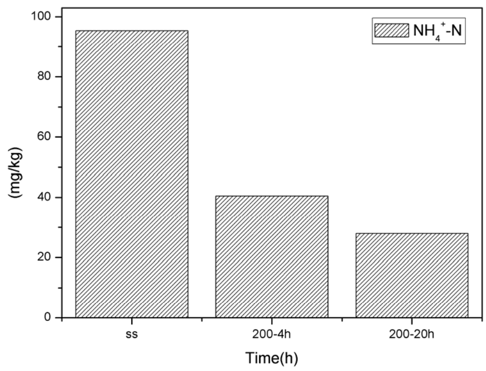


Figure 2. NH_4^+-N content in raw sludge and its hydrochar under different carbonization conditions.

As shown in figure 2, the content of NH_4^+-N in raw sludge was 95.37 mg/kg. The inorganic nitrogen content decreased after hydrothermal carbonization. With the hydrothermal carbonization temperature rising from 180 °C to 220 °C, the content of NH_4^+-N in hydrochar decreased from 44.75 mg/kg to 37.99 mg/kg. And with the increase of the carbonization time from 4 h to 20 h, the content of NH_4^+-N in hydrochar decreased. The reason is that some inorganic nitrogen compounds in the sludge undergo thermal decomposition to release NH_3 at a temperature of 100 °C to 300 °C. With the increase of the carbonization temperature and carbonization time, the gas yield increases. Therefore the inorganic nitrogen content in the hydrochar tends to decrease.

4 Conclusion

Most of the nitrogen in the sludge is organic nitrogen, and it contains a small amount of inorganic nitrogen (mainly ammonium nitrogen and nitrate nitrogen). After hydrothermal carbonization of the sludge, the total nitrogen and inorganic nitrogen content in the solid phase are reduced. The reason is that during the hydrothermal carbonization of the sludge, part of the inorganic nitrogen undergoes thermal decomposition to release NH_3, and some organic nitrogen will be hydrolyzed to produce ammonia nitrogen into the liquid phase.

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