Remediation of Emerging Heavy Metals from Water Using Natural Adsorbent: Adsorption Performance and Mechanistic Insights

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Abstract: The presence of potentially toxic metals in water causes a strong impact on environment and human health. In this study, activated biochar was produced by using chemical oxidation method from wheat straw as natural adsorbent and was employed for heavy metals competitive remediation. The morphology, structure, and chemical properties of biochar before and after adsorption were characterized by FTIR, XRD, SEM and EDX mapping techniques. The competitive adsorption efficiency of adsorbent for divalent cadmium (Cd) and lead (Pb) from contaminated water was investigated by using wide range of several initial metal concentration, contact time and pH. Maximum adsorption of Cd(II) and Pb(II) was found in the pH range of 6–8. The adsorption capacity for Cd(II) and Pb(II) was 8.85 and 9.03 mg/g, respectively. Thermodynamics parameters and kinetic models were applied to adsorption data. The isotherm data followed Langmuir model, corresponding to monolayer adsorption of the two ions in the contaminated water. The kinetic data followed the pseudo 2nd order kinetics model, which authenticates the chemisorption nature. The thermodynamic study indicated that Cd adsorption is a spontaneous exothermic process while Pb adsorption is an endothermic process. Mineral precipitation, surface complexation, and cation-π interactions are the major remediation strategies for Cd(II) and Pb(II).

Keywords: wastewater treatment; emerging contaminants; environmental remediation; adsorption; heavy metals

1. Introduction

The occurrence of heavy metals in industrial wastes, pesticides, fertilizers, metal mining, and energy utilization process are among the most hazardous pollutants to human beings due to their toxicity and non-degradable nature [1]. Water containing heavy metals causes serious irritation to the respiratory tract, and damage the liver, kidney and human olfactory sense through prolonged contact. Cr(V), Fe(III), Ni(II), Zn(II), Cd(II), Hg(II), and Pb(II) are the most well-known toxic heavy metal pollutants in wastewater, which need to be removed by appropriate methods before water recycling and reuse [2].
Cd(II) and Pb(II) have been considered most critical environmental pollutants due to their carcinogenic nature and longer persistent in the environment. It has been found that the excessive intake of Cd(II) can cause kidney, lungs, and bone problems, whereas Pb(II) can potentially damage the genital and nervous systems [3]. Thus, cost-effective methods to remove Cd(II) and Pb(II) from wastewater are urgently demanded. Up to now, several nominal approaches have been developed for heavy metals removal [4], including ion exchange [5], electrochemical [6], neutralization precipitation [7], membrane filtration [8], nanofiltration [9], flotation [10], and adsorption [11], of which adsorption is considered as one of the most environment-friendly and highly-efficient option [12]. To achieve good adsorption performance, the selection of adsorbents is very crucial. Activated carbon [13], and molecular sieves [14] were widely used because of their distinctive adsorption properties, resulting from firm micro and mesoporous structures. However, their high cost, complex preparation and recycling methods make it difficult to be conducted on a large-scale.

Natural adsorbent as biochar is a non-toxic material synthesized from agricultural wastes by the pyrolysis of biomass during carbonization and is considered as a good candidate to supplant the high-cost adsorbents for the expulsion of heavy metals from wastewater [15]. The biochar poses high organic carbon contents and aromatic structures that intensify its adsorption capacity [16]. Moreover, the higher oxygen content and acidic groups of biochar also plays a part in increasing its metal sorption efficiency [17]. Biomass type and carbonization conditions are important parameters that affect the pore size and chemical properties of biochar. The world annual production of wheat straw is about 529 million tons/year [18], and it contains high values of cellulose (34–40%), hemicellulose (20–25%) and lignin (20%) [19]. The low cost and abundance of organic functional groups in the wheat straw make it a potential adsorbent for the binding of heavy metals after carbonization. Usually, the pristine biochar derived from wheat-straw has a lower surface area due to the narrow microspores and poor heavy metals removal efficiency. Hence, an activation step is required to enlarge the porosity and enhancement of mass transfer fluxes and active loadings [20].

