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Facile one-step synthesis of magnetically modified biochar with enhanced removal capacity for hexavalent chromium from aqueous solution

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A B S T R A C T

This study explored a new facile one-step method of preparing magnetically modified biochar (NMBC) with easy separation characteristics for the improvement of Cr (VI) removal. The prepared NMBC was characterized by scanning electron microscopy, elemental analysis, Fourier transform infrared spectroscopy, and superconducting quantum interference device. Results showed that NMBC processed a rough and uneven surface with high N and amine contents, as well as magnetization for the separation. The kinetics, isotherm and thermodynamic analysis of Cr (VI) adsorbed on the prepared materials were also investigated, as well as the effect of initial pH. NMBC showed a high Cr (VI) adsorption capacity of 48 mg g^{-1}, which is twice higher than that of traditional magnetic biochar (MBC, 19 mg g^{-1}). The different mechanisms of MBC and NMBC were also discussed.

1. Introduction

Large quantities of various heavy metals (*e.g.*, chromium, copper, and arsenic) are inevitably discharged in the environment due to mining, processing, and related commercial activities. More than 4 billion cubic meters of Cr–containing wastewater is released annually from more than 10,000 electroplating factories in China [1]. Different techniques, such as chemical sediment, ion exchange, and electrolysis, have been used to attenuate chromium concentration in water. In particular, adsorption is commonly applied for chromium removal [2].

Biochar is a porous carbon-rich product prepared through the thermochemical conversion of biomass, such as plants, animal, and even microbes, under oxygen-free or anoxic conditions. Magnetic biochar (MBC) is used for easy separation and recycling. However, enhanced adsorption capacity is needed because of the limited affinity between MBC and chromium [3]. In the past research, the nitrogen-containing groups have been proved to exhibit strong adsorption ability for heavy metals through complexation or electrostatic interaction [4]. In addition, diethylenetriamine (DETA), consisting of amine, was widely used as nitrogen donor [5]. Thus, compared with traditional MBC, magnetically DETA-modified biochar can not only show magnetism, but also display improved adsorption capacity to heavy metals.

So far, methods to make magnetic biochar and modified biochar are independent [7,8]. The study in the one-step synthesis of magnetically modified biochar has seldom been reported. Therefore, this work proposed a facile one-step method to produce magnetically modified biochar with improved functional adsorption.

2. Material and methods

Cr (VI) stock was prepared from analytical reagent potassium dichromate. Waste bamboo collected from Dahu Mountain in Ilan County (Taiwan) was crushed and washed repeatedly. After being dried at 105 °C for 12 h, the bamboo was sieved to a 200–300 mesh as the precursor of biochar.

Magnetically modified biochar was prepared by modifying the approach to pyrolysis of $FeCl_3$-laden biomass [6]. In brief, the precursor (2 g) was soaked into $FeCl_3$ aqueous solution (3% w/v) for 1.5 h under magnetic stirring. Different amounts of DETA (1–8 mmol) were added into the solution. After impregnation for 0.5 h under magnetic stirring, the solution was filtered and dried at 105 °C for 12 h. The samples were then pyrolyzed at 600 °C for 1 h under N_2 atmosphere. The obtained products were washed with ultrapure water until the pH of the washing water became steady.

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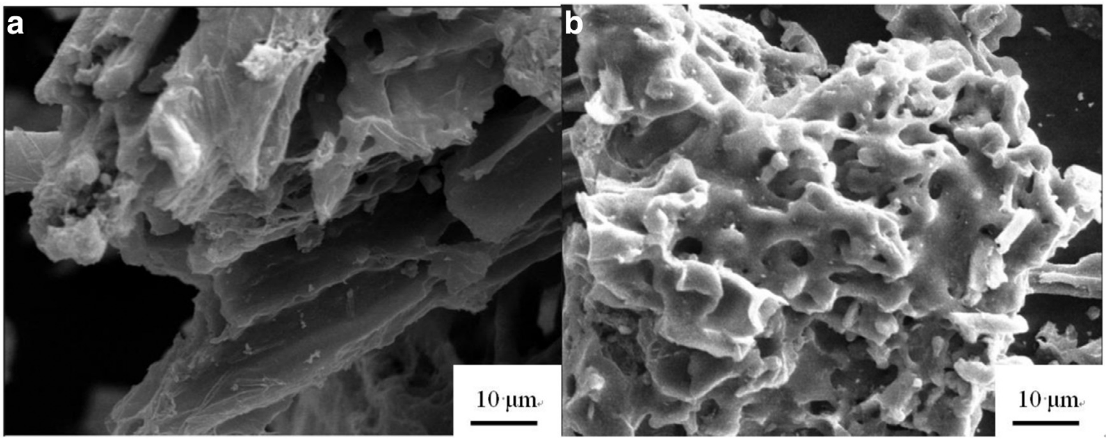

Fig. 1. SEM images of (a) MBC and (b) 4NMBC.

