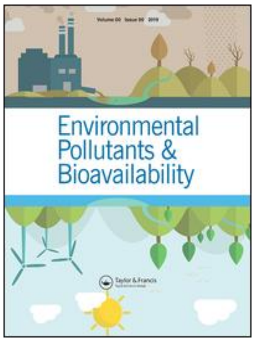

Environmental Pollutants and Bioavailability

ISSN: (Print) 2639-5940 (Online) Journal homepage: https://www.tandfonline.com/loi/tcsb21

Nutrient stability and sorption of sewage sludge biochar prepared from co-pyrolysis of sewage sludge and stalks / mineral materials

Xing-Yu Duan, Yang Cao, Tao-Ze Liu, Ling Li, Bing Wang & Xiao-Dan Wang

To cite this article: Xing-Yu Duan, Yang Cao, Tao-Ze Liu, Ling Li, Bing Wang & Xiao-Dan Wang (2020) Nutrient stability and sorption of sewage sludge biochar prepared from co-pyrolysis of sewage sludge and stalks / mineral materials, Environmental Pollutants and Bioavailability, 32:1, 12-18, DOI: 10.1080/26395940.2019.1710259

To link to this article: https://doi.org/10.1080/26395940.2019.1710259

Published online: 03 Jan 2020.

ENVIRONMENTAL POLLUTANTS AND BIOAVAILABILITY
2019, VOL. 32, NO. 1, 12–18
https://doi.org/10.1080/26395940.2019.1710259

Taylor & Francis
Taylor & Francis Group

Nutrient stability and sorption of sewage sludge biochar prepared from co-pyrolysis of sewage sludge and stalks / mineral materials

Xing-Yu Duan[a,b], Yang Cao[a], Tao-Ze Liu[b,c], Ling Li[b], Bing Wang[b] and Xiao-Dan Wang[c]

[a]School of Chemistry and Chemical Engineering, Guizhou University, Guiyang, China; [b]State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, China; [c]Institute of Karst Wetland Ecology, College of Eco-Environmental Engineering, Guizhou Minzu University, Guiyang, China

ABSTRACT
The pyrolysis treatment can effectively reduce the sewage sludge volume and fix its nutrients for land application. The synergistic effect on the fixation of nutrients can be better exerted by the sewage sludge biochars (SSB) prepared by the co-pyrolysis method. In this study, SSB was prepared by adding stalks and mineral materials in to sewage sludge that was used as the base material. The element composition, nutrient stability, and adsorption effect of SSB, as well as the feasibility of applying modified SSB in reducing soil nutrients leaching, were discussed in this study. The results indicate that the modified SSB reduced the amount of nitrate leaching and has the ability to remove nutrients in the solution, among which the removal effect of nitrate is better. Moreover, the modified SSB is added to the soil by leaching experiments in soil columns, which can reduce the leaching of nutrients.

ARTICLE HISTORY
Received 14 August 2019
Accepted 19 December 2019

KEYWORDS
Sewage sludge biochar; Nutrients; Removal; Leaching

1. Introduction

The sewage sludge is rich in organic matter, nitrogen, and phosphorus; the soil fertility can be effectively improved when it was applied to the soil. Therefore, the on-land disposition is the main method of sewage sludge treatment [1]. However, it would cause secondary pollution and harm the environment if the sludge is directly entered into the soil without treatment because dehydration is difficult and contains a large number of pathogens and microorganisms [2]. Therefore, how to deal with sludge has become a hot social issue.

Recent studies have revealed that the preparation of biochar from sludge through pyrolysis can effectively reduce the volume of sludge, remove or passivate harmful substances, and kill pathogenic bacteria in the sewage sludge; it is a clean and efficient sewage sludge disposal method [3–5]. Sewage sludge biochar not only maintains its fertility but also has a good pore structure that makes it have good adsorption performance [6]. Applying it to the soil improves soil texture and slows the release of nutrients from the soil [7].

There are many advantages to treating sewage sludge by pyrolysis. However, the addition of biomass and mineral materials co-pyrolysis has significant effects on improving the nutrient content and stability of biochar compared with the single sewage sludge pyrolysis treatment method [8,9]. Besides, co-pyrolysis can not only reduce the water content of sludge and improve the quality of SSB but also synergistically promote the process of sludge pyrolysis [10].

