Cd(II) removal from aqueous solutions by pomelo peel derived biochar in a permeable reactive barrier: modelling, optimization and mechanism

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Abstract
Biochar can have multiple benefits, such as solid waste recycling, water pollution treatment, carbon fixation and sustainability, and it is green, friendly, inexpensive and highly efficient. Therefore, the present study aimed to investigate Cd(II) removal from aqueous solutions using pomelo peel derived biochar combined with a permeable reactive barrier (PRB). Meanwhile, the materials were characterized using SEM, FIIR, XRD, N2 adsorption, Zeta potential, TGA and XPS. The removal conditions were optimized by a response surface methodology (RSM) and a back propagation combined with genetic algorithm (BP-GA). The results show that there were slight changes in the structure of the pomelo peel derived biochar before and after activation, while the variation was not significant. The specific surface areas of the not activated and activated pomelo peel derived biochars were 3.207 m² g⁻¹ and 6.855 m² g⁻¹, respectively. The pore diameter of the former was 4.165 nm and that of the latter was 4.425 nm, indicating that the two materials are mainly mesoporous. BP-GA is more suitable than RSM for optimizing the removal conditions of Cd(II) using the prepared materials combined with PRB. The maximum removal efficiency of Cd(II) was 90.31% at biochar dosage = 4.84, reaction time = 53.75 min, initial Cd(II) concentration = 19.36 mg l⁻¹ and initial pH = 6.07. The verification experiment was 88.74% under these experimental conditions, and the absolute error was 1.57%. The saturated adsorption capacity of quartz sand for Cd(II) is approximately 0.08 mg g⁻¹ when reaching equilibrium. The saturated adsorption capacity of biochar for Cd(II) is approximately 29.76 mg g⁻¹. Pseudo second order kinetics and Langmuir isotherm adsorption were more suitable for describing the Cd(II) adsorbed from an aqueous solution by activated pomelo peel derived biochar. The adsorption process of Cd(II) by the prepared biochar was spontaneous, endothermic and entropy driven. Our results suggest that the modified pomelo peel derived biochar can be regenerated within the fourth cycle and that it has application prospects as a useful adsorbent for water treatment in PRB systems. This finding provides a reference for relieving Cd pollution and for its large scale removal from wastewater when combined with a PRB system.

1. Introduction
Biochar, a solid material with a high carbon content and a high aromatization, is produced by the pyrolysis of biomass in a completely or partially anoxic state (approximately 700 °C) [1, 2]. After entering the environment, biochar may be degraded rapidly through biological and abiotic processes, or the surface of biochar will be
oxidized rapidly, impacting the environmental efficacy of biochar [3]. Meanwhile, the specific surface area, pore volume, surface morphology and other surface chemical properties of biochar will change in the process of environmental ageing [4]. The increase in oxygen containing functional groups, e.g., hydroxyl and phenolic hydroxyl groups, on the surface of biochar after ageing can promote its adsorption of heavy metals [5]. However, the decrease in the specific surface area and pH will lead to a reduction in heavy metal adsorption by biochar. Therefore, it is necessary to take several measures to activate biochar after environmental ageing.

Due to various human production activities, such as smelting, mining, chemical production, and fertilization, wastewater containing Cd is discharged into the water environment, causing serious Cd pollution in many areas [6–8]. Cd is persistent and enriched, and it is difficult to degrade in the environment, causing great harm to humans, animals and plants [9]. Currently, the main methods for removing Cd from water include chemical precipitation, redox reactions, ion exchange, biological filtration, activated sludge and adsorption [10–12]. Among them, the adsorption method has the advantages of an excellent purification effect and a simple operation and is also regarded as an effective and efficient treatment method [13]. It is widely used in the removal of Cd from urban wastewater and industrial wastewater. Based on the characterization of the original biochar and magnetic biochar, Hu et al [14] explored the adsorption and removal effects of the 2 types of biochar on Cd(II) in polluted water and the possibility of recycling biochar. The results showed that the adsorption of Cd(II) via biochar first increased and then decreased with an increasing solution pH, and the adsorption of Cd(II) by MSB and MMSB reached a maximum at a pH value of 5. Yin et al [15] prepared pristine biochar and MgCl₂ modified biochar using Pennisetum sp. straw used to remove Cd²⁺ from aqueous solutions. The results suggested that MgCl₂ impregnation during synthesis enhanced the specific surface area and pore volume of the biochar. Batch adsorption experiments indicated that the Cd²⁺ adsorption data of MBC fit the Langmuir isothermal and pseudo second order kinetic models, indicating that chemical adsorption occurred in the system. The maximum adsorption capacity of Cd²⁺ on MBC was 763.12 mg g⁻¹, which was 11.15 times higher than that of pristine BC. Liu et al [16] exhibited the Cd²⁺ sorption dynamics of alginate encapsulated water hyacinth biochar generated at different temperatures and modified using ferric/ferrous sulphate. The Cd²⁺ sorption followed pseudo first order kinetics (R² = 0.926 to 0.991) with a greater removal efficiency using treatments with biochar generated at temperatures ≥500 °C. Therefore, biochar is an effective material for Cd removal from wastewater.

In addition to the influence of raw materials and preparation methods on the adsorption performance of biochar, the influence of external factors on the adsorption capacity is also critical, especially the pH, dosage, temperature and adsorption time [17]. Controlling the best adsorption conditions is an effective way to maximize the adsorption capacity of biochar. Currently, artificial neural networks have been employed to assist Cd pollution removal from water environments. Wu et al [18] explored an efficient and rapid method for removing Cd(II) from aqueous solution, and prepared graphene oxide supported ferroferric oxide nanocomposites were used to remove Cd(II) from the aqueous solutions. Single factor experiments were used to determine the level of operating factors (initial Cd(II) concentration, operating temperature, contact time and initial pH). The operating parameters (4 factor and 3 level) of Cd(II) removal from an aqueous solution were optimized by response surface methodology (RSM) and an artificial neural network combined with genetic algorithm (ANN-GA). Deng et al [19] described the statistical optimization designs used to optimize Cd(II) removal from an aqueous solution with modified corn straw biochar. According to the single factor experiment under a Plackett–Burman design, they screened three main influencing factors for the Cd(II) adsorption process: pH, initial Cd(II) concentration, and biochar dosage. Overall, the objective of the present study is to 1) select the highest removal efficiency of Cd(II) without various activated means in an as prepared PRB system; 2) obtain the maximum removal efficiency of Cd(II) from an aqueous solution optimized by RSM and BP-GA; and 3) reveal the mechanism of Cd(II) adsorption onto activated biochar using kinetics, thermodynamics, adsorption isotherms and x-ray photoelectron spectroscopy (XPS) (Shimazu-Kratos Analytical, UK).

2. Experimental section

2.1. Preparation of biochar
Pomelo peel (PP) was washed with tap water and distilled water, dried at 70 °C to a constant weight, and crushed. The pomelo peel used in this experiment was agricultural waste Shatian pomelo peel. First, the pomelo peel was cut into pieces, cleaned with distilled water to remove the surface impurities, and dried in a drying oven at 80 °C for 24 h to a constant weight. 10 g of dried pomelo peel were weighed and put into a vacuum tube furnace. The temperature was programmed to 500 °C at a rate of 2 °C/min and calcined for 3 h. After the end of cooling, biochar cracking at 500 °C was obtained. The obtained fresh biochar was placed for two weeks.
Five methods, including C₂H₂OH and NaOH (PP1), C₂H₂OH, NaOH and MgCl₂ (PP2), C₂H₂OH and MgCl₂ (PP3), C₂H₂OH and CaCl₂ (PP4), and C₂H₂OH, NaOH and CaCl₂ (PP5) solutions, were used to activate the prepared pomelo peel derived biochar.

(1) 40 g of pomelo peel derived biochar were accurately weighed and put into a 500 mL beaker. Then, 200 mL of absolute ethanol and 100 mL of a 0.5 mol l⁻¹ NaOH solution were added to the beaker. The mixture was successively stirred for 30 min, soaked for 24 h and washed with pure water until the pH was near neutral. Finally, the suspension was dried at 70 °C for 24 h (PP1).