The activation process is classified into physical and chemical methods based on the activation mechanism [21]. Physical activation is the process in which oxidizing agents (H₂O, O₂, or CO₂) are used to develop porosity by controlled carbon gasification, while chemical activation uses chemical agents to enhance the gasification rate of biochar [22]. The frequently used chemicals for chemical activation are HCl [23], NaOH [24], KOH [25], H₃PO₄ [26], and ZnCl₂ [27]. Ahmed et al. [28] revealed that chemical modification of biochar can enhance its surface properties and produce a higher number of oxygenated functional groups where alkaline modification improves the surface aromaticity and removes the organic and inorganic contaminants efficiently. Naeem et al. [29] investigated wheat straw biochar (WSB) and activated wheat straw biochar (AWSB) by using batch and column methods for the removal of Cd(II) and found that AWSB removes Cd(II) more efficiently from contaminated water. Stasi et al. [20] reported that physically activated wheat straw by CO₂ has good catalytic ability and stability. Recently, Yu et al. [3] explored the sulfonated biochar for the removal of heavy metals. Previously, Inyang et al. [30] investigated the anaerobically digested biomass-derived biochar for the remediation of heavy metals. Although it is meaningful and economical to transform agricultural wastes into biochar for sorting the environmental risks, however the understanding of heavy metals adsorption by biochar remains challenging, due to the interaction between biochar and heavy metals, the long-term attachment of heavy metals, and the release of heavy metals from biochar. Furthermore, activation through the chemical oxidation process is less/never investigated for competitive bi-heavy metals remediation.

In this study, AWSB was prepared by activating the WSB through the chemical oxidation process which increases the surface functionalities like oxygen-containing groups and hydrophilicity of WSB after activation. Activation by chemical oxidation can also increase the pore size, resulting in improved competitive adsorption capacity of polar adsorbates, i.e., Cd(II) and Pb(II). Batch experiments and characterizations were performed
to evaluate the remediation and competitive adsorption of Cd(II) and Pb(II) by using AWSB. The uptake ability of biochar as well as the effect of metal concentration, contact time, and pH on Cd and Pb adsorption was evaluated. Moreover, the adsorption isotherms, thermodynamics, kinetics, and the adsorption mechanism were investigated in detail.

2. Materials and Methods

2.1. Preparation and Characterization of AWSB

Wheat straw was used as a feedstock for biochar preparation and was collected from the KOND farm of the Pir Mehr Ali Shah (PMAS) Arid Agriculture University, Rawalpindi, Pakistan. Firstly, wheat straw was washed several times with deionized water to remove all impurities and then dried in an oven at 333 K for 24 h. Then, 15 g of dried wheat straw was transferred to a ceramic crucible and pyrolyzed in a muffle furnace at 673 K for 2 h. The sample was cooled to room temperature and crushed into fine powder. The WSB was activated with 1 mol/L HCl solution for 1 h and then washed with deionized water several times until pH 7. After drying at 333 K for 4 h, the resultant powder was obtained and named as AWSB.

The AWSB was characterized before and after adsorption by several innovative techniques including scanning electron microscopy (SEM; Tescan Vega 3), energy dispersive X-ray (EDX) analysis, Fourier transforms infrared spectroscopy (FT-IR) (Bruker IFS-66), and X-ray Diffraction (XRD) analysis (X’Pert, DY-3805).

2.2. Adsorption Experiments

The stock solution of the bimetallic equimolar aqueous solution of Cd and Pb was prepared by dissolving cadmium nitrate (A.R., Cd(NO$_3$)$_2$; 8.90 mM) and lead nitrate (A.R., Pb(NO$_3$)$_2$; 4.80 mM) in deionized water. Standard solutions (2, 4, 8, 15, 30, and 50 ppm) were then precisely prepared from the stock solution and kept at room temperature for further tests. To evaluate the adsorption of Cd and Pb on AWSB (0.5 g), 50 mL of standard solutions of various concentrations were used. The mixture was then incubated at 180 rpm in a shaker for 2 h and later filtered. The Cd and Pb concentrations before and after adsorption were analysed by atomic absorption spectrophotometer (AAS; model AA-6300, GFA-Ex-71 Shimadzu). The pH of standard solutions was adjusted to 2, 4, 6, 8, 10, and 12 by 1 mol/L HCl and 1 mol/L NaOH solutions to study the influence of pH on Cd and Pb adsorption. The impact of Cd and Pb concentrations on adsorption was studied employing standard solutions with metal concentrations of 2, 4, 8, 15, 30, and 50 ppm. The effect of contact time was analysed after shaking for 0–16 h. The removal efficiency of each AWSB for Cd and Pb was calculated using the following Equation (1):

$$\text{Removal Efficiency (\%) } = \frac{C_0 - C_e}{C_0} \times 100$$

2.3. Adsorption Isotherms

Isotherm modelling has vital significance while planning a sorption-based system which identifies the metal division as a function of the metal concentration between solid adsorbent and aqueous media. The concentration of metals over the adsorbent increases till equilibrium and thereafter the metal ion concentration constantly distributes between the solid-liquid phase. Three models were frequently used to fit the heavy metal adsorption isotherms. The Langmuir model shows the perfect monolayer adsorption which demonstrates that there is no mutual interaction between adsorption of metals because of equivalent adsorption energy of all adsorption sites [31]. The Freundlich model explains the heterogeneous absorption with continuously increasing adsorption degree at higher concentrations [32]. The Temkin model is suitable for the system in which there is a linear decline in the adsorption heat by the coverage of adsorption because of the interaction between adsorbate and adsorbent [33]. The Langmuir, Freundlich, and Temkin isotherm’s linear forms are mentioned in Equations (2)–(5) [34]:
\[ \frac{1}{Q_e} = \frac{1}{Q_m} + \left[ \frac{1}{K_L Q_m} \right] \frac{1}{C_e} \]  
\[ \ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \]  
\[ Q_e = \frac{RT}{b} \ln (AC_e) \]  
\[ B = \frac{RT}{b} \]  
\[ R_L = \frac{1}{1 + \frac{K_L C_0}{C_e}} \]

