Chemical Engineering Journal 350 (2018) 1000–1009

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Classical theory and electron-scale view of exceptional Cd(II) adsorption onto mesoporous cellulose biochar *via* experimental analysis coupled with DFT calculations

Quan Chen[a], Jiewei Zheng[a], Liuchun Zheng[c], Zhi Dang[b], Lijuan Zhang[a,*]

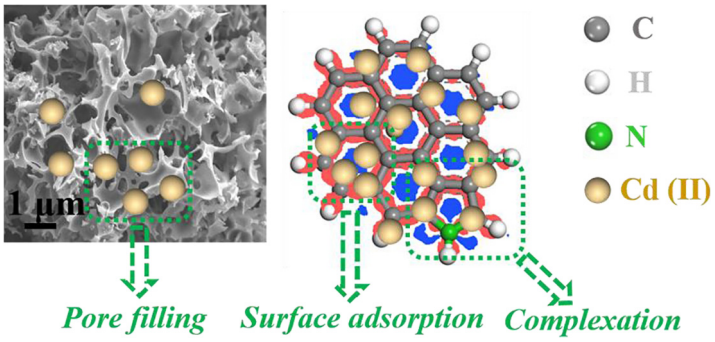
[a] School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, PR China
[b] School of Environment and Energy, South China University of Technology, Guangzhou 510006, PR China
[c] School of Chemistry and Environment, South China Normal University, Guangzhou 510006, PR China

HIGHLIGHTS

- Three mesoporous cellulose biochar (MCB) adsorbents were prepared.
- The structure-performance relationship in Cd(II) adsorption was elucidated.
- A new strategy for understanding adsorption micro-mechanism was proposed.
- Provided theoretical guidance for the subsequent biochar preparation.

GRAPHICAL ABSTRACT

Illustration of Cd(II) adsorption mechanism onto mesoporous cellulose biochar.



ARTICLE INFO

Keywords:
Mesoporous cellulose biochar
Cd(II)
Classical theory
Density functional theory
Micro-mechanism

ABSTRACT

The micro-mechanism of heavy metal cations adsorption onto biochar is critical for the renovation of heavy metal contamination. In this work, we prepared three mesoporous cellulose biochar (MCB) adsorbents with different surface area, O and N functionalities content properties through a 300 °C carbonization-KOH activation-700 °C carbonization-HNO_3 oxidation process. The Cd(II) adsorption performance of three MCB was compared, the MCB-1h exhibited best Cd(II) adsorption capacity (368.8 mg/g), and even remained 89% after 5 cycles. DFT calculations identified that MCB-1h had comparatively stronger Cd(II) binding ability, and the results were well consistent with the experimental data. The adsorption micro-mechanism was analyzed in the view of classical theory and electron-scale. The classical theory results proposed that the adsorption process was dominated by chemisorption, and electron sharing or exchange between Cd(II) and biochar occurred. Electron-scale mechanism analysis found that the functional groups and aromatic could provide lone pair electrons and π electrons for the Cd(II) adsorption, respectively. The N functionalities such as amino, pyridine and pyrrole groups could raise the adsorption ability of the biochar adsorbent. Overall, our results not only provide new insights into the heavy metal adsorption, but also has significant reference value for the subsequent biochar adsorbent preparation.

* Corresponding author.
E-mail address: celjzh@scut.edu.cn (L. Zhang).

https://doi.org/10.1016/j.cej.2018.06.054
Received 11 April 2018; Received in revised form 7 June 2018; Accepted 9 June 2018

1. Introduction

In recent decades, heavy metal cadmium containing waste has been directly or indirectly discharged into the environment with the rapid development of metallurgy, batteries, mining, electrolysis, electrical appliance manufacturing industries [1,2]. Cadmium is a human non-essential element with high chemical activity, toxicity and non-degradable, and easy to enter the plant and human body, triggering a variety of illnesses [3]. In order to reduce the harm of cadmium to the environment and human, many techniques have been used for cadmium removal, including adsorption, membrane separation, ion-exchange, chemical precipitation, penetration, animal and plant restoration [4,5].

Among the above techniques, adsorption has been broadly concerned due to its simplicity of operation, high removal efficiency, and low cost [6,7]. It should be pointed out that its practical application heavily depends on the adsorption efficiency of adsorbent, which needs to be inexpensive, having strong sorbate affinity and large number of active adsorption sites. Among the numerous adsorbents, biochar have been most frequently mentioned due to its economic advantages, large surface area, and good adsorption performance [8,9]. However, if a large fraction of the pores in the biochar are micropores (< 2 nm), its adsorption ability might be restricted by hydrothermal unstable, low adsorption capacity, and relatively slow diffusion kinetic [10]. Mesoporous biochar is a very promising heavy metal adsorbent with high adsorption capacity and hydrothermal stability, while retaining the large surface area and pore volume [11,12]. On the other hand, biochar is usually prepared using bioresource waste as precursors. Cellulose is a cheap biomass, and its content in wheat straw, corn straw, and rice straw are 33–40%, about 45% and about 40%, respectively [13]. Regarding cellulose as raw material to prepare biocahr adsorbent could not only remove heavy metals, but also take full advantage of biomass resources, and turn “waste” into treasure [14,15].