(2) PP2 was treated in the same way as the above method; however, it was soaked in 200 mL of absolute ethanol and 100 mL of 1.0 mol l⁻¹ MgCl₂ solution for 24 h (PP2).

(3) For PP3, 200 mL of absolute ethanol and 100 mL of 1.0 mol l⁻¹ MgCl₂ solution were added to the bake and stirred for 30 min (PP3).

(4) The bake was added to 200 mL of absolute ethanol and 100 mL of 1.0 mol l⁻¹ CaCl₂ solution, which was mixed and stirred for 30 min (PP4).

(5) The bake was added to 200 mL of absolute ethanol and 100 mL of 0.5 mol l⁻¹ NaOH solution, which were mixed and stirred for 30 min, and then the mixture was added to 100 mL of 1.0 mol l⁻¹ CaCl₂ solution and soaked for 24 h (PP5).

### 2.2. Adsorption experiment

The stock solution of Cd(II) was prepared from CdCl₂·5H₂O (analytical purity). The 1000 mg l⁻¹ stock solution of Cd(II) was gradually diluted to 10, 15, and 20 mg l⁻¹, which was regarded as simulated wastewater in the present study. Figure 1 exhibits the structure of the permeable reaction barrier (PRB) designed in the present study, which is used to remove Cd(II) in an aqueous solution [20]. The filler in zone I is quartz sand, which is used for filtration, buffering and protection. In zone II, pomelo peel derived biochar and sand core were used as the filler and middle separator, respectively. Most of the structures of the PRB were made of plexiglass. The simulated wastewater entered from the right water inlet, and a pump was installed on the right side to control the current velocity of the simulated wastewater passing through the reaction device. 20 mg l⁻¹ Cd(II) was selected as the initial concentration of the simulated wastewater and the flow rate was controlled at approximately 20 mL/min, with water samples taken at the outlet at different times to determine the Cd(II) contents.

According to the fitting equation of the standard curve, the equilibrium concentration of Cd(II) in the filtrate was calculated, and then the adsorption capacity (Q) and the removal rate (P) were calculated with equations (1) and (2), respectively [21]. The adsorption of Cd(II) on quartz sand was studied via batch tests. In total, 5 g of quartz sand were weighed into zone I, and then 50 ml of the Cd(II) solution with mass concentrations of 0, 2.5, 5.0, 10, 20, 40, 60, 80 and 100 mg l⁻¹ were added. The pH value of the system was adjusted to 7.0 with the 0.1 mol l⁻¹ HNO₃ and NaOH solution and shaken at room temperature for 48 hours. The Cd(II) concentration in filter liquor was determined using a 5300v inductively coupled plasma optical emission spectrometer (Perkin Elmer company, USA)(ICP-OES). The adsorption capacities of Cd(II) on quartz sand were evaluated by equation (1):

$$ Q = \frac{(C_0 - C_e) \times V}{M} $$

(1)

$$ P = \frac{C_0 - C_e}{C_0} \times 100\% $$

(2)

where C₀ is the concentration of Cd(II) in the solution before adsorption, mg l⁻¹; Cₑ is the concentration of Cd(II) in the solution after adsorption (mg l⁻¹); M is the mass of pomelo peel derived biochar (g); Q is the equilibrium adsorption quality of biochar (mg g⁻¹); and P is the adsorption efficiency. The Cd(II) concentration was determined using ICP-OES.

**Figure 1. Structural diagram of PRB.**

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G Xiang et al
2.3. Kinetic model, isothermal adsorption and thermodynamic parameters for Cd(II) removal from aqueous solutions containing Cd

To explore the adsorption mechanism of pomelo peel derived biochar, a kinetic model was used to fit the experimental data. In this study, the pseudo first order kinetic model and pseudo second order kinetic model are as follows [22]:

Pseudo first order kinetic model:
\[
\ln (q_e - q_t) = \ln q_e - k_1 t
\]

Pseudo second order kinetic model:
\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]

where \(q_e\) and \(q_t\) are the adsorption capacity (mg g\(^{-1}\)) of modified pomelo peel derived biochar for Cd(II) at equilibrium and time \(t\), respectively; \(k_1\) is the first order kinetic rate constant, min\(^{-1}\), which is obtained by the linear relationship between \(\ln (q_e - q_t)\) and \(t\); and \(k_2\) is the pseudo second order kinetics rate constant, g/(mg \cdot min).

Langmuir and Freundlich equation models are used to fit the experimental data. The Langmuir isotherm assumes that the adsorbate monolayer is adsorbed on the mean site of the adsorbent surface, and each molecule on the surface has the same adsorption activation energy. The Freundlich isothermal adsorption equation is used to describe the multilayer adsorption phenomenon on the not uniform surface in the not ideal state. The equations are as follows [23]:

Langmuir adsorption isothermal:
\[
\frac{c_e}{q_e} = \frac{1}{K_L q_{\text{max}}} + \frac{c_e}{q_{\text{max}}}
\]

Freundlich adsorption isothermal:
\[
\ln q_e = \ln K_f + \frac{1}{n} \ln c_e
\]

where \(q_e\) is the equilibrium adsorption capacity of Cd(II) on pomelo peel derived biochar (mg g\(^{-1}\)); \(C_e\) is the equilibrium concentration of Cd(II) solution (mg l\(^{-1}\)); \(q_{\text{max}}\) is the maximum adsorption capacity of the adsorbent monolayer, mg g\(^{-1}\); \(K_L\) is the Langmuir adsorption constant, l mg\(^{-1}\); \(K_f\) ((mg g\(^{-1}\))/(mg l\(^{-1}\))) and \(1/N\) are Freundlich constants; and \(K_f\) is the binding force of the adsorbent to the adsorbate.

Adsorption thermodynamics can provide key information to evaluate the spontaneous or exothermic nature of a removal process at different temperatures. Their equations [24] can be expressed as:

\[
\ln K_D = \frac{\Delta S^0}{R} = \frac{\Delta H^0}{RT}
\]

\[
K_D = \frac{C_0}{C_e}
\]

\[
\Delta G^0 = \Delta H^0 - T \Delta S^0
\]

where \(K_D\) corresponds to the thermodynamic equilibrium constant; \(C_0\) and \(C_e\) are the initial and equilibrium concentrations of Cd(II), respectively; \(\Delta H^0\) is the enthalpy change; \(\Delta S^0\) is the entropy change; \(R\) is the gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)); and \(T\) is the temperature. The values of \(\Delta H^0\) and \(\Delta S^0\) are determined from the slope and intercept of the linear plot of \(K_D\) versus \(1/T\) (K), respectively.

2.4. Response surface methodology and BP-GA experimental design

Based on the single factor experiment, the Box–Behnken design (BBD) model of RSM was used to design the experiment with 4 factors and 3 levels (table 1). The back propagation combined with genetic algorithm (BP-GA) design was performed according to Xie et al [25] and run in MATLAB 2016a.

\[
f = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_i (x_i)^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} \beta_{ij} x_i x_j
\]
3. Results and discussion

3.1. Adsorption capacity and material characterization of pomelo peel derived biochar under different treatment methods

By comparing the adsorption capacity of pomelo peel derived biochar on Cd(II) under the five treatment methods, it was determined that pomelo peel derived biochar activated by PP3 had the best adsorption of Cd(II) (Figure 2). Therefore, in this study PP3 will be used for the following experiments.

Scanning electron microscopy (SEM) shows that pomelo peel derived biochar retains a certain straw scale skeleton structure (Figure 3(a)). Biochar fragments are strip shaped, have a clear outline and have a rich pore structure. The uneven surface of biochar particles may be due to the accumulation of minerals in biomass on the biochar surface during the preparation process. In the scanning image, the particle size of biochar particles is essentially between 1 and 50 μm (Figure 3(b)). The surface pores of biochar are more abundant and may have a larger specific surface area after MgCl2 activation (Figure 3(c)). Compared with common commercial biochar, the specific surface area of biochar prepared in the experiment is smaller [26], which is probably caused by the mesopores and inner pores in the inner layer of biochar not being fully opened under the pyrolysis condition of grapefruit peel biomass at 500 °C [27]. The material shows small particles and gully like rod crystals after activation. It has been reported that the accumulation of these small particles renders the biochar surface to have mesoporous pores (Figure 3(d)). These particles increase the surface roughness of the material, which plays an important role in the adsorption of Cd(II) by the prepared biochar. In addition, pomelo peel derived biochar contains a large amount of cellulose, hemicellulose, lignin and other substances, and cellulose pyrolysis occurs at 240~350 °C, which will produce dehydrated cellulose and L-glucose. The pyrolysis temperature of hemicellulose is 200~260 °C, and the main products are volatiles, tar and carbon. After 400 °C, lignin begins to pyrolyze and the product is coke [28].

