



Article Single and Binary Adsorption Behaviour and Mechanisms of Cd²⁺, Cu²⁺ and Ni²⁺ onto Modified Biochar in Aqueous Solutions

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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Abstract: The chitosan–EDTA modified magnetic biochar (E–CMBC) was successfully used as a novel adsorbent to remove heavy metals. The adsorption behaviour and mechanisms of E–CMBC to Cd²⁺, Cu²⁺ and Ni²⁺ were performed in single and binary system in aqueous solutions. In single–metal system, the adsorption process of Cd²⁺, Cu²⁺ and Ni²⁺ on E–CMBC fitted well with the Avrami fractional–order kinetics model and the Langmuir isotherm model. The measured maximum adsorption capacities were 61.08 mg g⁻¹, 48.36 mg g⁻¹ and 41.17 mg g⁻¹ for Cd²⁺, Cu²⁺ and Ni²⁺, respectively. In binary–metal system, coexisting ions have obvious competitive adsorption behaviour on E–CMBC when the concentration of heavy meal beyond 20 mg L⁻¹. The maximum adsorption capacities of the heavy metals were found to be lower than that in single–metal system. The order of the competitive adsorption ability was Cu²⁺ > Ni²⁺ > Cd²⁺. Interestingly, in Cd²⁺–Cu²⁺ system the earlier adsorbed Cd²⁺ could be completely replaced by Cu²⁺ from the solution. Different competitive adsorption ability of those heavy metal were due to the characteristics of heavy metal and resultant affinity of the adsorption sites on E–CMBC. The adsorption mechanism indicated that chemical adsorption played a dominating role. Therefore, E–CMBC could be a potential adsorbent for wastewater treatment.

Keywords: modified biochar; heavy metals; competitive adsorption; mechanisms

1. Introduction

With the rapid development of industry, various organic and inorganic industrial pollutants are discharged into the environment, leading to a series of environmental and ecological problems [1–3]. Among them, heavy metal pollution in wastewater has attracted widespread attention for its mobility, non–degradability and toxicity in aquatic environment [4]. Heavy metal ions (such as Cu²⁺, Cd²⁺, Ni²⁺) can accumulate in human organisms, which will have serious impact on human health when its levels exceed the permissible limits [5]. Numerous treatment technologies, such as chemical precipitation [6], membrane filtration [7], electrochemical treatment [8], ion exchange [9], biological treatment [10], have been applied to remove the heavy metal ions from wastewater. However, there still exists many defects in each technology, such as low adsorption efficiency, low selectivity, high cost, and secondary pollution, which restrain its large–scale application [11,12]. Currently, adsorption is considered one of the best choice due to its easy operation, low cost and high efficiency [13]. Therefore, it is particularly important to develop a cheap, efficient and widely available adsorbent.

Biochar as a carbon–rich adsorbent has attracted more attention due to its unique properties, such as high surface area, high porosity and cation exchange capacity [14]. Biochar has been used widely as a multifunctional material in environmental remediation, soil reclamation, and energy recovery [15,16]. The adsorption performance of biochar for heavy metals is greatly affected by feedstock types (pinewood, dairy manure, rice husk, etc.) and pyrolysis conditions (temperature, heating rate, residence time, etc.). However, the relatively low heavy metal adsorption ability and difficulty to separate from aqueous solution are regarded as the major disadvantages which limit its application in the treatment of heavy metal polluted wastewater [17]. Acid/base treatment, surface oxidization, chemical graft, physical modification, and magnetic modification, are the main methods to modify and enhance the adsorption performance of biochar [18]. In particular,

