Functionalized moso bamboo powder adsorbent for Cd(II) complexes with citric acid/tartrate acid: characterization, adsorptive performance, and mechanism

Qinju Sun¹, Shaohua Lin^{2*}, Guohua Liu^{3*}, Yue Xuan², Liping Gao², Pingping Li¹

¹College of Biology and the Environment, Nanjing Forestry University, Nanjing 210037

²School of Civil Engineering, Nanjing Forestry University, Nanjing, Jiangsu Province 210037, China

³Bamboo Research Institute, Nanjing Forestry University, Nanjing, Jiangsu Province 210037, China

*These authors contributed equally to this work.

ABSTRACT

A new amine group functionalized moso bamboo powder adsorbent (AMBP) was prepared using a facile procedure to remove Cd(II) complexes with citric acid (CA) and tartrate acid (TA). The properties of the AMBP were characterized using SEM, FTIR, XPS, BET, and an elemental analysis. The adsorptive performances of the AMBP toward Cd(II)-CA/TA were investigated. The results indicated that amine group was successfully introduced, and the AMBP with a BET specific surface area of 0.463 m²/g was effective in adsorbing Cd(II)-CA/TA under pH 4.0–10.0. The removal of Cd(II) increased significantly when the Cd(II)/ligand molar ratio changed from 1:0.5 to 1:2. The adsorption processes of Cd(II)-CA/TA were endothermic and fit well with the pseudo-second-order kinetic model ($R^2 > 0.999$). The Langmuir model ($q_{\max}$ of 14.41 and 7.58 mg/g for Cd(II)-CA and Cd(II)-TA, respectively) fit the isotherms better than the Freundlich model. The AMBP could be regenerated by HCl and reused at least 4 times. The uptake mechanisms of Cd(II)-CA/TA were proposed to be physisorption and the chemisorption of the coordination between $-\text{NH}_2$ –NH and the Cd(II). This work shows that the AMBP is an adsorbent with high practical value to remove Cd(II) in water or wastewater containing CA/TA.

Keywords: Adsorption mechanism, Cd(II) complex, Facile preparation, Functionalized moso bamboo waste

1. Introduction

Cadmium (Cd), one of the most toxic heavy metals, can cause many diseases and body damage even at a very low concentration, such as cancer, bronchiolitis, emphysema, fibrosis, skeletal damage, brain damage, and kidney damage [1, 2]. Increasing industrial Cd discharges originating primarily from metal mining, refining, smelting, metal plating, electrolysis, electroplating, and other industries have deteriorated the aqueous environment [3]. Due to its non-biodegradable nature, Cd can accumulate in the environment and food chain; thus, it has adverse effects on ecosystems and human safety [4]. Therefore, Cd contamination has drawn an increasing amount of concern around the world.

To eliminate heavy metal ions in wastewater and surface water, various methods have been developed, such as chemical precipi-

itation [5], adsorption [6], and ultrafiltration [7]. Unfortunately, wastewater and surface water often contain small molecule organic compounds such as citrate and tartrate, which are widely used to enhance the solubility of metals in industries or are derived from many natural processes, such as the decay of plant and animal residues, microbial metabolism, canopy drips, and root activity [8, 9]. All of these processes tend to form metal complexes. In general, heavy metal complexes are considerably stable [10]; therefore, once in the environment, they are extremely tough to remove and result in the persistent pollution of aquatic systems [11]. Therefore, heavy metal complexes have become an important problem in wastewater and raw water treatment processes [10].

Typical treatment processes for the removal of heavy metal complexes involve complicated steps, including pre-oxidation, membrane separation, and ion exchange [12, 13]. Due to its ease of

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† Corresponding author

E-mail: franklinsh@njfu.edu.cn; ghliu@njfu.edu.cn

Tel: +86-25-8542-7691, +86-25-8542-7231 Fax: +86-25-8542-8984

ORCID: 0000-0003-4264-5969

operation, energy-savings, and non-selectivity toward contaminants, adsorption is considered to be an attractive technology for heavy metal complexes removal [12]. Nevertheless, some commonly used adsorbents, such as activated carbon, mesoporous silica, and montmorillonite, have shown poor performances for the removal of heavy metal complexes [14]. Some new different types of adsorbents have been reported recently, such as pentaethylene-hexamine-modified copolymers and chitosan-based adsorbents [15, 16]. The amine groups in these adsorbents have exhibited strong chelating ability that even allows them to compete with complex for heavy metal ions in wastewater [15, 17]. Currently, to improve the practicality of adsorption technology, agricultural and forestry wastes have gained more and more attention due to their natural abundance, low costs, and ease of modification [18-21].

