EFFECT OF POTASSIUM PERMANGANATE AND PYROLYSIS TEMPERATURE ON THE BIOCHAR PRODUCED FROM RICE STRAW AND SUITABILITY OF BIOCHARS FOR HEAVY METAL (CD & PB) IMMOBILIZATION IN PAPER SLUDGE

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ABSTRACT

The paper industry produces a large volume of paper sludge as a byproduct of the paper making process. This results in a substantial environmental burden to the industry from the high levels of heavy metals contained in the sludge and can limit land management applications. Biochar may have the potential to reduce environmental impacts of paper sludge by immobilizing heavy metals in soil. In this study, modified rice straw biochars were produced using a gradient of heat treatments and potassium permanganate activation levels. The physio-chemical and morphological properties of the produced biochars were characterized by FT-IR, ESEM-EDAX, BET, etc. The performances of the biochar on the immobilization of Cd and Pb in paper sludge were also studied by percolation leaching columns experiments to determine the potential use of biochars for remediation of soil contaminated by paper sludge. Results indicated that both pyrolysis temperature and $KMnO_4$ concentration significantly affected the physical and chemical properties of the biochars. The biochar yield decreased with the increase of heating temperature, while increased with the increase of $KMnO_4$ concentration. The pH and ash content of the biochar samples increased with the increases of both heating temperature and $KMnO_4$ concentration. The SSA value increased with the increase of pyrolysis temperature, while SSA decreased with the increase of $KMnO_4$ concentration. The Cd concentration of leachates with the addition of rice biochars was about 13-25% lower than the control. However, the biochars used in this study did not reduce the leaching Pb. The rice biochar additions showed clear potential for Cd immobilization, but were not suitable for immobilization of Pb.

KEYWORDS:
Pyrolysis temperature, Potassium permanganate, Biochar, Characterization, Heavy metals, Paper sludge

INTRODUCTION

The pulp and paper industry is considered to be one of the biggest and fastest growing industries in the world, and is expected to continue in the near future [1-2]. Due to the large volume of wastewater produced in this industry, a concurrent large quantity of paper sludge is produced as a byproduct, resulting in a massive environmental burden [2]. For example, on average, over seven and eleven million tons of paper sludge are produced annually in the European Union and China respectively [3-4], and sludge production will continue to increase in the foreseeable future [5]. Therefore, the disposal of paper sludge byproducts are a considerable concern for the pulp and paper industry.

The use of paper sludge as an agricultural soil amendment is seen as a potential win-win solution to the large volumes produced by the industry, and as a result, is receiving more and more attention [6]. It is estimated that around 15% of paper sludge byproducts are reused for land management applications [3]. For example, paper sludge has been successfully used as amendment in agricultural soils [7]. Unfortunately, paper sludge is also rich in heavy metals and can cause serious contamination of soil and groundwater from leaching into the environment, which in turn, can have far-reaching consequences after application [8-9].

In recent years, biochar products have attracted increased attention due to its potential use for the remediation of contaminated soils. Recent studies have highlighted biochar's role in immobilizing heavy metals in soil and by reducing heavy metal accumulation in plants [10-13]. In contrast to other organic materials, biochar is remarkably recalcitrant which could result in an extremely beneficial long-term immobilization effect [14-16].

Biochar is an insoluble, highly aromatic, and carbon-rich solid material commonly derived from different biomass under an oxygen-limited environment [17-19]. Biochar has been successfully obtained from different types of feedstocks including corn, canola, soybean, peanut, barley and wheat straws, switchgrass, pecan shells, poultry litter and peanut hulls, sugarcane bagasse, coconut coir, safflower seed press cake, hardwood and softwood tree species, and some other biowastes [17]. The beneficial features of biochar include high porosity, high inner surface area, large number of micropores, diverse surface sites, and high pH [18-19]. Biochar generally exhibits high ion exchange capacity and adsorption capabilities for heavy metal ions [11, 20]. Besides the feedstock type, pyrolysis conditions, such as residence time, temperature, heating rate, and reactor type, also have great influence on the chemical and physical properties of biochar [21]. In order to improve pore structure, surface area and functionality, biochar has also been modified by steam activation, heat treatment, and chemical activation [22-24].

The addition of biochar created from feedstocks to paper sludge land applications may provide long-term immobilization of heavy metals in soils. However, the effects of biochar additions to the mobility of heavy metals in paper sludge remains unexplored. The main objectives of this study are: ⅰ) to prepare and characterize the modified biochar produced from rice straw by $KMnO_4$ activation; ⅱ) to investigate the immobility of cadmium (Cd) and lead (Pb) in paper sludge by the addition of biochars prepared under optimized conditions.