to meet the individual requirements of environmental restoration [19]. In recent years, plenty of researches have confirmed chemical grafted biochar have promising adsorption properties for heavy metals. Li et al. [20] synthesized an aminothiourea chitosan modified magnetic biochar composite which had higher affinity for Cd²⁺ than the raw biochar. Further, the composite adsorbent presented an excellent adsorption efficiency for other heavy metal ions from real mining water. Ly et al. [21] found that the maximum adsorption capacities for Cu^{2+} increased from 6.85 mg g⁻¹ to 42.19 mg g⁻¹ by the EDTA—functionalized bamboo activated carbon. Sajjadi et al. [22] developed an urea functionalization of ultrasound-treated biochar and investigated its capability in adsorbing Ni^{2+} . It was found that the modified biochar could remove more Ni^{2+} in six hours than that using the raw biochar in twelve hours. However, most of the present research focused on the adsorption behaviour of heavy metals by biochar in a single-metal system [23–25]. In fact, wastewater often contains more than one type of heavy metal, and the coexist ions will influence the adsorption of target ions by biochar [26]. However, studies focused on the adsorption of biochar in multi-metal systems are still lacking. Deng et al. [27] have synthesized the chitosan-pyromellitic dianhydride modified biochar to remove heavy metal ions (Cd^{2+} , Cu^{2+} and Pb^{2+}) from mixed-metal aqueous solutions. It focused on the comparison of adsorption capacity and the selectivity sequences of the three metal ions while the competitive absorption behaviour and mechanisms of heavy metals in binary-metal systems is still not clear.

chemical graft receives more attention as it can add different functional groups on biochar

Our previous study found that chitosan–EDTA modified magnetic biochar (E–CMBC) had an excellent adsorption performance for Pb^{2+} in the single–metal system [28]. However, its efficiency to remove Cd^{2+} , Cu^{2+} and Ni^{2+} from single–metal (non–competitive) and binary–metal (competitive) systems are yet to be investigated. The purposes of this study were: (1) to investigate the adsorption capacities of Cd^{2+} , Cu^{2+} and Ni^{2+} on E–CMBC in single–metal systems; (2) to evaluate the competitive adsorption behaviour of Cd^{2+} , Cu^{2+} and Ni^{2+} on E–CMBC in binary–metal systems; (3) to elucidate the adsorption mechanisms of Cd^{2+} , Cu^{2+} and Ni^{2+} on E–CMBC.

2. Materials and Methods

2.1. Materials

The raw biomass measurements of the peanut shells were obtained from an agricultural field (Taian, Shandong, China). The chemicals used in the present research, including FeCl₃·6H₂O, copper nitrate trihydrate (Cu(NO₃)₂·3H₂O), cadmium nitrate tetrahydrate (Cd(NO₃)₂·4H₂O), nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O), 1–ethyl–3–(3– dimethylaminopropyl) carbodiimide hydrochloride (EDAC), and ethylenediaminetetraacetic acid (EDTA), acetic acid, chitosan, NaOH, HCl, were purchased from Aladdin Reagent Co. Ltd. Shanghai, China. All of these chemicals were analytically grade without extra treatment. De–ionized water was used to prepared solutions in all experiments.

2.2. Preparation and Characterization of Modified Biochar

The milled peanut shells were immersed into FeCl₃ solution (1 mol L⁻¹). After 24 h, the immersed biomass was oven–dried, then pyrolyzed at 500 °C for 2 h in N₂ atmosphere. The biochar obtained were milled and added to the acetic acid solution of chitosan (1%, g v⁻¹) and reacted for 2 h, then the mixture solution was adjusted to pH 10 by adding 1% NaOH solution. After stirring overnight, the filter residue was washed with plenty of de–ionized water, oven–dried, and milled. Equal quality of the sample and EDTA (1.0 g) were stirred at 60 °C in de–ionized water for 4 h. Then NaOH and EDAC were added when the reacted solution cooled down to 40 °C. The solution was stirred for 2 h and then naturally cool down to room temperature and keep the reaction overnight. The filtered solid composite was washed to be neutral, and oven–dried and sieved through a 100–mesh, which was referred to as E–CMBC.

The E–CMBC sample was characterized by SEM (Zeiss, Oberkochen, Germany), BET (Quantachrome, Boynton Beach, FL USA), XPS (Thermo, Waltham, MA USA), FTIR (Thermo, Waltham, MA USA), XRD (Rigaku, Tokyo, Japan),VSM (Lake Shore, Dunkirk, NY, USA), and Zeta potential (Malvern, Worcestershire, UK). Detailed synthesis process and physico–chemical characteristics of the E–CMBC had been reported in our previous study [28].