This study demonstrates a facile procedure for the transformation of the moso bamboo granules into an efficient amine group functionalized adsorbent for the adsorption of Cd(II) complexes with CA/TA. In addition, the adsorption characteristics are investigated. Moso bamboo was chosen as the base material because it is a very potentially renewable biomass resource, and has the outstanding advantage of a high yield and short growth cycle. In addition, bamboo is primarily composed of cellulose and lignin, which makes it easily modified through the reaction of different chemical moieties with its hydroxyl groups [22]. Specifically, the modification of agricultural and forestry waste to adsorb heavy metals from wastewater fit in with the concept of “waste control by waste” [23]. This study provides new insights for the development of heavy metal complexes removal technologies and advances the application of agricultural and forest residues for the treatment of wastewater containing heavy metals.

2. Materials and Methods

2.1. Materials and Chemicals

The culm waste of moso bamboo (*Phyllostachys pubescens*), aged five years, was collected from the Xiashu Experiment Base of Nanjing Forestry University (N32°07', E119°13'), Jiangsu, China. The culms waste was first cut into blocks with sizes of (2–3) × (2–3) cm, then washed using deionized water. Each block was dried under 105 ± 2°C and further ground into particles. Finally, the moso bamboo powder (MBP) was sieved to obtain a powder size between 60 and 100 mesh.

All of the chemicals used were of analytical grade and used without further purification. The epichlorohydrin (ECH), tetraethylenepentamine (TEPA), CdSO₄·8/3H₂O, NaOH, nitric acid, Na₂CO₃, tartrate acid (TA), citric acid (CA), and absolute ethyl alcohol were obtained from the Sinopharm Chemical Reagent Co. Ltd, China. Deionized (DI) water was obtained from the Millipore Milli-Q System (Millipore Corporation, United States of America).

2.2. Preparation of the Modified MBP

The MBP was first mercerized using 2 mol/L of NaOH solution to remove the impurities and increase the specific surface area, which made the hydroxyl groups more easily approachable for

further modification. A total of 3 g of mercerized MBP was mixed with 100 mL of 8% NaOH and 15 mL of ECH in a three-necked flask and placed in a constant-temperature water bath at 40°C for 8 h. The product was thoroughly washed using absolute ethyl alcohol and DI water successively. The epoxidation product was designated as EMBP. In the next step, 5 mL of TEPA was added dropwise into the flask with 100 mL of 1% Na₂CO₃ at 40°C for 2 h. The product was thoroughly washed with absolute ethyl alcohol and DI water to remove impurities. Finally, the adsorbent was dried at 60°C and named AMBP.

2.3. Characterization and Chemical Analysis

Elemental analysis of the native and modified MBP samples were acquired using a 2400 II analyzer (Perkin Elmer, USA). The Fourier transform infrared (FT-IR) spectra of the studied samples were obtained using a VERTEX 80 v (Bruker Corporation, Germany) Fourier transform infrared spectrometer using the KBr pellets method. The characterization of the surface morphology of the samples was determined using a scanning electron microscope (SEM, FEI QUANTA 200, Netherlands) at 10-15 kV, while EDS analysis was operated at 20 kV. All of the samples were sputter-coated with gold prior to the SEM analysis. Brunauer-Emmett-Teller (BET) specific surface areas were determined by nitrogen adsorption at the temperature of liquid nitrogen with ASAP 2020 (Micromeritics, USA). X-ray photoelectron spectroscopy (XPS) measurements were performed in a Kratos AXIS ULTRADLD spectrometer that was equipped with a monochromated Al K α X-rays source (1486.6 eV) and operated at 150 W for excitation. The C 1s level at 284.8 eV was used as an internal standard to correct the shift in the binding energy due to relative surface charging. The Zeta potential of adsorbent was instrumented with a Zeta potential analyzer (Zetasizer NANO ZS, Malvern, UK). The heavy metal concentration was determined using atomic adsorption spectroscopy (TAS-990 Super F, Beijing Pursee General Instrument Co. Ltd., China). The concentration of total organic carbon (TOC) was measured by TOC Analyzer (multi N/C 2100 BU, Analytic jena, Germany).

