Synthesis of Amino-Functionalized Waste Wood Flour Adsorbent for High-Capacity Pb(II) Adsorption

Yi Tan,† Kaili Wang,† Qian Yan,† Shifeng Zhang,*†‡ Jianzhang Li,*†‡ and Yong Ji‡

†College of Material Science and Technology, MOE Key Laboratory of Wooden Material Science and Application, Beijing Forestry University, Beijing 100083, China
‡College of Water Conservancy and Ecological Engineering, Nanchang Institute of Technology, Nanchang 330099, China

ABSTRACT: An innovative wood flour-based adsorbent for Pb(II) removal was synthesized via a cost-effective and environment-friendly method, which could be high on the priority list owing to its high absorption capacity. By increasing the specific surface and introducing functional groups through delignification and amination, the experimental adsorption capacity of the prepared adsorbent could reach 189.9 mg/g in 180 min (pH = 4, T = 293 K, dosage = 1 g/L, and ion concentration = 300 mg/L). This value is higher than most of those achieved in previous studies on wood-based adsorbents. Pseudo-second-order and Langmuir models were utilized to describe the adsorption kinetics and isotherms, respectively. The effects of solution pH, adsorbent dosage, and temperature on the adsorption efficiency were also evaluated. With a low decrease rate of 20.2% in five cycles, the adsorbent possessed reusability. The adsorbents exhibited high selectivity in the Pb(II), Cu(II), and Zn(II) mixed solution, and the selectivity coefficient k of adsorbents to Pb(II) could reach approximately 2.74 in triad. The method could prompt the development of cost-effective methods for the removal of heavy metals from wastewater.

1. INTRODUCTION

The removal of heavy metal ions from wastewater has been a concern for a long time.1 With the continuous development of electroplating, smelting, battery-making, and mining industries, vast heavy metals, including Pb(II), Zn(II), and Cu(II), are discharged into the water environment as wastes.2,3 These heavy metals are toxic, nondegradable, and often deposited in organisms,4 entering animals, plants, and human bodies through the ecological system, resulting in serious damages to the current ecological environment and human health. Thus, there is an urgent need to develop in order to address these serious environmental problems.5 As the United States Environmental Protection Agency stipulates, Pb(II) could damage the nervous system in children, affecting their intelligence, hearing, and hematopoietic ability.6 When the Pb(II) level increases, the probability of contracting cardiovascular diseases is increased, leading to death.7 Therefore, it is desired to create new materials and technologies for heavy-metal wastewater treatment.

Studies have been conducted on the development of various methods, such as chemical precipitation, ion exchange, membrane filtration, and adsorption, to remove heavy metals from wastewater.7−11 During chemical precipitation, heavy metals could be removed by forming insoluble precipitates. This method provides process simplicity, good compatibility, and low cost. However, it involves disposal and separation challenges.7 Ion exchange treatment removes the dissolved heavy metal ions via the cation or anion exchange between specific resins and heavy metals. The approach exhibits high capacity, selectivity, fast kinetics, and high regeneration; however, the technique is highly sensitive to pH and is not suitable for highly concentrated metal solutions.8 Membrane filtration treatments, including ultrafiltration, reverse osmosis, and nanofiltration, could achieve high removal efficiency and involve no phase change, but the cost is relatively high.9 Meanwhile, specific adsorbents are used to adsorb heavy metals by physical and/or chemical interactions. Among various processes, adsorption seems to exhibit the greatest potential because of its good operational flexibility, high efficiency, and low cost.10

Currently, the common adsorbents prepared from heavy metal ions mainly include activated carbon,12 diatomaceous earth,13 resin adsorbents,14 and so on. These adsorbents exhibit good performance, but their preparation requires strict conditions and high energy consumption. Recently, increasing efforts have been devoted to search for low-cost adsorbents with high efficiency. Bioadsorbents, including tree bark, sawdust, eggshell, lignin, cellulose, algae, and microbes, among others, have drawn considerable attention.15 Among these bioadsorbents, wood flour (WF), which is composed of natural polymers such as lignin, cellulose, hemicellulose, and other extractives, is available in large
quantities with low cost. It is a multiscale porous material with a definite specific surface area and abundant hydroxyl groups. In the process of cutting and pruning trees and manufacturing of wood products, numerous WF wastes could be produced. Burning or grinding of WF could result in environmental pollution and waste of resources. Therefore, the reasonable utilization of WF waste also presents a challenge.

