



Migration and transformation mechanism of nitrogen in the biomass–biochar–plant transport process

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ABSTRACT

In this paper, we reviewed several biochar studies to systematically examine the complete transport of nitrogen from biomass to biochar to plants. The results can be summarised as follows. (1) Nitrogen from biomass to biochar: the pyrolysis temperature of high-quality biochar for soil improvement is approximately 400 °C, the best preparation atmosphere is CO₂, and the retention rate of nitrogen in biochar is greater than 64.94%. More than 70% of the nitrogen in straw exists in the form of proteins, while the remainder is in the form of alkaloid-N, free amine-N, and inorganic NH₄⁺-N. When biochar is prepared from straw, the organic nitrogen species are pyrrole-N (43.75%), pyridine-N (22.69%), amino-N (11.25%), and nitrile-N (7.48%). In addition, inorganic nitrogen is present as NH₄⁺-N (14.82%). (2) Nitrogen from biochar to soil: there are two main functions of biochar applied to soil. First, biochar reduces nitrogen leaching from the soil. Second, biochar increases the soil nitrogen content linearly with the amount of biochar applied ($R^2 = 0.9767$). (3) Nitrogen from biochar to crops: biochars prepared from straw under different pyrolysis conditions were applied to soil, and crops were cultivated. We found that crops grew best in soil treated with biochar prepared at 400 °C under CO₂ atmosphere. The effect of adding straw biochar to the soil is significantly better than the direct addition of plant matter (straw). This paper focuses on the systematic study of the complete nitrogen cycle; that is, nitrogen is taken from plants and then returned to plants. In this way, this study can not only help make full use of biochar to improve soil fertility but also has great significance for biomass energy utilisation, especially for the divided utilisation of biomass energy elements (C and H) and nutrient elements (N and S).

1. Introduction

Nitrogen is the most important nutrient for the growth of crops, and the contribution of nitrogen fertiliser to increasing agricultural production in developed countries is more than 40% [1], while in developing countries, it is as high as 55% [2]. In the 1960s, Steiner et al. [3] found that biochar increased not only the fertility of Amazonian soil but also the amount of nitrogen absorbed by plants, which increased from 280% to 400%. Since then, the effect of biochar on increasing soil fertility has been gradually recognised. Biochar is an abbreviation of bio-charcoal and became the unified name for this material at the first International Conference on Biochar in Australia in 2007 [4]. Biochar is the solid remnant of pyrolysis and is formed by heating biomass at high temperatures under hypoxic conditions [5,6]. Previous studies have shown that biochar has excellent properties, such as an enormous specific surface area, rich pore structure, and strong adsorption capacity, which can reduce the loss of nutrients by absorbing nutrient ions, preventing leaching from the soil [7]. Consequently, to date, research has mostly focused on the impact of biochar on nitrogen leaching

(Table 1), and the nutrient elements in biochar itself have not been investigated. Existing studies concerning the nutrient elements in biochar have only investigated the preparation and nutrient return processes of biochar and have lacked systematic analysis and comparison.

In fact, biochar is rich in many kinds of nutrients and can play a vital role in improving soil fertility. In addition, China has an abundance of biochar resources. For example, more than 700 million tonnes of straw is produced annually – an equivalent nitrogen fertiliser amount of 350 million tonnes [8]. Therefore, starting from the preparation of biochar, we studied the transformation and migration process of nitrogen from biomass to biochar and then to plants. This review not only provides an effective basis for tracking the fate of nitrogen in biochar but also lays the foundation for improving the utilisation of nitrogen.

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Table 1
The effect of biochar on nitrogen leaching from soils.

Experimental type or material	Type and amount of biochar	Experimental results	References
A simulation test of soil column leaching.	Eucalyptus biochar; the application was 1%.	Effectively reduced the leaching of ammonium nitrogen ($\text{NH}_4^+\text{-N}$) and nitrate nitrogen ($\text{NO}_3^-\text{-N}$).	[9]
Soil column leaching, isothermal adsorption experiment of ammonium nitrogen ($\text{NH}_4^+\text{-N}$).	Biochar was added to soil at a rate of 1, 3, and 5%.	The leaching loss of ammonium nitrogen ($\text{NH}_4^+\text{-N}$) in yellow-brown soil was decreased by 22, 39, and 47%, respectively.	[10]
Leaching of ammonium nitrogen ($\text{NH}_4^+\text{-N}$).	The application of biochar was 5%.	When 5% biochar was added to the silt loam, the leaching loss of ammonium nitrogen ($\text{NH}_4^+\text{-N}$) was effectively reduced.	[11]
Indoor leaching and pot experiments.	Membrane coated with bamboo biochar.	The membrane coated with bamboo biochar reduced the leaching loss of nitrogen and improved the utilisation rate of nitrogen by 10–25%.	[12]
Adsorption experiments.	Bamboo biochar.	In a 20-cm soil layer, the loss of $\text{NH}_4^+\text{-N}$ was reduced by 15.2%.	[13]
Leaching of ammonium nitrogen ($\text{NO}_3^-\text{-N}$).	The application of biochar was 7%.	Reduced the loss of nitrate nitrogen ($\text{NO}_3^-\text{-N}$) and total nitrogen caused by runoff losses from the soil, thus improving the quality of the runoff.	[14]
Soil leaching experiment in chernozem and purple soil.	Addition of 50 and 100 t/ha biochar.	Reduced the leaching of nitrogen by 29% and 74% in chernozem and 41% and 78% in purple soil, respectively.	[15]