2.3. Batch Adsorption Experiments

The standard stock solutions (1000 mg L^{-1}) of Cd²⁺, Cu²⁺ and Ni²⁺ ions were prepared by dissolving the exact amounts of respective salts. The standard solutions were diluted to a specific concentration by de-ionized water when used. Both single-metal and binary–metals batch adsorption experiments of Cd²⁺, Cu²⁺ and Ni²⁺ were conducted. In single-metal systems, batch experiments were performed in 50 mL conical flask by mixing 25 mg E–CMBC with 25 mL heavy metal solution. The effect of initial pH on the adsorption capacity of E-CMBC were investigated in the range of 2-6. The pH of the solution was adjusted by adding negligible volumes of either HCl or NaOH. Adsorption kinetics experiments were examined at different time intervals (5 min-1440 min) with heavy metals concentration of 100 mg L^{-1} at pH 6. Adsorption isotherms were determined within different initial concentrations of the heavy metals (10 mg L^{-1} -500 mg L^{-1}) for 24 h. In binary-metal systems, the initial concentration of the two metals is the same. Batch experiments were conducted with the same procedure of single-metal systems. Kinetics experiments were conducted with the same time intervals as the experiment in single-metal systems. Adsorption isotherms were determined with initial concentrations of the heavy metals varying from 10 mg L^{-1} to 200 mg L^{-1} .

After adsorption, the residual heavy metal was detected by atomic absorption spectrometer (Agilent 240FS AA). All adsorption experiments were conducted in triplicates. The adsorption amount of metal q_e (mg g⁻¹) were evaluated using the following equation:

$$q_e = \frac{(c_0 - c_e) \times V}{m} \tag{1}$$

where $c_0 \pmod{\text{L}^{-1}}$ and $c_e \pmod{\text{L}^{-1}}$ are the initial concentration and the concentration at equilibrium, respectively; *m* (g) and *V* (L) are the weight of E–CMBC and the volume of metal solution, respectively.

3. Results and Discussion

3.1. Adsorption of Cd^{2+} , Cu^{2+} and Ni^{2+} in the Single–Metal System

Batch adsorption experiments were conducted to investigate the adsorption potential of E–CMBC to Cd^{2+} , Cu^{2+} and Ni^{2+} in a single–metals system. The effects of pH on the adsorption capacity of E–CMBC to Cd^{2+} , Cu^{2+} and Ni^{2+} were illustrated in Figure 1. To avoid the precipitation of heavy metal ions, the pH range of the solution were selected between 2–6. The adsorption capacities of E–CMBC to Cd^{2+} and Cu^{2+} were 39.75 mg g⁻¹,

30.72 mg g⁻¹ at pH 2, and the adsorption capacity increased with the raise of the pH, finally increased to 60.35 mg g⁻¹, 48.05 mg g⁻¹ at pH 6. It may be due to the stronger positive charge on the surface of E–CMBC at lower pH which will repel the metal cations [29]. With the pH increases (pH_{PZC} 3.25), the surface of E–CMBC gradually changes from positively charged to negatively charged, which will provide more adsorption sites and improve the adsorption capacity to heavy metal ions [30]. However, the adsorption capacity to Ni²⁺ exhibited a slight increase from 37.75 mg g⁻¹ to 40.7 mg g⁻¹ when the pH increased from 2 to 6. It suggested that the adsorption of E–CMBC to Ni²⁺ is less affected by pH, and the electrostatic interactions is not the key role in the process of Ni²⁺ adsorption, we found the similar adsorption behaviour of E–CMBC to Pb²⁺ in single–metal system [28].



Figure 1. Effect of initial solution pH and zeta potential on Cd²⁺, Cu²⁺ and Ni²⁺ for E–CMBC.