In this paper, SSB was prepared by adding different stalks and mineral materials for co-pyrolysis; the nutritional stability of SSB was investigated. Simultaneously, the nutrient leaching, removal effect of nitrate, ammonium, and phosphate in aqueous solution, and slow-release in soil were studied by performing adsorption and soil column leaching experiments [11]. Thus, the retention of fertilizer efficiency and the improvement of the adsorption performance of SSB were explored to provide a reference for the resource utilization of sewage sludge.

2. Materials and methods

2.1. Materials

The sludge was taken from a sewage treatment plant in Guiyang. Manganese ore powder (MO), graphite powder (GP), and clay (CB) were purchased from Tianjin Beilian fine chemical Co., Ltd. KNO_3, NH_4Cl, and KH_2PO_4 were purchased from Fisher Scientific. Maize stalk (MS), tobacco stalk (TS), and chili stalk (CS) were collected from the Guiyang city suburb. The stalks were oven-dried (80°C) after rinsed with water. Then, all stalks were crushed over 10 mesh screen and stored in a dryer for later use.

2.2. Characterizations

The total contents of carbon (C), nitrogen (N), and hydrogen (H) in the biochar samples were analyzed with an elemental analyzer (Perkin Elmer PE2400 series II). Major

CONTACT Yang Cao caoyang@gzu.edu.cn; Tao-Ze Liu liutaoze@foxmail.com

inorganic elements were determined by acid digestion of the samples followed by an X-ray fluorescence spectrometer (WD-XRF) (Axios mAX, PANalytical).

2.3. Preparation and characterization of sewage sludge biochar

The sewage sludge-stalks (MS, TS, CS) were mixed at a mass ratio of 5:1 (stalk 20%). Sewage sludge-mineral materials (MO, GP, CB) were mixed in mass ratios of 15:1 (ore 6.67%) and 20:1 (ore 5%). A granulator was used to make the mixed sewage sludge and the original sewage sludge into round particles with a diameter of 0.5cm. A charcoal furnace was employed to oven-convert the materials were biochar through slow pyrolysis in an N_2 environment at temperatures of 450°C, with the heating rate of 10°C min^{-1}. At 450°C, the sewage sludge pyrolysis biochar is called SS450. The other SSB samples are henceforth referred to as MS20%, TS20%, CS20%, Mo6.67%, MO5%, GP6.67%, GP5%, CB6.67%, and CB5%. The yield of biochar was calculated by mass loss of samples before and after pyrolysis.

2.4. Nutrient leaching of sewage sludge biochar

All SSB samples were oscillated in deionized (DI) water for 24 hours in a ratio of 1:40 (w/v) in a centrifuge tube and filtered through a 0.45μm nylon membrane filters. Concentrations of nitrate and phosphate in the leachate were determined using ion chromatograph (Dionex Inc. ICS90) and ICP-OES (Vista MPX, Varian Inc.), respectively. Concentrations of ammonium in the leachate were measured using the Nessler's reagent spectrophotometry form national environmental protection standards of China (HJ 535–2009) with a UV/VIS spectrophotometer (Thermo Scientific, EVO 60).

2.5. Sorption of nitrate, ammonium, and phosphate

Batch sorption experiments were conducted in a 100 mL centrifuge tube at room temperature (25 ± 1°C). Solutions with nitrate nitrogen of 20mg L^{-1}, ammonium nitrogen of 10mg L^{-1}, and total phosphorus of 50mg L^{-1} were prepared using KNO_3, NH_4Cl, and K_2HPO_4. About 1g of each SSB sample was added into the centrifuge tube and mixed with 50mL prepared solution. The mixtures were shaken at 100 rpm in a mechanical shaker for 24h and then filtered through 0.45μm nylon membrane filters. The detection method is the same as above.