where “\( Q_e \)” is the total Cd and Pb adsorbed at equilibrium on AWSB (mg/g); “\( Q_m \)” is the maximum adsorption capacity of Langmuir (mg/g); “\( K_L \)” is the affinity constant of Langmuir (L/mg); “\( C_e \)” is the equilibrium concentration of Cd and Pb in solution (mg/L); “\( K_F \)” is the Freundlich constant (mg/g·(L/g)^n); “\( n \)” is the dimensionless constant; “\( R \)” is the constant of universal gas (8.314 J/mol); “\( T \)” is the temperature (K); “\( b \)” is the constant of Temkin isotherm; “\( A \)” is the constant of Temkin equilibrium binding (L/g); “\( R_L \)” is the separation parameter as calculated by Equation (6), which might be 0 (irreversible), 1 (linear), 0–1 (favorable) or >0 (unfavorable); “\( C_0 \)” is the initial concentration of Cd and Pb [35]. Freundlich dimensionless constant describes the favorable adsorption and strong interaction between heavy metal and AWSB when its value varies between 1 to 10 [33].

2.4. Thermodynamics

Thermodynamic investigations can explain the effect of temperature on adsorption performance. The equilibrium constant (\( K \)) is determined by Equation (7) [34], while Gibbs free energy (\( \Delta G^\circ \)), entropy (\( \Delta S^\circ \)), and enthalpy (\( \Delta H^\circ \)) are calculated by the Equations (8)–(10) [34].

\[ K = K_F^n \times M \times 1000 \times 55.5 \]  
\[ \Delta G^\circ = -RT \ln K \]  
\[ \Delta G^\circ = \Delta H^\circ + T\Delta S^\circ \]  
\[ \ln K = -\frac{\Delta H^\circ}{R} \left( \frac{1}{T} \right) + \frac{\Delta S^\circ}{R} \]

where “\( M \)” is the metal’s molecular weight (Cd: 112.41 g/mol; Pb: 207.2 g/mol); “55.5” is the molar concentration of water; “\( R \)” is the constant of the universal gas (8.314 J/mol K); “\( T \)” is the temperature (K).

2.5. Kinetics

Adsorption kinetics was studied to evaluate the mechanism of metal adsorption on the surface of AWSB. The rate of reaction and degree of adsorption was well explained by kinetic equations. The pseudo 1st order kinetics, pseudo 2nd order kinetics, power function, and intraparticle diffusion are mentioned in Equations (11)–(14).

\[ \log (q_e - q_t) = \log q_e - \frac{K_t t}{2.303} \]  
\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \]  
\[ \ln q_t = \ln b + k_f (Lnt) \]  
\[ q_t = k_{dif} \sqrt{t} + C \]
where “qₑ” shows the amount of metal adsorbed by the adsorbent; “qₜ” indicates the quantity of Pb and Cd adsorbed at a standardized time (mg/g); “K₁” and “K₂” corresponds to the pseudo 1st order kinetic and pseudo 2nd order kinetic models; “t” represents time (h); “kᵢ” represents power function rate constants, “kᵢ” represents constant intraparticle diffusion (mg/g·min⁻⁰.⁵); “C” is a constant related to the border layer thickness (mg/g).

3. Results and Discussion

3.1. Characterizations of AWSB

The surface morphology and porous structure of pristine/pre-adsorbed WSB and AWSB were studied by SEM technique. As shown in Figure 1A and Figure S1, the pre-adsorbed AWSB has a heterogeneous structure with large bulk and smaller cracks as compared to pristine WSB. The bulk cracks contain parallel pores with a pore size of ~5 µm with a smooth pore wall. SEM-EDX mapping was performed to study the composition of pristine WSB and AWSB (Figure S2 and Figure 1B). The elemental percentage is shown in Table 1.