The influence of the contacting time on the adsorption capacity of E–CMBC to Cd^{2+} , Cu^{2+} and Ni^{2+} were also investigated. As shown in Figure 2a, the adsorption capacity of E–CMBC to Cd^{2+} , Cu^{2+} and Ni^{2+} within 60 min accounted for approximately 91.76%, 90.03%, and 91.89% of the equilibrium capacity. It may be attributed to the abundant available adsorption sites on the surface of the adsorbent at the beginning of the adsorption process. With the adsorption time increases, the available adsorption sites become less, therefore the adsorption rate slows down gradually.



Figure 2. (a) Adsorption kinetics of Cd^{2+} , Cu^{2+} and Ni^{2+} on E–CMBC in single–metal system; (b) adsorption isotherms of Cd^{2+} , Cu^{2+} and Ni^{2+} on E–CMBC in the single–metal system.

To evaluate the adsorption rates and explore the adsorption mechanism, the adsorption kinetics of E–CMBC to Cd^{2+} , Cu^{2+} and Ni^{2+} were fitted by three classic kinetic models, namely pseudo–first–order, pseudo–second–order, and Avrami fractional–order models. The formula and parameters are listed in Table S1 and the kinetic models fitting results are list in Table 1. The coefficient of determination (R^2) of the Avrami fractional–order model for Cd^{2+} , Cu^{2+} and Ni^{2+} was 0.99, 0.95, and 0.99, respectively, which were greater than that of pseudo–second–order and pseudo–first–order model for Cd^{2+} (0.98, 0.81), Cu^{2+} (0.88, 0.62), and Ni^{2+} (0.97, 0.82). According to the Avrami fractional–order model, the theoretical adsorption capacity of Cd^{2+} , Cu^{2+} and Ni^{2+} were 59.57 mg g⁻¹, 47.64 mg g⁻¹ and 40.24 mg g⁻¹, which were approximately the experiment results of Cd^{2+} (60.35 mg g⁻¹), Cu^{2+} (48.05 mg g⁻¹) and Ni²⁺ (40.7 mg g⁻¹), respectively. Therefore, the Avrami fractional–order model order model could more accurately describe the adsorption process. All the above findings suggested that the adsorption of E–CMBC to Cd^{2+} , Cu^{2+} and Ni^{2+} on was a multiple kinetics process, and the chemical adsorption played a dominating role [31,32].

Table 1. Adsorption kinetic model parameters for Cd^{2+} , Cu^{2+} and Ni^{2+} on E–CMBC in the single–metal system.

Metal Ion	Pseudo–First–Order Model		Pseudo–Second–Order Model		Avrami Fractional–Order Model	
Cd ²⁺	$q_e ({ m mg g}^{-1}) \ k_1 ({ m min}^{-1}) \ R^2$	57.0 0.17 0.81	$q_e (\mathrm{mg g^{-1}}) \ k_2 (\mathrm{g mg^{-1} min^{-1}}) \ R^2$	59.0 0.0048 0.98	$q_e \ ({ m mg g}^{-1}) \ k_3 \ ({ m min}^{-1}) \ R^2$	59.75 0.17 0.99
Cu ²⁺	$\frac{q_e \ (\text{mg g}^{-1})}{k_1 \ (\text{min}^{-1})} \\ R^2$	45.0 0.22 0.62	$ \frac{q_e (\text{mg g}^{-1})}{k_2 (\text{g mg}^{-1} \text{min}^{-1})} \\ \frac{R^2}{R^2} $	46.3 0.0089 0.88	$ \frac{q_e (\text{mg g}^{-1})}{k_3 (\text{min}^{-1})} \\ R^2 $	47.64 0.36 0.95
Ni ²⁺	$q_e (\mathrm{mg \ g}^{-1}) \ k_1 (\mathrm{min}^{-1}) \ R^2$	38.48 0.17 0.82	$\begin{array}{c} q_e \ (\mathrm{mg \ g^{-1}}) \\ k_2 \ (\mathrm{g \ mg^{-1} \ min^{-1}}) \\ R^2 \end{array}$	39.84 0.0072 0.97	$q_e (\mathrm{mg \ g}^{-1}) \ k_3 (\mathrm{min}^{-1}) \ R^2$	40.24 0.18 0.99