Biochar is mainly composed of cellulose and hemicellulose. Among them, the wide and slow dispersion peaks at 8° to 16° and 18° to 30° are mainly the (101) and (002) crystal planes of cellulose [29]. Referring to the composition of graphite microcrystals, it is considered that the graphite like microcrystals in the pyrolysis residue are superimposed by several aromatic layers. The 20 in wide and slow dispersion peaks between 15° and 36° are called with (002) diffraction peaks, which are used to describe the stacking of monatomic carbon layers in microcrystals [29]. Figure 4 shows the XRD spectra before and after activation. There is a sharp peak at 26°,
which is more obvious after activation. In addition, there is a broad peak type of nearly 43°, which is more significant after activation. Similarly, Sima et al.[28] found that $2\theta = 26^\circ$ and $43^\circ$ appeared in rice husk biochar. Combined with previous studies and this study, it is inferred that the two peak types are the (002) and (100) crystal faces of graphite, respectively. The increase in the peak type after activation indicates that the
Graphitization is intensified. At high temperatures, a large amount of salt in biochar precipitates due to water loss or split decomposition, resulting in carbonate diffraction peaks. Because grapefruit peel contains more salt, its carbonate absorption peak is strong. The diffraction peak intensity of calcite and sylvite was reduced after the activation of the MgCl₂ solutions. The MgCl₂ solution belongs to the metal impregnation method. An et al. [30] suggested that it can increase the surface active sites of biochar and improve the specific surface area and pore size of biochar. Various active sites on the modified biochar interface interact with the adsorbed substances through electrostatic attraction and ion exchange. Zhang et al. [31] prepared biochar/MgAl LDH using MgCl₂ and AlCl₃ solutions and treated biochar with aluminium salt. Modified biochar can effectively remove phosphate, methylene blue and arsenic in solution with excellent effects.

Figure 5 demonstrates the FTIR spectrum of pomelo peel derived biochar. The stretching vibration peak of aliphatic C-H is mainly in the range of 300–500 cm⁻¹. After activation, the absorption peak at 2845 cm⁻¹–2975 cm⁻¹ is weakened, which implies that less stable substances, such as cellulose and hemicellulose, are continuously dehydrogenated in this stage, thereby enhancing their aromatization structure. There are open chain fatty anhydrides C–O–C at 300 cm⁻¹ to 500 cm⁻¹. After modification, their stretching vibration is weakened, which indicates that the deoxidation reaction was found in pomelo peel derived biochar [32]. At 700 cm⁻¹, the vibration peaks of the carbon containing functional groups were weakened, and the degree of graphitization was increased. The vibration peak at approximately 3400 cm⁻¹ is the stretching vibration of OH, which is increased after activation. At approximately 1500 cm⁻¹, the vibration absorption peak is the C=O functional group, and the change in the vibration peak is not obvious after modification. At approximately 1030 cm⁻¹, there are stretching vibrations of OH of phenolic hydroxyl groups and OH of carboxyl groups, which are weakened after modification. The structure of pomelo peel derived biochar slightly changed before and after modification; however, this variety was not obvious.

Figure 6 shows the N₂ adsorption characterization when activated and not activated by PP3. With the mass decomposition of cellulose, hemicellulose and lignin after modification, several groups (hydroxyl, hydrocarbon and aromatic rings) in pomelo peel derived biochar are broken, resulting in the generation of a large number of volatile gases. These gases increased the surface pores of biochar, thus forming more pores and enhancing the roughness and surface area of the material. The specific surface area of the not activated pomelo peel derived biochar was 3.207 m² g⁻¹, while the specific surface area of the activated pomelo peel derived biochar was 6.855 m² g⁻¹. The pore size of the former is 4.165 nm and that of the latter is 4.425 nm. The results showed that the specific surface area of the activated pomelo peel derived biochar was increased by MgCl₂ activation, while the pore size of the activated pomelo peel derived biochar was not greatly affected, and the material was the main mesopores (2–50 nm).

The thermogravimetric analysis of pomelo peel derived biochar is shown in figure 7. The weight loss process of pomelo peel derived biochar before and after MgCl₂ activation is similar. The first stage of weight loss is between 30 °C and 100 °C, and the weight loss is approximately 10%, which may be caused by volatilization of adsorbed water. The second stage of weight loss is between 100 °C and 300 °C, and the weight loss is approximately 5%. The third stage was between 300 and 500 °C, which is the slow decomposition of lignin, and the decomposition process, accompanied by the cracking of aromatic nuclei. The mass loss rate of this process is
Figure 6. The characterization of N2 adsorption of activated (a) and non activated (b) pomelo peel derived biochar.

Figure 7. TGA of activated (a) and non activated (b) pomelo peel derived biochar.

Figure 8. Zeta potential of pomelo peel derived biochar under PP3 treatment.
approximately 50%. The last stage is from 500 °C to the end of heating, which is a 10% slow decomposition process.

The Zeta potential is an important index to evaluate whether materials can be stably dispersed in the medium, which is of great significance for the application system of materials [33]. Zeta potential is the potential between the shear plane of colloidal nanoparticles and the bulk solution. A positive value detected by Zeta potentiometer indicated that the material as a whole was positively charged, as was the surface. If the measured value was negative, it indicated that the entire material shows a negative charge. In this study, the surface of pomelo peel derived biochar was negatively charged, and the zeta potential was $-29.2 \text{ mV}$ (figure 8).

XPS is a widely used surface analysis technology that can provide accurate information on the material structure, surface composition and chemical state. After the activated biochar was used for the adsorption of Cd(II), a Cd3d peak was found at 406.8 eV, which indicates that Cd(II) was successfully adsorbed into the pomelo peel derived biochar compared with that before Cd(II) adsorption (figure 9(a)). Figure 9(b) shows that there is a sharp main peak in the C 1s narrow region spectrum near 284.88 eV, which is the C atom in the aliphatic or aromatic C–H, C–C or C=C carbon group, and they are the main form of carbon [34]. The characteristic peaks at 285.27 and 288.41 eV indicate the existence of hydroxyl carbon (C–OH) and carbonyl carbon (C=O). Figures 9a and b show that the characteristic peak at 284.88 eV does not shift after Cd$^{2+}$ adsorption onto the activated biochar, indicating that the C atom in the form of C–H, C–C or C=C does not

Figure 9. XPS characterization of full spectrum (a), and magnified C1s (b), Mg2s, (c), O1s (d) and Cd(II) (e) after Cd (II) adsorption by PP3 treatment.
participate in the process of Cd(II) adsorption. The electron binding energy of carbonyl carbon decreases from 286.39 eV to 286.00 eV, and the electron binding energy of hydroxyl carbon increases from 288.27 eV to 288.71 eV, indicating that carbonyl carbon and hydroxyl carbon participate in the adsorption process of activated biochar for Cd(II). The characteristic peak of Mg2s is obviously changed to be sharp after Cd(II) adsorption (figure 9(c)). Furthermore, hydroxyl carbon (C–OH) and carbonyl carbon (C=O) combined with Cd(II) is a surface complexation chemical reaction (figure 9(d)). Figure 9(e) shows that the characteristic peaks of Cd3d5/2 are at 405.69 eV and 406.24 eV, and the characteristic peaks of Cd3/2 are at 412.42 eV and 412.99 eV. The binding energies of Cd5/2 and Cd3/2 after adsorption are 405 eV and 412 eV, respectively, and the binding energies increase after Cd(II) adsorption onto the activated biochar, indicating that Cd(II) has an obvious tendency to lose electrons in the adsorption process [35].