Table 1. Elemental analysis of the pristine WSB and AWSB and post-adsorbed AWSB (2 ppm).

| Element | WSB | AWSB | Post-Adsorption |
|---------|-----|------|-----------------|
|         | Weight % | Atomic % | Weight % | Atomic % | Weight % | Atomic % |
| K       | 35.20 | 30.53 | 35.84 | 37.00 | - | - |
| Mg      | - | - | 5.74 | 9.54 | - | - |
| Si      | 42.75 | 51.62 | 32.74 | 47.05 | - | - |
| Ca      | 20.85 | 17.65 | - | - | 8.62 | 9.09 |
| Al      | - | - | - | - | 50.67 | 79.32 |
| Cd      | 1.21 | 0.20 | 8.56 | 3.07 | 19.18 | 7.21 |
| Pb      | - | - | - | - | 21.52 | 4.39 |

As a result of pyrolysis treatment, the carbon content of the biochar increases. FTIR spectrum was used to investigate the functional groups on the surface of pristine WSB and AWSB. As shown in Figure 2A and Figure S3A, the—OH stretching peaks at 3373 cm⁻¹ and 3356 cm⁻¹ and C=C stretching vibrations of aromatic rings at 1577 cm⁻¹ and 1637 cm⁻¹.
were observed on the pristine WSB and AWSB [33]. The O—H stretching peak becomes stronger after activation. The peak at 1380 cm⁻¹ is allotted to CH₃ bending for pristine WSB where 1602 cm⁻¹ is assigned to C=C stretching [29,31,33], while the peak around 650 cm⁻¹ corresponds to CO₃²⁻ [36] for pre-adsorbed AWSB. The number and classes of functional groups can decide the sorption capacity of the biochar and govern its adsorption mechanism [31]. The C=C functional groups of biochar were usually considered favorable for metal adsorption by forming a surface complex through inter-metal-π-interactions [37].

XRD technique was used to study the crystallographic structure of the AWSB sample. The XRD pattern in Figure 2B and Figure S3B shows inorganic moieties with the sharp and strongest peak of SiO₂ on 10° for AWSB and about 28° for pristine WSB at 2-theta degree [29]. The biochar attains a well-arranged crystal face, shape, and degree of graphitization after activating. The XRD peak around 28° on pristine WSB shifts to the lower 2-theta degree around 10° on AWSB, indicating the changes in the structural morphology which is in well accordance with SEM micrographs. Hence, the XRD results of pristine WSB and pre-adsorbed AWSB well explained the change in the structural morphology of biochar. The surface of pristine WSB and pre-adsorbed AWSB might be heterogeneous, according to XRD findings.

![Figure 2. (A) FTIR spectra and (B) XRD pattern of the pre-adsorbed AWSB.](image)

### 3.2. Adsorption Performance

#### 3.2.1. Effect of the Initial Metal Concentration

The important factor in the study of contaminant removal from the aqueous media is the removal efficiency of biochar with respect to initial heavy metals concentration. The Cd and Pb concentrations were increased from 2 mg/L to 50 mg/L with a constant AWSB dosage of 2 g. The Figure 3A presented a surge in the removal efficiency with an increase in the concentration of heavy metals until 30 mg/L. AWSB showed maximum removal efficiency (98.3% and 98.7%) for both Cd and Pb at 30 mg/L, respectively. Further increase in the metals concentration reduces the removal efficiency for Cd, which could be due to the saturation of AWSB active sites at higher metal concentrations [31,38]. The adsorption sites after a certain time get to be depleted and reaches an equilibrium which encourages adsorption from aqueous media is not conceivable. Initial metal ion accumulation contributes to the conquest of all metal transfer resistances within solid and liquid, which means a higher probability of collision between Cd, Pb, and active sites of AWSB. At the higher metal concentration of 50 mg/L, the Pb adsorption still maintains at high level (98.2%), whereas the Cd adsorption has decreased to 83.5%, indicating that competitive adsorption of Cd and Pb occurred over the active sites of AWSB.
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Figure 3. (A). Effects of initial metal concentration on Cd(II) and Pb(II) removal efficiency of AWSB. (B). Effects of contact time on Cd(II) and Pb(II) removal efficiency of AWSB. (C). Effects of pH on Cd(II) and Pb(II) removal efficiency of AWSB.

3.2.2. Effect of Contact Time

For remediation of Cd and Pb from contaminated water using AWSB, contact time also plays a crucial role. The impact of contact time is studied by fixing the usage of AWSB (0.05 g in 20 mL solution), and Cd and Pb concentrations (15 mg/L). As shown in Figure 3B, in the first hour, the removal rate rapidly increases to the maxima and then gradually slows down and attains equilibrium. The Cd and Pb maximum adsorption after 2 h were 1.9 and 5.6 mg/g, respectively. Rapid adsorption of Cd and Pb indicates a fast reaction rate within a short contact time due to the high availability of active sites on AWSB [34]. The efficiency of the material is shown by the accomplishment of the adsorption equilibrium in a small contact time. Small contact time is prioritized in wastewater treatment, as the strength of the procedure proficiency can be improved with less operating time and the total cost of the metal evacuation procedure can be reduced [39]. Hence, for the removal of Cd and Pb, AWSB proved to be a cost and time-effective adsorbent. The quick initial adsorption rate also proposes that adsorbent and adsorbate have high reactivity, thus
defining the interaction between the active surface and the metal ions, which is suggested to be chemisorption rather than the slow physisorption process.