Considerable efforts have devoted to the heavy metal removal using biochar adsorbent. Huang and his co-workers prepared biochar adsorbent using peanut hull as raw material. When the Cd(II) initial concentration was 200 mg/L, the removal percentage was up to 90%, and the adsorption isotherm theoretical maximum adsorption capacity was 28.99 mg/g [16]. A cellulose biochar was reported by Reddy and his co-workers, the Pb(II) adsorption process of the adsorbent was in accordance with pseudo-second-order kinetic model, and the maximum adsorption capacity was 316.3 mg/g [17]. However, much work has focused on preparation of adsorbent, evaluation of adsorption properties, factors that affect the adsorption performance, and adsorption model. Nevertheless, the structure-performance relationship in Cd(II) adsorption onto biochar has not yet been systematically cleared, and further efforts are required.

Moreover, heavy metals adsorbed onto biochar were controlled by a number of mechanisms, such as physical sorption, complexation, ion exchange, precipitation, and electrostatic interactions (chemisorption) [18]. But rarely systematic study concerned the adsorption micro-mechanism, especially at the electron-scale. Whereas, the micro-mechanism is extremely helpful to guide the preparation of high-efficiency heavy metal biochar adsorbent, thus reducing the practical cost of adsorption method. There is thereby an urgent need to investigate the adsorption mechanism. It’s generally established that the traditional theoretical analysis could propose the adsorption mechanism, but it remains challenge to understand on the basis of experimental data alone. In recent years, computer calculations based on density functional theory (DFT) have been employed to better study the adsorption micro-mechanism, which is a quantum mechanic method for studying the electron structure of multi-electron systems, and hold the advantages in wide applications and simple algorithm [19]. Yu et al. investigated the adsorption of organic compounds onto MOFs to rationalize the difference in adsorption performance and interpret the adsorption micro-mechanism by DFT calculations [20]. In Liang’s work, DFT calculations were studied to explore the surface interactions between heavy metal ions and different active sites of Mn-doped α-Fe_2O_3 nanocrystals, and to further understand the ion exchange mechanism in the adsorption [21]. Unfortunately, the clearly adsorption mechanism of Cd(II) onto modified biochar has not yet been revealed.

Taking the aforementioned aspects into consideration, we herein show our attempt to produce three mesoporous cellulose biochar (MCB) adsorbents with different surface area and morphology, O and N functionalities content adsorbents, evaluate and compare their Cd(II) adsorption performance, inspect the structure-performance relationship and factors that affect adsorption performance. The adsorption micro-mechanism is to be investigated by the combination of classical theory (based on the experimental data) and electron-scale (based on DFT calculations). In addition, our DFT calculations not only interpret the adsorption micro-mechanism, but also rationalize the differences in adsorption performance. Our mechanistic study provides meaningful insights into the preparation of efficient biochar adsorbents for environmental renovation.

2. Materials and methods

2.1. Materials

Cellulose (Cellulose, Powder, Sigma-Aldrich), Cadmium chloride hemi(pentahydrate) ($CdCl_2{\cdot}2.5H_2O$, 99%, J&K), Copper(II) chloride dihydrate, $CuCl_2$ $2H_2O$, 99%, J&K). Potassium hydroxide (KOH, AR, Guangzhou Chemical Reagent Factory), ethylene diamine tetraacetic acid (EDTA, AR, Guangzhou Chemical Reagent Factory), nitric acid (HNO_3, AR, Guangzhou Chemical Reagent Factory). Cadmium standard solution was purchased from Tianjin Kemiou Chemical Reagent Co., Ltd, China. All the chemicals are of analytical grade and used without further treatment or purification.

2.2. Preparation of mesoporous cellulose biochar

Typically, dried cellulose powder was evenly spread in the crucible and placed in the central of tube furnace. The heating rate was 5 °C/min, the nitrogen flow rate was 50 mL/min, the temperature was raised from room temperature to 300 °C and maintained for 1 h, and then cooled to room temperature to obtain cellulose biochar (designated CB). The CB and KOH solids were mixed at a mass ratio of 1:3, and deionized water was added and stirred (KOH concentration: 30%), then placed in 80 °C oven to obtain a cellulose alkali (named CB-KOH). The CB-KOH was calcined in the tube furnace. The heating rate was set as 5 °C/min and the nitrogen flow rate was 50 mL/min, the temperature raised from room temperature to 700 °C, and kept for 1 h, 2 h, 3 h to ensure the formation of aromatic structure, then cooled to room temperature to achieve cellulose activated carbon (designated CB-1h, CB-2h, CB-3h). Then, 30% nitric acid solution was slowly mixed with 20 g of CB-1–3h and stirred at 70 °C for 3 h. The reaction solution was diluted with large amount of deionized water and filtered. And then washed with a large amount of deionized water to neutral. The samples were dried in a vacuum oven to obtain the targeting product (named MCB-1h, MCB-2h, MCB-3h).

2.3. Characterizations

FTIR (Vector 33-IR, Bruker) was employed to analyze functional groups in the samples obtained by the KBr pellet technique. The spectrums were collected with wavenumber from 400 to 4000 cm^{-1}. N_2 adsorption-desorption isotherms were obtained from an ASAP 2010 analyzer (Micromeritics) at 77 K. The surface area was determined based on BET analyses. Pore size distribution was derived from the desorption branches of the isotherms based on BJH model, and the total pore volume was calculated using BJH analysis. The surface morphology, microstructure and elements of the samples were observed by