Several studies have explored the application of wood in wastewater remediation.20-23 On the one hand, the adsorption properties of natural wood have been extensively studied. Poplar wood sawdust has been utilized to remove copper, zinc, and cadmium from electroplating wastewater.24 Maple wood sawdust has been used in Cu(II) adsorption; at pH = 6.0, the maximum adsorption of 9.5 mg/g was obtained.22 On the other hand, wood could be modified to expand its applications in water remediation. Meranti sawdust could be used as adsorbents; it could adsorb Cu(II), Cr(III), Ni(II), and Pb(II) ions from aqueous solutions with concentrations in the 1–200 mg/L range.23 Bulk beech wood after esterification was explored for the remediation of Cu(II) from water.25 At low concentrations, the material could remove up to 95% of Cu(II) from aqueous solutions. Moreover, iron- and zinc-doped sawdust biochar was investigated for simultaneous removal of Cu(II) and tetracycline from aqueous solutions via sole and binary systems, with the help of sorption isotherms and adsorption kinetics models.26 These studies have continuously promoted the application of wood in the wastewater treatment; however, the adsorption capacity of these methods is relatively low, probably owing to the existence of wood fillers with a relatively small specific surface area and a small number of chelating groups.

To address the aforementioned problems and optimize wood processing residues, delignification and amination were employed to modify WF in this study. Delignification could remove hemicellulose and lignin to enhance the porous and loose structure of wood to enlarge its specific surface area and increase the contact area of heavy metal ions and absorbents. Simultaneously, the amino group could be introduced on the wood structure surface by amination, which could be used as the active site for chelating heavy metal ions in aqueous solutions.

The objective of this study is to synthesize a novel wood-based adsorbent by delignification and amination and evaluate the adsorption capacity for Pb(II) in aqueous solutions. The effects of pH, contact time, adsorption temperature, and initial Pb(II) concentration on the adsorption behavior of the adsorbent were also evaluated. Moreover, the adsorption mechanism was explored by kinetics and isotherm analysis.

2. EXPERIMENTAL SECTION

2.1. Materials and Chemicals. Balsa wood flour was supplied by Zhuhai DE CHI Technology Co., Ltd. (Zhuhai, China). All chemicals were used without further purification. Sodium sulfite (Na₂SO₃, 98%), acryloyl chloride (AC) (C₃H₅ClO, 98%), and tetraethylenepentamine (TEPA) (C₄H₈N₅) were purchased from Heowns Biochemical Technologies Co., Ltd. (Tianjin, China). Sodium hydroxide (NaOH, 96%, AR), ethanol (CH₃CH₂OH, 99.7%, AR), hydrochloric acid (HCl, 37%, AR), dichloromethane (DCM) (CH₂Cl₂, 99.5%, AR), and hydrogen peroxide (H₂O₂, AR) were obtained from Beijing Chemical Works (Beijing, China). Lead nitrate (Pb(NO₃)₂, 99%, AR) was purchased from Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China). Zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, 99%, AR) was provided by Xilong Chemical Co., Ltd. (Shantou, China), and copper nitrate trihydrate (Cu(NO₃)₂·3H₂O, 99%, AR) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China).