MATERIALS AND METHODS

Feedstock Preparation and Biochar Production. The rice straw used for biochar or modified biochar preparation was collected from the Xiashu Experiment Base of Nanjing Forestry University (N32°07′, E119°13′), Jiangsu, China. The rice straw was cut into 3-4 cm long pieces and dried for 6 h at 110 °C before using.

The raw material was converted into biochar by a tube resistance furnace. During each slow pyrolysis, approximately 50 g of organic matter was filled into the furnace tube. Slow pyrolysis was conducted at three different treatment temperatures: 300, 500, and 700 °C respectively. High purity nitrogen (> 99.999 %) at the flow rate of 100 mL/min was used as protective gas. The heating temperature increased from ambient temperature to the predetermined treatment temperature at the heating rate of 10 °C/min, and held at the final temperature for 2 h. The temperature was then dropped to room temperature. Each treatment was repeated three times, and the three biochar samples from the same treatment were mixed into one sample for analysis. To produce modified bio-char samples, the rice straw pieces were pretreated by impregnating with potassium permanganate ($KMnO_4$) solution of different concentration (i.e. 0.05, 0.1, and 0.2 mol/L). After 24 h impregnation, the obtained material was dried at 103±2°C for 24 h in a convection-drying oven. The pyrolysis treatment was the same as the preparation of biochar without modification.

In this study, the biochar samples pyrolyzed under x temperature without modification was named as C-x, while those pyrolyzed under x temperature with potassium permanganate activation at y mol/L concentration was named as y-C-x.

Percolation Leaching experiments. Percolation leaching experiments were conducted in order to assess the effects of biochar addition on mobility of Cd and Pb introduced by paper sludge in land applications. Plexiglass columns with an inner diameter of 9.0 cm were used for the leaching experiments. The bottom of each column was packed with a quartz sand layer of 3 cm, with glass wool placed on top of the quartz. To remove any heavy metals and organic matter, the quartz sand and glass wool were thoroughly heated at 450 °C in a muffle furnace and then washed by diluted hydrochloric acid and deionized (DI) water.

The columns were packed with composted paper sludge with or without biochar addition, which were used to simulate contaminated soil with or without the amendment of biochar. The composted paper sludge was collected from Guizhou Chitianhua Paper Co., Ltd, Guizhou, China. The biochar chosen for leaching experiments were C-500 and 0.05-C-500, according to the results of biochar characterization. The composted paper sludge was mixed with 1 %, 2 % and 5 % (w/w) of biochar. Each of the three biochar addition treatments were compared to the untreated (control). Each treatment was replicated three times.

Each leaching column was packed to a total height of 40 cm. The average bulk density was 0.796 kg/L. The packed columns were saturated by DI water, and equilibrated for 7 days before the experiments started. Elution of the stimulated soil columns was driven by gravity. The adjustable infusion sets were applied to control the outflow rate. For each application, 200 mL DI water was applied to each of the columns. During the first 3 weeks, the leaching experiment was conducted every 3 days, then every 5-7 days thereafter. A total of 13 leaching experiments were conducted over the course of the study.

Analytical methods. The elemental composition of C, H, O, N and S of each biochar sample was determined by an elemental analyzer (2400 II, Perkin Elmer, USA). The calorific values (CV) of biochar samples were measured by the automatic fast calorimetry instrument (WELL8000, Shanghai Ouri Instrument Company, China). Biochar ash content was determined after drying the biochar for 4 hours at 105◦C. For dry combustion, a muffle furnace was used at 450±2°C for 4 hours.

The specific surface area (SSA) of each biochar sample was analyzed by using the Brunauer, Emmett and Teller (BET) method. A ground biochar sample (approximately 200 mg) was degassed for 20 h at 200 °C and then determined using N_2 as the adsorbate at -196°C or 77 K in a relative pressure of 0.025-0.30 (Micromeritics ASAP2020, USA) [25]. SSA values were determined on a Quan-tachrome ASiQ (Quantachrome Instruments, Boynton Beach, FL, USA). FT-IR analysis was used to measure the organic functional groups of biochar samples. KBr pellets method (200 mg KBr and biochar loading of 0.1 % by weight) was used for the analysis. A VERTEX 80 v system (Bruker Corporation, Germany) was used to analyze the pellets for an average of 16 scans from 400 to 4000 cm^{-1} at 4 cm^{-1} resolution. FT-IR data was analyzed by the software of OMNIC 8.0 (Nicolet Analytical Instruments, USA) [26]. Surface morphologies of each biochar sample were analyzed by an environmental scanning electron microscope (FEI QUANTA 200, Netherlands). Mineral content of each type of biochar sample was measured by an X-ray energy dispersive spectrometer (INCA250X, UK) [17].