2.4. Adsorption Experiments

Batch adsorption experiments were conducted to investigate the influence of initial pH, temperature, and the molar ratios of the heavy metal and ligands on the Cd(II) complex adsorption. Cd(II) complexes with citric acid and tartrate acid were labeled as Cd(II)-CA and Cd(II)-TA, respectively. Stock solutions of Cd(II)-CA and Cd(II)-TA with different molar ratios of Cd(II) and ligands were prepared by mixing cadmium sulfate with CA and TA, respectively. Diluted NaOH and HNO₃ solutions were used to adjust the initial pH.

The adsorption experiments were conducted in a series of 150 mL polypropylene tubes using the different Cd(II) complexes. In a typical experiment, 0.2 g of adsorbent was added into each polypropylene tube with 50 mL of the working solution with molar ratios of heavy metals and ligand agents 1:1 of pH 6.0. The tubes were then shaken at 150 rpm under 25±2°C on a water-bath sway gyratory shaker (CHA-SA, Jintan Honghua Instrument Plant, Jiangsu Province, China). In the pH experiment, the initial pH was adjusted

to 2.0, 4.0, 6.0, 7.0, 8.0, and 10.0. In the temperature experiment, the water-bath temperature was adjusted to $5\pm2^\circ\text{C}$, $25\pm2^\circ\text{C}$, and $45\pm2^\circ\text{C}$. To investigate the effects of the molar ratios of the heavy metals and ligands, the molar ratios were adjusted to 1:0.5, 1:1, and 1:2. After 24 h adsorption, the water sample was filtrated using a $0.45\ \mu\text{m}$ membrane filter prior to sample analysis. All of the single factor experiments were performed in duplicate.

In kinetics experiments, after a prescribed contact time, the working solution was sampled and filtrated immediately using a $0.45\ \mu\text{m}$ membrane filter. Different concentrations of solutions were prepared to conduct the isotherm experiments.

The adsorption capacity of Cd was calculated using the following equation:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

where q_t represents the amount of Cd adsorbed per unit mass of AMBP (mg/g) at a given time of t , the same below; C_0 is the initial concentration of Cd (mg/L); C_t is the concentration of Cd (mg/L) at a given time t ; and m is the mass of the adsorbent (g).

2.5. The Ability to Reuse

The AMBP that had adsorbed Cd(II)-CA/TA was transferred to 100 mL of 1 M HCl. It was then stirred continuously for 24 h at room temperature. The adsorbent was obtained after filtration. Then it was washed with DI water until the pH was stable. Finally, the sample was dried for 720 min at a temperature of 60°C to obtain the regenerated adsorbent. The reusability of the adsorbent through four cycles of experiments was examined. The reusability experiment was conducted as follows: 0.2 g adsorbent was added into 50 mL of the working solution with the molar ratios of Cd(II) and ligand agents 1:1 of pH 6.0. This was then shaken at 150 rpm under $25 \pm 2^\circ\text{C}$.

3. Results and Discussions

3.1. Adsorbent Characterization

3.1.1. SEM and elemental analysis

Fig. 1 illustrates the SEM images of the MBP, the mercerized MBP,

the EMBP, and the AMBP. The SEM image for the MBP (Fig. 1(a)) shows a surface characterized by good interlocking between fibers and the polymer matrix. The surface of the mercerized MBP (Fig. 1(b)) indicates that the polymer matrix was removed or extracted by the NaOH, and a hollow porous structure was exposed. However, the fiber bundles showed good adhesion at interface. The surface of the fibers of the EMBP with hollow porous structures was partially filled (Fig. 1(c)), and it was coarser than that of mercerized MBP due to the epoxidation. The fiber image in the AMBP sample was similar to that in EMBP and even smoothed, as shown in Fig. 1(d).

