Sorption and transport of Mn\(^{2+}\) in soil amended with alkali modified pomelo biochar

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Abstract

Owing to its effectiveness and environment-friendly, biochar has been used for adsorbing and immobilizing pollutants in soil in recent years of studies, which is also suitable for manganese pollution in soil caused by manganese mining and processing activities. In this research, alkali modified pomelo biochar (MBC) was regarded as a soil amendment, the improvement of soil physicochemical properties as well as Mn$^{2+}$ sorption and transport in soil by modifying with MBC were investigated. In incubation experiment, 0-10% (w/w) MBC addition amount significantly improved the physicochemical properties of soil. Due to the amelioration of soil physicochemical properties along with the oxygen-containing functional groups and the developed pore structure of MBC itself, the adsorption capacity of MBC modification soil towards Mn$^{2+}$ ($q_e$) was enhanced in batch adsorption experiment, and $q_e$ increased by 10-108% when MBC ratio grew from 0 to 10% at 300 mg·L$^{-1}$ Mn$^{2+}$ solution. In column migration experiment, the Mn$^{2+}$ retention rate climbed by 13-106% from 0 to 10% MBC addition proportion when adopted the MBC filling way that placed MBC on the soil upper layer, and the reinforced restriction on Mn$^{2+}$ transport in soil amended with MBC might ascribe to the enhanced $q_e$ as well as the reduced saturated hydraulic conductivity. These results proved that MBC effectively augmented adsorption ability and suppressed transport of Mn$^{2+}$ in soil, which could provide an available mind on prevention and remediation of soil Mn contamination.

Key words: Soil; Biochar; Manganese; Adsorption; Transport
1 Introduction

Manganese (Mn), as the fourth metal in terms of average annual consumption (Yu et al., 2019), is extensively used in the production of stainless steel, dry batteries, glass, and specialty chemicals (Duan et al., 2010; Zhang et al., 2020). In recent decades, with the rapid development of modern industry, the global mining and processing of Mn ore gets more and more frequent. During these activities, a large amount of Mn will enter the topsoil around the mining area through surface runoff, wind-borne transportation and atmospheric deposition (Jiang et al., 2018). Part of the Mn accumulated in the soil surface will infiltrate into the deep soil with rainfall, and even migrate to the groundwater aquifer. Excessive Mn will be eventually adsorbed by the organism via the food chain (Duan et al., 2011). Although Mn is one of the essential trace elements for the organism, when the Mn uptake is too high, there will be symptoms of Mn poisoning in organism, examples include iron deficiency in algae, death of fish embryos, adverse effects on terrestrial plants, and human neurological diseases (Du et al., 2019; Sabina et al., 2019). Therefore, how to effectively inhibit the migration of Mn in the soil remains to be resolved.

Chemical immobilization has been used for stabilizing soil pollutants to restrict their transport extensively for which is of convenience, effectiveness and can be applied on a large scale in recent years (Gong et al., 2018). Compared with other cheap chemical stabilizer, biochar, a high temperature pyrolysis product of waste biomass, mostly possesses higher specific surface area (SSA), pH, cation exchangeable capacity (CEC), total organic carbon (TOC) and richer functional groups, redox couples etc., has been demonstrated an unique superiority to mitigate the mobility of pollutants in soil by growing studies. Khorram et al. (2015) found that migration of fomesafen was restrained due to the enhanced adsorption capacity in biochar-amended soil. In a column leaching test, Daryabeigi Zand and Grathwohl (2016) observed that after the biochar was added to contaminated soil, the leaching of polycyclic aromatic hydrocarbons was remarkably decreased. The application of
biochar derived from pig significantly reduced the mobility of cadmium, lead and dibutyl phthalate in soil with low organic carbon content, Qin et al. (2018) attributed it to the high SSA, surface alkalinity, pH, and mineral contents of biochar.

Adsorption is a decisive factor in controlling the transport of pollutants in the soil (Lei et al., 2020), and adsorption of Mn by soil is closely related to the physicochemical properties of the soil itself, and pH as well as redox potential (Eh) is the most critical among all the soil physicochemical properties since they control the mutual transformation of divalent Mn (soluble and high mobility) and Mn oxide (insoluble and relatively stable). Hue et al. (2001) claimed that Mn toxicity and mobility often occurred in those high Eh soil for long-term flooded or excessive use of organic amendments and acid soil. In addition, similar to other heavy metals, soil CEC and TOC might also affect Mn adsorption (Bradl, 2004).