Concentration of Cd and Pb in leachates were determined using inductively coupled plasma optical emission spectroscopy (ICP-OES, PE 2000DV, USA) according to the Chinese standards method [27]. The pH was measured using a digital pH meter (PB10, Sartorius, Germany), calibrated with standard buffer solutions. Before the pH of each biochar sample was measured, 20 g aliquot of biochar in 80 mL of DI water in 125 mL Erlenmeyer flasks were suspended by shaking at 100 rpm at 25 °C for 48 h.

RESULTS AND DISCUSSION

Proximate and Ultimate Analysis. Table 1 shows the changes of moisture content, CV, and elemental composition of biochar produced at different conditions. In general, with the increase of $KMnO_4$ concentration, the CV decreased. Compared with those of biochar samples without $KMnO_4$ pretreatment, the C and N contents of modified biochar samples decreased significantly. The reduction of C and N in the activated biochar might be ascribed to the strong oxidating effect of $KMnO_4$ on the feedstock. Another reasonable explanation is that loading of MnO_x particles onto the surface of the modified biochar might also reduce the proportion of other elements, which is similar to the finding of a previous study [28]. The occurrence of Mn on the surface of the modified biochar was confirmed by SEM-EDS analysis (Fig 4). On the other hand, the C content in the biochar samples did not increase or decrease steadily with increasing heating temperature or $KMnO_4$ concentration. The maximum value of C content was 49.75 % for C-500 and the minimum was 36.12 % for 0.05-C-500. The H/C value of the modified biochar treated at 500 °C were generally higher than those treated at 300 °C and 700 °C, which indicated that samples pyrolyzed at 500 °C were highly carbonized with a highly aromatic structure. The H and S contents did not show any clear regularity.

The effects of pyrolysis temperature and potassium permanganate concentration on the biochar yield, ash content, pH, and SSA is shown in Fig. 1. The biochar yield decreased with the increase of heating temperature from 300 °C to 700 °C (Fig. 1(a)) due to the greater primary or more thorough secondary decomposition [29]. At certain pyrolysis temperatures, the yield of modified biochar was also observed to be higher than that of unmodified. Furthermore, the yield of modified biochar increased with the increase of $KMnO_4$ concentration, which means pretreatment with higher concentration solution of $KMnO_4$ was beneficial. The ash content increase with the increasing of $KMnO_4$ concentration and heating temperature (Fig. 1(b))

TABLE 1
Elemental analyses of different biochars produced at different conditions

Samples	Moisture content(%)	CV/J·kg^{-1}	C(%)	H(%)	N(%)	S(%)	H/C
C-300	4.71	19.7	43.94	1.026	1.3	0.109	0.280
C-500	4.36	21.09	49.75	0.272	1.01	0.112	0.066
C-700	6.58	20.12	44.34	0.049	1.055	0.12	0.013
0.05-C-300	5.55	15.94	40.04	0.875	0.845	0.077	0.262
0.05-C-500	3.4	16.5	36.12	0.098	0.665	0.067	0.033
0.05-C-700	3.92	14.88	38.51	0.028	0.836	0.084	0.009
0.1-C-300	5.53	14.47	48.94	0.799	1.37	0.016	0.196
0.1-C-500	5.66	14.88	37.71	0.970	0.75	0.226	0.309
0.1-C-700	5.81	13.65	40.28	0.055	0.79	0.17	0.016
0.2-C-300	6.38	12.47	37.56	0.562	0.65	0.32	0.180
0.2-C-500	7.39	11.57	39.36	0.880	0.86	0.34	0.268
0.2-C-700	8.46	11.52	40.35	0.695	0.95	0.291	0.207

indicating that both increase of heating temperature and $KMnO_4$ pretreatment influenced feedstock mineralization. The effect of $KMnO_4$ pretreatment might be due to the stronger oxidating effect of higher solution concentration.

