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Preparation of biochar from co-pyrolysis of carbide slag and swine manure for adsorption of heavy metal cadmium

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Abstract. Carbide slag residue is an alkaline waste rich in calcium, typically managed through open-air storage, sun-drying, or landfilling. These disposal methods not only increase costs and land use but also severely pollute soil, water bodies, and the atmosphere. Thus, efficient processing and resource utilization of carbide slagresidue have become urgent issues to address. In recent years, heavy metal pollution, particularly water pollution, has become severe in China, making the search for efficient and economical materials for heavy metal removal a research hotspot. This study aims to explore the preparation method of biochar derived from the co-pyrolysis of carbide slagresidue and swine manure and its adsorption performance for cadmium (Cd) ions. Initially, swine manure and carbide slagresidue were subjected to co-pyrolysis at ratios of 10%, 25%, 50%, and 75%, with pyrolysis temperatures set at 300°C, 500°C, and 700°C. The morphology and structure of the biochar were characterized using scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET) surface area and porosity analysis, elemental analysis (CHNS), and Fourier-transform infrared spectroscopy (FTIR) to reveal its microstructural characteristics. The results showed that the biochar surface possesses abundant pore structures and functional groups, which facilitate cadmium ion adsorption. Under optimal preparation conditions, the maximum adsorption capacity of the biochar for cadmium reached 28.4 mg/g. In summary, the biochar produced from the co-pyrolysis of carbide slagresidue and swine manure exhibits high cadmium adsorption capacity, indicating its potential application in heavy metal pollution remediation.

Keywords: Biochar, Carbide slag, Manure residues, Meavy metal adsorption.

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1. Introduction

Heavy metal cadmium pollution is threatening the environment and public health [1]. Therefore, the top priority for improving the environment is to find effective adsorption materials to remove cadmium from contaminated water and soil.

With the gradual deterioration of the environment and the lack of existing environmentally friendly materials, biochar has been discovered. Biochar is inexpensive and environmentally friendly and can be used for a variety of purposes, such as soil remediation, waste management, greenhouse gas emission reduction, and energy production. It has appeared in many journals as a research hotspot in recent years [2]. Nevertheless, biochar derived from individual biomass sources frequently demonstrates constraints in terms of adsorption effectiveness. The process of co-pyrolysis, comprising the simultaneous pyrolysis of many feedstocks, has been recognized as an effective approach for enhancing the properties of biochar [3].

Carbide slag, the leftover produced during acetylene manufacturing, is rich in calcium and alkaline substances. Conversely, swine manure is abundant in organic carbon and vital nutrients [4]. The objective is to produce biochar with improved adsorption capability for cadmium in order to facilitate the use and environmental mitigation of industrial waste and animal husbandry waste.

The aim of this work is to examine the procedure of synthesizing composite biochar by the simultaneous combustion of carbon slag and swine manure. An analysis was conducted on the produced biochar to ascertain its properties and measure its ability to adsorb cadmium. The objective of this work was to assess the advancements achieved in the application of biochar-based materials for enhancing the effectiveness of heavy metal remediation.

2. Materials and Methods

2.1. Biochar preparation

A bench-scale chamber-type atmospheric furnace prepared the biochar (GSL-1100×, Hefei Ke Jing Materials Technology Co. Ltd., China). Equal weights of Carbide sludge and swine manure were fully blended (0,10,25,50,75%, dw/dw). After this, the heating was started at 10 °C min^{-1} until the target temperature (300, 500, and 700 °C) was attained. The samples were retained at the target treatment temperature for 1 h before slowly cooling them down. The N_2 flow of 100 mL min^{-1} was maintained throughout the whole run. Biochar is marked as MB, CM700, CM500, CM700, and the subscripts indicate the pyrolysis temperature of 300℃, 500℃ and 700℃[5].

2.2. Biochar characterization

The biochar yield at various temperatures was determined by measuring the dry weight of swine manure and carbide slag, as well as the weight of biochar obtained by pyrolysis. The pH of the biochar and swine dung mixture (with a ratio of 1:10, weight/volume) was determined using a pH meter (FE20, Mettler-Toledo Group, USA). The elemental composition (carbon, hydrogen, nitrogen, sulfur) of biochar and swine dung was determined using an elemental analyzer (Thermo Scientific, Flash EA 1112, Italy)[6]. Following degassing at a temperature of 200 °C, nitrogen gas adsorption-desorption tests were conducted at a temperature of 77 K using a TriStar II 3020 surface area analyzer. These experiments aimed to determine the specific surface area (SSA) using the Brunauer-Emmett-Teller method, as well as the pore volume (PV) and pore diameter (Dap) of the biochar. The biochar samples were examined for their surface functional groups using Fourier transform infrared spectroscopy (FTIR) with a Nicolet iS50 instrument from Thermo, USA. The analysis of the surface structure of biochar was conducted using scanning electron microscopy (SEM) with a ProX instrument from Phenom, a company based in The Netherlands.