2.6. Leaching of nutrients from soil columns

Two biochar samples MS20% and GP5% were selected to study their effects on nutrients retention in soil. The SSB was mixed with soil in accordance with the mass ratio of 1:10 (w/w); then, it was placed in the soil column with a length of 12cm and an inner diameter of 3cm. Besides, the bottom of the columns was covered with quartz sand in order to prevent soil loss (Figure 1). These columns were flushed with DI water before use. Then, a nutrient solution containing 25mg L^{-1} nitrate, ammonium, and phosphate was applied to these laboratory soil columns in order to study the effect of biochar on nutrients retention and transport. Leaching was performed at a rate of 50 ml · d $^{-1}$ for five consecutive days; leachate samples were collected from the outlet at the bottom of the columns and immediately filtered through 0.45μm filters for further analyses. The nitrate, ammonium, and phosphate concentrations in leachate samples were measured using the same method described above.

3. Results and discussion

3.1. Characterization of sewage sludge biochar

The yield, element composition, and other physical and chemical properties of SSB are shown in Table 1.

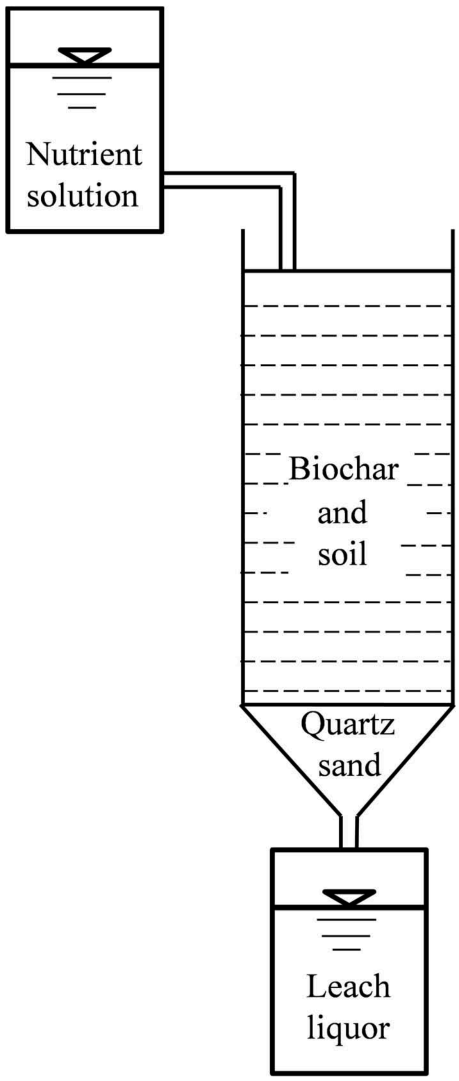

Figure 1. Diagram of leaching experiment.

Table 1. Summary of the physicochemical properties of sewage sludge biochar.

		Elemental composition (%)										
	Yield (%)	C	H	N	P	K	Ca	Mg	Si	Mn	Fe	Al
SS450	51.7	11.9	1.16	1.19	1.37	1.80	14.2	4.30	37.0	0.29	6.03	14.7
MS20%	43.1	14.9	1.19	1.14	1.26	2.38	12.9	3.98	36.8	0.30	6.63	14.8
TS20%	45.2	16.3	1.65	1.44	1.21	2.67	10.4	3.23	36.0	0.38	6.63	14.3
CS20%	45.6	16.6	1.46	1.22	1.23	2.61	11.2	3.49	36.6	0.28	6.63	14.7
MO5%	49.0	11.5	1.07	0.99	1.21	1.75	12.5	3.90	36.9	3.81	6.62	14.9
MO6.67%	49.5	10.1	1.06	0.88	1.20	1.70	12.4	3.88	36.6	5.83	6.67	15.1
GP5%	51.2	12.6	1.46	0.94	1.31	1.77	13.0	3.98	37.7	0.38	6.94	14.3
GP6.67%	50.3	22.4	3.34	1.97	1.00	1.70	7.39	2.36	34.7	0.39	6.43	16.0
CB5%	54.3	10.6	1.17	0.95	1.32	1.82	12.8	4.07	38.1	0.32	7.19	16.0
CB6.67%	50.2	10.7	1.27	0.95	1.30	1.74	11.9	3.99	37.8	0.31	7.28	16.2