The elemental analysis was used to characterize the nitrogen change during the preparation of the AMBP. The elemental analysis results are listed in Table S1. The nitrogen content decreased from 0.3% to 0.14%, 0.1% after mercerization and epoxidation. It then increased to a percent of 0.9%, confirming the insertion of the TEPA onto the moso bamboo fiber.

3.1.2. FTIR analysis

To analyze the changes in the functional groups during the chemical modification process, the MBP, mercerized MBP, EMBP, and AMBP were characterized using the FT-IR spectra, as shown in Fig. 2. In the spectrum of the MBP, the peaks at 3,200–3,450, 1,632, and $1,330\ \text{cm}^{-1}$ could be attributed to the stretching vibrations of the hydroxyl group (O-H). The peak at 3,200–3,450 cm^{-1} may also correspond to the stretching vibration of N-H and N-H₂ [24], because bamboo, a type of natural lignocellulose plant, is made up of approximately 47% cellulose, 26% lignin, and 27% of other types of substrates [22].

In the spectra of the mercerized MBP, the EMBP, and the AMBP, the peak at $1,736\ \text{cm}^{-1}$ disappeared. This was because some substrates, such as lignin and polyoses, could have been removed by mercerization reaction. In the EMBP, the peak at 3,200–3,450 became strong and wide, which could have been attributed to the hydrogen bonds after epoxidation [25]. In the spectrum of the AMBP, the peak at 3,200–3,450 cm^{-1} became stronger and widened further, indicating the MBP had been successfully modified by the TEPA due to the introduction of new hydroxyl group (O-H) and amine (NH₂) group at $3,140\ \text{cm}^{-1}$, $3,275\ \text{cm}^{-1}$, and $3,448\ \text{cm}^{-1}$ and a secondary amine (N-H) at approximately $3,400\ \text{cm}^{-1}$ [24–26].

Fig. 1. SEM micrographs of (a) the MBP; (b) the mercerized MBP; (c) the EMBP; and (d) the AMBP.

3.1.3. BET surface area analysis

BET surface area analysis and Barrett-Joyner-Halenda (BJH) pore size and volume analysis were applied to evaluate the specific surface properties of MBP and AMBP (Table S2). The BET specific surface area calculations showed that the AMBP has a higher surface area (0.463 m²/g) than that of the MBP (0.253 m²/g). The increase of the specific surface area may be mainly due to the alkali treatment before the chemical modification, which remove most impurities. In addition, the results indicated that MBP is macroporous materials, while AMBP is mesoporous material.

Fig. 2. The FTIR spectrums of the MBP, the mercerized MBP, the EMBP, and the AMBP.

3.2. Adsorption Performances

3.2.1. Effect of pH

The adsorption performance of AMBP was compared with MBP control test before the investigation of the single-factor effects (Fig. S1). AMBP showed an obviously better performance than MBP. Since the reactive epoxy groups have reacted with TEPA, the results suggested that the amine groups were the functional group in AMBP.

The pH value of the solution is an important control variable that may influence the adsorption process on the solid-liquid interface. The effect of the initial pH on the adsorption capacity of Cd (II)-CA/TA was investigated. Fig. 3(a) and (b) show that the adsorption removal of Cd (II)-CA and Cd (II)-TA increased significantly from pH 2.0 to 6.0, then further increased steadily to 10.0. These results could be attributed to the effects of the concentration of protons on the adsorbent surface charge and the speciation of the heavy metals and the fraction of ligand anionic forms [10, 27].

To clarify the effect of proton on the adsorbent surface charge, Zeta potential change was determined (Fig. S2). The surface charge of AMBP decreased with the increasing of pH value, while the removal of Cd (II)-CA and Cd (II)-TA increased. The results suggested that electrostatic action played an important role. The concentration of protons affects the distribution of surface groups. The pK_a of the -NH₂ protonation constant is 6.5 at a pH < 6.5, the predominant

