Adsorption Behavior of Pb(II), Cd(II), and Zn(II) onto Agave Bagasse, Characterization, and Mechanism

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ABSTRACT: Biosorption is an alternative procedure to remove metal ions from aqueous media using agricultural waste. In this work, the adsorption capacity and removal efficiency of agave bagasse (AB) toward Pb(II), Cd(II), and Zn(II) were analyzed. Parameters such as equilibrium pH, particle size, AB dosage, time, and initial metal ion concentration were discussed. The results showed that pH 5.5, 0.4 g (<250 μm), and only 15 min of contact assured conditions for maximum adsorption capacity. The kinetic studies were fitted to the pseudo-second-order model, whereas the isotherms showed good agreement with the Langmuir model. AB has a higher affinity for Pb(II) over Cd(II) and Zn(II), and the maximum adsorption capacities were 93.14, 28.50, and 24.66 mg g⁻¹, respectively. The results of the characterization evidenced two adsorption mechanisms. Scanning electron microscopy and X-ray diffraction displayed adsorption via the ion exchange mechanism by releasing Ca(II). The ¹³C cross-polarization mode with magic-angle spinning nuclear magnetic resonance analysis demonstrated a complexation mechanism by cellulose, hemicellulose, and lignin. AB is a good alternative for the removal of metals without prior thermal or chemical treatment, with rapid kinetics, suitable adsorption capacity, and high removal efficiency contributing to waste management.

1. INTRODUCTION

Water pollution has been increasing because of population growth, anthropogenic activities, urbanization, industrialization, and excessive use of water. The treatment of industrial effluents or wastewater is complex due to the variety of pollutants such as the heavy metals, Pb, Cd, Zn, Cr, Hg, and Ni in different oxidation states, besides other organic compounds that are commonly used in the stages of the productive processes. The heavy metals cause several health problems in humans, animals, and plants, and their elimination is imperative. Several methods for their removal have been proposed, such as chemical precipitation, ion exchange, membrane filtration, and adsorption.¹−³ Nevertheless, adsorption has advantages over other methods in terms of effectiveness and feasible regeneration.⁴ Different sorbents have been developed and evaluated for the removal of heavy metals, including minerals such as aluminosilicates or vermiculites and activated carbon.⁵ The latter has limited use because of its high cost.

Other kinds of sorbents with a relatively recent application are the residues from food or agriculture industries. These wastes are considered as biosorbents,⁶,⁷ and so far, studies show that longer adsorption times⁸−¹⁰ and preliminary chemical treatments are required,¹¹−¹³ which undoubtedly affect their further application. Notwithstanding, the feasibility of the adsorption process has been reported in a continuous system besides at a pilot scale.¹⁴,¹⁵

In Mexico, thousands of tons of agave bagasse (AB) are discarded annually due to the high production of tequila spirit or mezcal, and it is close to 40% of the total processed agave.¹⁶ AB is a porous material mainly composed of cellulose, hemicellulose, and lignin.¹⁷ It has been proposed for different applications such as animal feed¹⁸ or reinforcement for composite materials.¹⁹ Because of its active sites, AB is capable to adsorb heavy metals.¹²,²⁰ However, the adsorption kinetics and isotherms in a wide range of concentration as well as the role of AB compounds (cellulose, hemicellulose, and lignin) in the adsorption of metal ions have not been evaluated.

The present research is focused on the behavior of AB as a biosorbent for the heavy metals Pb(II), Cd(II), and Zn(II), evaluating different parameters in the system such as pH, particle size, biosorbent dosage, time, and metal ion concentration. The adsorption capacity of the metal ions from single and binary mixtures was discussed. In addition, the characterization of AB before and after the adsorption process

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was performed by scanning electron microscopy (SEM), X-ray diffraction (XRD), and solid-state $^{13}$C cross-polarization mode with magic-angle spinning nuclear magnetic resonance (CP/MAS NMR) to evidence the influence of cellulose, hemicellulose, and lignin in metal ion adsorption.

2. RESULTS AND DISCUSSION

2.1. Effect of pH. In Figure 1, the adsorption capacities and removal efficiencies are presented, which were calculated using the equations described in the Experimental Section. It is possible to see in Figure 1a that the adsorption capacity ($q_{M(II)}$) increases with equilibrium pH and reaches a maximum around pH 5.5. After this, it remained without significant changes for all metal ions. In Figure 1a, it is notable that AB has more affinity for Pb(II) than Cd(II) and Zn(II). For instance, at pH 5.5, $q_{Pb(II)}$ was 11.28 mg g$^{-1}$, whereas Cd(II) and Zn(II) exhibited similar behavior, obtaining 4.06 and 4.15 mg g$^{-1}$, respectively. The removal efficiency showed the same trend as that of the adsorption capacity (Figure 1b). At pH 5.5, 96.8% Pb(II), 41% Cd(II), and 40% Zn(II) were removed.

These results can be explained by the biosorbent surface charge as it is affected by pH. The point of zero charge (pH$_{PZC}$) of AB was evaluated, and the result is shown in Figure 2.

pH$_{PZC}$ of 4.7 indicates that at pH < 4.7, the ΔpH values (and the biosorbent surface) are positive, whereas at pH > 4.7, the surface is negative. pH$_{PZC}$ is indicated by the vertical dashed line in Figures 1a and 2.