3.2. RSM optimization
According to the BBD design of RSM, x1, x2, x3 and x4 represent the four independent variables, i.e., reaction time, biochar dosage, initial Cd(II) concentration and initial pH, and Cd(II) removal rate, which was used as the response value. Table 2 shows a total of 29 experimental data points, including 5 datasets as zeros and 24 datasets as factorial points. The quadratic polynomial regression equation between the Cd(II) removal rate (y) and each factor is obtained:

\[
y = 78.42 + 0.31x_1 + 1.20x_2 - 2.14x_3 + 0.025x_4 - 0.47x_1x_2 + 6.61x_1x_3 - 6.29x_2x_4 + 4.88x_2x_3 - 7.33x_2x_4 - 3.89x_3x_4 + 0.50x_1^2 + 0.40x_2^2 - 0.34x_3^2 + 0.64x_4^2
\]

(11)

According to the F value, x3 > x2 > x1 > x4 indicates that the initial Cd(II) concentration > biochar dose > reaction time > initial pH. Table 3 exhibits that the developed model is significant (F = 175.65 and p = 0.001) and has a higher R² value (0.9943). This indicates that the predicted value is close to the experimental value, and a lack of fit also implies that the established model is of significance. Among them, linear terms x1 and x2 (p < 0.001) and interaction terms, including x1x3, x1x4, x2x3, x2x4 and x3x4 (p < 0.001), have extremely significant effects on the developed model. In addition, the difference between the adjusted R² value (0.9887)
Table 3. Response surface variance analysis result.

| Source      | Sum of squares | Degree of freedom | Mean square | F value | P value |
|-------------|----------------|-------------------|-------------|---------|---------|
| Model       | 784.66         | 14                | 56.05       | 175.65  | < 0.0001 Significant |
| $x_0$       | 1.13           | 1                 | 1.13        | 3.53    | 0.0812  |
| $x_1$       | 17.21          | 1                 | 17.21       | 53.93   | < 0.0001 |
| $x_2$       | 55.17          | 1                 | 55.17       | 172.9   | < 0.0001 |
| $x_3$       | 7.65 x 10^{-3} | 1                 | 7.65 x 10^{-3} | 0.024   | 0.8792  |
| $x_0x_2$    | 0.87           | 1                 | 0.87        | 2.74    | 0.1201  |
| $x_0x_3$    | 174.5          | 1                 | 174.5       | 546.89  | < 0.0001 |
| $x_1x_4$    | 158.17         | 1                 | 158.17      | 495.69  | < 0.0001 |
| $x_2x_3$    | 95.26          | 1                 | 95.26       | 298.33  | < 0.0001 |
| $x_2x_4$    | 214.62         | 1                 | 214.62      | 672.61  | < 0.0001 |
| $x_3x_4$    | 60.45          | 1                 | 60.45       | 189.45  | < 0.0001 |
| $x_1^2$     | 1.62           | 1                 | 1.62        | 5.09    | 0.0405  |
| $x_2^2$     | 1.02           | 1                 | 1.02        | 3.19    | 0.0958  |
| $x_3^2$     | 0.75           | 1                 | 0.75        | 2.37    | 0.1463  |
| $x_4^2$     | 2.62           | 1                 | 2.62        | 8.21    | 0.0125  |
| Residual    | 4.47           | 14                | 0.32        |         |         |
| Lack of Fit | 2.47           | 10                | 0.25        | 0.49    | 0.8327  |
| Pure Error  | 2              | 4                 | 0.5         |         |         |
| Cor Total   | 789.12         | 28                |             |         |         |

$R^2 = 0.9943; Adj. R^2 value = 0.9887; Pre.R^2 value = 0.9780; Adequate precision = 43.557; Coefficient of variation = 0.56%$

and the predicted $R^2$ value (0.9780) is slight. The larger precision (43.557) and lesser coefficient of variation (0.56%) elaborate that the model has a higher fitting accuracy and a small error. Figure 10 shows that the 3D response surface analysis concerning the interaction between the four factors affected the Cd(II) removal efficiency. The steeper the 3D surface is, the greater the interaction between the two factors is. The removal rate of Cd(II) by pomelo peel derived biochar reached 87.70% under an initial pH = 6.14, a reaction time = 50.86 min, an initial Cd(II) concentration = 17.16 mg l$^{-1}$ and a biochar dosage = 4.66 g. To verify the reliability of the model, the experimental Cd(II) removal rate was 85.14% under these conditions. The validation value of the model is close to the predicted value, and the error is 2.56%. It is proven that the response surface method is accurate and feasible for finding the optimal conditions of Cd(II) removal by pomelo peel derived biochar. Musa et al. [36] reported that the production of activated carbon from sugarcane bagasse is used to remove Cd(II) using a central composite design of RSM, which revealed the interaction of the three selected factors of temperature, time and nitrogen/steam flow rate at different levels. The correlation coefficients were 0.957 for removal and 0.985 for yield, showing the sufficiency of the model in predicting a response within 13 experimental runs. Kashi et al. [37] investigated RSM and central composite design used for Cd(II) removal by natural clinoptilolite and natural bentonite and studied the effect of pH and contact time on the adsorption efficiency and process optimization. They suggested that the Cd(II) adsorption model was highly significant and had low $p$ values. The pH (5.35 and 3.89), contact times (20.49 and 16.27 h), and adsorption efficiency (94.86% and 87.42%) were found to be optimum for Cd(II) ion adsorption on natural clinoptilolite and natural bentonite, respectively. Men et al. [38] reported that to explore the adsorption mechanism of humin for heavy metals, lignite was selected as the material for preparing humin and optimized the adsorption conditions. The results showed that the pH, the dose of HM and the initial concentration of Cd$^{2+}$ had the greatest effect on Cd$^{2+}$ adsorption by humin. This result indicated that the optimum adsorption conditions were obtained at 308 K, 107.82 min, pH of 5.55, a humin dosage of 0.05 g and a Cd$^{2+}$ initial concentration of 95.56 mg l$^{-1}$.

3.3. BP-GA optimization

The BP neural network contains the forward propagation of information and the back propagation of error, which has input, hidden and output layers [39]. The number of neurons in the hidden layer is higher, and the model may be overfitted, thus leading to a decline in the generalization ability. The number of neurons is fewer, the model fitting is insufficient, and the prediction ability is weakened. In the present study, GA combined with is used to optimize the number of neurons in the hidden layer of the BP network through the lowest MSE value. Three neurons were used in the hidden layer (figure 11). Referring to Xie et al. [25], in our proposed model several parameters are set, including epoch (2000), learning rate (0.1), goal (1 x 10^{-5}) and momentum factor (0.9). The model established by the BP neural network is a ‘black box model’, and the $R^2$ value of the established model is 0.99872, indicating that the experimental value of the model is in high agreement with the predicted value (figure 12).
Figure 10. Relationship between removal efficiency and reaction parameters.