2.2. Preparation of Wood Flour Adsorbent. 2.2.1. Delignification of Wood Flour. Balsa wood sawdust was ground to 100 meshes to obtain WF. Delignified wood flour (DFW) was prepared as described in the study by Hu et al.27 The WF was dispersed in a boiling solution with 2.5 M NaOH and 0.4 M Na₂SO₃ and reacted for 2 h under magnetic agitation. Deionized water was then used to remove chemical residues and neutralize the solution. The upper suspension was removed by suction filtration, and the treated WF was retained. Subsequently, to adopt more radical measures to remove the lignin and hemicellulose, the treated WF was dispersed in 3 M H₂O₂ boiling solution for 2 h and then washed to neutral pH, filtered, and freeze-dried. The freeze-drying process could protect the wood physical structure from full degradation and could ensure porosity. After these delignification procedures, DWF was obtained.

2.2.2. Grafting Carbon—Carbon Double Bond onto Delignified Wood Flour. The amount of AC used was calculated as a 3-fold excess (mol) in glucopyranose equivalents (MW = 162 g/mol)28 under the assumption that DWF is 100% cellulose. Theoretically, 1 mol of cellulose contains about 3 mol of hydroxyl groups and could react with 3 mol of AC. Subsequently, 0.3 mol of AC (27.15 g) and 0.1 of mol DWF (16.2 g) reacted in 1 mol of DCM (84.93 g) for 24 h under magnetic agitation at an ambient temperature. After being washed with isopropyl alcohol three times, the samples were freeze-dried to obtain DWF—C=C.22

2.2.3. Amination of DWF—C=C. To modify DWF—C=C with amino groups, 16.2 g of WF—C=C was dispersed in 200 g of ethyl alcohol, and 0.15 mol of TEPA (28.40 g) was added dropwise. The reaction continued for 1 h under magnetic stirring at ambient temperature. The sample was then washed with ethyl alcohol several times and freeze-dried to obtain DWF—NH₂ (Scheme 1).

Scheme 1. Delignification and Amination Process of Wood Flour

2.3. Characterization. The morphological features, element percentages, and distribution of adsorbents were observed by field emission scanning electron microscopy (FE-SEM) (Hitachi SU8010 instrument, Japan) and energy-dispersive X-ray spectroscopy (EDS; EX-350, Horiba Scientific, Japan). The Brunauer—Emmett—Teller (BET) surface area, total pore volume, and pore diameter distribution were measured with a computer-controlled nitrogen gas adsorption analyzer (Quantachrome AUTOSORB IQ). To achieve high test accuracy, samples were further milled to 200-mesh particles and then analyzed with a FTIR device (Nicolet 6700 Thermo Scientific, United States).

2.4. Adsorption Study. Stock solutions of Pb(II) were prepared by dissolving Pb(NO₃)₂ in deionized water and
further diluted to the concentrations required for the experiments. The DWF–NH$_2$ adsorbent was mixed with a 100 mL of Pb(NO$_3$)$_2$ solution under constant magnetic stirring.

The adsorption kinetics was determined at a Pb(II) concentration of 300 mg/L and pH = 4, with a DWF–NH$_2$ dosage of 1 g/L for 10–180 min at 293 K. The adsorption isotherms were determined with different initial Pb(II) concentrations (100–400 mg/L) and pH = 4, with a DWF–NH$_2$ dosage of 1 g/L at 30 °C for 180 min. The pH effect was investigated by varying the pH value from 2 to 5, being adjusted with 0.1 M HCl or NaOH solutions at 293 K for 180 min, with a dosage of 1 g/L and an ion concentration of 300 mg/L. For the adsorbent dosage study, the adsorbent was examined at the dosages ranging from 0.05 to 0.4 g and pH = 4 at 293 K for 180 min, with an ion concentration of 300 mg/L. Meanwhile, the temperature study was determined at 293–333 K and pH = 4 for 180 min, with a dosage of 1 g/L and an ion concentration of 300 mg/L. For competitive adsorption experiments, Cu(NO$_3$)$_2$·3H$_2$O and Zn(NO$_3$)$_2$·6H$_2$O were also dissolved to obtain a 300 mg/L solution. For the regeneration study, the concentration was 200 mg/L. After the adsorption under optimal conditions, the Pb(II) ions on the adsorbents were desorbed by 1 M HCl for 2 h, and the adsorbents were freeze-dried, ready for subsequent test cycles. The regeneration study was repeated five times. After filtration,
the metal ion concentration was determined by atomic absorption spectrophotometry (AAS6300 Shimadzu). The adsorption capacity \( q_e \) adsorption amount \( q_d \) and the removal rate \( R \) could be calculated using eqs 1–3. The pH values were measured using an OHAUS ST20 pH detector.