It can be seen that the yield of stalks-SSB with the addition of modified materials is lower than that of minerals-SSB. Since stalks-SSB are rich in C, H, N, K, and other elements compared with the original biochar [12], the proportion of C, H, N, and K in biochar increases correspondingly; the increasing range of C and K are 20.3%~28.3% and 24.4%~32.6%, respectively. The results showed that the nutritive elements in biochar could be further improved by adding stalks. However, with the addition of mineral materials, the content of Mn, Fe, and Al of minerals-SSB in biochar increased; the increasing range of Fe and Al were 6.22%~17.2% and 2.03%~13.7%, respectively. Relevant studies have shown that the increase in the content of Mn, Fe, Al, and other metal cations leads to the increase of adsorption sites on the surface of biochar, resulting in improving its surface charge capacity. Therefore, the adsorption capacity of modified biochar on anions was significantly improved [13].

3.2. Leaching experiment

The leaching amounts of nitrate, ammonium, and phosphate were measured in this experiment (Table 2). The leaching amounts of nitrate in different SSBs were 0.14 ~ 4.02 mg L^{-1}; the leaching amounts of ammonium in different SSBs were 0.29 ~ 6.41 mg L^{-1}; the leaching amounts of phosphate root in different SSBs were 0.05 ~ 1.44 mg L^{-1}. Lu et al. (2015) reported that sewage sludge biochar made at 500°C has the nitrate leaching amount of 31.2 mg L^{-1}, the ammonium leaching amount of 25.4 mg L^{-1}, and the phosphate root leaching amount of 12.8 mg L^{-1}. They are higher than those of this experiment research result [14]. Compared with the original biochar, the modified SSB reduced the amount of nitrate leaching (except for graphite) by 83.2 ~ 96.0%. The decrease in available N in biochar was caused by the loss of TN and heterocyclization of N during pyrolysis [15]. The amount of nitrate leaching from graphite-sewage sludge biochar was increased, which may be due to the condensation of the carbon matrix. The number of nitrogen atoms in the graphene layer to replace the carbon atoms was reduced by the addition of graphite reduces; therefore, the heterocyclization of nitrogen was weakened [16]. This results in an increase in nitrate leaching, indicating that the addition of graphite powder is not conducive to reducing the nitrate leaching amount in SSB. The leaching amounts of ammonium of CS20% and GP6.67% SSBs were lower than that of SS450; the leaching amounts of other SSBs were higher than that of SS450 (Table 2). Moreover, the phosphate leaching amount of modified SSB was all higher than that of original biochar; the insoluble phosphorus in the original SSB may be activated by the addition of modified materials. Therefore, Phosphate is easily dissolved into the water during leaching, resulting in higher leaching amounts of ammonium and phosphate in the modified SSB [17,18]. However, the nutrient leaching amount of SSB is lower than the first grade discharging standard compared with the National integrated wastewater discharge standard (GB 20,425–-2006) (Table 2).

Table 2. Nutrient leaching amount of sewage sludge biochar.

	Nutrients (mg L^{-1})		
	Nitrate(N)	Ammonia	Phosphorus(P)
SS450	0.78	0.69	0.02
MS20%	0.12	1.24	0.47
TS20%	0.08	2.96	0.19
CS 20%	0.13	0.22	0.20
MO6.67%	0.03	4.98	0.31
MO5%	0.03	3.59	0.17
GP6.67%	0.91	0.73	0.47
GP5%	0.70	0.27	0.45
CB6.67%	0.06	4.77	0.24
CB5%	0.03	2.05	0.16
GB 20,426-2006	10.00	5.00	0.50

3.3. Adsorption of nutrient by sewage sludge biochar

Related researches illustrated that biochar added to fertilizer had a slow release effect on nutrients [19,20]; it is also widely used to remove nutrients from the water. Especially, the adsorption effect of nutrient elements in water after modification is better. Li et al. (2018) reported that iodine removal value of sewage sludge biochar is 278.60mg g^{-1} while that of sludge-peanut shell biochar is 395.64mg.g^{-1} [21].