Cellulose, hemicellulose, and lignin are the main compounds of AB, and they contain functional groups such as hydroxyl $\text{–OH}$ and carboxyl $\text{–COOH}$. The pKa value for the hydroxyl group is in the range of 9.5$-13$. Therefore, the negative charges found on the biosorbent surface between 4.7 and this range (9.5$-13$) of pH should be predominantly because of the carboxylate groups, whereas those below should be because of the phenolate groups. As the present study involves metal ions, the regions more basic than pH 7$-8$ was avoided, aiming to minimize the formation of metallic hydroxocomplexes and other related complexes. Therefore, the phenolate groups do not contribute to the surface charge in the pH region studied in the paper.

The carboxylic groups must be deprotonated to generate negative charges on the surface and H$^+$ in aqueous media and permit the adsorption of different metal ions. This is carried out from pH 1.7 ($pK_a$: 1.7$-4.721$), thus promoting a rise in the metal ion adsorption by a complexation mechanism that explains the moderate adsorption capacities at pH < pH$_{PZC}$.

The results are in agreement with the pH range reported for cucumber peel, rapeseed biomass, and bamboo, presenting the higher adsorption capacity at pH between 5 and 6.

2.2. Effect of Particle Size. Figure 3 shows the variation of $q_{M(II)}$ as a function of particle size. It can be observed that the adsorption capacity increases when the particle size range diminishes from >250 to 250–180 μm for Cd(II) and Zn(II). This is related to the milling process that exposes the active sites in AB inducing more contact area during the adsorption experiments. However, a greater reduction in particle size does not represent a higher adsorption capacity, obtaining 9.6 and 9.2 mg g$^{-1}$ for Cd(II) and Zn(II), respectively. For Pb(II), the adsorption capacity remains constant at 10.9 mg g$^{-1}$ for all the particle size ranges analyzed. It means that the adsorption of Pb(II) is independent of this parameter.

The removal efficiencies are presented in Table 1. Particle sizes <250 μm exhibited a very good performance, removing around 99% of Pb(II), 91% of Cd(II), and 80% of Zn(II). The results show that with smaller particle size, the contact area increases, improving adsorption, unlike the results shown in Figure 1 where only 41 and 40% were reached for Cd (II) and
Therefore, particle sizes lower than 250 μm were selected for further experiments to assure better conditions for the metal ion adsorption capacity.

2.3. Influence of Dosage AB. The adsorption capacity and removal efficiency as a function of AB dosage are displayed in Figure 4 for Pb(II), Cd(II), and Zn(II). The results indicate that the adsorption capacity increases significantly at lower AB amounts. \( q_{M(II)} \) reaches 42.6, 27.27, and 24.2 mg g\(^{-1}\) for Pb(II), Cd(II), and Zn(II), respectively, with 0.1 g of AB (Figure 4a). The lower adsorption capacity and little difference for the three metal ions are observed with 0.6 g AB. The diminution in adsorption capacity is attributed to the increase of active sites when the AB mass is augmented, and then a higher concentration of metal ions is required to allow the saturation of the biosorbent.

In Figure 4b, the difference in removal efficiency is distinguished when the AB dosage is modified. For Cd(II) and Zn(II), the removal efficiency increases with the AB mass. Cd(II) showed better results from 0.3 g with approximately 95%, whereas Zn(II) required 0.4 g of AB to reach 83%. For Pb(II), it can be observed that the removal efficiency is very similar around 99.4% for all amounts of AB. These results demonstrate the high adsorption capacities of AB and the preference for Pb(II) compared to Cd(II) and Zn(II).

Based on the above results, the amount of 0.4 g of AB was selected as the best condition for the removal efficiency with acceptable adsorption capacities for all metal ions, and it was kept constant for kinetic studies and isotherms.

2.4. Adsorption Kinetics. Figure 5a shows the adsorption capacity of Pb(II), Cd(II), and Zn(II) onto AB as a function of time. The plot displays that \( q_{M(II)} \) for all metal ions remained constant from the first 5 min of contact with AB. The adsorption capacities are 11.11 ± 0.22, 10.04 ± 0.20, and 9.60 ± 0.17 mg g\(^{-1}\) for Pb(II), Cd(II), and Zn(II), respectively, with 0.1 g of AB (Figure 4a). The lower adsorption capacity and little difference for the three metal ions are observed with 0.6 g AB. The diminution in adsorption capacity is attributed to the increase of active sites when the AB mass is augmented, and then a higher concentration of metal ions is required to allow the saturation of the biosorbent.

In general, the biosorbents have been identified as materials that need long times of contact to reach the adsorption equilibrium with moderate efficiency. For example, Taro (Colocasia esculenta (L.) Schott) adsorbs Pb(II) in 120 min,\(^{24}\) Posidonia oceanica fibers uptake Pb, Cd, and Zn in 80 min,\(^{25}\) whereas 60 min is necessary with cucumber peel for Pb(II) and Cd(II).\(^{22,23}\) Therefore, the results found in this work demonstrate that AB reaches the adsorption equilibrium in a very short time as compared to other biosorbents. The following experiments were set up at 15 min to assure the equilibrium at different conditions.