2.5. Determination of Adsorption Capacity and Removal Rate. The metal ion adsorption performance of adsorbents was determined by the adsorption capacity \( q_d \) adsorption amount \( q_e \) and removal rate \( R \), which could be calculated using the following equations

\[
q_e = \frac{(C_0 - C_e)V}{M} \tag{1}
\]

\[
R = \frac{(C_0 - C_e)}{C_0} \times 100\% \tag{2}
\]

\[
q_t = \frac{(C_0 - C_d)V}{M} \tag{3}
\]

where \( q_e \) (mg/g) and \( q_t \) (mg/g) represent equilibrium adsorption amount and that of time \( t \), respectively, \( R (\%) \) is the removal rate, \( C_0 \) (mg/L), \( C_e \) (mg/L), and \( C_d \) (mg/L) represent the initial, residual, and equilibrium concentrations of the adsorbate, respectively, \( V \) (L) is the volume of adsorbate solution, and \( M \) (g) represents the dosage of the adsorbent.

3. RESULTS AND DISCUSSION

3.1. Morphology and Structure of Samples. The morphologies of the WF samples are shown in Figure 1. In Figure 1a, WF indicated that despite several embossments, the surface was generally smooth and close-knit. The lignin and hemicellulose were intertwined, able to connect and fix the wood cell structure. In Figure 1b, the DWF surface contained numerous warped folds, indicating that the delignification loosened the tight connections.\(^{39}\) In Figure 1c,d, similar loose fibrous structures appeared, with an average fiber diameter of about 3 μm. Moreover, the morphologies of DWF—NH\(_2\) after Pb(II) adsorption under different magnifications are shown in Figure 1e–g. As pointed by the yellow arrows, hexagon pieces were scattered over the surface, with a diameter of about 2.5 μm. These pieces may be the chelate of Pb(II) with the amidogen on DWF—NH\(_2\) adsorbents.\(^{30}\) This finding demonstrated that the Pb(II) ions were successfully adsorbed.

As shown in Figure S1, FE-SEM observations around the wood pits of DWF—NH\(_2\), the chelate with a larger size was easily blocked around the pores. Due to the different microstructures of wood powder, hydroxyl accessibility of crystalline and amorphous regions of wood powder fibers, and the solution infiltration process, the chelate groups would not be equally distributed. Actually, acryloyl chloride and tetraethylenepentamine had less molecular weight, easily penetrated into wood, and reacted with the hydroxyl of amorphous regions.

The FE-SEM observation and the EDX spectrum of DWF—NH\(_2\)–Pb are depicted. In Figure 1g, hexagonal pieces were scattered over the wood-based adsorbent surface. The corresponding element distribution is presented in Figure 1h. The red luminous point reflected the distribution of Pb elements, and the intensity of hexagonal pieces pointed by yellow arrows was relatively higher, confirming Pb(II) adsorption.