On the one hand, it is universally acknowledged that biochar is both pollutant adsorbent and soil amendment, which may improve the adsorption performance of soil through its own excellent adsorption ability and modification on soil physicochemical properties to weaken pollutant transport. Vu et al. (2015) observed the adsorption capacity of soil for rhamnolipid was enhanced as the biochar was added to soil, which result from the improvement of soil organic matter caused by biochar, thus the migration of rhamnolipid was mitigated. Kim et al. (2015) explained that decline in the NH₄NO₃-extractable heavy metal of biochar modification soil was caused by the increment in soil pH and heavy metal adsorption ability induced by biochar in a soil incubation experiment. On the other hand, biochar also affects soil hydraulic characteristics to influence the transport of pollutants as well. Lei et al. (2020) thought it was one of reasons for the restricted migration of 3,5,6-trichloro-2-pyridinol in biochar modified purple soil that the soil diffusion coefficient and convection velocity were decreased by biochar addition. According to Trinh et al. (2017), an intensified interaction between pollutant and soil following biochar addition caused by the declining pore-water flow rate gave rise to a
nonreversible retention of pollutant. Few studies have focused on the influence of biochar on Mn\textsuperscript{2+} sorption and transport in soil so far on the basis of collected literature. The type, dosage and application method of biochar are three influence factors needed to be considered carefully affecting pollutant sorption and transport in biochar modified soil (Li et al., 2018). Alkali modified pomelo biochar (MBC) exhibited an excellent adsorption for Mn\textsuperscript{2+} in aqueous solution, whose saturated adsorption capacity was up to 163.194 mg·g\textsuperscript{-1} according to a previous study (An et al., 2020). In the present study, MBC was further selected as a soil amendment, several tasks were completed: 1) the impact on soil properties with different dosage MBC addition; 2) the adsorption of Mn\textsuperscript{2+} by soil amended with MBC; 3) the influence of MBC addition amount and filling way on Mn\textsuperscript{2+} migration in soil. Based on the former study, this study aimed to further explore the application value of MBC in soil Mn contamination.

2 Materials and method

2.1 Soil and MBC

The soil was collected from 0-20cm layer of an uncontaminated field in Chongqing Municipality (29°32′N, 106°27′E), China. Removed impurity, air-dried for days, and crushed to pass through a 2-mm sieve, the soil was pretreated before experiment was start up (Xu et al., 2016).

Details of MBC preparation was described in a previous study (An et al., 2020). In short, pomelo peels modified with NaOH solution were pyrolyzed at 500 °C for 2 h under oxygen-free environment in a furnace (GF11Q-B, Nanjing Boyuntong Instrument Technology Co., Ltd, China), then the pyrolysis products were collected and sieved for less than 0.38 mm, which was named MBC.

Determination of samples (soil and MBC) physicochemical property: deionized water was added to sample at 2.5:1 (v/w) for soil and 20:1 (v/w) for MBC respectively,
agitating them by glass rod for 1 min, then standing for 30 min, pH value and Eh value was measured using a desktop acidimeter (PHS-3C, Shanghai INESA Scientific Instrument Co., Ltd. China). In the case of CEC, hexamminencobalt trichloride solution-spectrophotometric method (Ministry of Ecology and Environmental of PR China, HJ 889-2017) was applied. TOC was determined by K₂Cr₂O₇ – H₂SO₄ oxidation method (Ministry of Agriculture of PR China, GB 9834-88). The bulk density of undisturbed soil was tested by the cutting ring method (Ministry of Agriculture and Rural Affairs of PR China, NY/T 1121.4-2006), while dividing the dry mass of MBC by the packed volume to estimate that of MBC. Soil texture was measured according to a simplified method described by Kettler et al. (2001). The elemental composition was conducted by energy dispersive spectroscopy (EDS; VEGA 3, TESCAN Inc., Czech Republic). The detailed data were listed in Table 1. Part of data about MBC derived from previous study (An et al., 2020).