Adsorption kinetics for metal ions onto AB have not been previously reported; the experimental results were fitted to pseudo-first- and pseudo-second-order models. The pseudo-first-order or Lagergren equation\(^{26}\) is expressed by

\[
\ln(q_e - q_t) = \ln q_e - k_1t
\]

The plot displays that \( q_{M(II)} \) for all metal ions remained constant from the first 5 min of contact with AB. The adsorption capacities are 11.11 ± 0.22, 10.04 ± 0.20, and 9.60 ± 0.17 mg g\(^{-1}\) corresponding to Pb(II), Cd(II), and Zn(II). The removal efficiencies calculated from Figure 5a are 99, 93, and 82% for Pb(II), Cd(II), and Zn(II), respectively, in only 5 min. Then, the adsorption of metal ions onto AB rapidly proceeded with high removal efficiencies.

Table 1. Removal Efficiency (%) for Pb(II), Cd(II), and Zn(II) at Different Particle Size Ranges\(^a\)

| particle size range (μm) | Pb(II) | Cd(II) | Zn(II) |
|--------------------------|--------|--------|--------|
| >250                     | 96.81 ± 0.17 | 41.09 ± 1.15 | 37.14 ± 1.57 |
| 250–180                  | 99.21 ± 0.14 | 91.78 ± 0.23 | 78.34 ± 1.62 |
| 180–150                  | 99.21 ± 0.09 | 91.80 ± 0.13 | 80.07 ± 0.81 |
| <150                     | 99.40 ± 0.28 | 90.94 ± 0.47 | 80.79 ± 1.60 |

\(^aC_0 = 100 \text{ mg L}^{-1}, w_{AB} = 0.4 \text{ g}, t = 30 \text{ min}, \text{ and } pH 5.5.\)

Figure 3. Adsorption capacity of AB as a function of particle size range. \( C_0 = 100 \text{ mg L}^{-1}, w_{AB} = 0.4 \text{ g}, t = 30 \text{ min}, \text{ and } pH 5.5.\)

Figure 4. Effect of AB dosage on (a) adsorption capacity and (b) removal efficiency. \( C_0 = 100 \text{ mg L}^{-1}, t = 30 \text{ min}, \text{ pH } 5.5, \text{ and AB particle size } <250 \mu m.\)
is not observed (correlation coefficient, \( R^2 < 0.93 \)) unlike that of the pseudo-second-order equation. Figure 5b presents the fitting according to eq 2. The adsorption of metal ions is described by the pseudo-second-order model with remarkable agreement to the correlation coefficient (\( R^2 \)) higher than 0.99. The results of adsorption kinetics from both models are resumed in Table 2. The \( k_1 \) values for Pb(II), Cd(II), and Zn(II) were 1.0602, 1.2910, and 0.8969 g mg \(^{-1}\) min, respectively, which corroborates a very good agreement between the experimental and predicted values of adsorption capacity. The solid lines in Figure 5a correspond to the predicted adsorption capacity based on the obtained parameters of the pseudo-second-order model. This model is representative of the adsorption behavior of divalent metal ions such as Pb(II), Cd(II), and Zn(II).28

### Table 2. Calculated Parameters for Kinetic Models

|     | Pb(II) | Cd(II) | Zn(II) |
|-----|--------|--------|--------|
| \( q_e \) (mg g \(^{-1}\)) | 11.11 ± 0.22 | 10.04 ± 0.20 | 9.60 ± 0.17 |
| \( k_1 \) (min \(^{-1}\)) | 0.0720 | 0.0578 | 0.0933 |
| \( R^2 \) | 0.7876 | 0.9265 | 0.8147 |
| \( k_2 \) (g mg \(^{-1}\) min \(^{-1}\)) | 0.0112 | 0.0111 | 0.0157 |
| SE  | 12.1255 | 10.9493 | 10.4309 |

#### 2.5. Adsorption Isotherms

Figure 6a presents the adsorption isotherms for each metal ion in an interval of the initial concentration of 10–1000 mg L \(^{-1}\). At low concentrations, it is notable that \( q_{\text{exp}} \) increases with the equilibrium concentration. In this case, the mass-transfer resistance between solid and liquid phases is diminished through driving force by concentration effect enhancing adsorption capacity. However, at higher concentrations, the adsorption capacity achieves a plateau that matches with the maximum adsorption capacity (\( q_{\text{max,exp}} \)), as the active sites are occupied, inducing the biosorbent saturation. For Pb(II), \( q_{\text{max,exp}} \) was 93.14 ± 3.38 mg g \(^{-1}\) at 560 mg L \(^{-1}\) as the equilibrium concentration. When the concentration is higher, it is observed that the adsorption capacity is lower than the maximum adsorption capacity (indicated with an arrow in Figure 6a). This phenomenon is attributed to the high amount of Pb(II) on the surface promoting the desorption of metal ions from the saturated active sites.29 In the case of Cd(II) and Zn(II), the adsorption behavior is similar, and the plateau is rapidly achieved at 28.50 ± 3.72 and 24.66 ± 2.97 mg g \(^{-1}\) respectively. An extended comparison with other references is presented in Table 3, and it is noticed that the majority of biosorbents do not have the high adsorption capacity exhibited by AB in this work in a very short time. Comparable results have been reported using mango or cucumber peel after 60 min.22,23,31,32 In this work, the experiments only required 15 min for similar adsorption capacities. The results reported by other authors for AB without treatment indicate that the adsorption capacity for Pb(II), Cd(II), and Zn(II) are 35.6, 13.27, and 7.84 mg g \(^{-1}\), respectively.12 These values are lower