3.2.3. Effect of pH

pH is another essential parameter that affects the acid-base property, degree of ionization, and surface charge, which directly affects the ionic strength of metal ions in the solution [40]. The pH of the aqueous media varied between 2 to 12 in this study. The Figure 3C showed that as the pH of the aqueous solution increases from 2 to 8, the Cd and Pb adsorption capacities of AWSB also increases. Maximum Cd and Pb adsorption of 98.0% is obtained by AWSB at pH = 8, while remediation efficiency decreases with further increasing the pH. The poor adsorption efficiency at low pH may be caused by the repulsion between the Cd and Pb on the surface of biochar and acidic functional groups. In contrast, the competition between Cd and Pb and hydronium ions decreases at high pH, and the biochar surface gradually turned to be negatively charged, which provides an active surface for Cd and Pb adsorption. Our findings are in good agreement with the literature study, which reported that there is a direct relation between heavy metal adsorption and pH, i.e., an increase in pH improves the adsorption of heavy metals [41]. Notably, AWSB shows high removal efficiency for Pb as compared to Cd, indicating that Cd adsorption is more sensitive to pH.

3.2.4. Adsorption Isotherms

Adsorption isotherm was studied to evaluate the mechanisms and total adsorption capacity of AWSB. The equilibrium isotherm is the foremost noteworthy phy-chem-method in a solid-liquid framework, which is mostly used to investigate the adsorption behavior [42]. The adsorption equilibrium isotherm is studied using the linear form of Langmuir, Freundlich, and Temkin models. Linear correlation coefficients and constant parameters are elucidated in Table 2. The Langmuir model suits Cd and Pb adsorption on AWSB better than Freundlich and Temkin model at temperatures of 298, 310, and 322 K (Figure 4A–C and Figures S4–S9). The adsorption behavior of AWSB fitted well with the Langmuir model suggests a monolayer adsorption process rather than heterogeneous coverage on homogenous sites [43]. For Cd and Pb adsorption, the Langmuir maximum monolayer adsorption capacity (Qm) value is 9.3 and 0.6 mg/g at 298 K, respectively. Moreover, the R_L value for Cd and Pb adsorption with a concentration of 15 ppm at 298 K is 0.940 and 0.953, explaining that both the heavy metals favorably adsorbed on AWSB. Freundlich dimensionless constant n values for Cd (1.949) and Pb (2.865) are greater than 1, which indicates their favorable adsorption on AWSB.

### Table 2. Constant parameters and correlation coefficients of isothermal models for Cd(II) and Pb(II) adsorption onto AWSB.

| Heavy Metal | Temperature (K) | Langmuir Model | Freundlich Model | Temkin Model |
|-------------|-----------------|----------------|------------------|--------------|
|              | K_L (L/mg) | Q_m (mg/g) | R² | K_F (mg/g) | n | R² | B (J/mol) | A (L/g) | R² |
| Cd          | 298     | 1.048 | 9.285 | 0.939 | 0.725 | 1.949 | 0.900 | 318.1 | 0.188 | 0.811 |
|             | 310     | 1.103 | 9.009 | 0.928 | 0.702 | 1.954 | 0.913 | 335.8 | 0.176 | 0.807 |
|             | 322     | 0.635 | 3.724 | 0.911 | 0.705 | 1.954 | 0.909 | 348.6 | 0.177 | 0.804 |
| Pb          | 298     | 0.736 | 0.621 | 0.943 | 0.498 | 2.865 | 0.930 | 169.9 | 0.269 | 0.923 |
|             | 310     | 0.161 | 0.191 | 0.935 | 0.513 | 2.884 | 0.924 | 179.6 | 0.267 | 0.903 |
|             | 322     | 0.028 | 0.172 | 0.926 | 0.519 | 2.895 | 0.919 | 196.5 | 0.269 | 0.815 |
3.2.5. Adsorption Thermodynamics