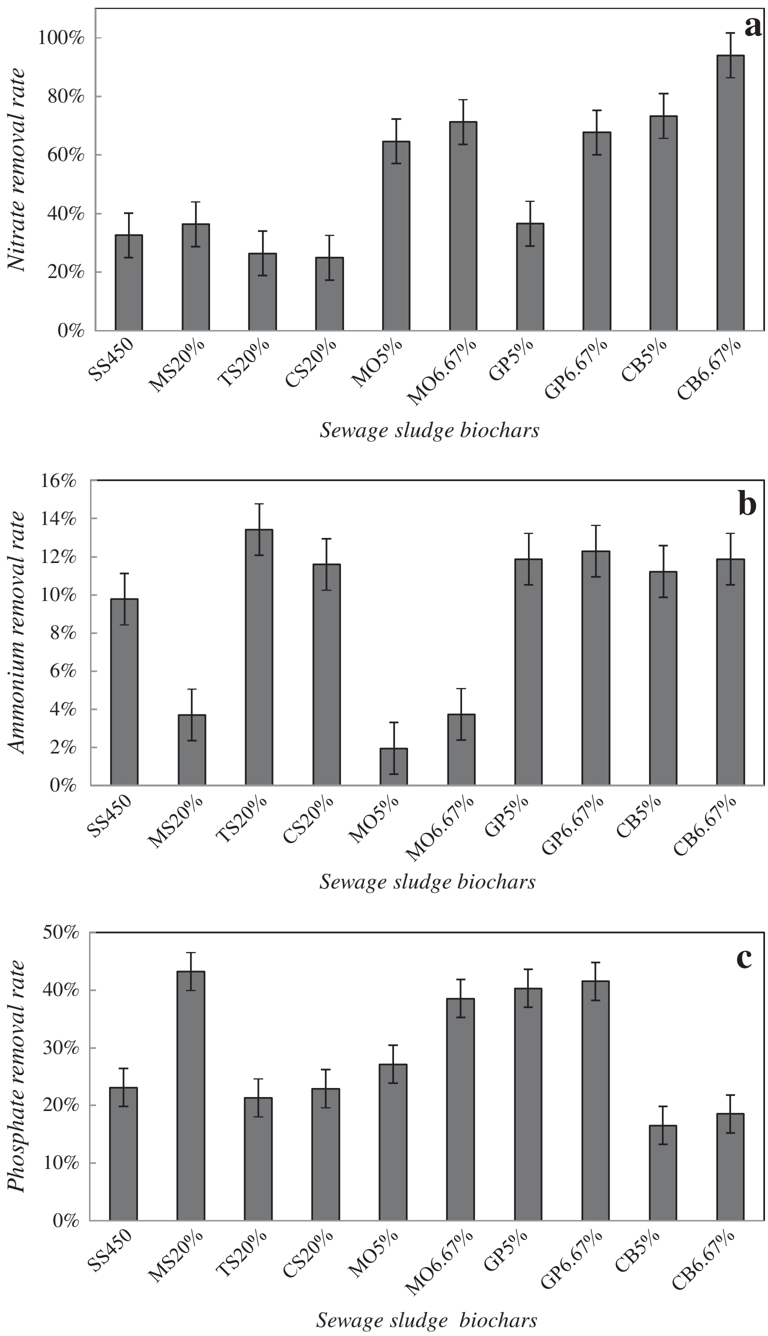

Figure 2. Removal of nitrate (a), ammonium (b), and phosphate (c) by different modified sewage sludge biochar in aqueous solution (1 g of each biochar sample was added into the vessels and mixed with 40mL prepared solution).

The adsorption effect of SSB on nutrients is displayed in Figure 2. It can be seen from Figure 2(a) that the removal capacity of nutrients in an aqueous solution of modified SSB has been significantly increased; however, there are obvious differences in removal effect. The removal rate of nitrate was 24.9% ~94.0%; besides, the removal rate of nitrate in minerals-sewage sludge biochar was higher than that in stalks-sewage sludge biochar. The main reason is that the mineral elements are positively charged; moreover, the physical adsorption of NO_3^- is conducted by means of electrostatic adsorption [22]. In minerals-sewage sludge biochar, the removal rate of nitrate increased from 64.7%, 36.6%, and 73.3% to 71.2%, 67.7%, and 94.0% as the proportion of mineral materials (MO, GP, CB) increased from 5% to 6.67%.