2.2 Incubation experiment

Soil was treated in glass container at 25 ± 2 °C with different ratios of MBC: 0, 1, 3, 5, 10% (w/w). To ensure relative constant water content (60% field water holding capacity), spraying water every 3 d during incubation period for 30 d (Xu et al., 2016).

The modified soils were air-dried then crushed to pass through a 2-mm sieve once incubation experiment was finished, and they were here referred as B0-S, B1-S, B3-S, B5-S, B10-S corresponded to the MBC ratios of 0, 1, 3, 5, 10% (w/w) respectively. pH, Eh, CEC and TOC of modified soils were determined, and micro-morphology of B0-S and B10-S were measured by scanning electron microscope (SEM; VEGA 3, TESCAN Inc., Czech Republic).

2.3 Adsorption experiment

Adsorption kinetics experiment: Mn²⁺ solution in here was prepared with
MnCl₂·4H₂O. Mn²⁺ concentration was set to 300 mg·L⁻¹, and the pH value of Mn²⁺ solution was adjusted to 7.0±0.1 by 0.1M HCl and NaOH solutions. 1 g of modified soils (including B0-S, B1-S, B3-S, B5-S, B10-S) was added to 50 mL Mn²⁺ solution in conical flask, which were next respectively oscillated for 10, 30, 60, 120, 180, 300, 420, 540, 720, 960, 1200 and 1440 min in a constant temperature oscillator (ZMY-2102C, Shanghai Zhicheng Analytical Instrument Inc, China) at a temperature of 30 °C and a rotating speed of 120 rpm. Once the adsorption time reached the set value, the solution was centrifuged for 10 min at 3000 rpm with centrifuge (TG16-WS, Xiangyi Centrifuge Instrument Co., Ltd, China) and then filtered through a 0.45 μm filter membrane, and Mn²⁺ concentration in the filtrate was determined by flame atomic absorption spectrophotometer (AA800, PerkinElmer Inc, America) based on the standard (Ministry of Ecology and Environmental of PR China, GB 11911-89).

Adsorption isotherm experiment: Mn²⁺ concentration gradient was set to 50, 100, 150, 200, 250, 300 mg·L⁻¹. 0.1M HCl and NaOH solution were used to adjust the initial pH of the Mn²⁺ solution to 7.0 ± 0.1. 1 g of modified soils (including B0-S, B1-S, B3-S, B5-S, B10-S) was added to 50 mL Mn²⁺ solution in conical flask, which were next oscillated for 24 h in a constant temperature oscillator at a temperature of 30 °C and a rotating speed of 120 rpm. After the adsorption was completed, the solution was centrifuged, filtered and determined as the above procedure. In addition, soil itself wouldn’t release Mn²⁺, which was proved by an adsorption experiment with soil and deionized water.

The adsorption capacity of soil towards Mn²⁺ was expressed as follow (An et al., 2020):

\[ q_e = V \times \frac{C_0 - C_e}{M} \]

Where \( q_e \) (mg·g⁻¹) is the amount of adsorbed Mn²⁺ per unit mass of soil in the adsorption equilibrium stage, \( V \) (L) is the volume of Mn²⁺ solution, \( C_0 \) and \( C_e \) (mg·L⁻¹) are the initial and equilibration Mn²⁺ concentration respectively, \( M \) (g) is the mass of soil.
To analyze the adsorption mechanism of B0-S for Mn\(^{2+}\), attenuated total reflection Fourier transform infrared spectroscopy (FTIR; Nicolet iS5, Thermo Fisher Scientific Inc., USA) and X-ray diffraction (XRD; D/MAX 2500pc Rigaku Instrument Co., Japan) was applied to measure the change of functional groups and mineral crystal structure in B0-S before and after adsorption of Mn\(^{2+}\).