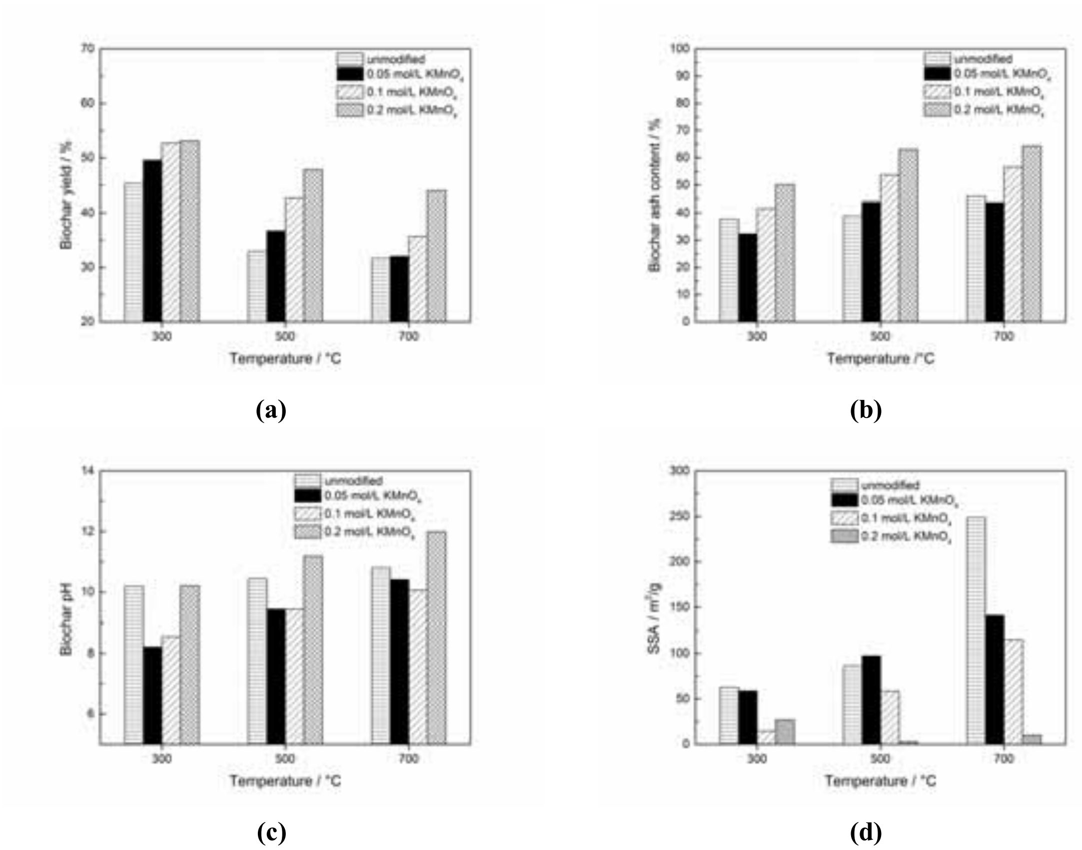
The pH value of the biochar samples was found to increase with the increases of both heating temperature and $KMnO_4$ concentration (Fig. 1(c)), which was consistent with the enhanced ash content as the temperature and $KMnO_4$ concentration increased. Ash component has been thought to be an important factor contributing to biochar high pH [30].

Increasing the heating temperature or $KMnO_4$ concentration helps to improve the alkalinity of biochar. Fig. 1(d) indicated that both pyrolysis temperature and $KMnO_4$ concentration had significant impacts on SSA. In general, the SSA value increased with the increase of pyrolysis temperature, while SSA decreased with the increase of $KMnO_4$ concentration.

FT-IR Analysis. FT-IR spectroscopy was used to determine the effects of heating temperature and $KMnO_4$ concentration on surface functional groups changes. Figure 2 depicts the FT-IR spectra of the biochars produced from different conditions. All biochars produced in the study demonstrated a similar trend with a broad band between 3300 and 3600 cm^{-1} (peak at 3409 cm^{-1}) and between 900 and 1200 cm^{-1} (peak vibrated between 1000 cm^{-1} to 1100 cm^{-1}), and with a smaller band from 2800 to 2950 cm^{-1} (peak at 2920, 2850 cm^{-1}).

The broad band between 3200 and 3600 cm^{-1} is corresponding to the cellulosic hydroxyl -OH stretching vibration [31]. The intensity of the peak at 3409 cm^{-1} decreased with increasing temperature, indicating that some cellulosic hydroxyl groups were gradually decomposed [32]. However, the intensity of the peak at 3409 cm^{-1} was observed to increase with the increase of $KMnO_4$ concentration, which showed that more cellulosic hydroxyl groups could be produced by treatment of high concentration of $KMnO_4$.

The aliphatic –CH_2– stretching vibrations of methylene methyl, and methoxyl groups with the peak of 2920, 2850 cm^{-1} are apparent [33]. Various aromatic C=C stretching vibrations, C-H plane deformations, CH_2 and C=O were also detected within the wavelength range between 1400 and 1600 cm^{-1} (peak at 1401, 1600 cm^{-1}) [31, 34]. The intense bands between 1400 and 1600 cm^{-1} decreased with heating to higher temperatures. But the intense bands between 1400 and 1600 cm^{-1} increased with the increase of the concentration of $KMnO_4$, which could be explained that more C=O was produced by the activation of $KMnO_4$.



(a) **(b)** **(c)** **(d)**

FIGURE 1
Changes in yield, ash content, pH, and SSA of biochar prepared under different conditions.