Figure 5. (a) Effect of time on the adsorption capacity of AB. (b) Pseudo-second-order kinetic model according to eq 4. \( C_0 = 100 \) mg L \(^{-1}\), \( \omega_{\text{AB}} = 0.4 \) g (<250 μm), and pH = 5.5.

\[
\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2q_e^2}
\]

where \( q_t \) and \( q_e \) are the adsorption capacity at time \( t \) and at equilibrium (mg g \(^{-1}\)), respectively, and \( k_1 \) is the pseudo-first-order rate constant. According to eq 1, the plot of \( \ln(q_t - q_e) \) against \( t \) gives a straight line, where the slope matches with \( k_1 \).

The linear form of the pseudo-second-order kinetic model is

\[
SE = \frac{\sum (q_{\text{exp}} - q_{\text{calc}})^2}{N - 2}
\]

where \( q_{\text{exp}} \) and \( q_{\text{calc}} \) represent the experimental and predicted adsorption capacity by the model, respectively, and \( N \) is the number of experiments.

According to eq 1, an acceptable fitting to experimental data is not observed (correlation coefficient, \( R^2 < 0.93 \)) unlike that of the pseudo-second-order equation. Figure 5b presents the fitting according to eq 2. The adsorption of metal ions is
than those obtained in this work owing to different experimental conditions used by the authors, such as narrow concentration interval, higher particle size, and lower pH.

The Langmuir and Freundlich equations were considered to represent the experimental systems in terms of equilibrium concentration, \( C_e \), and adsorption capacity, \( q_e \). The first one in linear form is defined by

\[
\frac{C_e}{q_e} = \frac{1}{q_{\text{max}}} + \frac{1}{K_L q_{\text{max}}} \left(\frac{C}{q_{\text{max}}} \right)
\]

(4)

where \( q_{\text{max}} \) is the saturated monolayer adsorption capacity and \( K_L \) is the Langmuir constant. According to eq 4, the plot of \( C_e/q_e \) against \( C_e \) gives a straight line whose slope is equivalent to \( 1/q_{\text{max}} \), and from the intercept, it is possible to calculate the \( K_L \) value.

Freundlich isotherm describes heterogeneous systems by the following equation

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]

(5)

where \( n \) is the adsorption intensity and \( K_F \) is the Freundlich isotherm constant. The logarithmic graph of \( q_e \) versus \( C_e \) gives a straight line, where the slope is related to \( n^{-1} \) value and the intercept corresponds to \( \log K_F \). The experimental data were analyzed considering both models.

The results of the fitted data such as slope, intercept of the straight line, correlation coefficient, and the obtained parameters of eqs 4 and 5 are given in Table 4.

In Figure 6b, it is possible to see that the experimental data for Pb(II), Cd(II), and Zn(II) have a very good agreement with the predicted isotherms for the Langmuir model.

### Table 3. Adsorption Capacities Reported in the Literature for Pb(II), Cd(II), and Zn(II) and the Results Obtained in This Work

| Biosorbent                  | Time (min) | pH  | Concentration Interval (mg L\(^{-1}\)) | \( q_{\text{Pb(II)}} \) (mg g\(^{-1}\)) | \( q_{\text{Cd(II)}} \) (mg g\(^{-1}\)) | \( q_{\text{Zn(II)}} \) (mg g\(^{-1}\)) |
|-----------------------------|------------|-----|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|
| AB (this work)              | 15         | 5.5 | 10–1000                              | 93.14 ± 3.38                         | 28.50 ± 3.72                         | 24.66 ± 2.97                         |
| AB\(^{12}\)                 | 30–60      | 5   | 1–100                                | 35.6                                 | 12.5                                 | 112.3                                |
| Agave Americana fibers\(^{25}\) | 60         | 5   | 20–300                               | 133.6                                | 68.92                                | 28.21                                |
| Cucumber peel\(^{13}\)      | 80         | 6–8 | 30–250                               | 48.33                                | 30.22                                | 37.90                                |
| P. oceanica fibers\(^{25}\) | 60         | 5   | 10–600                               | 99.05                                | 68.92                                | 28.21                                |
| Mango peel\(^{14}\)        | 60         | 5   | 5–6                                  | 21.29                                | 13.9                                 | 39                                   |
| Rapeseed biomass\(^{9}\)    | 180        | 5.2 | 5–250                                | 39                                   | 39                                   | 13.9                                 |
| Peanut shell\(^{9}\)        | 180        | 5.5 | 100–350                              | 291.56                               | 291.56                               | 291.56                               |
| Rice straw\(^{26}\)         | 180        | 5   | 25–350                               | 13.9                                 | 13.9                                 | 13.9                                 |
| Taro\(^{24}\)               | 120        | 6   | 10–500                               | 291.56                               | 291.56                               | 291.56                               |
with the Langmuir model (eq 4). The correlation coefficient is higher than 0.99, which indicates that this model is suitable to predict the adsorption capacity of AB for the three metal ions. The Langmuir constant for Pb(II), Cd(II), and Zn(II) is 0.0748, 0.0695, and 0.0432 L mg\(^{-1}\), respectively. Then, the adsorption onto AB is brought out by the monolayer formation to reach the saturation of the biosorbent, and this is associated with a complex mechanism.\(^{37}\) Despite the higher constant obtained for Pb(II), SE is also elevated. This is attributed to the wide concentration interval evaluated. At higher concentrations, the adsorbed Pb(II) onto AB raises and significant interactions take place. Thus, deviations from the Langmuir model were observed, increasing the SE.