### 2.4 Adsorption model fitting

Pseudo-first-order, pseudo-second-order and intra-particle diffusion model were utilized to describe the adsorption kinetics, which were written as Eqs. (2)-(4) (An et al., 2019):

\[
q_t = q_e (1 - e^{-k_1 t})
\]

\[
q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}
\]

\[
q_t = k \times t^{0.5} + b
\]

Where \(t\) (min) is adsorption time, \(q_t\) (mg·g\(^{-1}\)) is the amount of adsorbed Mn\(^{2+}\) per unit mass of soil at time \(t\), \(k_1\) (min\(^{-1}\)), \(k_2\) (g·mg\(^{-1}\)·min\(^{-1}\)) and \(k\) (mg·g\(^{-1}\)·min\(^{0.5}\)) respectively represent pseudo-first-order, pseudo-second-order and intra-particle diffusion rate constant, \(b\) (mg·g\(^{-1}\)) is intercept.

For adsorption isotherm, Langmuir and Freundlich model, two of the most typical models, were applied, and they were as Eqs. (5)-(6) (An et al., 2018):

\[
q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e}
\]

\[
q_e = K_F C_e^n
\]

Where \(q_{max}\) (mg·g\(^{-1}\)) is the saturated adsorption capacity, \(K_L\) (L·mg\(^{-1}\)) is the affinity constant between adsorbent and adsorbate, \(K_F\) (mg·g\(^{-1}\)·L\(^n\)·mg\(^{-n}\)) is the Freundlich equilibrium constant, \(n\) is the constant that reflects the strength of adsorption.
2.5 Transport experiment

The filling way (MBC was laid on the upper, lower layer and uniformly mixed with soil, which were respectively denoted as LUP, LLO and UMS for convenience, and CK meant no MBC addition.) and dosage (0, 1, 3, 5, 10%) of MBC were taken into account in Mn\textsuperscript{2+} transport experiment, whose detailed design were listed in Table 2. A total of 3 g of natural soil and MBC were filled in a 12×100 mm (D×H) chromatography column. In order to evenly distribute the influent solution and prevented the loss of substance in column, the bottom and top of the column were both filled with 2 g of fine quartz sand, a 300 meshes polyester screen was additionally packed between quartz sand in the column bottom and the mixture of soil and MBC (Chen et al., 2017). The bulk density of the mixture of soil and MBC was calculated by the respective bulk density of the soil and MBC, then the column filling height could be determined according to the mixture bulk density (Li et al., 2018). The filling of the materials in the column were performed by wet-packed method to ensured uniformity and no interspace (Chen et al., 2017). Prior to the transport experiment, materials in the column were incubated for 1 week like the above incubation test. Deionized water was pumped slowly into the column for 12 h to saturated it by peristaltic pump (BT-600EA, Chongqing Jieheng Peristaltic Pump Co., Ltd, China), then the pore volume and porosity of the column could be gravimetrically calculated (Chen et al., 2018). After the soil column was saturated, 300 mg·L\textsuperscript{-1} of Mn\textsuperscript{2+} solution with a volume of 200 mL continuously injected into the column. During the test, the flow rate of the peristaltic pump was adjusted so that the height of the liquid level above the column was always maintained at 1~2 cm (Tan et al., 2015a), and the effluent was collected regularly to measure the Mn\textsuperscript{2+} concentration by flame atomic absorption spectrophotometer. The transport experimental device was shown in Fig. S1.
2.6 Transport parameters calculation

\[ K_s = \frac{Q}{A} \cdot \frac{L}{\Delta H} \]  \hspace{1cm} (7)

In the above Eq. (7), where \( K_s \) (cm·min\(^{-1}\)) is the saturated hydraulic conductivity, \( Q \) (mL·min\(^{-1}\)) is the flow rate provided by peristaltic pump, \( A \) (cm\(^2\)) is the cross section area of the column, \( L \) (cm) is the filling height of the column, \( \Delta H \) (cm) is the water head difference between the water level and the outlet of the column, (Tan et al., 2015a).

\[ q_{total} = \frac{Q}{1000} \int_0^{t_{total}} (C_0 - C_t) dt \]  \hspace{1cm} (8)

\[ R = \frac{q_{total}}{m_{total}} \times 100 \]  \hspace{1cm} (9)

Eqs. (8)-(9) were used for estimating the mass balance of Mn\(^{2+}\), where \( q_{total} \) (mg) is the amount of Mn\(^{2+}\) retained in column, \( t_{total} \) (min) is the total time of an integrated test, \( C_t \) (mg·L\(^{-1}\)) is the Mn\(^{2+}\) concentration in effluent at time \( t \), \( m_{total} \) (mg) is the total amount of Mn\(^{2+}\) injected in column.. \( R \) (%) is the Mn\(^{2+}\) retention rate in column.