The ammonium removal rate of modified SSB is between 1.95% and 13.42% (Figure 2(b)). TS20% has the best removal effect on ammonium. In minerals-sewage sludge biochar, the removal rate of ammonium increased from 1.95%, 11.9%, and 11.2% to 3.73%, 12.3%, and 11.9% as the proportion of mineral materials added increased from 5.00% to 6.67%. Among them, SSB with graphite powder not only has a lower ammonium leaching rate but also has the best removal rate of ammonium in aqueous solution.

The modified SSB exhibited a certain ability to remove phosphate from aqueous solution, with the removal rate of

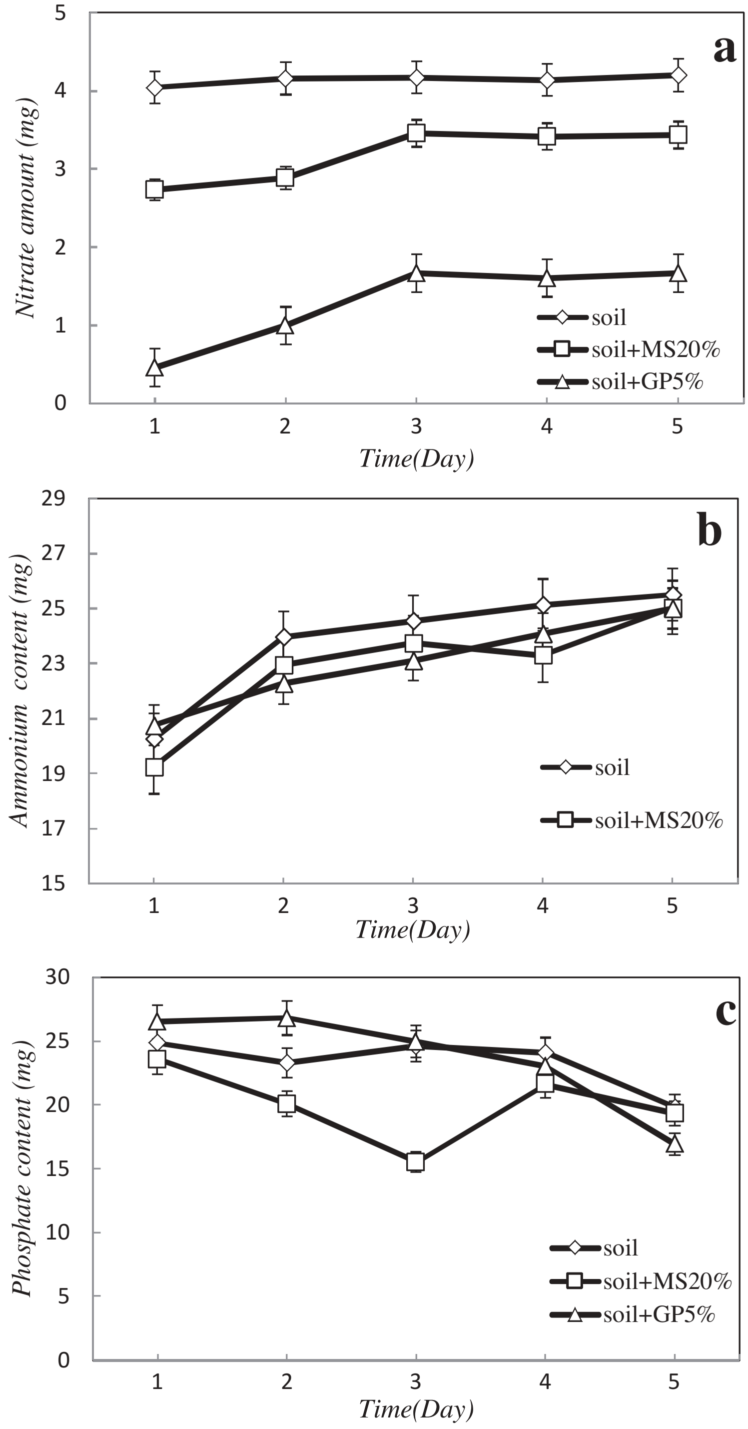

Figure 3. Accumulation of nitrate (a), ammonium (b), and phosphate (c) in leachate of different sewage sludge biochar soil column.