With regard to the calculated parameters for the Freundlich model (Table 4), the correlation coefficients do not exceed the value of 0.95, indicating an acceptable fitting. A high \(n\) value suggests a stronger interaction of the biosorbent with the heavy metal.\(^{38}\) In this context, Pb(II) results in an \(n\) value equal to 1.90, which is higher for Cd(II) and Zn(II), that is, 2.79 and 2.60, respectively. This shows the stronger interaction of AB with Cd(II) and Zn(II) than that with Pb(II) in contrast to the experimental results. It is associated with the low correlation coefficient that implies differences between the experimental data and the model.

Although the experimental data satisfactorily fitted with both models, for the Freundlich model, the correlation coefficients are lower than that of the Langmuir equation (Table 4), and the main deviations are for the higher concentrations. AB is not a homogeneous biosorbent, but the adsorption data fitted well to the Langmuir model, and it is related to the small particle size used in the adsorption experiments. In consequence, the active sites of AB are available homogeneously to adsorb metal ions.

### 2.6. Adsorption Behavior in Binary Mixtures

The results discussed above correspond to the adsorption behavior of Pb(II), Cd(II), and Zn(II) onto AB from single solutions without considering the interaction with other ions. Figure 7 includes the adsorption capacities of Pb(II), Cd(II), and Zn(II) in binary mixtures and their comparison with single solutions. The adsorption capacity of Pb(II) is improved in the presence of Cd(II) from 10.5 to 13.41 mg g\(^{-1}\), whereas the obtained adsorption capacity is 8.28 mg g\(^{-1}\) for the mixture Pb(II) + Zn(II) (Figure 7a). In contrast, slight changes are observed in the adsorption capacity of Cd(II) when Pb(II) or Zn(II) is included in the solution (Figure 7b). In the case of Zn(II), a diminution in adsorption capacity is remarkable when Pb(II) or Cd(II) is present (Figure 7c).

The competition effect in the adsorption capacity in binary mixtures was calculated by the following relationship

\[
r = \frac{q_e^m}{q_e^0} = \frac{q_e^{Pb+Cd}}{q_e^0} = \frac{q_e^{Pb+Zn}}{q_e^0} = \frac{q_e^{Cd+Zn}}{q_e^0}
\]

where \(q_e^m\) and \(q_e^0\) are the adsorption capacities of the metal ion in a mixture (superscript \(m\) = Pb + Cd, Pb + Zn, or Zn + Cd) and single solution (superscript 0), respectively.\(^{39}\) Thus, when \(r\) is higher than unity, the adsorption of the metal ion improves in the mixture or a synergistic effect is observed. In contrast, a value smaller than 1 implies a diminished adsorption capacity or an antagonistic effect of metal ions, and finally \(r = 1\) indicates that there is no interaction between two metal ions. The calculated values of \(r\) using eq 6 are condensed in Table 5.

| metal ion | \(q_e^{Pb+Cd}/q_e^0\) | \(q_e^{Pb+Zn}/q_e^0\) | \(q_e^{Cd+Zn}/q_e^0\) |
|-----------|-----------------|-----------------|-----------------|
| Pb(II)    | 1.19            | 0.74            |                 |
| Cd(II)    | 1.07            | 1.05            |                 |
| Zn(II)    | 0.63            | 0.75            |                 |

\(^\text{a}\)C\(_0\) = 100 mg L\(^{-1}\), \(w_{AB} = 0.4\) g (<250 \(\mu\)m), \(t = 15\) min, pH = 5.5.
According to that described above, the synergistic effect is found for Pb(II) in the presence of Cd(II), obtaining a ratio of 1.19, whereas in the presence of Zn(II), it diminished considerably (r = 0.74). There is no significant competence for the active sites on AB by the other ions over Cd(II) as r is very close to 1. In the case of Zn(II), the presence of Pb(II) or Cd(II) induces an antagonistic effect, obtaining an r value of 0.63 and 0.75, respectively. It is reported in the literature that the hydrated ion radius of Pb (401 pm) which is smaller than that of Cd and Zn (426 and 430 pm, respectively), along with its higher covalent-bonding character, promotes a highly favorable interaction with ligands such as the carboxyl groups.