species of adsorbent is RNH₃⁺ at a pH > 6.5, and the predominant species is RNH₂ [28]. The N atom in -NH can also be protonated when the pH < 3.1 [29, 30]. However, the distribution of heavy metal species and ligands species would change with pH increasing. At pH 2.0, Cd was primarily present in the form of free cadmium (cationic form) [31], which is electrostatically repelled by protonated amine groups. Therefore, the adsorption removal was the lowest. Then a series of complex of cadmium and citrate/tartrate appeared with increasing pH to 6.0. For example, in the presence of citrate, the species of Cd(H₂cit)⁺, Cd(Hcit)⁰, and Cd(cit)⁻ had less positive charge or even a negative charge that would enhance their ability to approach the protonated amine groups [31]. However, the partially dissociated ligand of citrate existing as anions may have involved a supplementary competition due to the attraction by protonated amine groups [28]. However, these anions adsorbed onto the adsorbent surface may have formed coordination with Cd(II) and facilitated the adsorption of Cd(II).

When the pH increased to 7.0 and higher, the Cd(II) existed as anionic species Cd(cit)⁻, Cd(cit)₂⁴⁻, and Cd(cit)OH²⁻, and the predominant adsorbent species was -NH₂/-NH. The high removal efficiency could have been attributed to the strong complexation competition of -NH₂/-NH with Cd(II) from Cd(II)-CA besides physisorption [18]. A similar phenomenon of Cd(II)-TA adsorption could also be explained in a similar manner.

In summary, the AMBP was effective at adsorbing Cd(II) complexes with CA and TA under a wide pH range from 4.0 to 10.0.

3.2.2. The effect of temperature and thermodynamics

The effect of temperature on the adsorption of Cd(II) complexes with CA and TA was investigated. Fig. 3(c) and (d), shows the adsorption removal of Cd(II)-CA and Cd(II)-TA on the AMBP at different temperatures. The removal ratio increased with an increase in temperature from 5 to 45°C, which meant that the adsorption of Cd(II)-CA and Cd(II)-TA on the AMBP was an endothermic process. The Cd(II) removal increased with an increase in temperature, since the increased temperature could facilitate molecular motion and enhance the interaction between the adsorbate and the adsorbent [32]. Therefore, a better adsorption removal of the Cd(II) complexes with CA and TA was achieved by raising the adsorption temperature from 5 to 45°C.

The thermodynamic parameters were calculated using the following equations [33].

$$K_C = C_{ads}/C_e \quad (2)$$

where K_C is the Langmuir constant, C_{ads} is the concentration of adsorbed metal ions (mg/L) and C_e is the equilibrium concentration (mg/L).

$$\Delta G_{ads}^0 = -RT \ln K_C \quad (3)$$

$$\ln K_C = (\Delta S_{ads}^0/R) - (\Delta H_{ads}^0/RT) \quad (4)$$

where ΔG_{ads}^0 is the change in Gibbs free energy (kJ/mol), ΔH_{ads}^0 is the change in enthalpy (kJ/mol), ΔS_{ads}^0 is the change in entropy (J/(mol·K)), R is the universal gas constant (8.314 J/(mol·K)) and

Fig. 3. The effects of the solution pH, temperature, and the Cd(II)/ligand molar ratio on Cd(II) complexes adsorption on the AMBP (initial Cd(II) concentration 30 mg/L): (a), (b) pH on Cd(II)-CA and Cd(II)-TA adsorption, respectively; (c), (d) temperature on Cd(II)-CA and Cd(II)-TA adsorption, respectively; (e), (f) the Cd(II)/ligand molar ratio on Cd(II)-CA and Cd(II)-TA adsorption, respectively.

T is the temperature (K). From the plot of $\ln K_c$ vs. $1/T$, values of ΔH_{ads}^0 and ΔS_{ads}^0 can be calculated from the slope $-(\Delta H_{ads}^0/RT)$ and the intercept $(\Delta S_{ads}^0/R)$, respectively. The thermodynamic parameters are summarized in Table S3.

The positive values of ΔH_{ads}^0 also indicated that the adsorption processes were endothermic. The negative values of ΔG_{ads}^0 showed that the adsorption process were feasible and spontaneous. In addition, the positive values of ΔS_{ads}^0 implied that the randomness were increasing at the solid-liquid interface during the adsorption process.