3. Results and discussion

3.1. Physical and chemical properties of biochar

The figures in Table 1 display the yield, elemental analysis, atomic ratios, surface area (SA), pore volume (PV), and pore diameter (PD) of biochar produced by co-pyrolysing carbide slag and swine dung. Considerable diversity in carbon content (C%) is seen among the samples, with the highest carbon content recorded in CM700-25% (47.04%) and the lowest found in CM700-75% (15.78%). The aforementioned observation implies that the carbon content is influenced by both the concentration of the raw materials and the pyrolysis temperature. The hydrogen content (H%) shows a declining pattern as the concentration increases, with CM700-10% displaying the highest hydrogen content at 4.67%. These results indicate that increased concentrations may result in reduced hydrogen retention in the biochar. The nitrogen content (N%) varies between 0.34% in CM700-75% and 3.24% in CM700-10%. The elevated nitrogen content seen in samples with lower quantities may indicate that the swine excrement has a composition abundant in nitrogen. The samples demonstrate a very uniform sulfur content (S%), varying between 0.53% and 1.13%. The Sulphur concentration of the CM700-25% sample is the highest, measured at 1.13%[7]. Across all samples, the H/C ratio, which quantifies the aromaticity and hydrophilicity of the biochar, remains consistently low. Among the samples, the CM700-10% sample has the lowest H/C ratio of 0.03. Low H/C ratio biochars have greater stability compared to higher ratio biochars[8].The biochar yield (%) decreased with the increase of concentration and pyrolysis temperature, especially the CM700-75% sample had the lowest yield of

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18.02%, while the CM700-25% sample had the highest yield of 42.63%. As the pyrolysis temperature increases, the degree of decomposition of cellulose and hemicellulose in swine manure increases, resulting in a decrease in biochar yield[9]. The specific surface area (SSA), pore volume (PV), and pore diameter (Dap) values of biochar are in the range of 5.01~75.95 m2g-1, 1.13~7.11 m3 g-1 and 9.61~24.76 nm, respectively. According to previous studies, the SSA and PV of biochar are related to the pyrolysis temperature and the properties of biochar[10]. As the temperature increases from 300°Cto 700°C, the SSA and PV of different carbide slag and swine manure ratios also show similar changes. At high temperatures, inorganic compounds in the ash are released, and the pores on the surface of biochar are blocked, resulting in a decrease in SSA and PV in biochar[7], [9].

Table 1 Yield, elemental analysis, atomic ratio and pore properties of biochar from co-pyrolysis of carbide slag and swine manure

Biochar	**Yield (%)**	**C (%)**	**H (%)**	**N (%)**	**S (%)**	**H/C**	**SA (m^2 g^{-1})**	**PV (CM700 g^{-1})×10^{-2}**	**PD (nm)**
CM700-10%	39.61	34.08	4.67	3.24	0.91	0.14	5.01	1.13	9.95
CM500-10%	37.14	29.15	3.65	2.16	0.57	0.13	62.04	5.67	9.61
CM700-10%	35.63	21.98	0.74	0.70	0.70	0.03	75.95	7.11	15.52
CM700-25%	42.63	47.04	2.08	1.95	0.53	0.04	5.61	1.39	20.09
CM500-25%	32.92	44.29	1.91	3.16	1.03	0.04	11.57	2.48	17.43
CM700-25%	22.33	40.27	1.48	1.87	1.13	0.04	55.80	5.52	14.45
CM700-50%	36.89	22.39	2.02	1.62	0.54	0.09	5.55	1.42	24.09
CM500-50%	28.72	19.20	0.96	0.90	0.67	0.05	15.83	3.83	17.96
CM700-50%	20.99	17.37	0.71	0.48	0.64	0.04	44.42	4.98	13.88
CM700-75%	30.71	18.61	1.86	1.30	0.55	0.10	6.11	2.13	24.76
CM500-75%	25.96	17.42	0.90	0.73	0.59	0.05	12.50	3.02	21.89
CM700-75%	18.02	15.78	0.56	0.34	0.63	0.04	27.43	3.82	18.45

3.2. SEM images of swine manure biochar and co-pyrolysis biochar of swine manure and carbide slag

Figure 1 displays the findings of scanning electron microscopy (SEM) examination of swine manure biochar, carbide slag, and swine manure co-pyrolysis biochar, with a 25% sample size selected for comparison. Although the surface of swine manure charcoal (MB) is smooth, the surface image of carbide slag (CS) is rough and irregular. In contrast to MB and CS, the surface of CM-25% biochar exhibits more porosity and roughness, suggesting that the co-pyrolysis process has generated a substantial quantity of pores in the raw material. As the temperature of pyrolysis rises, the specific surface area of co-pyrolysis biochar progressively grows, leading to a shift from a less porous structure (300℃) to a bigger porous structure (500℃), and ultimately to a more porous structure (700℃). The aforementioned result aligns with the documented evidence, namely that biochar at elevated pyrolysis temperatures exhibits a greater specific surface area and pore volume, as illustrated in Table 1.