2. Conversion of nitrogen-containing species during the process of biochar preparation (biomass to biochar)

2.1. Biomass pyrolysis for energy products (biochar, biogas and biooil)

Biomass refers to the various organisms produced by photosynthesis, and it is the only renewable carbon source on Earth [16]. In recent years, with the development and application of renewable energy, biomass pyrolysis and carbonisation technology has developed rapidly and become a hot topic in academia. Nader et al. [17] found that when the pressure was 20 P, the yield of pyrolysis products (biogas, biooil and biochar) produced from wheat straw is the highest. Wu et al. [18] observed that when the temperature was in the range of 450–500 °C, the calorific value of biogas prepared by maize straw is higher, approximately 1.3–1.7 kJ/m³. The research of Wang et al. [19] showed that the mixed pyrolysis of corn and millet straw is useful for biooil production. Zhang [20] suggested that to produce more biochar by rapeseed pyrolysis, the pyrolysis temperature should be 400 °C. Moreover, some scientific research groups have performed many studies on optimising the heat carrier, catalyst, solvent, reaction conditions, etc. [21–27] to improve the yield and quality of biooil. In view of this, most studies on biomass pyrolysis were performed to obtain more energy products and didn't consider the ability of biochar to improve soil fertility. There is no systematic research on the preparation conditions of biochar with good quality for nutrient translocation.

As early as the 19th century, Amazon Valley ancestors discovered that cultivating crops on special black soil called “Terra Preta” could increase production. Studies have shown that the black soil is rich in stable biochar, which is the main cause of the increased soil fertility and crop yield [28–30]. Therefore, the ability of biochar to improve soil has attracted worldwide attention. In the 1990s, the whole world began to research biochar preparation technology [18], hoping to improve soil fertility by applying large-scale biochar to fields. However, biochar was prepared by conventional pyrolysis techniques developed with the aim of energy products, which resulted in a non-obvious effect of biochar on the soil fertility and crop production, and even negative effects appeared [31]. Kishimoto et al. [32] found that when 5 t hm⁻² and 15 t hm⁻² biochar was applied to soil, the yield of soybean decreased by 37% and 71%, respectively; too much biochar will reduce the yield of crops that are sensitive to pH, such as corn and so on. Zhang et al. [33] suggested that biochar observably inhibits the growth of maize at the seedling stage [34]. The reason for this negative effect was partly due to the loss of nutrient elements (mainly nitrogen) during the conventional pyrolysis preparation of biomass.

This paper is very important for biomass energy utilisation, especially for the divided utilisation of biomass energy elements (C and H) and nutrient elements (N and S), and will help us develop better thermal chemical transfer processes in biomass for energy utilisation. Fig. 1 shows the significance of the divided utilisation of biomass

elements.

2.2. Nitrogen in biomass

2.2.1. The nitrogen content of biomass

Biochar has a wide range of sources, from agricultural waste, such as wood and straw, to organic waste produced by industrial and municipal activities, such as garbage and sludge (although other waste materials can be used as raw materials for biochar preparation) [35,36]. Biochar is classified according to the source of the raw material, for example, charcoal, bamboo charcoal, straw charcoal, rice husk carbon, animal faecal charcoal, etc. [37,38]. At present, biomass is the most important raw material for biochar preparation.

The content of nitrogen in biomass is not low, between 0.02% and 2.5%, which is close to that in coal (0.2–2.5%) [39]. Because there are many kinds of natural biomass, the content and distribution of nitrogen in biomass from different sources differs significantly. The nitrogen contents in common biomass sources are listed in Table 2 [40].

As shown in Table 2, the source materials for biochar preparation are quite varied and include agricultural waste and herbs. There are differences in the nitrogen content of different raw materials; for example, the nitrogen content in wheat stalks, rice husk, corn cobs, and other commonly used materials is relatively low, less than 1.5%. Therefore, some studies have shown that biochar can only improve the nutrient content in nutrient poor soils and has a smaller effect on fertile soils [65].

2.2.2. The nitrogen species in biomass

Lv et al. [66] showed that the content of nitrogen in biomass is between 0.5% and 1.5%, and 80–85% of this nitrogen is present in the form of proteins, 10% in the form of nucleic acids, and 5% in the form of water-soluble ammonia compounds [67]. Many researchers have tried to determine the nitrogen species in biomass directly using methods such as NMR, X-ray absorption near edge structure (XANES) spectroscopy, and X-ray photoelectron spectroscopy (XPS), although this has proven very difficult, yielding results with significant uncertainty. Consequently, current investigations into the nitrogen species in biomass mostly use indirect inference methods [40]; that is, they infer the speciation of nitrogen in biomass by studying the pyrolysis products of biomass. However, some researchers still use direct measurement methods [68]. Tian et al. experimented with sludge, finding that the species of nitrogen in sludge are mainly divided into four types: pyrrolic-N, protein-N, amine-N, and pyridinic-N. The nitrogen content in sludge was analysed by examining the XPS survey spectrum, and four peaks were obtained by fitting. The nitrogen contents of the four species were similar (Table 3), in which pyrrolic-N was derived from proteins, amine-N was derived from carbohydrates, and pyrrolic-N and pyridinic-N were derived from the decomposition of nucleic acids [69]. The process of sludge pyrolysis mainly produced heterocyclic-N, amine-N,

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