The effect of the initial concentration of single Cd^{2+} , Cu^{2+} and Ni^{2+} on adsorption capacity was shown in Figure 2b. Two widespread–used nonlinear isotherms including Langmuir and Freundlich were fitted by experimental data to evaluate the adsorption type and the adsorption capacity. The formula and parameters of the two isotherm models were shown in Table S2. Obviously, the adsorption capacity increased with the initial concentration of single Cd^{2+} , Cu^{2+} and Ni^{2+} and gradually progresses to equilibrium. From Table 2, the R² of the Langmuir model for Cd^{2+} , Cu^{2+} and Ni^{2+} were higher than that of the Freundlich model. It was clear that the Langmuir model describes the adsorption behaviour better than the Freundlich model. This indicated that the adsorption of E–CMBC to Cd^{2+} , Cu^{2+} and Ni^{2+} in the single–metal system mainly occurred in monolayer [25]. Further, the Langmuir maximum adsorption capacities of E–CMBC to Cd^{2+} , Cu^{2+} and Ni^{2+} in the single–metal system (q_{max}^{0}) were higher than that of some previous reported adsorbents [33–36]. Furthermore, the Langmuir maximum adsorption capacity order is $Cd^{2+} > Cu^{2+} > Ni^{2+}$ in single–metal system, which is different from the results of other researchers [37,38].

Table 2. Adsorption isotherm model parameters for Cd^{2+} , Cu^{2+} and Ni^{2+} on E–CMBC in the singlemetal system.

Metal	Langmuir Model			Freundlich Model		
Ion	q_m (mg g ⁻¹)	K_L (L mg ⁻¹)	<i>R</i> ²	K_F (L mg ⁻¹)	п	R^2
Cd ²⁺	61.95	3.24	0.98	36.35	0.11	0.62
Cu ²⁺	48.73	1.72	0.97	27.89	0.11	0.68
Ni ²⁺	40.38	6.61	0.96	26.15	0.094	0.73

3.2. Adsorption of Cd^{2+} , Cu^{2+} and Ni^{2+} in the Binary–Metal System

The competitive adsorption behaviour in binary–metal systems (Cd²⁺–Ni²⁺, Cu²⁺–Ni²⁺, Cd²⁺–Cu²⁺) were studied in the same initial concentrations. Some characteristic properties of Cd²⁺, Cu²⁺ and Ni²⁺, such as the hydrated radius, electronegativity, absolute hardness, and binding constant with EDTA, were listed in Table 3. The results showed that the maximum adsorption capacities of the three metals in the binary system (q_{max}^{mix}) were all lower than q_{max}^0 . The characteristic properties of E–CMBC and the heavy metal ions may be responsible for the different performances [38].

Metal Ion	Hydrated Radius (Å)	Electronegativity (Pauling)	Absolute Hardness	Binding Constant with EDTA
Cd ²⁺	4.26	1.69	10.3	16.5
Cu ²⁺	4.19	1.90	8.3	18.8
Ni ²⁺	4.04	1.91	8.5	18.7

Table 3. The properties of Cd^{2+} , Cu^{2+} and Ni^{2+} [38–40].