Furthermore, \( V_b \) and \( V_s \) (mL) are the breakthrough and saturation volume which are defined as an accumulated volume when \( C_t/C_0 \) reached 0.05 and 0.90 respectively (Singh et al., 2012).

2.7 Statistical analyses

All treatment and measurement were carried out in triplicate. Experimental data were analyzed by SPSS software. One way analysis of variance was used to compare mean values, and significant differences were statistically considered when \( P < 0.05 \). Pearson correlation coefficients were calculated to determine relationship between parameters.
3 Results and discussion

3.1 The impact of MBC on soil physicochemical properties

The chemical properties of soil were significantly changed by modified with MBC (p<0.05), and the variation degree increased with the augment of MBC addition ratio except for CEC (Fig. 1). MBC modification increased the soil pH by 14-67%, which could attribute to the reason that high alkalinity and pH of biochar caused the release of alkali metal salts after biochar was applied to soil, and the hydrolysis of alkali metal salts increased the soil pH (Kelebemang et al., 2017). Biochar was composed of mineral phase, amorphous carbon, graphite carbon and unstable organic molecules, many of which could be electron donors or acceptors in the soil (Joseph et al., 2015), and applying MBC greatly descended the soil Eh by 21-59%, which suggested MBC possess stronger reducibility than soil. When MBC addition rate enhanced from 0 to 10%, the soil TOC grew by 47-578%, which might be due to the complexation between the metal and the oxygen-containing functional groups in the biochar (He et al., 2019). The soil CEC raised by 13-26% after MBC treatment, and this was likely to be relevant to the growing surface variation charges, which resulted from the increased pH, and resulted in the intensified adsorption affinity for cation (Liu et al., 2018). It was also observed that MBC improved the physical properties of soil, as was revealed in Fig. S2, the surface micro-morphology of B0-S was flat and homogenous, while irregular and porous structure was found in that of B10-S. The improvement on soil physical properties was linked to the porous characteristic of biochar itself, which could interact with the soil aggregate to establish a relatively developed pore structure (Tan et al., 2015b). Abdelhafiez et al. (2014) found the physicochemical properties of a metal-polluted soil (including the soil aggregate stability, water holding capacity, CEC and TOC) amended with biochar originated from organic wastes were significantly ascended after incubation. As stated by Tan et al. (2015b), incubated with biochar for 1 year, the pH, CEC and micro-morphology of
ultisol were ameliorated a lot. Zheng et al. (2020) reported that it was an effective measurement to augment the soil fertility that applied biochar to soil since the physicochemical properties of soil would be polished.

3.2 Mn$^{2+}$ adsorption by soil with MBC modification

3.2.1 Adsorption kinetics

The adsorption of soil towards 300 mg·L$^{-1}$ Mn$^{2+}$ solution in different reaction time within 24 h was investigated. As was revealed in Fig. 2(a), regardless of the MBC dosage, the adsorption rate dropped rapidly with time, which was likely to relate to the available adsorption sites. Because of the finite adsorption sites, the unit time consumption of the adsorption sites would gradually decrease, which corresponded to the reduction of the adsorption rate with time (An et al., 2020). The adsorption equilibrium time of each group of soil was about 700 min, except for B10-S, there were more adsorption site in B10-S, so, it took more time for Mn$^{2+}$ to occupy them. The kinetics fitting parameters were listed in Table S1, according to the correlation coefficients ($R^2$), pseudo-second-order ($R^2=0.620-0.970$) and intra-particle diffusion model ($R^2=0.702-0.952$) were fitting better. The former result indicated there was chemical sorption, while the latter consequence implied a diffusion mechanism, which belonged to physical sorption (An et al., 2019), hence, a combination of physical and chemical sorption existed in the adsorption process. It was noteworthy that the effect of intra-particle diffusion was reinforced with the augment of MBC dosage according to the trend of $R^2$ of intra-particle diffusion model, which suggested the pore structure of modified soil was developed with the increase of MBC addition rate, and the result was in keeping with the conclusion obtained from the incubation experiment.