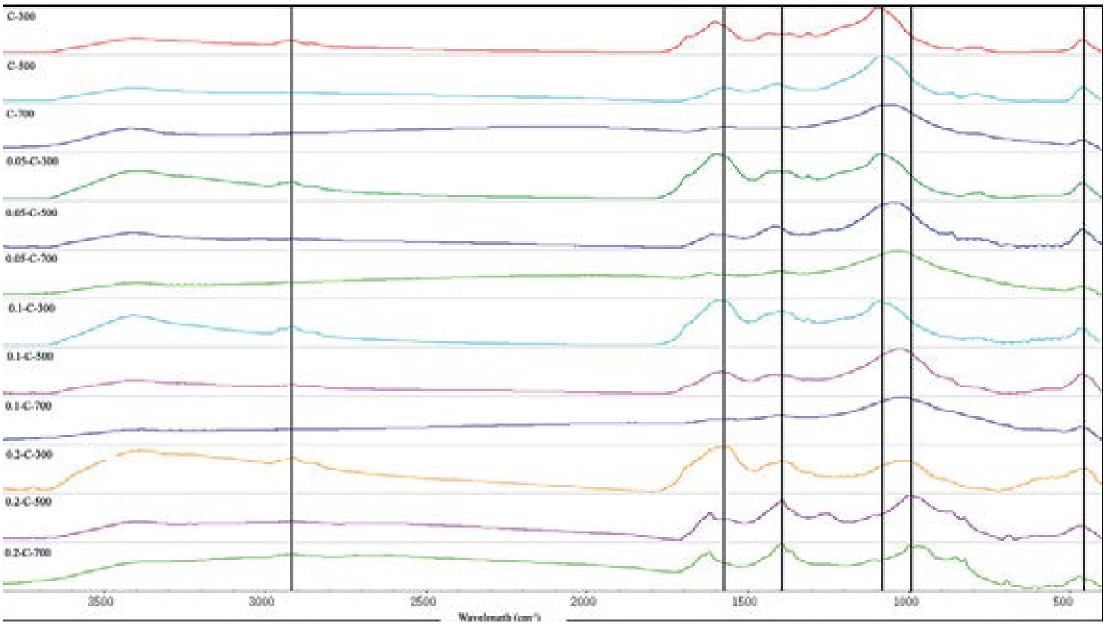


FIGURE 2
FT-IR spectroscopy of biochar prepared under different conditions.

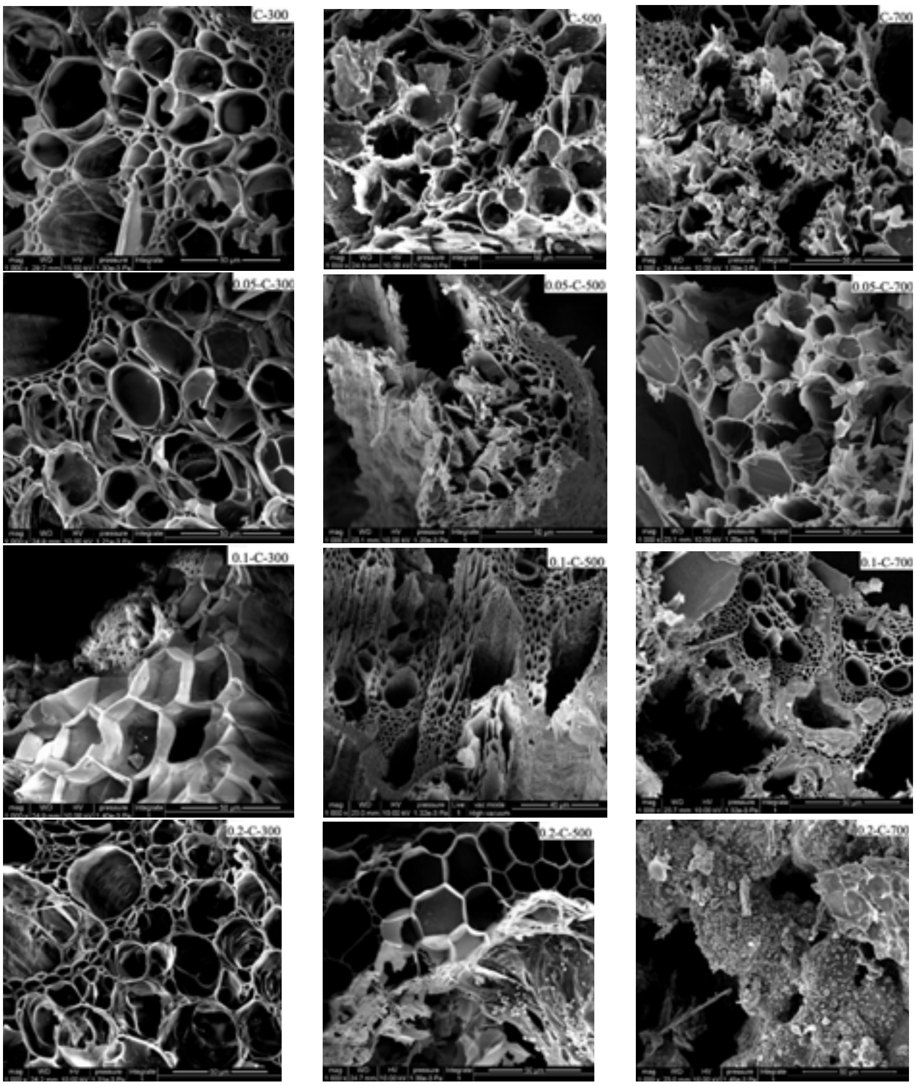
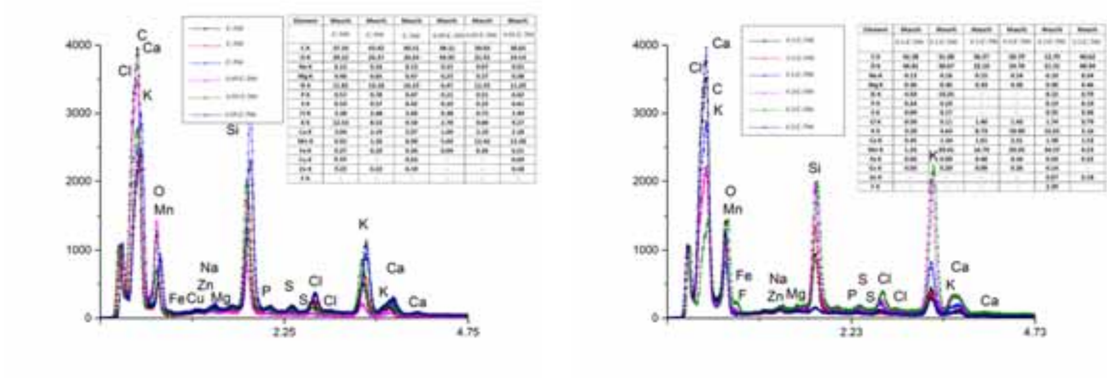