3.2.3. The effect of the Cd(II)/ligand molar ratio

The effects of the Cd(II)/ligand molar ratio on the adsorption of cadmium from solutions were investigated. Fig. 3(e) and (f) shows the adsorption removal of Cd(II) from the CA/TA solutions under different molar ratios. When the Cd(II)/ligand molar ratio changed from 1:0.5 to 1:1, the adsorption removal of Cd(II) increased significantly. This phenomenon may be because the anionic ligand species of CA and TA were adsorbed onto the adsorbent surface. To determine the effects of CA and TA adsorption by AMBP on Cd(II) removal, TOC concentration was measured (Table S4). The decrease of TOC value indicated that CA/TA was involved in Cd(II) adsorption. In addition, ΔTOC increased when the Cd(II)/ligand molar ratio changed from 1:0.5 to 1:1. These adsorbed anionic ligand species increased the carboxylic acid groups on the surface of the adsorbent, thereby causing an increment in the adsorption of Cd(II) [34]. This result was consistent with the XPS characteristic of the AMBP after adsorption (Fig. 7, a new carboxylic acid group

appeared).

However, further increase of the ligand concentration may have different effects on Cd(II) removal. When the Cd(II)/ligand molar ratio changed further from 1:1 to 1:2, the Cd(II) removal from the TA solution increased from 75.4% to 82.3%. However, the Cd(II) removal from the CA solution nearly remained stable, which indicated that the enhancement of the ligand concentration increase on the Cd(II) removal was not unlimited.

3.2.4. Kinetic studies

Time-dependent experiments were conducted to understand the adsorptive rate of the Cd (II) complexes onto the AMBP. Fig. 4 shows the kinetic curves of Cd (II)-CA and Cd (II)-TA adsorption on the AMBP. For the Cd(II) complexes adsorption, q_t increased rapidly within the initial 120 min, and then increased at a much slower rate and gradually stabilized at approximately 480 min.

The kinetic curves were simulated using the pseudo-first-order kinetics, the pseudo-second-order model, and the intra-particle diffusion model [35]. The pseudo-first-order kinetics is commonly expressed as follows:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \quad (5)$$

In this model, q_e (mg/g) is the equilibrium adsorption capacity, the same below; the plot of $\log(q_e - q_t)$ versus t , k_1 is the equilibrium constant of the pseudo-first order adsorption (min^{-1}).

The pseudo-second-order model is described as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

where k_2 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$) is the rate constant.

The empirical equation of the intra-particle diffusion model, commonly applied to characterize the diffusion mechanism, is presented as Eq. (7):

$$q_t = K_p t^{0.5} + C \quad (7)$$

where K_p ($\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1/2}$) is the constant rate of the intra-particle diffusion model, and the constant of C (mg/g) represents the boundary layer effect, which is proportional to the extent of the boundary layer thickness.

Table S5 shows the calculated values of k_1 , k_2 , K_p , C , and R^2 , as well as the values of the regression coefficients for the aforementioned three kinetic models. It is generally accepted that the mass transfer of adsorption process may be controlled by four independent processes: (i) bulk diffusion; (ii) film diffusion;

(iii) intra-particle diffusion; and (iv) chemical reaction (adsorption at a special site on the surface) [36]. In this work, the process of bulk diffusion was not proposed to be the limiting step due to the rapid mechanical mixing. The R^2 values (between 0.81 and 0.87) of the intra-particle models suggested that the internal diffusion was not the only rate-determining step, and some other mechanism may also be involved. However, the higher R^2 values (> 0.999) of the pseudo-second-order (fitting results are shown in Fig. 4, the inserted graph) than the other two models showed that the pseudo-second-order model fitted the adsorptive rate data better. Hence, the adsorption process of Cd (II)-CA and Cd (II)-TA adsorption on the AMBP may have been controlled predominately by chemical processes (adsorption at a special site on the surface) [37]. Consequently, the pseudo-second-order model explained the mechanism of the sorption process of the studied Cd (II) complexes on the AMBP.

3.2.5. Adsorption isotherms

The Langmuir and Freundlich models were used to simulate the isotherms data. The Langmuir model expression is the following [32]:

$$q_e = \frac{q_{\max} K_L C_e}{(1 + K_L C_e)} \quad (8)$$

where $q_{\max}$ (mg/g) is the maximum adsorption capacity; C_e (mg/L) is the equilibrium Cd concentration, the same below; and K_L is a constant related to the binding energy.