3.2.1. Cd²⁺-Ni²⁺ System

The adsorption kinetics of Cd²⁺–Ni²⁺ on E–CMBC were showed in Figure 3a. For both Cd^{2+} and Ni^{2+} , the adsorption capacities increased with the contact time and the adsorption process included a fast stage and a slow stage. The adsorption capacities of E-CMBC to Cd²⁺ and Ni²⁺ increased rapidly in the initial 60 min as there were plenty of binding sites on the surface of the adsorbent. After the binding sites were occupied by heavy metals, the adsorption gradually slows down and finally reaches the adsorption equilibrium. From Table S3, the experiment data fitted the pseudo-second-order and Avrami fractional-order model perfectly. It revealed that the adsorption of E-CMBC to Cd²⁺ and Ni²⁺ in Cd²⁺–Ni²⁺ systems was a multiple kinetics process too. The adsorption isotherms of E–CMBC to Cd^{2+} and Ni^{2+} in binary–metal systems were investigated and shown in Figure 3d, the parameters fitted by the Langmuir and Freundlich models were shown in Table S4. The \mathbb{R}^2 values (>0.94) suggested that the Langmuir model provided a better fit than the Freundlich model for both Cd^{2+} and Ni^{2+} in $Cd^{2+}-Ni^{2+}$ systems. It demonstrated that Cd²⁺ and Ni²⁺ were absorbed to distinct sites, in which each site could only combine one ion [31]. Competition between Cd^{2+} and Ni^{2+} affected the adsorption capacity of each other on E–CMBC. The Langmuir maximum adsorption capacities of Cd²⁺ and Ni²⁺ decreased from 61.95 mg g^{-1} and 40.38 mg g^{-1} in the single-metal systems to 32.63 mg g⁻¹ and 26.93 mg g⁻¹ in Cd²⁺–Ni²⁺ systems. The decrease in the amplitude of Cd²⁺ adsorption (47.33%) was larger than that of Ni²⁺ (33.31%), which suggesting that Cd²⁺ adsorption was more affected by Ni²⁺ competition. The resultant affinity of adsorption sites and chemical characteristics of the heavy metals may be responsible for this performance. A reasonable explanation for this result is that the hydrated radius of Ni²⁺ (4.04 Å) is smaller than that of Cd²⁺ (4.26 Å), that means Ni²⁺ has greater affinity for most functional groups on surface of E-CMBC (such as amino and carboxylic groups) [41]. Furthermore, the electronegativity of Ni^{2+} (1.91) is higher than Cd^{2+} (1.69), which ensure that Ni^{2+} is more favorably adsorbed than Cd²⁺. Ni²⁺ has the larger binding constant with EDTA compared with Cd^{2+} (Ni²⁺ logK = 18.7, Cd^{2+} logK = 16.5). Therefore, Ni²⁺ is more likely to combine with EDTA on the of the surface of E-CMBC.



Figure 3. Adsorption kinetics of Cd²⁺, Cu²⁺ and Ni²⁺ on E–CMBC in binary–metal system: (a) Cd²⁺–Ni²⁺ system; (b) Cu²⁺–Ni²⁺ system; (c) Cd²⁺–Cu²⁺ system. Adsorption isotherms of Cd²⁺, Cu²⁺ and Ni²⁺ on E–CMBC in binary–metal system; (d) Cd²⁺–Ni²⁺ system; (e) Cu²⁺–Ni²⁺ system; (f) Cd²⁺–Cu²⁺ system.

3.2.2. Cu²⁺-Ni²⁺ System

The relationship between adsorption capacity with contact time was established in $Cu^{2+}-Ni^{2+}$ system. Figure 3b showed the quantity of Cu^{2+} and Ni^{2+} with time. The adsorption capacities of Cu^{2+} and Ni^{2+} increases with time, and the adsorption process also includes a fast and slow stage too (Figure 3b). The pseudo–second–order and Avrami fractional–order model fit the Cu^{2+} and Ni^{2+} adsorption data well in the $Cu^{2+}-Ni^{2+}$ system (Table S3). The effect of initial concentration on the adsorption capacity and selectivity was shown in Figure 3e. With the initial heavy metal concentration increased, the adsorption capacity of Cu^{2+} gradually increased and approached equilibrium. However, the adsorption capacity of Ni^{2+} increased at first and then decreased to equilibrium. At low initial concentration (≤ 20 mg L⁻¹), the adsorption capacities of Cu^{2+} and Ni^{2+} in $Cu^{2+}-Ni^{2+}$ system were almost same to those in the single–metal systems. The results

suggested that there were excess binding sites on E–CMBC at low heavy metal concentration. Cu^{2+} and Ni^{2+} could bind to different sites without competition. With the heavy metal concentration increased (>20 mg L⁻¹), the adsorption capacity of Cu^{2+} gradually increased and approached equilibrium adsorption capacity, but it was still lower than the q_{max}^0 of Cu^{2+} . However, the adsorption capacity of Ni^{2+} decreased to equilibrium with the increase of the Ni^{2+} concentrations. Similar results have also been reported by other researchers [38]. These indicated that the adsorption of Cu^{2+} and Ni^{2+} could be inhibited by each other at the high initial concentration (>20 mg L⁻¹). Although the hydrated radius is larger and the electronegativity and binding constant with EDTA are similar, Cu^{2+} have stronger competitive adsorption performance than Ni^{2+} . It may be attributed to the lower polarizability and absolute hardness of Cu^{2+} than that of Ni^{2+} in the theory of hard and soft acids and bases [38].