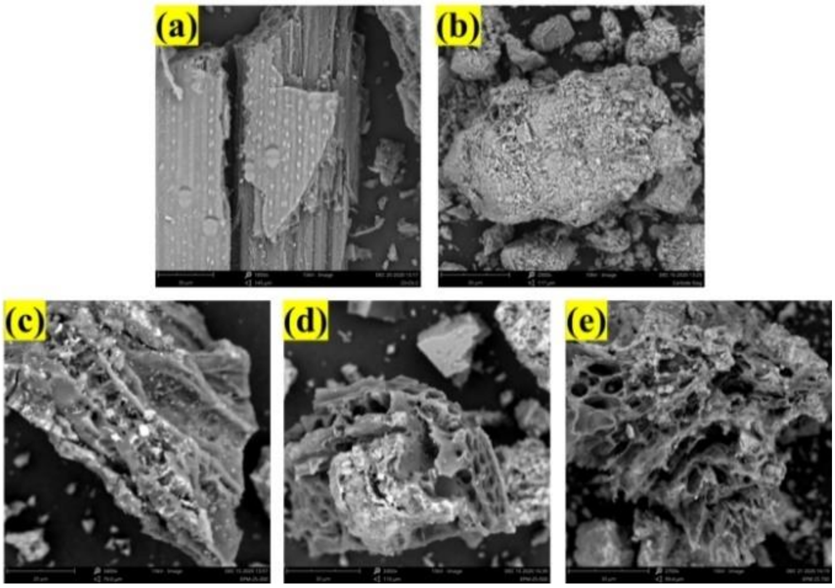

Fig. 1. SEM images of (a) MB, (b) CS, (c) CM700-25%, (d) CM500-25%, (e) CM700-25%.

3.3. FTIR of swine manure biochar and co-pyrolysis biochar of swine manure and carbide slag

Significant changes were seen in the chemical functional groups of biochars comprising varying proportions of swine dung and carbide slag. An rise in the carbide slag ratio resulted in a substantial decrease in the O-H stretching band (3200 cm^{-1}), suggesting a reduction in hydroxyl-containing chemicals. The observed reduction indicates that the pyrolysis process resulted in dehydration and decarboxylation, therefore facilitating the development of more robust aromatic structures. An observed reduction in intensity of the C-H stretching band at 2925 cm^{-1} suggests a depletion of aliphatic hydrogen. Furthermore, this observation provides additional evidence of the rise in aromaticity and the development of more densely packed carbon structures in biochar. The observed displacement of the peak at around 1650 cm^{-1} and its correlation with C=O stretching suggests a modification in the carbonyl-containing groups, most likely caused by the formation of aromatic C=C bonds by pyrolysis. The peak observed at 876 cm^{-1} exhibited a progressive increase in intensity, which represents the out-of-plane bending vibration of the aromatic ring. This observation provides more evidence supporting the development of aromatic structures throughout the process of pyrolysis.

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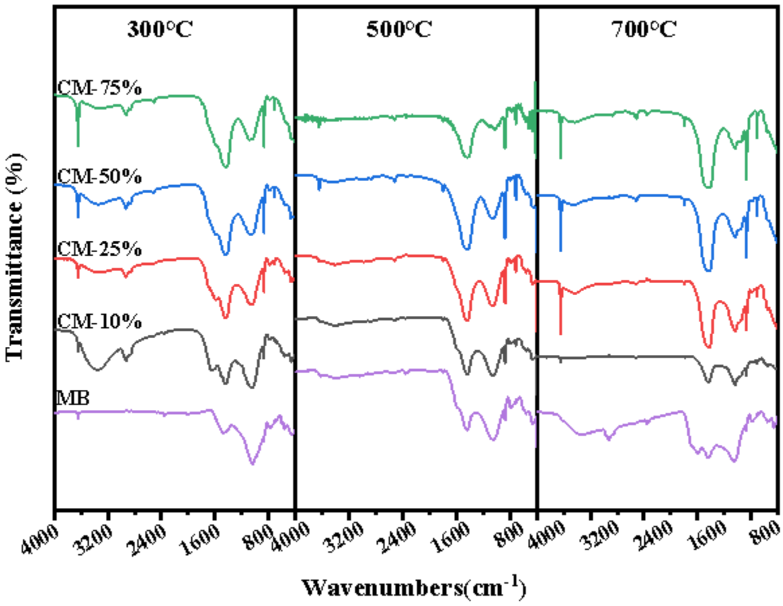

Fig. 2. FTIR of swine manure biochar and co-pyrolyzed biochar with carbide slag.