The thermodynamic analysis is examined to explore the nature and energetic changes in Cd and Pb adsorption over AWSB. The obtained thermodynamic parameters are tabulated in Table 3. Negative $\Delta G^\circ$ indicates that Cd and Pb adsorption on AWSB is a spontaneous process. The adsorption becomes more spontaneous and favorable at low temperatures with the decline in $\Delta G^\circ$ under promoting temperature. The $\Delta G^\circ$ value of 4–10 kJ/mol indicates the existence of Van der Waal forces of interaction, hydrogen bonding from 2–40 kJ/mol, dipole force of interaction from 2–29 kJ/mol and >60 kJ/mol chemical bonding is the dominant force of interaction [34]. In this case, $\Delta G^\circ$ ranges from $-35.44$ to $-37.67$ kJ/mol for Cd and $-32.04$ to $-34.47$ kJ/mol illustrates hydrogen bonding as the major interactive force between heavy metals and AWSB. The graph between $\ln K$ and $1/T$ is plotted to extract the values of $\Delta H^\circ$ and $\Delta S^\circ$ as shown in Figure 5. Positive $\Delta S^\circ$ value (3.49 J/mol K for Cd and 119.26 J/mol K for Pb) expresses the good affinity between AWSB and Cd and Pb with the disordered solid-liquid interface. The disorder-ness between solid-liquid might be because of the discharge of water molecules due to the migration of positive and negative ions generated by the transfer of heavy metals on the surface of AWSB. Compared to Cd, the higher $\Delta S^\circ$ for Pb indicates its stronger affinity with AWSB. Negative $\Delta H^\circ$ value for Cd ($\Delta H^\circ = -1.90$ kJ/mol) reveals that the adsorption process is exothermic while a positive amount of $\Delta H^\circ$ for Pb ($\Delta H^\circ = 112.42$ kJ/mol) illustrates its adsorption on AWSB is endothermic. Generally, $\Delta H^\circ$ value for physical adsorption ranges from 2.1 to 20.9 kJ/mol where the chemical adsorption process ranges from 80 to 200 kJ·mol$^{-1}$, respectively [44], thus $\Delta H^\circ$ values for Cd and Pb adsorption well fits in physical adsorption process.

| Heavy Metal | Temperature (K) | $\Delta G^\circ$ (kJ/mol) | $\Delta H^\circ$ (kJ/mol) | $\Delta S^\circ$ (J/mol K) |
|-------------|-----------------|--------------------------|--------------------------|--------------------------|
| Cd          | 298             | $-35.44$                 | $-1.90$                  | 3.49                     |
|             | 310             | $-36.46$                 |                          |                          |
|             | 322             | $-37.67$                 |                          |                          |
| Pb          | 298             | $-32.04$                 |                          |                          |
|             | 310             | $-33.28$                 | 112.42                   | 119.26                   |
|             | 322             | $-34.47$                 |                          |                          |
3.2.6. Adsorption Kinetics

Adsorption kinetics governs a crucial role in designing the adsorption process and forecast the solution rejected adsorbate. Adsorption kinetics was examined for the removal of heavy metals based on the adsorption time. Pseudo 1st order and pseudo 2nd order are two renowned equations used on the adsorption data to achieve the kinetic process presented in Figure S10 and Figure 6 and the measured kinetic parameters are presented in Table 4. For Cd and Pb, the quantity of correlation coefficient ($R^2$) for pseudo 2nd order is higher than pseudo 1st order, power function (Figure S11), and intraparticle diffusion (Figure S12). Thus, Cd and Pb adsorption on AWSB fits best on pseudo 2nd order kinetics. It is described that for the adsorption process of Cd and Pb, the chemisorption is the rate-controlling mechanism on AWSB by sharing electrons between heavy metals and biochar [41]. The $q_e$ experimental and calculated values for pseudo 2nd order are very close to each other expressing that the mechanism of adsorption depends upon the limited rate of chemisorption, such as precipitation and complexation [45]. The maximum Cd and Pb adsorbed on AWSB is 8.9 and 9.0 mg/g at 298 K, respectively. AWSB showed superior adsorption capacity in comparison to other adsorbents in literature (Table 5) [14,30,41,46–50]. The lower $R^2$ value of power function and intraparticle diffusion reveals that Cd and Pb adsorption never progress through power function and intraparticle diffusion model.
Figure 6. Pseudo 2nd order fittings of Cd(II) and Pb(II) adsorption data for AWSB.

Table 4. Kinetic parameters of Cd(II) and Pb(II) adsorption on activated wheat straw biochar at 298K.

| Adsorbent | Kinetic Models | Parameters | Cd | Pb |
|-----------|----------------|------------|----|----|
| AWSB      | Pseudo 1st order | $q_e$ (Exp) mg/g | 6.064 | 6.921 |
|           |                 | $q_e$ (Cal) mg/g | 7.644 | 7.872 |
|           |                 | $K_1$ | 0.005 | 0.004 |
|           |                 | $h$ | 0.268 | 0.267 |
|           |                 | $R^2$ | 0.983 | 0.993 |
| AWSB      | Pseudo 2nd order | $q_e$ (Exp) mg/g | 7.53 | 8.142 |
|           |                 | $q_e$ (Cal) mg/g | 8.85 | 9.03 |
|           |                 | $K_2$ | 0.004 | 0.003 |
|           |                 | $h$ | 0.277 | 0.272 |
|           |                 | $R^2$ | 0.984 | 0.996 |
| AWSB      | Power function | $k_f$ | −0.233 | −0.090 |
|           |                 | $b$ | 1.530 | 1.893 |
|           |                 | $R^2$ | 0.782 | 0.839 |
| AWSB      | Intraparticle diffusion | $k_{dif}$ | 0.620 | 0.988 |
|           |                 | $c$ | 0.269 | 0.262 |
|           |                 | $R^2$ | 0.814 | 0.839 |