Figure 8. Micrographs and SEM/EDS of (a,b) AB, (c,d) AB−Pb, (e,f) AB−Cd, and (g,h) AB−Zn at maximum adsorption capacity.
of AB, inhibiting the adsorption of other metal ions. This explains the diminution in the adsorption capacity of Zn(II). Similar effects have been found in the adsorption of Pb and Ni mixtures onto coconut shell and water hyacinth or Pb and Cd mixtures onto cucumber peel.

2.7. Characterization of Biosorbent and Adsorption Mechanisms. 2.7.1. Scanning Electron Microscopy. Figure 8 shows the scanning electron micrographs for AB and the biosorbent after metal ion adsorption at a maximum adsorption capacity. The AB particles shown in Figure 8a present several ducts in the transversal section, whereas the longitudinal section has a rough surface which promotes a large area of contact to perform the adsorption process. The morphology of AB after the adsorption process is not modified (Figure 8c,e,g). A SEM/energy-dispersive spectrometry (EDS) analysis was carried out in the samples. For AB, the presence of calcium besides carbon and oxygen is notable (Figure 8b). The peaks of copper are due to the metallization treatment of the samples to make them conductive on the surface.

The calcium percent in AB corresponds to 2.3 wt %, whereas after the adsorption process, values of 0.77, 0.94, and 0.86 wt % were obtained for AB−Pb, AB−Cd, and AB−Zn, respectively (Figure 8d,f,h). The variation in the calcium percent indicates an ionic exchange mechanism in which calcium is exchanged by the metal ions during the adsorption process. The SEM/EDS mapping of micrographs are included in Figure 9 for AB−Pb, AB−Cd, and AB−Zn. The different elements in the samples were identified by color: carbon, red; oxygen, green; calcium, cyan; and Pb, Cd, or Zn in blue. It is observed that heavy metals are homogeneously distributed in AB, confirming the adsorption of metal ions onto AB, as predicted by the Langmuir model.

2.7.2. X-ray Diffraction. Figure 10 exhibits the XRD patterns of AB and those acquired after the adsorption process at maximum capacity. The peaks observed in the AB patterns at 14.7, 15, and 20° are associated with cellulose. The lignocellulosic component gives a peak at 24.14°, whereas peaks at 29.88, 37.97, and 45.63° were indexed to calcium oxalate monohydrate or whewellite, CaC₂O₄·H₂O (COD 9000763). Similar results were reported by other authors. No peaks were related to lignin because it is an amorphous macromolecule.

The difference between the XRD patterns of AB and those after the adsorption of metal ions, AB−Pb, AB−Cd, and AB−Zn, is notable. The pattern of AB−Pb displays a lower intensity of peaks associated with cellulose in comparison with those of AB−Cd and AB−Zn. The metal ions adsorbed on AB induce a variation in the cellulose structure by linking through functional groups, which reflect a change in the peak intensity. The van der Waals halo (broad peak at 15−20°) is also modified. This is attributed to the presence of metal ions on the polymeric structure, reducing the interaction by van der Waals forces, as is mainly observed for Pb(II). The foregoing results confirm that adsorption is carried out by a complexation mechanism through the cellulose groups. Nevertheless, the effect of other compounds such as hemicellulose or lignin on AB must be analyzed by another technique.

With reference to CaC₂O₄·H₂O, all peaks show a decrease in intensity because of the cationic exchange of Ca(II), as has been proven by SEM/EDS (Figure 8). This effect indicates that Cd(II) and Zn(II) are mainly adsorbed onto AB by a cationic exchange mechanism. For Pb(II), the adsorption mechanism is also associated to complexation with the carboxyl and hydroxyl groups of cellulose. From the XRD analysis, it is possible to explain that AB has more affinity for Pb(II) because its adsorption is performed by two mechanisms, whereas the Cd(II) and Zn(II) adsorption depends mostly on calcium exchange. It was reported that the adsorption of heavy metals onto sugar beet pulp was brought out by complexation and cationic exchange mechanism.

2.7.3. Solid-State 13C CP/MAS NMR. In order to elucidate the role of AB compounds in the complexation mechanism during the adsorption, further characterization by solid-state 13C CP/MAS NMR was performed. Figure 11 shows the
obtained spectrum of AB. The peaks were identified at the carbon atoms of cellulose, lignin, and hemicellulose with the initials C, L, and H, respectively.

The solid-state $^{13}$C CP/MAS NMR spectra provide important evidence to the complexation mechanism for the metal ion adsorption onto AB. Then, Pb(II) is adsorbed by the cellulose, hemicellulose, and lignin groups. This explains the high affinity of AB for Pb(II). For the adsorption of Cd(II), the three compounds of AB participate in the adsorption process in a lesser grade than Pb(II). Zn(II) is adsorbed by the amorphous cellulose with a scarce contribution by the hemicellulose and lignin groups, which is in agreement with the low adsorption capacity of AB.