3.2. Porosity of Samples. The nitrogen adsorption–desorption isotherms of the samples are presented in Figure 2. All isotherms of the samples were similar to the Type II and III isotherms identified in the original IUPAC classification of 1985, indicating that the samples were nonporous or macroporous adsorbents with relatively weak adsorbent–adsorbate and adsorbed molecules clustered around most favorable sites. As a result of unrestricted monolayer–multilayer adsorption up to high \( p/p_0 \), a more gradual curvature indicated a significant overlap of monolayer and multilayer adsorption.\(^{31}\)

The shapes of hysteresis loops approximated the H3-type hysteresis loop identified in the original IUPAC classification of 1985, stating the existent capillary condensation, with numerous slits formed by the accumulation of flaky particles inside.\(^{31,32}\) The number of micropores in the material may be lower than the minimum value, and mainly mesopores and macropores were found in wood.\(^{33}\)

The curves of the pore diameter distribution obtained by the DFT method are presented in Figure S2. The results in Figure S2a,b indicate that the order of pore volume from large to small was DWF > DWF—C=C ≈ DWF—NH\(_2\) > WF. This tendency was consistent with the BET surface area data in Table 1. The pore volume of DWF was the maximum, reaching 0.019 cm\(^3\)/g, followed by 0.009, 0.008, and 0.004 cm\(^3\)/g. The average pore diameters of WF, DWF, DWF—C=C, and DWF—NH\(_2\) were 10.0, 55.5, 19.0, and 32.3 nm, respectively. The BET surface area and porosity were reduced by grafting modification at the late stage. Owing to the low molecular weight and strong polarity, the ethanol solvent could cause swelling in wood and increase its pore size.\(^{34}\) However, the pore in wood remained larger than that of pure WF. Delignification could remove fillers, such as lignin and hemicellulose, and increase porosity, pore diameter, and specific surface area. Grafting double bonds or amino groups could fill the pores of wood to a certain extent, resulting in the decreased pore size and specific surface area.

3.3. Constituent Analysis of Samples. The FTIR spectra of WF, DWF, DWF—C=C, and DWF—NH\(_2\) are presented in Figure 3. The clear transmittance peaks of the samples could be assigned as follows: 3407 cm\(^{-1}\) (–OH stretching vibration);\(^{35}\) 2900 cm\(^{-1}\) (–C–H stretching vibration of the –CH\(_2\) group);\(^{36}\) 1738 cm\(^{-1}\) (–C==O stretching of the acetyl group);\(^{37,39}\) 1595 and 1505 cm\(^{-1}\) (aromatic skeletal vibration) provided by residual lignin.\(^{38}\) After delignification, the weak peaks at 1235 cm\(^{-1}\) disappeared, confirming the successful removal of hemicellulose.\(^{41}\) The peaks of –C==O stretching of the acetyl group in DWF—C=C and DWF—NH\(_2\) could confirm the successful grafting of the carbon–carbon double bond onto DWF. The absorption peaks at 1566 cm\(^{-1}\) (–N–H bending vibration of amide) and 1635 cm\(^{-1}\) correspond to the carbonyl group of amide, demonstrating that these samples were indeed amidogen grafted onto wood.
(alkene) may overlap with the peaks of aromatic skeletal vibration from the bit residual lignin; thus, the peaks of the groups were not apparent. In the spectra of DWF–NH₂, the broad absorption bands at 3400 and 3200 cm⁻¹ attributed to the –NH₂ stretching vibration also overlapped with the OH stretching vibration bands.

To further explore the constituents, the weights and atomic percentages of the elements from the EDX spectra of the samples are listed in Table 2, which presents the averages of a specific area. After the delignification and grafting of the carbon–carbon double bond, the samples slightly changed, but no nitrogen element could be detected. However, after the introduction of amino, the nitrogen element could be evidently observed, confirming that the amino was grafted with wood by adding TEPA. The percentage of the N element that was ultimately obtained could change with the difference in the accessibility of wood cellulose, degree of reaction, and uniformity problem caused by penetration. Thus, 100% grafting would be difficult to achieve.