3.2.2 Adsorption isotherm

To examine the adsorption capacity of soil amended by different addition amount
of MBC towards Mn$^{2+}$ solution with varying initial concentration from 50 to 300 mg·L$^{-1}$, the adsorption isotherm test was carried out. As shown in Fig. 2(b), a higher $q_e$ was obtained in a larger $C_0$, when $C_0$ increased from 50 to 300 mg·L$^{-1}$, $q_e$ grew by 180% for B0-S, 181% for B1-S, 182% for B3-S, 197% for B5-S, and 259% for B10-S, because a larger $C_0$ could provide more Mn$^{2+}$ to adsorbent (An et al., 2018). In each $C_0$, the soil modified with more MBC always exhibited a better $q_e$, $q_e$ increased by 10-60%, 22-92%, 13-80%, 14-69%, 13-86% and 10-108% in $C_0$ of 50, 100, 150, 200, 250 and 300 mg·L$^{-1}$ respectively with the increment of MBC addition ratios from 0 to 10%, which meant that MBC modification strengthened the adsorption capacity of soil towards Mn$^{2+}$, and the enhancement degree became greater in higher MBC dosage. It was apparently logical that biochar amendment could boost the adsorption capacity of soil, for biochar was a specific adsorbent whose adsorption capacity was much larger than that of soil. This result was observed in other studies (Vithanage et al., 2014; Liu et al., 2015). The fitting parameters of Langmuir and Freundlich model were displayed in Table S2. In general, The Freundlich model ($R^2=0.929-0.998$) fitted the adsorption isotherm better than the Langmuir model ($R^2=0.818-0.976$), which showed that the adsorption was a kind of multilayer adsorption that occurred on a heterogeneous surface. Both adsorption ability and affinity were augmented as the MBC addition amount increased respectively certified by the change trend of $K_f$ and $n$ (An et al., 2018).

### 3.3 The enhanced mechanism on Mn$^{2+}$ adsorption in soil by MBC addition

To figure out the mechanism of intensification for adsorption MBC exert on soil towards Mn$^{2+}$, the distinction of adsorption of Mn$^{2+}$ by B0-S and MBC must be identified firstly. For B0-S, FTIR and XRD analysis were conducted to elucidate its adsorption towards Mn$^{2+}$ (Fig. 3). From Fig. 3 a, in terms of B0-S before adsorption towards Mn$^{2+}$, the peak at 3621 and 3424 cm$^{-1}$ were both associated with the stretching vibration of O-H in the clay minerals (Xu et al., 2020). The band centering...
at 1638 cm\(^{-1}\) originated from the C=C and C=O stretching vibration of amides and aromatics (Churchman et al., 2010). Those vibrations of peaks all represented Si-O at 1030, 797, 694, 525 and 468 cm\(^{-1}\), which belonged to the quartz, feldspar and kaolinite (Langford et al., 2011; Bernier et al., 2013; Chandrasekaran et al., 2015). After the adsorption of Mn\(^{2+}\) by B0-S, the bands at 797 and 525 cm\(^{-1}\) respectively became weakened and shifted to a lower wavenumber at 522 cm\(^{-1}\), which revealed that Si-O was involved in the adsorption process. According to MDI jade software, the main mineral crystal structure of B0-S was SiO\(_2\) (PDF# 99-0088), after adsorption, Mn\(_2\)SiO\(_4\) (PDF# 02-1327) was observed at peaks of 31.1°, 35.1° and 50.2°, corresponded to the crystal face of (111), (200), and (220) respectively (Fig. 3 b). Combining FTIR results, the SiO\(_2\) in B0-S was hydrolyzed and reacting with Mn\(^{2+}\) to form Mn\(_2\)SiO\(_4\), Yan et al. (2012) also drew the same conclusion. On the one hand, MBC modification might increase the oxygen-containing functional groups to enhance the adsorption ability of soil since there were many oxygen-containing functional groups on MBC and Mn\(^{2+}\) was adsorbed by CO\(_3^{2-}\) and -COO\(^-\) to form MnCO\(_3\) and -COO\(^{\text{Mn}^+}\) (An et al., 2020). On the other hand, the pore structure of the soil modified with MBC was ameliorated, which might also play a positive role in Mn\(^{2+}\) adsorption.