Table 5. Comparison of efficiency of adsorbents for remediation of Cd(II) and Pb(II) from polluted water.

| Adsorbents | Quantity Adsorbed (mg/g) | Reference |
|------------|--------------------------|-----------|
| Cd         |                          |           |
| Out-grassed magnesium composite (Mg-AC) | 0.094 | Yanagisawa et al. [42] |
| BC-300     | 4.41                     | Usman et al. [48] |
| Dairy manure | 0.28                     | Xu et al. [49] |
| Oak        | 0.05                     | Mohan et al. [50] |
| Pine       | 0.01                     | Mohan et al. [50] |
| Anaerobically digested sludge | 0.44 | Ni et al. [51] |
| Adsorption |                          |           |
| AWSB       | 8.85                     | Present work |
Table 5. Cont.

| Adsorbents          | Adsorbents                           | Quantity Adsorbed (mg/g) | Reference               |
|---------------------|--------------------------------------|--------------------------|-------------------------|
| Pb                  | Oxidized MWCNTs                       | 2.06                     | Xu et al. [49]           |
| Bagasse             |                                      |                          |                         |
| Digested whole sugar beet |                                    | 0.20                     | Inyang et al. [52]      |
| Rice husk           |                                      | 0.01                     | Liu and Zhang [53]      |
| Sesame straw        |                                      | 0.49                     | Park et al. [54]        |
| Pinewood            |                                      | 0.02                     | Liu and Zhang [53]      |
| Anaerobically       |                                      |                          |                         |
| digested sludge Adsorption |                                | 0.61                     | Ni et al. [51]          |
| AWSB                |                                      | 9.06                     | Present work            |

3.3. Insights of the Adsorption Mechanism

Generally, the adsorption mechanism of Cd and Pb on biochar governs surface complexation, mineral precipitation, and metal-π interaction. The key method for the removal of heavy metals by biochar is precipitation with minerals. Biochar possesses CaCO₃, Ca₃(PO₄)₂, a variety of additional substances and inorganic anions like OH⁻, CO₃²⁻ and PO₄³⁻ were released when Cd and Pb contacted the biochar within the aqueous environment, facilitating their precipitation. The precipitates from Pb²⁺ and inorganic anion reactions can be observed after adsorption in the XRD study according to previous literature. Therefore, a possible mechanism for Cd and Pb adsorption on AWSB could be their surface mineral precipitation [8,51]. The proof of biochar-derived precipitation with minerals is as follows.

(a) SEM images (Figure 7A) for post-adsorption of AWSB indicated the adsorption of Cd and Pb ions in the internal pores ultimately making the surface area of biochar well-arranged and least porous. The increased carbon content of the biochar due to pyrolysis thereby increases the adsorption area for the metals. The Cd and Pb adsorption on the AWSB surface were confirmed by using SEM-EDX (Figure 7B). The EDX results revealed that the Pb percentage on AWSB of the pre-adsorbed sample was 0% and increased to 21.52% after adsorption (Table 1). Similarly, the percentage of adsorption for Cd on AWSB surface for pre and post adsorption samples was increased from 8.56% to 19.18%. A high percentage of Si, K, and Ca was also observed on biochar surfaces in EDX analysis. These results strongly evidenced and confirmed the adsorption of heavy metals on AWSB surface where Pb results illustrate the strong adsorption on biochar surface. When Cd and Pb are adsorbed, the AWSB surface has certain particles or minerals crystal on it, showing that Cd and Pb related compounds are produced between Cd, Pb, and biochar, according to SEM spectra.

(b) XRD pattern of post-adsorbed Cd and Pb on AWSB is presented in Figure 8A. Post-adsorption of Cd(NO₃)₂, Pb(NO₃)₂, and pH controlling agent (HCl and NaOH), these XRD peaks become broader and stronger at about 2θ which corresponds to SiO₂ which are in-line with the EDX results [29,33]. The change in the structure of biochar after Cd and Pb adsorption accelerates the precipitation process at the time of adsorption and facilitates the surface precipitation which is an important adsorption mechanism for these metals. The new crystal peak was emerged at 42° after Cd and Pb adsorption on AWSB corresponds to CdCO₃ and PbCO₃ presence. The shape and characterization of CO₃²⁻ was consistent with the previous study [52].