The region between 120 and 160 ppm is reported as characteristic of carbon in the aromatic ring of lignin. At 153.3 and 150.8 ppm are displayed the peaks for L3 and L5, whereas the signal of the chemical shift at 121.5 ppm corresponds to L4. The methoxy groups −OCH$_3$ and the aldehyde −CHO give a signal in 167.6 and 150.8 ppm, respectively. In cellulose, the peaks at 167.8 and 154.8 ppm are assigned to the CH$_3$ in the acetyl groups overlapped by the cellulose peaks. CH$_3$ in the acetyl groups in hemicellulose can be assigned also at 20.6 ppm. At 24.9 ppm is designated to the α carbon in lignin. Table 6 presents the assignment of spectra.
3. CONCLUSIONS

The adsorption behavior of AB has been investigated to remove Pb(II), Cd(II), and Zn(II), and the results proved AB to be a potent biosorbent. The adsorption capacity is highly influenced by pH, particle size, dosage, time, and metal ion concentration. The kinetic studies demonstrated that adsorption rapidly proceeds with high removal efficiencies, that is, 99, 93, and 82% for Pb(II), Cd(II), and Zn(II), respectively, in only 5 min and follows the pseudo-second-order equation. The isotherms show a Langmuir behavior with the maximum adsorption capacity of 93.14, 28.50, and 24.66 mg g\(^{-1}\) in the case of Pb(II), Cd(II), and Zn(II), respectively. In binary mixtures, the presence of other ions affect the adsorption capacity of Cd(II) and Zn(II). Finally, better affinity for Pb(II) over Cd(II) and Zn(II) was evidenced from characterization by SEM/EDS and XRD. The results reveal a combined adsorption mechanism by complexation with cellulose functional groups and calcium exchange for Pb(II); meanwhile, Cd(II) and Zn(II) are mainly adsorbed onto AB by ionic exchange.

4. EXPERIMENTAL SECTION

4.1. Materials. The reagents used in this study were of analytical grade, without further purification. The aqueous solutions of metal ions were prepared by dissolving appropriate amounts of Pb(NO\(_3\))\(_2\), Cd(NO\(_3\))\(_2\), and ZnSO\(_4\) (J.T. Baker, US) in distilled water to obtain the desired concentration. The solutions were kept at ambient temperature in polyethylene flask until their utilization.

AB was obtained from the State of Jalisco (Mexico) as a residue of tequila spirit production. The content of cellulose, lignin, and hemicellulose in the same AB was reported elsewhere\(^{30}\) and corresponds to 42 ± 2, 15 ± 1, and 20 ± 1%, respectively. AB was dried in a furnace at 80 °C for 2 h to remove the moisture and to avoid further degradation. Prior to adsorption experiments, the organic compounds were removed according to the standard test method D-1103-96\(^{51}\) to avoid secondary reactions with metal ions. Then, AB was dried, milled, and sieved in a vibratory sieve shaker Retsch AS-200 (Germany) for 5 min to select the particle size.

4.2. Adsorption Behavior. A batch system was performed thrice with 0.4 ± 0.01 g of AB and 45 mL of a solution containing metal ions separately in 100 mg L\(^{-1}\) with magnetic stirring of 300 rpm at 25 °C for 30 min. The pH influence on adsorption capacity was studied in the range of 3–6.5. The pH was measured during all the experiments using an HI2550 equipment (Hanna Instruments, Germany) with a combined electrode, and it was adjusted by the addition of 0.1 mol L\(^{-1}\) NaOH or 0.1 mol L\(^{-1}\) HCl, as required. Four particle size ranges were used: >250, 250–180, 180–150, and <150 μm. Experiments were conducted at different AB dosages in a range of 0.1–0.6 g (<250 μm) at pH 5.5.

For kinetic studies, the adsorption of each metal ion was performed between 5 and 120 min, at pH 5.5, using 0.4 g of biosorbent (<250 μm). The pseudo-first- and pseudo-second-order models were discussed for experimental data.

The adsorption isotherm for each metal ion in a wide interval of concentration was obtained using 0.4 g AB, for 15 min, and at pH 5.5. For these experiments, solutions at different initial concentrations from 10 to 1000 mg L\(^{-1}\) were used. Langmuir and Freundlich equations were considered to predict the adsorption behavior.

The influence of metal ions on adsorption from binary mixtures was studied using 100 mg L\(^{-1}\) for [Pb(II)–Cd(II), Pb(II)–Zn(II), and Zn(II)–Cd(II)], maintaining the pH at 5.5, using 0.4 g of biosorbent (<250 μm), and holding for 15 min.

After all adsorption experiments, AB was separated, dried for 2 h in a furnace, and reserved for further characterization. The initial and final concentrations of metal ions were quantified using a 3100 (PerkinElmer, USA) atomic absorption spectrometer.