Furthermore, the improvement on soil physicochemical properties with MBC might response for the reinforced sorption capacity of soil towards Mn\(^{2+}\) as well. There was a significant correlation between \(q_m\) and pH (\(P < 0.05\)), \(q_m\) and TOC (\(P < 0.01\)) (Table S3). Some scholars also obtained that the improvement on soil physicochemical properties with biochar was one of the reasons for the augment of soil adsorption capacity towards heavy metals via correlation analysis (Gondek et al., 2016; Liang et al., 2017; Hailegnaw et al., 2020). The increase of pH overwhelmingly affected the solubility of Mn and could heighten the electrostatic adsorption on metal cations (Sparrow and Uren, 2014). For TOC, there were more organic matters in those high TOC soil, which might complex with metal cations to adsorb them (Palansooriya...
et al., 2020).

To sum up, owing to the nature of MBC (high SSA, pH, TOC, rich oxygen-containing functional groups and developed pore structure), the physicochemical properties together with the adsorption capacity were improved, and the detailed mechanism was illustrated in Fig. 4.

3.4 Mn²⁺ transport in soil affected by MBC addition

3.4.1 Effect of MBC filling way

Fig. 5 displayed the Mn²⁺ breakthrough curves (BTC) of different MBC filling methods at various biochar addition ratios. From the figure, no matter how MBC was added to the soil, its BTC was lower than that of CK, which showed that when MBC was added to the soil, the transport of Mn²⁺ was suppressed. When the MBC dosage was fixed, whatever the MBC filling methods was, the Mn²⁺ BTC of every filling method were basically identical. Ming et al. (2014) also reported that it was close to lock Cr(VI) in soil to place biochar on soil superstratum or to mix biochar with soil evenly. However, judging from Table 3, in spite of the MBC dosage, relative retention parameters of Mn²⁺ in column of LLO were significantly inferior to UMS and LUP (p <0.05), which demonstrated that LLO got the worst limit on Mn²⁺ migration, and the phenomenon might be connected with the contact between MBC and Mn²⁺ solution. Because of the presence of the quartz sand on the column, Mn²⁺ solution could be evenly dispersed on the material on the column upper layer, whereas the continuous downward infiltration of Mn²⁺ solution might trigger preferential flow (Zhang et al., 2019), causing the formation of specific channel for Mn²⁺ penetration, which resulted in Mn²⁺ inadequately in contacted with the material in lower layer of column. Obviously, LLO made the contact between Mn²⁺ solution and MBC the least, which leaded to the worst Mn²⁺ retention effect. Moreover, as displayed in Table 2, Kₛ of LLO was remarkably higher than that of the other two filling methods (p<0.05). Li et al. (2018) filled the apple tree biochar into the silty clay soil with the same application
ways as this article, the largest $K_s$ was observed with LLO filling way as well when
the biochar addition ratio was 1 or 2%. The $K_s$ value determined the residence time of
solution in soil, solution always attain more sufficient contact with those soil with
lower $K_s$ value (Singh et al., 2012). Therefore, another reason for the worst $Mn^{2+}$
retention effect of LLO might be that the $K_s$ value was the highest in this filling
method. In conclusion, the LLO filling way was not advisable in practical application.