4. EVALUATION OF THE ADSORPTION CAPACITY OF ADSORBENTS

4.1. Effect of Solution pH and Adsorbent Dosage on Pb(II) Adsorption of DWF–NH₂. Figure 4a shows the adsorption capacity and removal rate of Pb(II) by using the DWF–NH₂ adsorbent at varying pH levels. The solution pH could affect the metal ion ionization, hydrogen ion concentration of surface functional groups, adsorption equilibrium, and adsorption kinetics of heavy metals. When pH was lower than 4, adsorption was repressed because the high H⁺ concentration and protonated amino groups intensified the competition and repulsion between H⁺ and the metal ions for active sites on the adsorbent surface. At a higher pH value, the active sites passivated by H⁺ were released, and the adsorption was enhanced. Chelates were more easily formed between metal ions and nitrogen atoms in DWF–NH₂ because of the increased deprotonation of the amino group. Thus, with an increase in pH, qe and R of Pb(II) adsorption increased rapidly, reaching 186.6 mg/L and 62.18%, respectively, at pH = 4. The values obtained at pH = 4 and 5 were approximately equal. These variables were not evaluated at pH = 6 because of the precipitation of Pb(II) ions, forming Pb(OH)₂. Usually, wastewater containing heavy metals is acidic. Therefore, pH = 4 could be regarded as the optimal pH value for Pb(II) adsorption and used in all subsequent studies.

Figure 4b illustrates the effect of the adsorbent dosage on Pb(II) adsorption. When the dosage was 0.5 g/L, qe was only 87.4 mg/g. However, with an increase in dosage, qe increased until the maximum of 193.0 mg/g was reached because of the large number of unsaturated active sites accessible for interaction with Pb(II). As the dose increased from 0.5 to 1 g/L, the adsorption increased by a large margin; thus, the 1 g/L dose was chosen as the optimal dose in further adsorption studies.

4.2. Kinetic Study on Metal Ion Adsorption of DWF–NH₂ Adsorbents. The adsorption kinetics of metal ions on DWF–NH₂ was investigated at a constant of pH = 4 under ambient temperature and the Pb(II) starting concentration when the dose was 300 mg/L. In the Supporting Information, the pseudo-first-order (eq 1) and the pseudo-second-order models (eq 2) were used to fit the experimental data.

The nonlinear and linear fitting results of the different models are presented in Figure 5. The kinetic parameters and correlation coefficients R² of Pb(II) removal onto DWF–NH₂ were calculated and are listed in Table 3. As shown in Figure 5a and Table 3, adsorption quickly proceeded, and the adsorption reached equilibrium within 180 min. The experimental qe value of DWF–NH₂ was 189.9 mg/g, whereas that of DWF was only 106.7 mg/g. The R² value for the pseudo-second-order kinetic model was 0.9924, which was higher than that for the pseudo-first-order kinetic model (0.9403). The linear fitting results were the same as those in Figure 5b,c. These results indicated that the adsorption was dominated by chemical adsorption via the exchange or sharing of electrons between adsorbents and adsorbates.

4.3. Adsorption Isotherms of Metal Ion Adsorption of DWF–NH₂ Adsorbents. Adsorption isotherms could indicate the interaction pattern between the adsorbent and adsorbate, explaining the adsorption mechanisms. The adsorption process was fitted using the Langmuir (eq 4), Freundlich (eq 5), and Temkin (eq 6) models in the Supporting Information, and the raw isotherms of Pb equilibrium adsorbed amount with the equilibrium concentration (qe vs C₀) are presented in Figure 5.

The adsorption isotherm fitting results are shown in Figure 6 and Table 4. By linear fitting and comparison of results, the

Table 2. Weights and Atomic Percentages of the Elements of WF, DWF, DWF–C=\text{C}, and DWF–NH₂

| sample      | carbon weight | carbon atomic percentage | oxygen weight | oxygen atomic percentage | nitrogen weight | nitrogen atomic percentage |
|-------------|---------------|--------------------------|---------------|--------------------------|----------------|---------------------------|
| WF          | 49.4          | 56.5                     | 50.6          | 43.5                     |                |                           |
| DWF         | 52.2          | 59.2                     | 47.8          | 40.8                     |                |                           |
| DWF–C=\text{C} | 50.6      | 57.7                     | 49.4          | 42.3                     |                |                           |
| DWF–NH₂     | 50.9          | 57.7                     | 45.8          | 39.0                     | 3.3            | 3.3                       |