3.4. Adsorption effect of biochar from co-pyrolysis of swine manure and carbide slag on Cd^{2+}

Results indicate that with a higher carbide slag ratio, Cd(II) removal efficiency will be better than swine manure biochar alone. Besides, the trend is uniform at the pyrolysis temperatures in the experiments: 300℃, 500℃ and 700℃. The removal rates of CM700-25%, CM500-50%, and CM700-25% reached a maximum of more than 99%. Moreover, the equilibrium pH values slightly increased with a higher carbide slag ratio. This infers a possible effect of biochar on solution pH during the removal process, which states that because of the nature of the mineral elements such as Na^{+}, Mg^{2+}, and Al^{3+} on the surface ash of the biochar, H^{+} in the solution might have been displaced, hence increasing the pH post-reaction. The alkalinity itself in the biochar has been found to enhance its capacity in the adsorption of heavy metals through surface precipitation mechanisms[11], [12].

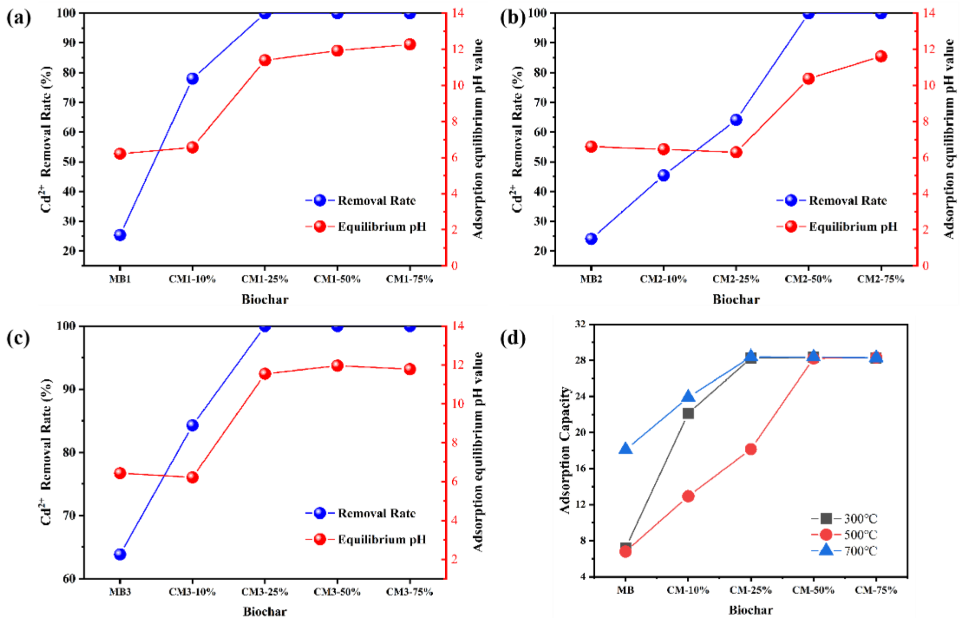

Fig. 3. Effects of biochar co-pyrolyzed with carbide slag and swine manure at 300°C (a), 500°C (b), and 700°C (c) on the removal rate, equilibrium pH value, and adsorption capacity (d) of Cd(II)

5. Conclusion

The present work produced composite biochar by co-pyrolysis of carbide slag and swine manure. This synthesis aimed to improve the adsorption capacity of cadmium (Cd) from a polluted environment. The results show that the addition of carbide slag improves the structural and chemical properties of the biochar, especially in terms of Cd adsorption capacity, and the composite biochar exhibits exceptionally superior efficiency and degree of purity compared to biochar produced from individual feedstocks. The cadmium removal rate was over 99% when biochar was produced at a ratio of 25%. Empirical evidence demonstrates that the simultaneous breakdown of carbide slag and swine dung exhibits exceptional adsorption properties. This biochar has a high pore count, a significantly large specific surface area, and many functional groups on its surface. These characteristics contribute positively to the effective absorption of heavy metals. This study establishes a foundation for the effective synthesis of biochar from industrial and agricultural wastes for environmental remediation. The present study provides evidence that biochar produced by the analysis of swine manure and carbide sludge presents a feasible and ecologically sound method for the removal of cadmium. Furthermore, it enhances the effective implementation of waste management and is in line with the concepts of a circular economy. Further investigation should analyze the long-lasting stability of cadmium adsorption in different environmental circumstances and assess the efficiency of production methods.

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