Figure 11. MSE values of different neurons.
BP-GA was used to optimize the conditions of pomelo peel derived biochar and Cd(II) adsorption in the PRB (figure 13). The parameters of GA by referring to Xie et al [25] are set as follows: population size = 20, cross probability = 0.8, mutation probability = 0.01, genetic probability = 0.9 and maxgen = 500. After BP-GA optimization, the removal rate of Cd(II) by pomelo peel derived biochar reached 90.31% under the optimal conditions: initial pH = 6.07, reaction time = 53.75 min, initial Cd(II) concentration = 19.36 mg l$^{-1}$ and biochar dosage = 4.84 g. According to the above conditions, the experimental removal efficiency of Cd(II) was 88.74%. The validation value of the model is close to the predicted value, and the absolute error between their removal efficiencies is 1.57%. The optimization results and the absolute error implied that BP-GA is more suitable for the removal of Cd(II) from simulated wastewater by pomelo peel derived biochar in the PRB. In general, RSM uses multiple quadratic regression equations to fit the functional relationship between the factors and response value, and finds the optimal process parameters through the analysis of regression equations while easily falling into local optima. For the GA, genetic operation applies certain operations (selection, crossover and mutation) to individuals according to their adaptability to the environment, thus realizing the evolutionary process of survival of the fittest [40]. Nag et al [41] described that three biowaste materials, jackfruit, mango and rubber leaves, are used for Cd(II) bioremediation from synthetic wastewater in a continuous down flow in packed bed columns. The applicability of hybrid artificial intelligence GA-ANN was attempted as a tool for the simulation and optimization of Cd(II) removal efficiency prediction as a function of influent variables. The
network performed appreciably well in terms of the cross correlation coefficient value (between 0.997 and 0.999) and the minimization of errors. Wu et al [18] reported that the predicted and confirmed values were 89.722% and 87.723% using ANN-GA with temperature \(= 29.96 \, ^\circ\text{C} \), initial pH \(= 5.49 \), initial Cd\({^{(II)}\}) concentration \(= 28.36 \, \text{mg l}^{-1} \) and contact time \(= 65.78 \, \text{min} \). According to the R\(^2\) value, the predicted maximum efficiency and confirmed experiment, the performance and predicted ability of the ANN-GA model was better than that of RSM. Xie et al [25] demonstrated that BP-GA was more suitable for Cu\({^{(II)}\}) removal from aqueous solutions because its absolute error between the experimental and predicted values was relatively smaller. For BP-GA optimization, the maximum removal efficiency of Cu\({^{(II)}\}) reached 91.35% at temperature \(= 29.73 \, ^\circ\text{C} \), contact time \(= 69.60 \, \text{min} \), initial pH \(= 6.46 \) and initial Cu\({^{(II)}\}) concentration \(= 100.00 \, \text{mg l}^{-1} \).

### 3.4. Kinetic model, isothermal adsorption and thermodynamic parameters for Cd\({^{(II)}\}) removal

According to the fitting parameters in Table 4 and Figure 14, the R\(^2\) value of Cd\({^{(II)}\}) adsorbed by activated pomelo peel derived biochar fitted by pseudo first order and pseudo second order kinetic models is greater than 0.9. However, compared with the pseudo first order kinetic model, the pseudo second order kinetic model can better describe the adsorption process of Cd\({^{(II)}\}) adsorbed by activated pomelo peel derived biochar, and the main factor affecting the second order kinetic adsorption is the formation of chemical bonds, showing that the process is mainly chemical adsorption. Moreover, the first order reaction kinetic equation has limitations, and \(q_e\) needs to be determined experimentally before drawing, while in the experimental process there are various errors and other factors that cannot be accurately measured [42]. The second order kinetic model includes all processes of adsorption. Therefore, the second order kinetic model can more truly and comprehensively reflect the kinetic mechanism of Cd\({^{(II)}\}) adsorption in a modified biochar solution [43]. Goswami et al [44] also found that the process of Cd\({^{(II)}\}) removal using Ipomoea fistulosa biochar for adsorption followed a pseudo second order kinetic model. Huang et al [45] suggested that the kinetics of adsorption were better described by pseudo second order kinetic models than pseudo first order kinetic and intraparticle diffusion models under different initial Cd\(^{2+}\) concentrations of 20, 50, and 100 mg l\(^{-1}\). Shao et al [46] reported that a pseudo second order kinetic model was suitable for describing the adsorption of Pb\(^{2+}\) by corn straw and sawdust mixed biochar because its R\(^2\) value is greater than the pseudo first order model. Table 4 Kinetics fitting parameters of Cd\({^{(II)}\}) adsorption onto pomelo peel derived biochar.

**Table 4.** Kinetics fitting parameters for Cd\({^{(II)}\}) adsorption onto pomelo peel derived biochar.

|                      | Pseudo first order kinetic model | Pseudo second order kinetic model |
|----------------------|----------------------------------|-----------------------------------|
| \(k_1\)              | \(q_e\)                          | \(R^2\)                           |
| 0.0645               | 4.140                            | 0.9141                            |
| \(k_2\)              | \(q_e\)                          | \(R^2\)                           |
| 0.0126               | 8.019                            | 0.9947                            |

![Figure 14](image-url) The fitting parameters of kinetic models for Cd\({^{(II)}\}) adsorbing by activated pomelo peel derived biochar.
Table 5 and figure 15 demonstrate that the fitting coefficients of the Langmuir and Freundlich models for Cd(II) adsorption by the activated pomelo peel derived biochar are greater than 0.95. The adsorption process of Cd(II) in solution by activated biochar can be well fitted by Langmuir and Freundlich isothermal adsorption models at 25 °C. The theoretical maximum adsorption capacity $q_m$ of the activated pomelo peel derived biochar fitted by the Langmuir isothermal adsorption equation is 29.76 mg g$^{-1}$, which is roughly consistent with the actual saturated adsorption capacity and is credible. Meanwhile, the $n$ value fitted by the Freundlich isothermal adsorption equation can reflect the adsorption capacity of biochar for Cd(II). $n < 1$, $n < 0.5$ and $n > 1$ represent difficult, extremely difficult and easy to adsorb, respectively [42]. The $n$ value of the activated pomelo peel derived biochar is 6.115, which is greater than 1, indicating that the activated biochar has a strong adsorption capacity for Cd(II). Table 6 shows the different maximum adsorption capacities of Cd(II) in comparison with the other materials.

Figure 16 shows that the adsorption capacity of quartz sand for Cd(II) increases with an increasing initial Cd(II) concentration and gradually tends to balance. The reason may be that the surface of quartz sand lacks functional groups that can combine with Cd(II); therefore, its adsorption capacity for Cd(II) is relatively weak. Biochar is a mesoporous molecular sieve with a highly ordered adjustable pore structure and a relatively uniform pore size distribution; therefore, biochar has a large adsorption capacity for Cd(II).

The adsorption of Cd(II) by biochar is a spontaneous process because $\Delta G^0 < 0$ (table 7). $-20 < \Delta G^0 < 0$ kJ mol$^{-1}$ is a physical adsorption process, and $-400$ kJ/mol $< \Delta G^0 < -80$ kJ mol$^{-1}$ is a chemical adsorption process; therefore, the adsorption process is a physical adsorption process (table 7) [58]. In addition, $\Delta H^0 > 0$ indicates that the adsorption process is endothermic, and heating is conducive to the adsorption process. $\Delta S^0$

![Figure 15. Comparison of Langmuir and Freundlich adsorption isotherm models (the biochar dosage = 3 g; contact time = 60 min; initial Cd(II) concentration = 10 mg l$^{-1}$ and initial pH = 7).](image)

Table 5. Adsorption isotherm fitting parameters for Cd(II) adsorption onto pomelo peel derived biochar.

| Langmuir | Freundlich |
|----------|------------|
| $q_m$    | $K_L$      | $R^2$  | $K_F$    | $1/n$     | $R^2$  |
| 29.76    | 0.4053     | 0.9976 | 6.115    | 0.5725    | 0.9620 |

Table 5 and figure 15 demonstrate that the fitting coefficients of the Langmuir and Freundlich models for Cd(II) adsorption by the activated pomelo peel derived biochar are greater than 0.95. The adsorption process of Cd(II) in solution by activated biochar can be well fitted by Langmuir and Freundlich isothermal adsorption models at 25 °C. The theoretical maximum adsorption capacity $q_m$ of the activated pomelo peel derived biochar fitted by the Langmuir isothermal adsorption equation is 29.76 mg g$^{-1}$, which is roughly consistent with the actual saturated adsorption capacity and is credible. Meanwhile, the $n$ value fitted by the Freundlich isothermal adsorption equation can reflect the adsorption capacity of biochar for Cd(II). $n < 1$, $n < 0.5$ and $n > 1$ represent difficult, extremely difficult and easy to adsorb, respectively [42]. The $n$ value of the activated pomelo peel derived biochar is 6.115, which is greater than 1, indicating that the activated biochar has a strong adsorption capacity for Cd(II). Table 6 shows the different maximum adsorption capacities of Cd(II) in comparison with the other materials.