The Freundlich model is expressed as the following [32]:

$$q_e = K_f C_e^{1/n} \quad (9)$$

Where K_f ($\text{mg/g})(\text{L/mg})^{-1/n}$; and n are parameters related to the adsorption capacity and the intensity of adsorption.

The adsorption isotherms are described as shown in Fig. 5. In addition, the linear regression method was used to determine the applicability of the two models. The fitting parameters are summarized in Table S6. The Langmuir model ($R^2 = 0.981\text{--}0.987$) fitted the adsorption isotherms better than the Freundlich model ($R^2 = 0.927\text{--}0.981$) for both Cd(II)-CA and Cd(II)-TA.

The maximum adsorption capacities of Cd-CA and Cd-TA estimated by the Langmuir model were calculated to be 14.41 mg/g and 7.58 mg/g , respectively. This result can be attributed to the molecular structure difference between CA and TA. CA and TA molecules contain 3 and 2 carboxyl groups, respectively, which are the primary chelating group. Therefore, in the equimolar concentration system of Cd(II) and CA/TA, when the partially dissociated ligand of citrate and tartrate adsorbed onto the adsorbent surface, a stronger coordination of CA with Cd(II) may have facilitated the adsorption of Cd(II). $1/n$ in the Freundlich isotherm model represents the curve of the isotherm or the energy distribution of the adsorption site. $2 < n < 10$ means an easier adsorption for both Cd(II)-CA and Cd(II)-TA [38]. The n values of Cd(II)-CA and Cd(II)-TA were 1.975 and 2.295, respectively, which suggested that the adsorptions of Cd(II)-CA and Cd(II)-TA on the AMBP were relatively easy.

The separation factor (R_L) was also used to confirm whether the adsorption process was favorable. R_L is given by Eq. (10):

$$R = \frac{1}{1 + K_L C_0} \quad (10)$$

Fig. 4. Kinetic curves of the Cd (II) complexes adsorption onto the AMBP (initial Cd(II) concentrations: (a) Cd (II)-CA: 20 mg/L and (b) Cd (II)-TA: 30 mg/L).

Fig. 5. Adsorption isotherms of (a) Cd(II)-CA and (b) Cd(II)-TA on the AMBP.

The value of R_L reflects the trend of adsorption: irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), and unfavorable ($R_L > 1$) [32]. In this experiment, the values of R_L for both Cd(II)-CA and Cd(II)-TA were 0.12 and 0.05, respectively, indicating that the adsorption process was favorable.

3.2.6. The ability to reuse

Reusability is a very important feature for an adsorbent in practical applications. Fig. 6 shows the results of the four cycles of Cd(II)-CA and Cd(II)-TA adsorption by the samples. The adsorption performance of the AMBP for Cd(II)-CA and Cd(II)-TA decreased obviously after the first cycle. However, then the adsorption capacity of Cd(II)-CA and Cd(II)-TA remained stable and at approximately 75% and 68%, respectively, after four cycles. This result suggested that the AMBP adsorbent could be recycled and reused at least 4 times.

3.3. Adsorption Mechanism

EDS analysis was carried out to identify the presence of Cd in the adsorbent surface after adsorption. The EDS spectra of AMBP

Fig. 6. The adsorption capacity recovery of Cd(II)-CA and Cd(II)-TA adsorption on the AMBP (initial Cd(II) concentrations: (a) 30 mg/L and (b) 30 mg/L).

and two typical AMBP samples after adsorption of Cd(II)-CA and Cd(II)-TA, are shown in Fig. S3. The new characteristic peaks of Cd in the spectra after adsorption confirmed the adsorption of Cd(II).

To investigate the mechanism of Cd(II) adsorption by the AMBP from the CA/TA solution, the samples were further characterized using XPS before and after adsorption. The results are shown in Fig. 7. There was no Cd element on the adsorbent prior to adsorption (Fig. 7(a)). The Cd 4d (405.3 eV) and Cd 3d (412.0 eV) appeared after adsorption [38] (Fig. 7(b) and (c)), which indicated that the Cd(II) in the solution was adsorbed to the AMBP.