In adsorption systems, the adsorption capacity (\(q_{\text{M(II)}}\), mg g\(^{-1}\)) and the removal efficiency for metal ions [M(II) = Pb(II),

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Table 6. Assigned Peaks in the Solid-State \(^{13}\)C CP/MAS NMR Spectra for AB, AB–Pb, AB–Cd, and AB–Zn. C: Cellulose; H: Hemicellulose; L: Lignin

| carbon atom       | AB        | AB–Pb     | AB–Cd     | AB–Zn     |
|-------------------|-----------|-----------|-----------|-----------|
| C1                | 104.4     | 104.5     | 104.4     | 104.6     |
| C2, C3            | 73.5      | 74.8      | 73.8      | 73.9      |
| C4 (crystalline)  | 88.2      | 88.2      | 88.1      | 88.3      |
| C4’ (amorphous)   | 82.4      | 83.2      | 83.0      | 83.1      |
| C5                | 71.8      | 71.8      | 71.6      | 71.8      |
| C6 (crystalline)  | 64.3      | 64.3      | 64.3      | 64.5      |
| C6’ (amorphous)   | 62.1      | 61.9      | 61.9      | 62.0      |
| H–COOH acetyl group | 173.3    | 173.0     | 173.3     | 173.6     |
| H–COO–M(II) acetyl group | 175.9    | 175.1     |           |           |
| H–CH\(_3\) acetyl group | 20.6     | 20.5      | 20.5      | 20.7      |
| H–C1 (shoulder)   |          | 101.6     | 101.2     | 101.0     |
| L3                | 153.3     | 152.9     | 152.6     |           |
| L5                | 150.8     | 150.6     | 151.6     | 151.2     |
| L4                | 121.5     |           |           |           |
| L–α               | 68.8      |           |           | 68.2      |
| L–OCH\(_3\) methosyl group | 55.3   | 55.2      | 54.9      | 55.3      |
| acetyl group      | 20.6      | 20.5      | 20.5      | 20.7      |
| L–αβ acetyl group | 24.9–32.3 | 29.6      | 29.6      | 29.8      |
| L–carboxyl group  | 167.6–168.3| 167.6–168.4| 167.5–168.4| 167.8–168.5|

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Table 6. Assigned Peaks in the Solid-State \(^{13}\)C CP/MAS NMR Spectra for AB, AB–Pb, AB–Cd, and AB–Zn. C: Cellulose; H: Hemicellulose; L: Lignin
Cd(II), or Zn(II)]) were calculated at different conditions by eqs 7 and 8, respectively

$$q_{M(II)} = \frac{C_0 V_0 - C_f V_f}{w_{AB}}$$  \hspace{1cm} (7)

Removal efficiency = $$\frac{C_0 V_0 - C_f V_f}{C_0 V_0} \times 100$$  \hspace{1cm} (8)

where, \(V_0\) and \(V_f\) are the initial and final volumes, in liters. \(C_0\) and \(C_f\) are the initial and final concentrations of metal ions \(M(II)\) expressed in mg L\(^{-1}\), whereas \(w_{AB}\) is the AB dosage in grams.

### 4.3. Characterization of Biosorbent

The solid addition method was used to determine the point of zero charge (pHpzc) of AB. Several 0.1 mol/L KNO\(_3\) solutions were adjusted at pH values between 2 and 8 by adding 0.1 HNO\(_3\) or NaOH. Each solution with 0.1 g of AB was placed in a sealed flask under constant stirring (150 rpm). After 48 h, the final pH was measured. The plot of \(\Delta p\text{H} (pH_f - pH_0)\) against the initial pH \((pH_0)\) was made to obtain pHpzc.

AB characterization was carried out before and after the adsorption experiments by SEM, XRD, and solid-state \(^{13}\)C CP/MAS NMR. The morphology of the biosorbent was evaluated by using a scanning electron microscope, JEOL JSM-6400 (US). EDS microanalysis was conducted to identify the elements in AB. The samples were weighed (0.2 g) and characterized with an X-ray diffractometer, Bruker D8 Advance Da Vinci (USA), using Cu Ka radiation at a step size of 0.03°. Nuclear magnetic resonance analysis was performed using CP/MAS for \(^{13}\)C nuclei in a 500 MHz spectrometer (Bruker, USA).

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### ABBREVIATIONS

- AB, agave bagasse; \(C_0\), initial concentration of metal ion; \(C_{eq}\), equilibrium concentration of metal ion; \(C_f\), final concentration of metal ion; CP/MAS, cross-polarization mode with magic-angle spinning; EDS, energy-dispersive spectrometry; \(k_f\), pseudo-first-order rate constant; \(k_p\), pseudo-second-order rate constant; \(K_f\), Freundlich constant; \(K_L\), Langmuir constant; \(M(II)\), metal ion Pb(II), Cd(II), or Zn(II); \(N\), number of experiments; \(n\), adsorption intensity; NMR, nuclear magnetic resonance; \(pH_0\), initial pH; \(pH_f\), final pH; \(\Delta pH\), differential of pH; \(q_{calc}\), predicted adsorption capacity by model; \(q_{exp}\), adsorption capacity at equilibrium; \(q_{exp}^{max}\), adsorption capacity of the metal ion in a binary mixture; \(q_{exp}^{max}\), adsorption capacity of the metal ion in a mixture; \(q_{exp}^{max}\), adsorption capacity at time \(t\); \(r\), ratio of adsorption capacities; \(R^2\), correlation coefficient; SE, standard error; SEM, scanning electron microscopy; \(V_0\), initial volume; \(V_f\), final volume; \(w_{AB}\), AB dosage; XRD, X-ray diffraction

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