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Langmuir model showed better adsorption of adsorbates with higher correlation coefficient $R^2$ (0.9864). This result indicated that DWF−NH$_2$ adsorbents had a homogeneous surface with identical sorption sites.\textsuperscript{2,8} The $R_L$ values for 100, 200, 300, and 400 mg/L were 0.722, 0.565, 0.464, and 0.394, respectively, which confirmed that the adsorption process was favorable.\textsuperscript{8,21} In addition, the $R^2$ value of the Temkin model was higher than 0.95; thus, strong interactions between the adsorbed metals and the adsorbent were observed during adsorption.

Table 5 shows the comparison of the maximum adsorption capacity of the resulting adsorbent toward Pb(II) (equilibrium condition), reported previously and in the current study. The adsorption capacity of DWF−NH$_2$ was relatively higher. Furthermore, the simple process and mild condition of DWF−NH$_2$ preparation provided a better application foreground.

4.4. Effect of Temperature on Pb(II) Adsorption of DWF−NH$_2$. To explore the thermodynamic characteristics of the DWF−NH$_2$ adsorbents, the adsorption isotherm experiments were conducted at different temperatures (293, 313, and 333 K) (Figure 7a). The industrial application usually requires a mild treatment temperature; temperatures close to ambient temperature, 293, 313, and 333 K, were selected, similar to those used in many previous studies.\textsuperscript{16,21} Figure 7a presents the change in $q_t$ as a function of time at different temperatures. Higher temperatures could contribute to the adsorption process. Room temperature was more feasible; thus, room temperature (293 K) was adopted for the test.

4.5. Regeneration Performance. In addition to excellent adsorption capability, recycling stability is vital for an adsorbent to be applicable. To evaluate the regeneration ability of DWF−NH$_2$, 1 M HCl was selected as the eluent for Pb(II) desorption, and desorption continued for 120 min. Figure 7b shows the adsorption performance of DWF−NH$_2$ for Pb(II) adsorption during five cycles. The $q_e$ value of
DWF−NH₂ for Pb(II) decreased by approximately 20.20% (from 174.8 to 139.5 mg/g) after five cycles. The decrease could be attributed to the irreversible combination and the protonation of partial functional groups in DWF−NH₂, leading to a reduction in the number of binding sites and weakening the electrostatic attraction between the adsorbates and the adsorbents. In the last cycle, the adsorption capacity was 139.5 mg/g, which was 3 times as high as that to Zn(II) and 10 times that to Cu(II). The adsorption capacity of the tested metal ions followed the order Pb(II) > Zn(II) > Cu(II), demonstrating a high adsorption selectivity for Pb(II) on DWF−NH₂. The covalent index and electronegativity of Pb was higher than other elements, suggesting that Pb(II) exhibited a stronger attraction than Cu(II) and Zn(II) to the lone pair of electrons in nitrogen atoms to form complexes.55

4.6. Competitive Adsorption Experiments. Competitive adsorption experiments were conducted by adding 0.1 mg/100 mL of DWF−NH₂ into a mixed solution consisting of Pb(II), Cu(II), and Zn(II) ions under the following conditions: individual concentration, 300 mg/L; pH 4; temperature, under 293 K; duration, 180 min. The selectivity coefficient k is calculated according to eq 8 in the Supporting Information. A selectivity value of >1 indicates adsorption selectivity toward that ion.