Finally, the products were dried at 60 °C for 12 h under vacuum environment. The resulting biochar was donated as xNMBC, where x represents the amount of DETA. MBC and NaOH-MBC were also prepared. NaOH was added to the latter sample to reach the same pH for comparison with 4NMBC.

The samples were characterized by scanning electron microscopy (SEM, HITACHI S-4800), elemental analysis (EA, Vario EL cube), Fourier transform infrared spectroscopy (FT-IR, Nicolet iS 10), and superconducting quantum interference device (SQUID, MPMS XL). Cr (VI) and total Cr were measured by UV–Vis spectroscopy (HITACHI U-3900) at 540 nm wavelength with 1,5-diphenylcarbazide chromogenic reagent and by microwave plasma atomic emission spectroscopy (MP-AES, Agilent 4100), respectively.

3. Results and discussion

3.1. Characterization

The SEM micrographs of MBC and 4NMBC are shown in Fig. 1a and b, respectively. The surface morphology of MBC is smooth, whereas that of 4NMBC is rough and uneven. And small pores can be observed from Fig. 1b. Besides, 1NMBC has similar surface with MBC, while 2NMBC shows a relatively rough one. However, SEM images suggest that structure folds and aggregates occurred on 8NMBC surface, as well as NaOH-MBC (Fig. S1). BET analysis indicated that the specific surface area of 4NMBC is 243.4 m^2 g^{-1}, which is slightly smaller than that of MBC (317.8 m^2 g^{-1}).

MBC consists of two relative obvious peaks at 1400 and 3132 cm^{-1}, assigned to C–H bending and N–H stretching vibration in ammonium [8], respectively, as shown in Fig. 2a. Other two inconspicuous peaks at 1630 and 3423 cm^{-1} represent a bit of amide (C=O stretching vibration and N–H stretching) [9]. As the impregnation of DETA increased, the peaks at 1400 and 3132 cm^{-1} became increasingly sharp. It illustrates more C–H and N–H was involved into materials. In addition, more obvious peaks at 1630 and 3423 cm^{-1} in NMBCs ascribed to amide are contributed from DETA introduced on the surface. The peak at 1630 cm^{-1} can also overlap contribution from the bending N–H due to amines [10]. Table 1 shows that the N content, H content and N/C increased with increasing DETA content, which agrees with the above results. Thus, many functional groups, such as amine and amide, are introduced on the surface of the biochars after adding DETA. It is worth noting that N content, H content and N/C of 8NMBC are similar with that of 4NMBC, although the former consumed more DETA than the latter.

Table 1
Elemental analysis of biochars.

Biochars	C (wt.%)	N (wt.%)	H (wt.%)	N/C
MBC	55.72 ± 2.25	0.37 ± 0.03	2.05 ± 0.33	0.01
1NMBC	59.57 ± 1.45	1.39 ± 0.19	2.04 ± 0.18	0.02
2NMBC	56.04 ± 3.92	2.49 ± 0.23	2.33 ± 0.20	0.04
4NMBC	51.61 ± 5.18	4.10 ± 0.61	2.59 ± 0.09	0.08
8NMBC	52.78 ± 2.14	4.22 ± 0.59	2.15 ± 0.37	0.08

Table 2
Isotherm parameters for Cr (VI) adsorbed on biochars.

Samples	Langmuir	Freundlich	Tempkin		
	R^2	R^2	R^2	A	K_T
MBC	0.985	0.976	0.993	1.01	1,015,712
1NMBC	0.936	0.913	0.966	1.33	266,529
2NMBC	0.970	0.788	0.943	3.01	9310
4NMBC	0.942	0.927	0.998	4.06	936
8NMBC	0.969	0.944	0.970	1.21	259,873

Magnetic hysteresis loops of MBC and 4NMBC were measured at room temperature (Fig. 2b). Results show that the saturation magnetization of 4NMBC is 17.49 emu g^{-1}, which is lower than that of MBC (32.49 emu g^{-1}). This phenomenon occurred because $FeCl_3$ was wrapped after adding DETA and thus affected the yield of $Fe(OH)_3$ and Fe(OH), the precursors of Fe_3O_4 during pyrolysis [6]. However, 4NMBC was easily separated from the solution by using a magnet because 4NMBC exhibits a high magnetic response as shown in Fig. 2b (inset).

3.2. Performance

3.2.1. Adsorption isotherm

The adsorption isotherm experiments were conducted with the initial concentration ranging from 10 to 200 ppm. Furthermore, Langmuir, Freundlich, and Tempkin models were developed to describe the adsorption process. Results show that the adsorption of Cr (VI) into biochars conforms to the Tempkin model, as shown in Table 2. The Tempkin model is given by the following equations [11]:

$$Q_e = A \ln(K_T C_e) \tag{1}$$

$$Q_e = A \ln K_T + A \ln C_e \tag{2}$$

where A is a constant related to the heat of adsorption and K_T is the Tempkin constant.