(c) Biochar metal cations (Ca²⁺, Mg²⁺, K⁺) are stored by complexation (e.g., —COOM, —R—O—M with —OH and COOH) or precipitation or by electrostatic attraction. During the adsorption process, Cd and Pb are exchanged through these cations in solution through surface complexation by metal exchange process, co-precipitation, or by an electrostatic exchange. Our findings are also supported by previous literature
that the concentration of cations and anions decreased after heavy metal adsorption on biochar [53].

A significant mechanism for metal sorption by biochar is also surface complexation with organic functional groups (OFGs). There are many types of OFGs found in biochar. The OFGs are affected greatly by pyrolytic temperatures. The types and content of OFGs have reduced markedly with increasing pyrolytic temperature. Interaction between Cd/Pb and OFGs occurred in this research due to a higher number of oxygen-containing functional groups, especially at low temperatures. The FTIR spectra (Figure 8B) showed the variation in absorbance peaks responsible for competitive adsorption between the two heavy metals eliminated from the self-contaminated water. The adsorption of Cd and Pb might occur by π-electrons offered by the aromatic ring. The post-adsorption peak for -OH stretching ranges from 3300 to 3500 cm\(^{-1}\) emerged due to water after physio-sorbed adsorption [29,36]. The C—O stretching vibrations of alcohols, phenols, ether, or ester groups refer to the peak at 1070.5 cm\(^{-1}\) where the peak around 650 cm\(^{-1}\) corresponds to CO\(_3^{2-}\) 36. According to the FTIR analysis, some peaks moved or vanished when Cd and Pb adsorbed onto AWSB, including C—C, C=C, C—O, and —OH. They followed the mechanism of surface complexation that occurred between Cd, Pb, and AWSB. AWSB was partially carbonized at low temperatures and some OFGs were reserved in the AWSB.

The cation-π interaction is another well-known mechanism for metal adsorption by biochars. Zhang et al., reported that the interaction of cation-π played a significant role during biochar heavy metal sorption [54]. The cyclic aromatic π-system’s π-electrons can act as a donor of the electrons, such donation becomes increased with the increase of the number of associated rings [55]. The peak for C=C groups shifted in the post-adsorption FTIR analysis, which confirms that the cation-π interaction indeed makes contributions to the Cd and Pb adsorption in our experiment.
Activated biochar was synthesized by chemical oxidation through HCl as an activating agent. A strong competitive Cd and Pb adsorption efficiency from aqueous media with an adsorption value of 8.9 and 9.0 mg/g was shown by the AWSB. The AWSB has a good porous structure and optimal adsorption was achieved with the concentration of 30 mg/L, pH = 8, and contact time of 2 h. Equilibrium, thermodynamic and kinetics were studied to investigate the feasibility and adsorption mechanism. Equilibrium isotherm studies revealed that all isotherms match well with experimental results, whereas amongst them for Cd and Pb Langmuir isotherm best fitted with highest fitting R² values of 0.939 and 0.943 at 298 K. The thermodynamic investigation exposed the spontaneous adsorption process by ΔG° values. Cd governs exothermic where the endothermic pathway was followed by Pb which was revealed by ΔH° values, respectively. As well, the entropy values reflected a decent affinity of AWSB for Pb and showed a decreased affinity for Cd. Furthermore, thermodynamic investigations also proved that adsorption was primarily a result of Van der Waal’s force interaction between heavy metals and AWSB. The adsorption kinetics confirmed the well-fitting of pseudo 2nd order kinetics. The mechanism regulating the AWSB for the remediation of Cd and Pb is minerals precipitation, surface complexation, and cation-π interaction.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/su13168817/s1, Figure S1: Scanning electron micrographs (SEM) of pristine WSB and pre-adsorbed AWSB (pyrolyzed at 673 K), Figure S2: EDX mapping of the pristine WSB, Figure S3: (A) FTIR spectra and (B) XRD pattern of the pristine WSB, Figure S4: Langmuir isotherm for the adsorption of Cd(II) and Pb(II) AWSB at 310K, Figure S5: Langmuir isotherm for the adsorption of Cd(II) and Pb(II) on AWSB at 322K, Figure S6: Freundlich isotherm for the adsorption of Cd(II) and Pb(II) on AWSB at 310K, Figure S7: Freundlich isotherm for the adsorption of Cd(II) and Pb(II) on AWSB at 322K, Figure S8: Temkin isotherm for the adsorption of Cd(II) and Pb(II) on AWSB at 310K, Figure S9: Temkin isotherm for the adsorption of Cd(II) and Pb(II) on AWSB at 322K, Figure S10: Pseudo 1st order fittings of Cd and Pb adsorption data, Figure S11. Power function fittings of Cd(II) and Pb(II) adsorption data for AWSB, Figure S12. Intraparticle diffusion fittings of Cd(II) and Pb(II) adsorption data for AWSB.

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