3.2.3. Cu²⁺–Cd²⁺ System

The competitive adsorption of Cu²⁺ and Cd²⁺ within specified intervals were shown in Figure 3c. For Cu²⁺, adsorption increased rapidly in the initial 60 min, then showed only a small increment over the subsequent period, which fitted the Avrami fractionalorder model better (Table S3). In contrast, the adsorption capacity of Cd^{2+} was initially reached a maximum, then gradually decreased with time and finally became zero. It could be attributed to the abundant sites on the surface of E-CMBC at the beginning for Cu^{2+} and Cd^{2+} ; subsequently, the initially adsorbed Cd^{2+} was replaced by Cu^{2+} in the solution. Similar results were reported by other researchers [38,39,41]. Figure 3f showed the competitive adsorption of Cu²⁺ and Cd²⁺ in specified concentrations. It was clear that the adsorption capacity of Cu^{2+} increased with the increasing equilibrium concentration. Compared with the single-metal system, the maximum adsorption capacities of Cu²⁺ hardly changes in Cu^{2+} – Cd^{2+} systems. However, the adsorption capacity of Cd^{2+} increased at first and then gradually decreased to zero. The above phenomenon showed that the competitive adsorption and replacement would occur when the Cu²⁺ and Cd²⁺ reached certain concentration in the binary-metal system. Furthermore, the adsorption of Cd²⁺ was greatly inhibited by the coexisting Cu^{2+} , but the adsorption of Cu^{2+} was slightly affected by Cd^{2+} . The higher affinity of Cu^{2+} over Cd^{2+} on E–CMBC could be attributed to that: Cu^{2+} has a smaller hydrated radius (4.19 Å) and absolute hardness (8.3) than that of Cd^{2+} (4.26 Å and 10.3) but a higher electronegativity (1.90) and binding constant with EDTA (18.8) than that of Cd^{2+} (1.69 and 1.65).

A replacement experiment was carried out to verify the hypothesis that the adsorbed Cd^{2+} on E–CMBC might be replaced by Cu^{2+} in the binary–metal systems. The Cd^{2+} saturated E–CMBC sample was collected and labelled as Cd–loaded sample. The Cd–loaded samples were used to adsorb Cu^{2+} at the same conditions as batch experiments. A blank control experiment was carried out in de–ionized water with the same pH as Cu^{2+} solution. After adsorption equilibrium, the concentration of Cu^{2+} was decreased by 45.89 mg L⁻¹, and the concentration of Cd^{2+} was measured by 55.93 mg L⁻¹ (Figure 4). While there was almost no Cd^{2+} could be detected in the blank control experiment. The XPS analysis detected the of peak of Cu^{2+} , while the peak of Cd^{2+} disappeared in the Cd–loaded sample after adsorption of Cu^{2+} (Figure 5b). These results further confirmed that Cd^{2+} on E–CMBC could be completely replaced by Cu^{2+} in the binary–metal system.



Figure 4. Replacement adsorption between Cu²⁺ and Cd²⁺ on Cd–loaded E–CMBC in Cu²⁺ solution.



Figure 5. (a) FTIR spectra of E—CMBC before and after adsorption of Cd^{2+} , Cu^{2+} and Ni^{2+} ; (b) XPS spectra of E–CMBC before and after adsorption of Cd^{2+} , Cu^{2+} , Ni^{2+} and replacement adsorption of Cd^{2+} – Cu^{2+} .