16.5%~43.2% (Figure 2). Among the stalks-sewage sludge biochar, MS20% SSB has the highest removal rate of 43.2%. In minerals-sewage sludge biochar, the removal rate of phosphate increased correspondingly as the proportion of minerals increased from 5.00% to 6.67%.

The removal rates of nitrate and phosphate in SSB are proportional to the content of Mn, Fe, Al, and other metal elements. Metallic elements may interact electrostatically with negatively charged anionic adsorbents and form mono-nuclear or multi-nuclear complexes, which can be bound to the active sites of biochar by chemical bonds or ion exchange [23].

3.4. Transport in soil columns

The effect of SSB on nutrient transport and retention was investigated by performing the soil column leaching experiment. According to the results of the nutrient adsorption experiment, two SSBs (MS20% and GP5%) with relatively good sorption ability for nutrients were selected for the soil column leaching study. MS20% and GP5% SSBs were mixed with soil at a ratio of 1:10 for soil column leaching analysis. The cumulative amounts of nutrients added to the leachate of different biochar soil columns are illustrated in Figure 3. It can be seen from Figure 3(a), MS20% and GP6.67% reduced the amount of nitrate leaching by 18.2% and 60.2% compared to the columns without biochar. During the initial leaching period (1-3d), the leaching amount of nitrate gradually increased and then stabilized. This is similar to the results of other studies [24]. Moreover, as can be seen in Figure 3(b,c), adding MS20% and GP5% can reduce the leaching of ammonium and phosphate, but only a slight decrease, the trend is not obvious.

Pore structure, large surface area, and abundant functional groups have been developed in Biochar. N and P in the leached filtrate were adsorbed on the surface of biochar by chemical bonds and electrostatic attraction [25]. However, the soil added with SSB has a poor effect on reducing the leaching amount of phosphate, which is mainly because the SSB has more phosphate leaching. Besides, the soil has a stronger nitrification effect, as well as a better adsorption effect on ammonium. Therefore, the adsorption effect of ammonium has not been significantly improved by the soil with biochar [26].

4. Conclusions

Biochar produced from sewage sludge pyrolysis has the potential to reduce nutrient leaching and improve soil fertility; co-pyrolysis has obvious synergistic effects on improving the stability and adsorption of biochar. It can be found from this study that the effects of sewage sludge biochar on the retention and release of nutrient ions such as nitrate, ammonium, and phosphate are very different. Of the ten SSB tested in this study, the nitrate leaching amounts in most modified SSB were lower compared to the original sewage sludge biochar. However, it has less effect on the leaching amounts of ammonium and phosphate. Moreover, the modified SSB have a significant difference in the removal of nutrients in the adsorption experiment; the removal rate of nitrate was the best while the removal rates of phosphate and ammonium are relatively little. The results obtained from the leaching soil column study were consistent with the finding from the adsorption experiments, that is, modified SSB (MS20% and GP5%) had better sustained release of nitrate compared to ammonium and phosphate.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported by the the Natural Science Foundation of China [41571130042; U1612441];the High-Level Overseas Talent Innovation and Entrepreneurship Project of Guizhou Province [201808];the National Key Research and Development Program of China [2016YFC0502602].