Figure 16 shows that the adsorption capacity of quartz sand for Cd(II) increases with an increasing initial Cd(II) concentration and gradually tends to balance. The reason may be that the surface of quartz sand can provide a large number of adsorption points when the Cd(II) concentration is lower. The adsorption points are not fully occupied at the moment, accelerating Cd(II) adsorption in the solution. With the continuous increase in the initial concentration of Cd(II) in this system, the adsorption point provided by the surface energy of quartz sand is gradually occupied by Cd(II) and tends to be saturated. The saturated adsorption capacity of quartz sand for Cd(II) is approximately 0.08 mg g$^{-1}$ when reaching equilibrium. The saturated adsorption capacity of biochar for Cd(II) is approximately 29.76 mg g$^{-1}$, indicating that biochar has a better adsorption capacity for Cd(II) than quartz sand. This result was consistent with Qin et al [56] and Guo et al [57]. This is because the surface of quartz sand lacks functional groups that can combine with Cd(II); therefore, its adsorption capacity for Cd(II) is relatively weak. Biochar is a mesoporous molecular sieve with a highly ordered adjustable pore structure and a relatively uniform pore size distribution; therefore, biochar has a large adsorption capacity for Cd(II).

The adsorption of Cd(II) by biochar is a spontaneous process because $\Delta G^0 < 0$ (table 7). $-20 < \Delta G^0 < 0$ kJ mol$^{-1}$ is a physical adsorption process, and $-400$ kJ/mol $< \Delta G^0 < -80$ kJ mol$^{-1}$ is a chemical adsorption process; therefore, the adsorption process is a physical adsorption process (table 7) [58]. In addition, $\Delta H^0 > 0$ indicates that the adsorption process is endothermic, and heating is conducive to the adsorption process. $\Delta S^0$
0 indicates that the adsorption process increases the disorder degree of the solid liquid interface, suggesting that the adsorption process easily occurs. The forces of the adsorption process may be hydrogen bonds, van der Waals forces and $\pi - \pi$ electron conjugation. In a spontaneous endothermic process, Cd needs sufficient energy to overcome the diffusion layer entering the pores. Properly increasing the adsorption temperature can effectively improve the adsorption capacity of biochar to heavy metals. However, an excessively high temperature can accelerate the thermal movement of ions, resulting in the desorption of biochar and decreasing the removal rate \[59\]. The removal rate of heavy metals increased with increasing temperature, which was in accordance with Saima et al \[60\]. However, unduly high temperatures are not conducive to adsorption. Liu et al \[61\] used peanut shell carbon as an adsorbent to study the effect of temperature on the adsorption of Cr$^{6+}$ and

### Table 6. Comparison of the different maximum adsorption capacities of Cd(II).

| Materials            | Initial Cd(II) Concentration (mg l$^{-1}$) | Maximum adsorption capacity (mg g$^{-1}$) | References |
|----------------------|--------------------------------------------|------------------------------------------|------------|
| Fe$_3$O$_4$          | 88.96                                      | 9.68                                     | \[47\]     |
| Fe$_3$O$_4$-SO$_3$H  | 88.96                                      | 80.9                                     | \[48\]     |
| CoFe$_2$O$_4$/SiO$_2$| 8.89                                       | 5                                        | \[49\]     |
| NiO                  | 117.92                                     | 97                                       | \[50\]     |
| ZrO$_2$              | 8.89                                       | 3.18                                     | \[51\]     |
| ZnO nanorods         | 889.6                                      | 147.25                                   | \[52\]     |
| nZVI                 | 444.8                                      | 188                                      | \[53\]     |
| CdS Np               | 444.8                                      | 141.5                                    | \[54\]     |
| Ag NP                | 44.8                                       | 4.67                                     | \[55\]     |
| Modified             | 10                                         | 26.96                                    | In the present study |
| pomelo peel based biochar |                                           |                                           |            |

### Table 7. The thermodynamic parameters for the adsorption of Cd(II) onto the biochar.

| Temperature (K) | $\Delta G^\circ$ (kJ mol$^{-1}$) | $\Delta S^\circ$ (J mol$^{-1}$K$^{-1}$) | $\Delta H^\circ$ (kJ mol$^{-1}$) |
|-----------------|----------------------------------|----------------------------------------|----------------------------------|
| 298             | $-6.1024$                        | 35.3                                   | 4.506                            |
| 308             | $-6.2028$                        |                                        |                                  |
| 318             | $-6.7324$                        |                                        |                                  |
| 328             | $-7.1017$                        |                                        |                                  |

$>0$ indicates that the adsorption process increases the disorder degree of the solid liquid interface, suggesting that the adsorption process easily occurs. The forces of the adsorption process may be hydrogen bonds, van der Waals forces and $\pi - \pi$ electron conjugation. In a spontaneous endothermic process, Cd needs sufficient energy to overcome the diffusion layer entering the pores. Properly increasing the adsorption temperature can effectively improve the adsorption capacity of biochar to heavy metals. However, an excessively high temperature can accelerate the thermal movement of ions, resulting in the desorption of biochar and decreasing the removal rate \[59\]. The removal rate of heavy metals increased with increasing temperature, which was in accordance with Saima et al \[60\]. However, unduly high temperatures are not conducive to adsorption. Liu et al \[61\] used peanut shell carbon as an adsorbent to study the effect of temperature on the adsorption of Cr$^{6+}$ and
The results show that the optimal adsorption temperatures of Cr\(^{6+}\) and Cu\(^{2+}\) are 30 °C and 40 °C, respectively. With a further increase in temperature, the removal rate decreased, and the adsorption of biochar appeared at a high temperature. Heavy metal wastewater is often a mixed system of all types of pollutants, and all types of pollutants will compete with heavy metal ions for adsorption sites. In particular, the competition between heavy metals with the same adsorption mechanism is the most obvious.

3.4.1. Mechanism of Cd\(^{2+}\) adsorption onto the modified biochar and regeneration of the materials

The adsorption of Cd\(^{2+}\) onto biochar is a relatively complex process. Based on the analysis of adsorption kinetics, the removal process includes physical action and chemical bonding, viz. external liquid film diffusion, surface adsorption and intraparticle diffusion processes [62] (figure 17). In addition, according to a thermodynamic study and combined with previous studies, the removal mechanism of Cd\(^{2+}\) onto biochar involves electrostatic interactions, ion exchange, chemical action and physical behaviour. In particular, FTIR analysis showed that abundant OH, COOH, CO, and CH functional groups existed on the surface of the biochar, which may be involved in Cd\(^{2+}\) binding. Surface complexation is quite an important function in the adsorption process between Cd\(^{2+}\) and biochar, containing hydrogen bonding and electronic attraction. Additionally, ion exchange plays an important role in Cd\(^{2+}\) adsorption onto biochar. Deionized water is regarded as a contrast, and heavy ions (Ca\(^{2+}\), Na\(^{+}\), K\(^{+}\) and Mg\(^{2+}\)) from biochars are released in mixtures of water and biochar, especially Ca\(^{2+}\) and K\(^{+}\) ions, which participate more in the ion exchange process [63].

The regeneration of biochar plays an important role in assessing the possibility for large scale utilization. The adsorption cycles of Cd\(^{2+}\) were performed three times with an eluent of 0.1 mol l\(^{-1}\) HCl. Figure 18 shows that the removal efficiencies of the first regeneration cycle, second regeneration cycle, third regeneration cycle and fourth regeneration cycle are 94.26%, 91.66%, 89.51% and 66.88%, respectively. The results reveal that the
gradual decline in the adsorption capacity of the modified biochar for MB occurred for four consecutive adsorption cycles, and a dramatic decline was observed after four regeneration cycles. Thus, modified pomelo peel derived biochar can be regenerated and has application prospects as a useful adsorbent for water treatment.