3.3. Analysis of Adsorption Mechanism

The FTIR was used to characterize the surface's groups of E–CMBC before and after the adsorption of heavy metal ions (Figure 5a). The overlapping peak around 3416 cm⁻¹ presented in E–CMBC, indicated the –OH and –NH₂ stretching vibrational modes, this peak decreased to 3399 cm⁻¹ (Cd²⁺), 3404 cm⁻¹ (Cu²⁺) and 3385 cm⁻¹ (Ni²⁺) after adsorption, which suggested that these groups had interacted with the heavy metal ions. The peaks appeared around 1630 cm⁻¹ and 1403 cm⁻¹ were related to the stretching vibration of C=O (–NHCO, –COOH). After the adsorption of heavy metal ions, these peaks shifted to low wavenumber, too. The results clearly revealed the interaction of the amides and carboxyl groups with the heavy metal ions during the adsorption process [42]. The oxygen–rich functional groups on the surface of E–CMBC, such as hydroxyl and carbonyl functional groups, could form organometallic complexes with heavy metals, through electrostatic surface and via inner–sphere complexation [43]. When the pH value of the solution was greater than Zeta potential, the adsorption capacity of heavy metal increased, which indicated that the electrostatic interaction with negatively charged functional groups on E–CMBC surface was also one of the adsorption mechanisms [31]. In Figure 5b, the heavy metal peaks (Cd3d, Cu2p, Ni2p) appeared on the full–range XPS spectra of E–CMBC after adsorption which indicated that E–CMBC had adequate sorption for heavy metal ions. The typical peak of Na1s at 1072.08 eV disappeared after adsorption, which indicated that the exchange reaction between Na⁺ and heavy metal ions occurred. In addition, physical adsorption was one of the common mechanisms for porous materials [21].

The possible mechanisms of heavy metal ions adsorption on E–CMBC in single–metal system can be summarized as follows: surface complexation; electrostatic interaction; ion exchange; physical adsorption. The isotherm, kinetic parameters for the adsorption of Cd^{2+} , Cu^{2+} and Ni^{2+} indicated that the adsorption process was mainly chemical adsorption [44], which is consistent with the introduction of active groups on the surface of the modified biochar. The adsorption mechanism in the binary–metal system is similar to the single–metal system, while the characteristics of different heavy metal ions will lead to different competitive adsorption ability.

4. Conclusions

In this study, E–CMBC was successfully used as an effective adsorbent to adsorb Cd^{2+} , Cu^{2+} and Ni^{2+} . The Langmuir isotherm model and the Avrami fractional–order kinetics model provided the better fit for the experimental data of the single–metal system. The Langmuir maximum adsorption capacities of Cd^{2+} , Cu^{2+} and Ni^{2+} were 61.95 mg g⁻¹, 48.73 mg g⁻¹ and 40.38 mg g⁻¹, respectively. In a binary–metal system, the coexistence of the two metal ions will suppress the adsorption ability of each other due to the competitive adsorption. The order of the competitive adsorption ability was $Cu^{2+} > Ni^{2+} > Cd^{2+}$. Moreover, the adsorbed Cd^{2+} could be replaced completely by Cu^{2+} in the solution, which shows E–CMBC has the potential to separate and purify Cd^{2+} – Cu^{2+} mixed ions. These results indicate that the difference in competitive adsorption ability is related to the properties of E–CMBC and also to the characteristics of heavy metal ions. The mechanistic analysis demonstrates that the adsorption is a monolayer and multiple kinetics process, and chemical adsorption was the dominant mechanisms. Our findings suggest that E–CMBC has the potential to remove a variety of heavy metal ions from aqueous solutions.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10 .3390/pr9101829/s1, Table S1: Adsorption kinetic models, equations and parameters for single and binary metal systems. Table S2: Adsorption isotherm models, equations and parameters for single and binary metal systems. Table S3: Adsorption kinetic model parameters for Cd²⁺, Cu²⁺ and Ni²⁺ on E–CMBC in binary–metal system. Table S4: Adsorption isotherm model parameters for Cd²⁺ and Ni²⁺ on E–CMBC in Cd²⁺–Ni²⁺ system.

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