The C1s, O1s, and N1s peaks of the AMBP before and after adsorption of Cd(II) were further analyzed. The C1s spectrum of the AMBP (Fig. 7(d)) could be deconvoluted into peaks at 284.8 eV and 285.4 eV, 287.7 eV, and 286.3 eV attributed to C-C(H), C=O, and C-N/C-O/C-OH, respectively [1, 39-41]. After adsorption, the primary change in the C1s spectra (Fig. 7(e) and (f)) was the appearance of a new peak at 288.7 eV. This was attributed to -COOH [2], which suggested that CA/TA was involved in the Cd(II) adsorption on the AMBP.

Compared with the peaks of N1s before and after adsorption, as shown in Fig. 7(a), (b), and (c), the changes occurred at the binding energy of C-NH₂/C-NH. The peak of the protonated amino group (-NH₃⁺) (401.8 eV) [27], which was produced during the course of the adsorbent purification rinse using the acidic DI water, significantly weakened after adsorption. The binding energy of C-NH₂/C-NH became larger after adsorption from 399.4 eV to 399.5 eV for Cd(II)-CA and 399.7 eV for Cd(II)-TA, since the lone pair of electrons in the N atom was shared between N and Cd(II), leading to the decrease of electron cloud density of the N atom, and a higher binding energy peak was observed [38]. Therefore, the XPS spectra of the N1s effectively confirmed that one of the adsorption mechanisms was the complexation between -NH₂/-NH and Cd(II) [38].

Based on the above results, it was concluded that $\text{-NH}_2\text{-NH}$ participated in the Cd(II) adsorption process to form complexes [38]. In addition, given that $\text{-COO-}/\text{-COOH}$ was present in the adsorption, the primary possible adsorption mechanisms for Cd(II)-CA/TA on the AMBP at pH = 6.0 were described, as shown in Fig. 8. The Cd(II) removal from the solution bearing CA/TA on the adsorbent could be adsorbed through physisorption. For example, the Cd(II)-CA/TA anions (for example, $\text{Cd}(\text{cit})^-$) could be adsorbed by the protonated amino groups of the adsorbent through the electrostatic interaction. $\text{Cd}(\text{Hcit})^0/\text{Cd}(\text{tart})^0$ could also be adsorbed through van der Waals forces. The nitrogen atom in the $\text{-NH}_2\text{-NH}$ may have further coordinated with the adsorbed Cd(II) in $\text{Cd}(\text{Hcit})^0$, $\text{Cd}(\text{tart})^0$, and even $\text{Cd}(\text{cit})^-$ due to chemical bonding.

4. Conclusions

A new functionalized moso bamboo powder adsorbent was successfully prepared using a facile procedure with the mild reaction conditions and the simple reaction equipment. The batch adsorption experiment demonstrated that the adsorption Cd(II) complexes with CA and TA on the AMBP is an easy process. The AMBP was effective for the adsorption of Cd(II)-CA/TA under a wide pH range. An increase of ligand concentration was favorable for Cd(II) removal. The adsorption process of Cd(II)-CA/TA on the AMBP followed a pseudo-second-order kinetic model which revealed that the rate-determining step was the chemisorption. The Langmuir model fitted the adsorption isotherms better than the Freundlich model for both Cd(II)-CA and Cd(II)-TA. XPS analyses indicated that the Cd(II) in the solution was adsorbed to the surface of AMBP. The uptake mechanisms of Cd(II)-CA/TA were proposed to be physisorption, and this included electrostatic interactions, van der Waals forces, and chemisorption of the coordination reaction between $\text{-NH}_2\text{-NH}$ and the Cd(II) complexes. The AMBP would be a low-cost and renewable adsorbent for Cd(II)-CA/TA removal.

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Author Contribution

Q.S. (Ph.D. student) Writing-Review & Editing. S.L. (Professor) Conceptualization, Methodology, Supervision. G.L. (Professor) Conceptualization, Methodology, Supervision. Y.X. (Master student) Data curation. L.G. (Master student) Software, Validation. P.L. (Professor) Writing- Review & Editing. All authors have read and agreed to the published version of the manuscript.

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