ORCID

Bing Wang http://orcid.org/0000-0002-2773-2370

References

[1] Sun N, Shang H, Ru S, et al. Effects of continuous application of sewage sludge compost on heavy metal accumulation and mobility characteristics in soil profile and on heavy metals uptake of wheat. Environ Sci. 2017;38:815–824.
[2] Hossain MK, Strezov V, Chan KY, et al. Influence of pyrolysis temperature on production and nutrient properties of wastewater sludge biochar. J Environ Manage. 2011;92:223–228.
[3] Tan C, Rong H, Hongtao W, et al. Adsorption of heavy metals by biochar derived from municipal sewage sludge. J Tsinghua Univ. 2014;54:1062–1067.
[4] Hossain MK, Strezov V, Chan KY, et al. Agronomic properties of wastewater sludge biochar and bioavailability of metals in production of cherry tomato (Lycopersicon esculentum). Chemosphere. 2010;78:1167–1171.
[5] Jin J, Li Y, Zhang J, et al. Influence of pyrolysis temperature on properties and environmental safety of heavy metals in biochars derived from municipal sewage sludge. J Hazard Mater. 2016;320:417–426.
[6] Dai L, Ren J, Tao L, et al. Properties of sewage sludge biochar produced under different pyrolysis temperatures and its sorption capability to Cd^{2+}. Chin J Environ Eng. 2017;11:4029–4035.
[7] Yuan H, Lu T, Wang Y, et al. Sewage sludge biochar: nutrient composition and its effect on the leaching of soil nutrients. Geoderma. 2016;267:17–23.
[8] Huang H, Yang T, Lai F, et al. Co-pyrolysis of sewage sludge and sawdust/rice straw for the production of biochar. J Anal Appl Pyrolysis. 2017;125:61–68.
[9] Xu X, Zhao Y, Sima J, et al. Indispensable role of biochar-inherent mineral constituents in its environmental applications: A review. Bioresour Technol. 2017;241:887–899.
[10] Wang D, Wang Y, Yu Z, et al. Synergistic effect on carbon and nitrogen fixation of biochar during co-pyrolysis of sewage sludge and rice straw. Acta Scientiae Circumstantiae. 2015;35:2202–2209.
[11] Wu Y, Xu G, Xu Y, et al. Effects of biochar amendment on soil physical and chemical properties: current status and knowledge gaps. Adv Earth Sci. 2014;29:68–79.
[12] Gao X, Ma W, Ma C, et al. Analysis on the current status of utilization of crop straw in China. J Huazhong Agric Univ. 2002;21(3):242–247.
[13] Wan X, Mei C, He L, et al. On the synthesis, characterization and phosphate removal of the biochar-based magnetic composites. J Safety Environ. 2017;17:1069–1075.
[14] Lu T, Yuan H, Wang Y, et al. Influence of pyrolysis temperature on biochar stability and leaching properties of nutrients contained in biochar. Ciesc J. 2015;66:2664–2669.
[15] Zheng H, Wang Z, Deng X, et al. Characteristics and nutrient values of biochars produced from giant reed at different temperatures. Bioresour Technol. 2013;130:463–471.
[16] Koutcheiko S, Monreal CM, Kodama H, et al. Preparation and characterization of activated carbon derived from the thermo-chemical conversion of chicken manure. Bioresour Technol. 2007;98:2459–2464.

[17] K C U, Inoue M, Andry H, et al. Effect of cow manure biochar on maize productivity under sandy soil condition. Soil Use Manage. 2011;27(2):205–212.

[18] Wang M, Zhou Q. Environmental effects and their mechanisms of biochar applied to soils. Environ Chem. 2013;32:768–780.

[19] J M N, Lima I, Xing B, et al. Characterization of designer biochar produced at different temperatures and their effects on a loamy sand. Ann Environ Sci. 2009;3:195–206.

[20] Yao Y, Gao B, Zhang M, et al. Effect of biochar amendment on sorption and leaching of nitrate, ammonium, and phosphate in a sandy soil. Chemosphere. 2012;89 (11):1467–1471.

[21] Li N, Zhang H, Meng J, et al. Preparation of biochar from sewage sludge with different biomass by co-pyrolysis and its land application. Renew Energy Resour. 2018;36:1423–1430.

[22] Lehmann J, J P DS, Steiner C, et al. Nutrient availability and leaching in an archaeological Anthrosol and a Ferralsol of the Central Amazon basin: fertilizer, manure and charcoal amendments. Plant Soil. 2003;249(2):343–357.

[23] Liu X, Jia B, Shen F, et al. Research progress of metal-modified biochar for phosphate adsorption. J Agro Environ Sci. 2018;37:2375–2386.

[24] Knowles OA, Robinson BH, Contangelo A, et al. Biochar for the mitigation of nitrate leaching from soil amended with biosolids. Sci Total Environ. 2011;409:3206–3210.

[25] Novak JM, Busscher WJ, Laird DL, et al. Impact of biochar amendment on fertility of a southeastern coastal plain soil. Soil Sci. 2009;174(2):105–112.

[26] Gao D, Zhang L, Liu Q, et al. Application of biochar in dryland soil decreasing loss of nitrogen and improving nitrogen using rate. Trans Chin Soc Agric Eng. 2014;30:54–61.