FIGURE 3
ESEM images of rice biochars produced under different conditions.



(a) (b)

FIGURE 4
Elements of different biochar samples analyzed using ESEM-EDAX spectrum. '-' means below detection limit.

At the band between 1000 and 1200 cm^{-1} with the peak of 1100 cm^{-1} was assigned to SiO_2. The peak at 870 cm^{-1}, which can be attributed to aromatic C-H bending [35], increased when heating temperature increased from 300 °C to 500 °C, and then decreased abruptly after 700 °C. The peak at 870 cm^{-1} also did not show sequential trend depending on the concentration of $KMnO_4$.

Surface Morphology and ESEM–EDAX Analysis. The surface morphologies of rice biochars is shown in Fig. 3. Significant differences among rice biochar samples produced under different conditions were observed. Compared to the biochars produced at lower temperatures, the pore size of the higher temperature biochars were relatively smaller, as found by Liu in the literature [17]. This observation was verified by the changes of SSA (Fig. 1), which could be attributed to more decomposition of volatile matters under higher treatment temperature. With the increase of $KMnO_4$ concentration, the walls of the biological tubular pores became thinner and more pore structures appeared. For example, in 0.2-C-300, new pores could be observed in the wall of tubular pores. However, as for 0.2-C-700, the biological tubular pores structures almost disappeared, which should be ascribed to the excessively combined effects of the etching of activation agent and heat treatment.

Surface elemental analysis of the biochars produced under different charring conditions was also preformed and is shown in Fig. 4. In addition to C and O, other elements such as Na, Mg, Si, P, S, Cl, K, Ca, Mn, Fe, and Zn were also found in the rice biochars. The remained elemental P, and K suggest that the biochars produced from rice straw have the potential to be applied as a soil fertilizer [36-37]. Overall, with increased $KMnO_4$ concentrations, the content of Mn also increased.

Percolation Leaching experiments. Based on the characterization results of biochars produced under different conditions, C-500 and 0.05-C-500 were chosen for leaching column experiments to study the performance on immobilization of Cd and Pb in paper sludge. The effects of the addition of rice biochars on leachate pH are shown in Fig. 5. Rice biochars were found to increase the pH values of leachates. After the forth elution, the pH values of all the other treatments were 0.1-0.5 units higher than that of the control treatment, which was 7.02. As the amount of biochar addition increased, the pH values of leachates increased correspondingly. The results indicated that rice biochars may serve as a promising alkalizing soil amendment under acidic soil situations [38-39].