4. Conclusions

Under PP3 treatment, i.e., C2H5OH and MgCl2, the structure of pomelo peel derived biochar changed slightly before and after activation, while the overall change was not significant. Compared with RSM, BP-GA is more suitable for the removal of Cd(II) from simulated wastewater by pomelo peel derived biochar in a PRB system. The developed RSM model showed that the influence of the four factors on the Cd(II) adsorption rate is initial Cd(II) concentration > biochar dose > reaction time > initial pH value. The maximum removal efficiency of Cd(II) was 90.31% at a biochar dosage = 4.84, reaction time = 53.75 min, initial Cd(II) concentration = 19.36 mg l⁻¹, and initial pH = 6.07. The verification experiment is 88.74%, and the absolute error is 1.57%. The saturated adsorption capacity of quartz sand for Cd(II) is approximately 0.08 mg g⁻¹ when reaching equilibrium. The saturated adsorption capacity of biochar for Cd(II) is approximately 29.76 mg g⁻¹. Pseudo second order kinetic and Langmuir isotherm adsorption were more suitable for describing the adsorption of Cd(II) in simulated wastewater by pomelo peel derived biochar. The adsorption process of Cd(II) by the prepared biochar was spontaneous, endothermic and entropy driven. Our results suggest that the modified pomelo peel derived biochar can be regenerated within the fourth cycle and has application prospects as a useful adsorbent for water treatment in PRB systems. This finding provides a reference for relieving Cd pollution and its large scale removal from wastewater combined with a PRB system.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Author contributions

Writing—original draft preparation, G. X.; writing—review, G. X.; S. L, X. W and H. L. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

The authors declare no competing interests.

Institutional review board statement

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Informed consent statement

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Ethical approval and consent to participate