3.4.2 Effect of MBC dosage

The BTC of different MBC dosage with UMS, LUP and LLO filling methods
were depicted in Fig. 6. It could be seen from the figure that the BTC with a larger
MBC addition ratio was often below the BTC with a smaller MBC addition ratio,
which illustrated that as the MBC dosage grew, the retention of $Mn^{2+}$ in column
enhanced, and the migration of $Mn^{2+}$ was more inhibited. Khorram et al. (2015) found
that biochar effectively reduced the mobility of fomesafen in soil, and this inhibitory
effect strengthened with the augment of biochar dosage. From the concrete parameters
in Table 3, when the filling ways were unaltered, in addition to the $V_b$, the $q_{total}$, $R$ and
$V_s$ values were improved significantly ($p<0.05$) with the augment of MBC addition
rate. With the MBC dosage increased from 0 to 10%, the $q_{total}$ and $R$ grew by 13-95%,
13-106% and 4-85%, the $V_s$ climbed by 115-175%, 115-175%, and 115-175%, but the
increment was only 18-35%, 24-35% and 12-29% for $V_b$ respectively in filling way of
UMS, LUP and LLO, and this improvement effects perhaps attributed to the following
two reasons. On the one hand, since the adsorption ability of MBC towards $Mn^{2+}$ was
much better than that of soil, the increase of MBC dosage would enhance the
adsorption affinity of the mixture for $Mn^{2+}$. The adsorption experiment has already
proved that the soil amended by larger MBC ratio possessed greater adsorption
capacity towards $Mn^{2+}$. On the other hand, in the same MBC filling method, with the
MBC addition ratio was grew from 0 to 10%, the $K_s$ values dropped by 10-21%. The
reduced $K_s$ could owe to the high SSA and low bulk density of biochar, which made
its pores, especially large pores, easy to be blocked, thereby reducing water permeability according to Lei et al. (2020). Consequently, on the premise of being economically feasible, increasing the MBC dosage as much as possible could better inhibit the migration of Mn$^{2+}$.

3.5 The intensified inhibition mechanism on Mn$^{2+}$ transport in soil by MBC addition

As shown in Table S4, the significant positive and negative correlation were respectively observed between R and $q_e$ along with R and $K_s$ ($p < 0.01$), which suggested Mn$^{2+}$ transport was closely connected with adsorption and saturated hydraulic conductivity. To explain the intensified inhibition mechanism on Mn$^{2+}$ in soil by MBC addition, the distinction of Mn$^{2+}$ migration between natural and MBC modification soil was illustrated in Fig. 7. Compared to natural soil, due to the good performance of MBC for Mn$^{2+}$ sorption and significant improvement for soil physicochemical property, the MBC modification soil had stronger adsorption ability towards Mn$^{2+}$, which allowed more Mn$^{2+}$ to be adsorbed and immobilized. Moreover, the porous structure of MBC was easily blocked, which leaded to a low water permeability and $K_s$ in the modification soil, and the contact and residence time of Mn$^{2+}$ with soil would be reinforced, then the Mn$^{2+}$ migration was inhibited. In a word, both strengthened soil adsorption capacity for Mn$^{2+}$ and decreased soil $K_s$ might be response for the restrain mechanism on Mn$^{2+}$ transport in soil by MBC.

4 Conclusions

MBC which presented prominent adsorption ability towards Mn$^{2+}$ in a past research was further to serve as soil amendment to adsorb and immobilize Mn$^{2+}$ in soil in this work. The chemical properties (pH, Eh, CEC, TOC) of soil modified with serval MBC dosage were significantly adjusted ($P < 0.05$), and its pore structure were
also improved through incubation. The chemical and physical sorption both existed in adsorption of Mn\(^{2+}\) by modified soils suggested by the R\(^2\) of pseudo-second-order and intra-particle diffusion model. The adsorption isotherm was well fitted by the Freundlich model (R\(^2\)=0.929-0.998), which implied the sorption of soil modified with MBC for Mn\(^{2+}\) was multilayer adsorption. MBC modification affected the adsorption of Mn\(^{2+}\) by soil rely on not only its’ superb adsorption capacity but improvement of soil pH and TOC. It was sensible to employ the MBC filling method of LUP or UMS and economical MBC dosage as much as possible, which could inhibit Mn\(^{2+}\) migration in soil to the utmost extent. The mechanism on Mn\(^{2+}\) restricted transport in soil amended with MBC might be associated with intensified adsorption ability and declined K\(_s\). The study gives some theoretical guidance and advice for soil Mn contamination remediated with chemical stabilization.

**Declarations**

**Ethics approval and consent to participate**
Not applicable.

**Consent for publication**
Not applicable.

**Availability of data and materials**
All data generated or analysed during this study are included in this published article [and its supplementary information files].

**Competing interests**
The authors declare that they have no conflicts of interest.

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**Authors' contributions**
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