The effects of rice biochars addition on leachate Cd are shown in Fig. 6. The Cd concentration of leachates with the addition of rice biochars was obviously lower than that of the control treatment without biochar. The leaching Cd concentration of the control treatment remained nearly 0.075 mg/L, while the leaching Cd concentrations with treatments including the addition of biochar were 0.055-0.065 mg/L, which results in about 13-25% lower Cd leaching concentrations. Results indicate that the addition of rice biochars will effectively reduce Cd leachates. This can be attributed to the sorption of Cd by biochars, thereby improving the retention of Cd in the simulated soil [40-41]. Furthermore, when biochars are added, soil pH increases, and the electronegativity of soil particles are enhanced, which would increase active adsorption sites for Cd, thus Cd is effectively fixed in soil. However, no difference was observed between biochars with and without $KMnO_4$ activation.

The effect of rice biochars additions on leaching Pb are shown in Fig. 7. Neither the unmodified rice biochar nor the modified showed the potential of reducing Pb leachates. In general, the concentration of leaching Pb remained stable at about 0.065 mg/L. Compared to the control treatment, during the early stages of the leaching experiment, the addition of biochar even increased the leaching Pb.

Three main mechanisms of cation exchange, complexation, and precipitation have been proposed for Cd and Pb sorption by biochars. The sorption mechanisms depend on the characteristics of biochar, which is affected by feedstock, pyrolysis temperature, and solution pH [30]. For rice straw biochar, cation exchange with Ca and Mg and precipitation with phosphate were the dominant mechanisms of Pb sorption [42-43]. When pyrolysis temperature is high, especially >500 °C, poorly soluble minerals (such as $Ca_2Mg(PO_4)_2 \cdot 2H_2O$, $Ca_2P_2O_7$, etc) are formed, which limit the sorption of Pb^{2+} [38]. Furthermore, biochar pyrolyzed at high temperatures containing less acidic groups such as carboxyl (-COOH) and hydroxyl (-OH), can effectively complex Pb^{2+}, thereby decreasing the ability of biochar to immobilize Pb^{2+} [30]. In addition, the competition for sorption sites on biochar surfaces between metals and other ions or organic pollutants can also influence the Pb^{2+} immobilization by biochar. In short, the findings in this study suggest that the tested hydrochar is not suitable for Pb immobilization.