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References
[1] Mei H, Li Z, Luo N, Ren Y, Wen J, Huang B and Zeng G 2019 Application potential of biochar in environment: Insight from degradation of biochar-derived DOM and complexation of DOM with heavy metals Sci. Total Environ. 646 220–28
[2] Lebrun M, Nandillon R, Maire F, Forestier L L, Morabito D and Bourgerie S 2021 Effects of biochar ochre and manure amendments associated with a metalliferous ecotype of Agrostis capillaris on As and Pb stabilization of a former mine technosol Environ. Geochim. Hlth 43 1491–505
[3] Zhong Y, Igalavithana A D, Zhang M, Li X D, Rinklebe J and Hou D Y 2020 Effects of aging and weathering on immobilization of trace metals/metalloids in soils amended with biochar Environ. Sci.-Proc. Imp 22 1790–808
[4] Mia S, Dijkstra F A and Singh B 2017 Aging induced changes in biochar’s functionality and adsorption behavior for phosphate and ammonium Environ. Sci. Technol. 51 8359–67
[5] Chen C, Cheng T, Zhang X, Wu R and Wang Q 2019 Synthesis of an efficient Pb adsorption nano-crystal under strong alkaline hydrothermal environment using a gemini surfactant as directing agent J. Chem. Soc. Pak. 41 1034–1038
[6] Zhao H, Huang X, Zhang G, Li G, He Z L and Ji P H 2020 Possibility of reducing cadmium pollution from the environment using a newly synthesized material coal fly ash Environ. Sci. Pollut. Res. 27 4997–5008
[7] Chen C, Cheng T, Wang Z L and Han C H 2014 Removal of Zn2+ in aqueous solution by Linde F (K) zeolite prepared from recycled fly ash J. Indian Chem. Soc. 91 285–291
[8] Peng Z D, Lin X M and Zhang Y L 2021 Removal of cadmium from wastewater by magnetic zeolite synthesized from natural low-grade molybdenum Sci. Total Environ. 772 135355
[9] Amoroso M J, Oliver G and Castro G R 2002 Estimation of growth inhibition by copper and cadmium in heavy metal tolerant actinomycetes J. Basic Microb. 42 231–7
[10] Vikrant K, Kumar V and Vellingiri K 2019 Nanomaterials for the abatement of cadmium (II) ions from water/wastewater Nano. Res. 12 1489–507
[11] Chen C, Cheng T, Shi Y S and Tian Y 2014 Adsorption of Cu(II) from aqueous solution on fly ash based linde F (K) Zeolite Iran. J. Chem. Eng. 33 29–35
[12] Sall M L, Diaw A K D and Gningue-Sall D 2020 Toxic heavy metals: impact on the environment and human health and treatment with conducting organic polymers a review Environ. Sci. Pollut. Res. 27 29927–42
[13] Vikrant K, Kumar V and Vellingiri K 2019 Nanomaterials for the abatement of cadmium(II) ions from water/wastewater Nano. Res. 12 1489–507
[14] Hu X Y, Chen Y J, Zhang S S, Wang X Q, Li C C and Guo X 2018 Cd removal from aqueous solution using magnetic biochar derived from maize straw and its recycle Transactions of the Chinese Society of Agricultural Engineering 34 208–18
[15] Yin G C, Tao L, Chen X X, Binoyssarkar B N S, Lin Q T and Wang H L 2021 Quantitative analysis on the mechanism of Cd2+ removal by MgCl2 - modified biochar in aqueous solutions J. Hazard. Mater. 420 126487
[16] Liu C, Ye J, Lin Y, Wu J and Wang Y 2020 Removal of Cadmium (II) using water hyacinth (Eichhornia crassipes) biochar alginat beads in aqueous solutions Environ. Pollut. 264 117485
[17] Cheng T, Chen C, Yang R, Han C H and Tian Y 2018 Competitive adsorption of Cu, Ni, Pb and Cd from aqueous solution onto flyash-based Linde F(K) zeolite J. Chem. Eng. 37 61–72
[18] Wu X L, Huang X F and Zhang Z M 2019 Influencing factors of Cd(II) removal from aqueous solution by Fe3O4/GO China Environmental Science 39 2411–21
[19] Deng X, Zhou H, Qu X N, Long J and Liao B H 2017 Optimization of Cd(II) removal from aqueous solution with modified corn straw biochar using Plackett-Burman design and response surface methodology Desalin. Water Treat. 70 210–9
[20] Han C H and Xie W F 2020 Study on Pb(II) removal from simulated wastewater by permeable reaction barrier combined with Co3O4/GO nano-composites and its adsorption mechanism Nonferrous Metals Engineering 10 120–8
[21] Wu J T, Zhao X P, Li Z P and Gu X P 2020 Thermodynamic and kinetic coupling model of Cd(II) and Pb(II) adsorption and desorption on goethite Sci. Total Environ. 727 138730
[22] Zhang S, Yang X J, Mu J and Zheng K 2019 Mercury adsorption to aged biochar and its management in China Environ. Sci. Pollut. Res. 26 4867–77
[23] Adnasa Sl, Shekari N and Mahsoudi A 2019 Optimization of arsenic removal with Fe3O4@Al2O3@ZnO-Fe LDH as a new magnetic nano adsorbent using box-behken design J. Environ. Chem. Eng. 7 102974
[24] Mustapha S, Tijani J O, Ndamtiso M M, Abdulkareem S A, Shauib D T, Mohammed A K and Sumaila A 2020 The role of kaolin and kaolinite in remediation of CuO nanoasorbents in adsorption studies for tannery wastewater treatment Sci. Rep. 10 13068
[25] Xie W, Cheng T and Chen C 2020 Optimizing and modelling Cu(II) removal from simulated wastewater using attapulgite modified with Keggin ions with the aid of RSM BP-ANN and GA-BP Desalin. Water Treat. 207 270–86
[26] Li M Y, Hu Y W, Lang C, Sang W J and Li D X 2020 Adsorption of Lead and Cadmium on Biochars Produced From Agroforestry Wastes Journal of Esoleyand Rural Environment 36 106–14
[27] Bruun E W, Hauggaard-Nielsen H, Ibrahim N, Eggaard H, Ambus P, Jensen P A and Dam-Johansen K 2011 Influence of fast pyrolysis temperature on biochar labile fraction and short-term carbon loss in a lysimeter soil Biomass and Bioenergy 35 1182–9
[28] Sima X F, Shen X C, Fang T, Yu H Q and Jiang H 2017 Efficiently reducing the plant growth inhibition of CuO NPs using rice husk-derived biochar: experimental demonstration and mechanism investigation Environmental Science Nano 4 1722–32
[29] Zheng Q F, Wang Z M, Chen B J, Liu G F and Zhao J 2016 Analysis of XRD Spectral Structure and Carbonization of the Biochar Preparation Spectroscopy and Spectral Analysis 36 3355–9
[30] An Q, Chen Z D, Qin P and Yue X 2021 Research progress of biochar activation technology and biochar catalyst China Environmental Science 41 1990–2001
[31] Yang X, Zhang S Q, Hou Q D, Wang Y N, Ju M T and Liu L 2018 The preparation of biochar and adsorption behavior of Mg-modified biochar to pollutants Acta Scientiae Circumstantiae 38 4032–43
[32] Zhang X Q, Hou G J, Zhang Y H and Zhao Y 2017 Structural and physico-chemical properties of biochars prepared from different rice straw Environmental Engineering 35 122–6
[33] Pang J S, Zhang H Y, Cao B, Song C, Mao L B and Chen J 2009 Research on dispersion of ZnO nanoparticles in aqueous coating system Bulletin of the Chinese Ceramic Society 01 114–8
[34] Hu Q, Zhu Y, Hu B, Lu S H and Sheng G D 2018 Mechanistic insights into sequestration of U(VI) toward magnetic biochar: batch, XPS and EXAFS techniques J. Environ. Sci. 70 220–8
[35] Wang X, Feng J and Cai Y 2020 Porous biochar modified with polyethyleneimine (PEI) for effective enrichment of U(VI) in aqueous solution Sci. Total Environ. 708 1–11
[36] Musa M, Kikuchi A, Majid Z A, Jaafar J and Salim M R 2014 Activated carbon production from agricultural biomass using response surface method (RSM) for Cd (II) Removal Journal Teknologi 69 59–64
[37] Kashif N, Fard E and Fazaelli R 2017 Empirical modeling and CCD-based RSM optimization of Cd(II) adsorption from aqueous solution on clinoptilolite and bentonite Russ J. Appl. Chem. 90 977–92
[38] Men S H, Huang Z B, Li F Z and Wang A 2020 Adsorption of Cd by humin: response surface methodology and mechanism study China Environmental Science 40 2615–26
[39] Yu S, Zhu K and Diao F 2008 A dynamic all parameters adaptive BP neural networks model and its application on oil reservoir prediction Appl. Math. Comput. 195 66–75
[40] Ibynaich S, Wakrim L and Hassani M M 2021 Nonuniform semi-patches for designing an ultra wideband PIFA antenna by using genetic algorithm optimization Wireless Pers. Commun. 117 957–69
[41] Nag S, Bar N and Das S K 2018 Sustainable bioremediation of Cd(II) in fixed bed column using green adsorbents: Application of Kinetic models and GA-ANN technique Environ. Technol. Innov. 13 130–45
[42] Chen C, Wang L, Cheng T, Zhang X and Tian Y 2021 Ag2PO4/Ag3SbO4 composite as novel photocatalyst with significantly enhanced activity through a Z-scheme degradation mechanism Mater. Res. 24 e20210100
[43] Li K Q, Zheng Z, Jiang J C and Zhang J B 2010 Adsorption kinetic and thermodynamic studies of lead onto activated carbons from cotton stalk Environmental Science 31 1402–8
[44] Goswami R, Shimi J, Deka S, Kumari D, Katakai R and Kumar M 2016 Characterization of cadmium removal from aqueous solution by biochar produced from Ipomoea Fistulosa at different pyrolytic temperatures Ecological Engineering 97 444–51
[45] Huang F, Gao L Y, Deng J H, Chen S H and Cai K Z 2018 Quantitative contribution of Cd(II) adsorption mechanisms by chicken-manne derived biochars Environ. Sci. Pollut. Res. 25 28322–34
[46] Shao Y, Chen J W, Wang W P, Cui J M, Li H Y, Wang L and Ma S C 2017 Adsorption of Pb(II) through different organic materials in aqueous solution Journal of Agro-Environment Science 36 1858–67
[47] Ethrabi S, Sulaymon A H, Saad and Alhares H 2016 Competitive removal of Cu(II), Cd(II), Zn(II) and Ni(II) ions onto iron oxide nanoparticles from wastewater Desalin. Water Treat. 57 20915–20929
[48] Chen K, He Y J, Li Y L, Cai X G, Zhang K S, Liu T, Hu Y, Lin D Y, Kong L T and Liu J H 2017 Removal of cadmium and lead ions from water by sulfonated magnetic nanoparticle adsorbents J. Colloid Interface Sci 494 307–16
[49] Wang Y, Tian T, Wang L and Hu X 2013 Solid-phase preconcentration of cadmium(II) using amino-functionalized magnetic-core silica-shell nanoparticles and its determination by hydride generation atomic fluorescence spectrometry Microchem Acta 180 235–42
[50] Behnoudnia F and Dehghani H 2014 Anion effect on the control of morphology for NiC2O4·2H2O nanostructures as precursors for synthesis of Ni(OH)2 and NiO nanostructures and their application for removing heavy metal ions of cadmium(II) and lead(II) Dalton. Trans. 43 3471–8
[51] Gusain D, Singh P K and Sharma Y C 2016 Kinetic and equilibrium modelling of adsorption of cadmium on nano crystalline zirconia using response surface methodology Environ. Nanotechnol. Monit. Manag. 6 99–107
[52] Kumar K Y, Murulidharana B, Nayaka Y A, Balasubramanayam J and Hanumanthappa H 2013 Hierarchically assembled mesoporous ZnO nanorods for the removal of lead and cadmium by using differential pulse anodic stripping voltammetric method Powder Technol. 239 208–16
[53] Su Y M, Adeleye A S, Huang Y X, Sun X Y, Dai C M, Zhou X F, Zhang Y L and Keller A A 2014 Simultaneous removal of cadmium and nitrate in aqueous media by nanoscale zerovalent iron (nZVI) and Au doped nZVI particles Water. Res. 63 102–11
[54] Das S K, Shome I and Ghua A K 2012 Surface functionalization of Aspergillus versicolor mycelia: In situ fabrication of cadmium sulphide nanoparticles and removal of cadmium ions from aqueous solution RSC Adv 2 3000–7
[55] Zuo Y, Chen G Q, Zeng G M, Li Z W, Yan M, Chen A W, Gao Z, Huang Z Z and Tan Q 2015 Transport fate and stimulating impact of silver nanoparticles on the removal of Cd(II) by Phanerochaete chrysosporium in aqueous solutions J. Hazard. Mater. 285 236–44
[56] Qin K, Wang L, Zhang Z Q, Yang Y T, Li Y H and Meng Z F 2014 Adsorption of Cd(II) ions in aqueous by triamine-modified SBA-15 particles pre-pared by using reed ash as silica resource Chinese Journal of Environmental Engineering 8 4393–401
[57] Guo Z Y, Guo T, Jiang Y H, Qin R, Zhang Z Q and Li R H 2017 SBA-15 Transport and its Effect on Cd(II) Mobility in Saturated Sand Media Acta Agriculture Boreali-occidentalis Sinica 26 1259–66
[58] Hank D, Azi Z, Hocine S A, Chalaal O and Hellal A 2014 Optimization of phenol adsorption onto bentonite by factorial design methodology J. Ind. Eng. Chem. 20 2225–63
[59] Zhang X, Cheng T, Chen C, Wang L, Deng Q, Chen G and Ye C H 2020 Synthesis of A Novel Magnetic Nanozeolite and Its Application as an Efficient Heavy Metal Adsorbent Mater. Res. Express 7 085307
[60] Saima B, Muhammad I, Qaiser H and Kong J 2017 Adsorption of copper(II) by using derived-farmyard and poultry manure biochars: Efficiency and mechanism Chem Phys Lett 689 190–8
[61] Liu Y N, Huang B and Zhang L 2017 Adsorption of Heavy Metal Cd2+ and Cu2+ in Aqueous Solutions by peanut shell Biochar Science Technology and Engineering 17 1671–85
[62] Deng H, Li Q and Huang M 2020 Removal of Zn(II) Mn(II) and Cu(II) by adsorption onto banana stalk biochar: Adsorption process and mechanisms Water Sci. Technol. 82 2962–74
[63] Zhou N, Zu J and Feng Q 2019 Effect of pyrolysis condition on the adsorption mechanism of heavy metals on tobacco stem biochar in competitive mode Environ. Sci. Pollut. Res. 26 26947–62