Figure 8a shows the adsorption quantity of the adsorbents for Pb(II), Cu(II), and Zn(II) ions at different times. Adsorption increased with time. Compared with adsorption in a single system, although the adsorption of Pb(II) was inhibited to a certain extent because of the competition for active sites, the adsorption selectivity to Pb(II) of the adsorbent still exhibited good performance with a higher selectivity coefficient k (Figure 8b). The selectivity coefficient k of the adsorbents to Pb(II) could reach approximately 2.74 in 180 min, which was 3 times as high as that to Zn(II) and 10 times that to Cu(II). The adsorption capacity of the tested metal ions followed the order Pb(II) > Zn(II) > Cu(II), demonstrating a high adsorption selectivity for Pb(II) on DWF−NH₂. The covalent index and electronegativity of Pb was higher than other elements, suggesting that Pb(II) exhibited a stronger attraction than Cu(II) and Zn(II) to the lone pair of electrons in nitrogen atoms to form complexes.55

5. CONCLUSIONS

A novel DWF−NH₂ adsorbent was synthesized by delignification and amination of waste WF. By characterizing the morphological characteristics and components of the samples, the successful introduction of −C=C and −NH₂ was confirmed. The adsorption capacity of DWF−NH₂ could reach 189.9 mg/g, higher than the values obtained in most existing studies. The adsorption process of Pb(II) on DWF−NH₂ was well described by the pseudo-second-order and Langmuir models, indicating that the adsorption of Pb(II) onto DWF−NH₂ was dominated by chemical adsorption via the exchange or sharing of electrons between the adsorbents and the adsorbates. With a slight reduction in adsorption capacity in the regeneration study, the DWF−NH₂ showed an unlimited potential as a reusable adsorbent for practical application. The result also revealed high selectivity to Pb(II) of the DWF−NH₂ adsorbent still exhibited good performance with a higher selectivity coefficient k (Figure 8b). The selectivity coefficient k of the adsorbents to Pb(II) could reach approximately 2.74 in 180 min, which was 3 times as high as that to Zn(II) and 10 times that to Cu(II). The adsorption capacity of the tested metal ions followed the order Pb(II) > Zn(II) > Cu(II), demonstrating a high adsorption selectivity for Pb(II) on DWF−NH₂. The covalent index and electronegativity of Pb was higher than other elements, suggesting that Pb(II) exhibited a stronger attraction than Cu(II) and Zn(II) to the lone pair of electrons in nitrogen atoms to form complexes.
environment-friendly, and reusable adsorbent based on waste WF, for the removal of heavy metals from wastewater.

**ASSOCIATED CONTENT**

* Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00920.

FE-SEM observations around the wood pit of DWF−NH₂; pore volume curves as a function of pore diameter isotherm of (qₑ) Pb equilibrium adsorbed amount with (Cₑ) equilibrium concentration; and calculation equations of adsorption isotherms analysis, adsorption kinetics study, and competitive adsorption experiments (PDF)

**AUTHOR INFORMATION**

**Corresponding Authors**
*E-mail: shifeng.zhang@bjfu.edu.cn. Phone/Fax: +86 010 62336072 (S.Z.).
*E-mail: lijzh@bjfu.edu.cn (J.L.).

**ORCID**
Yi Tan: 0000-0003-0299-833X
Shifeng Zhang: 0000-0003-1767-2041

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**Figure 7.** (a) Effect of temperature on adsorption capacity for Pb(II) (pH = 4, t = 180 min, dosage = 1 g/L, and ion concentration = 300 mg/L); (b) Pb(II) equilibrium adsorption capacity of DWF−NH₂ in the adsorption−desorption experiment (adsorption conditions: pH = 4, t = 180 min, dosage = 1 g/L, ion concentration = 300 mg/L, and T = 293 K; desorption conditions: HCl concentration = 1 M, t = 120 min).

**Figure 8.** Comparison of (a) qₑ and (b) k of Pb(II), Cu(II), and Zn(II) ions on DWF−NH₂ (pH = 4, dosage = 1 g/L, T = 293 K, and individual ion concentration = 300 mg/L).

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**Notes**
The authors declare no competing financial interest.

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Jianzhang Li: 0000-0002-4590-2919
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