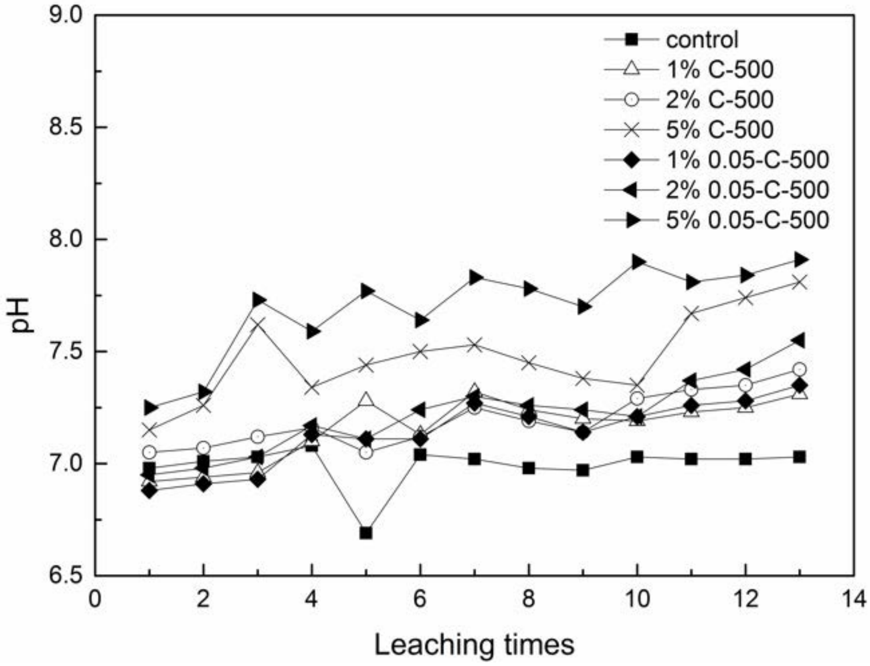


FIGURE 5
Effects of rice biochars addition on leachate pH

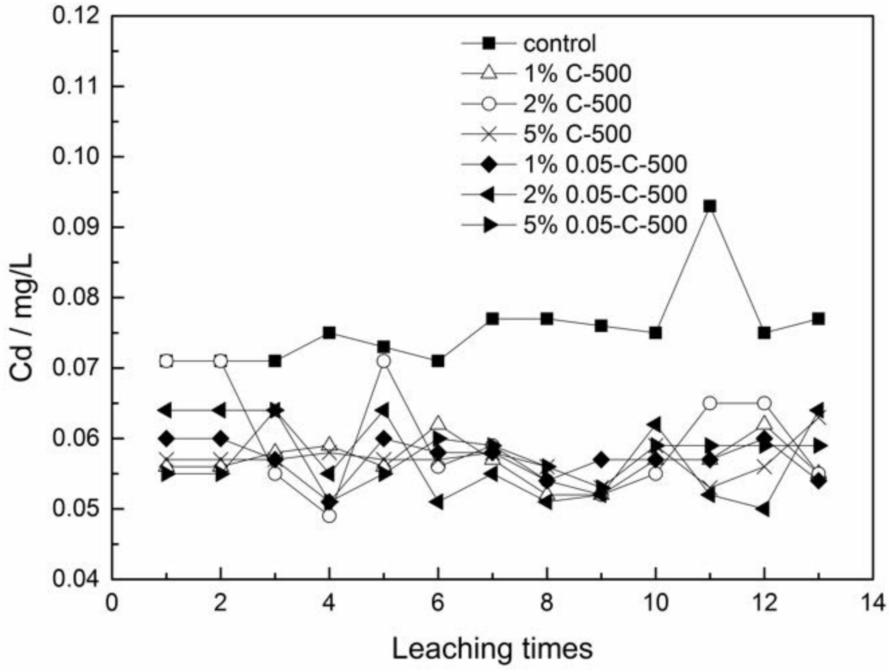


FIGURE 6
Effects of rice biochars addition on the leachate Cd

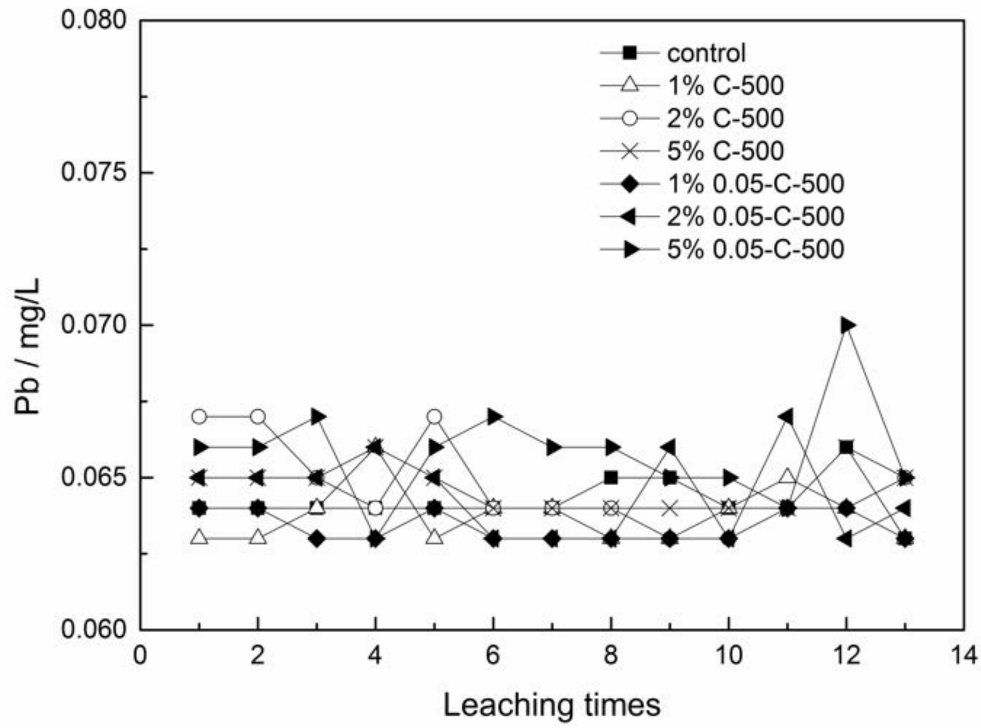


FIGURE 7
Effects of rice biochars addition on the leaching Pb

CONCLUSIONS

Both pyrolysis temperature and $KMnO_4$ concentration significantly affected the physical and chemical properties of the biochars produced from rice straw. With an increase in heating temperature, the yield, pH, SSA, and ash content of the derived biochars also increased. At higher temperatures, the surface of the derived biochar was less aliphatic due to the decomposition of dehydroxylation and O-containing functional groups, which was supported by FTIR spectra.

With increased $KMnO_4$ concentration, the yield, pH, and ash content of the derived biochars also increased, while SSA decreased. Due to the etching of activation agent new pores could be observed in the wall of tubular pores by ESEM.

The addition of rice biochars could increase pH values of leachates and effectively reduce Cd release from paper sludge. Rice biochars may serve as a promising soil remediation agent under acidic soil situations for Cd immobilization. However, rice biochars did not show obvious immobilization of Pb. In summary, rice biochars may be effective at reducing some heavy metals from leaching in paper sludge applications for land management. In general, rice biochars show promise to reduce Cd leachates, however, rice biochars do not appear effective at reducing the leaching of Pb.

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