# Adsorbent potential of cocoa pod husk activated charcoal to remove metals from the Ucayali River

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Abstract. The problem of river water contamination due to the presence of dangerous metals for ichthyological flora and fauna and human health has motivated the search for innovative and feasible solutions. Therefore, the production of activated carbon from cocoa pod husks was investigated to eliminate metals present in the Ucayali River. Response surface methodology was used to optimize the manufacturing of the adsorbent and test its effectiveness in removing metals from water using a factorial design of  $3^3$  and  $3^2$ , with three replicates each. The optimal amount of activated carbon (18.41 g) was obtained from 200 g of fresh cocoa pod husks. It was converted into activated carbon under the following conditions: thermal modification at 100, 150, and 200 °C; activation time of 1.0, 1.5, and 2.0 h; and pyrolysis and activation at 400, 500, and 600 °C. This allowed the elimination by efficient adsorption of 56.8% Fe<sup>2+</sup>, 68.4% Al<sup>3+</sup>, 65.9% Cu<sup>2+</sup>, and 55.5% Zn<sup>2+</sup> from Ucayali River, thus demonstrating its adsorbent power. The results will make it possible to manufacture filters to decontaminate water containing heavy metals, thus guaranteeing its consumption.

Key words: adsorption, heavy metals, pyrolysis, thermal modification, water pollution.

# **INTRODUCTION**

In most countries, the waters of rivers are effluent dumps, which carry pollutants, including heavy metals, that negatively affect the fish population by accumulating in the muscles, viscera, and other tissues (Adeyeye & Ashaolu, 2022; Akila et al., 2022; Zaghloul et al., 2022). They also affect the health of residents who use drink these waters and can have a carcinogenic effect. Therefore, it is considered a public health problem in Peru (Ccanccapa-Cartagena et al., 2021) and is also a prevalent problem worldwide (Mariana et al., 2021).

The development of cocoa (*Theobroma cacao*) cultivation has been increasing in the Ucayali-Peru region. In 2021, 20,046 t were harvested, and by February 2022, 1,213 t had been accumulated (López & Alva, 2022), of which 70–75% (Cruz et al., 2012) corresponded to the husks; therefore, between 14,032.2 and 15,034.5 t, and 849.1 and 909.8 t of residues, respectively, were left in the field, increasing environmental and landscape pollution.

Decontaminating the waters of the Ucayali-Peru river, due to the presence of metals, is approached from a perspective of reuse of lignocellulose waste from cocoa pod shells, which comprise 43.6% lignin, 34.4% cellulose, and 11.75% hemicellulose (Díaz-Oviedo et al., 2022), making them excellent raw materials for the production of activated carbon (Valdés-Rodríguez et al., 2022) using pyrolysis (Maulina & Iriansyah, 2018). They contribute to the formation of micropores of appropriate diameters, have a greater surface area, and have appropriate functional groups on their surface, making it a potential and efficient adsorbent for contaminant removal (González-García et al., 2013; Mariana et al., 2021).

Pyrolysis shows promise for dealing with agricultural waste by thermochemical conversion at high temperatures in the absence of oxygen (Mariana et al., 2021) into activated carbon, and has many important effects, particularly on its adsorption capacity, because increasing the temperature from 350 to 650 °C leads to a drastic increase in surface area and carbonisation with the loss of functional groups (Choi & Kan, 2019).

For the production of activated carbon, the values of surface area and micro pore volume, which are influenced by the type of raw material and pyrolysis temperature, obtained at 300–500 °C using coconut shell (*Cocos nucifera*) were 13.0 m<sup>2</sup> g<sup>-1</sup> and 0.021 cm<sup>3</sup> g<sup>-1</sup> (Solanki & Boyer, 2017), respectively; 120.0 m<sup>2</sup> g<sup>-1</sup> and 2.43 cm<sup>3</sup> g<sup>-1</sup>, respectively, using palm (*Elaeis guineensis*) activated carbon at 600 °C (Guo et al., 2016); 605.0 m<sup>2</sup> g<sup>-1</sup> and 0.421 cm<sup>3</sup> g<sup>-1</sup>, respectively, using wheat straw (*Triticum spp*) at 700 °C (Wu et al., 2018); and 904.1 m<sup>2</sup> g<sup>-1</sup> and 0.506 cm<sup>3</sup> g<sup>-1</sup>, respectively, using grapefruit peel (*Citrus paradisi*) at 600–900 °C (Chen et al., 2017).

The use of activated carbon made from lignocellulose waste to remove metals from water samples has been successfully tested; thus,  $Cu^{2+}$  has been removed from wastewater samples using activated carbon from green vegetables (Sabela et al., 2019). The removal of Fe<sup>2+</sup> from the Nag-India River was achieved using activated carbon from orange (*Citrus sinensis*) peels (Nandeshwar et al., 2016).

Liu et al. (2020) removed Hg<sup>2+</sup> from wastewater using activated carbon from rice husks (*Oriza sativa*); Yunus et al. (2020) removed  $Cr^{3+}$  and  $Zn^{2+}$  from mining effluents in the tile and electroplating industries using melon (*Cucumis melo*); and Olaoye et al. (2018) and Prastuti et al. (2019) removed  $Cu^{2+}$  and  $Cr^{6+}$  from textile wastewater, and Pb<sup>2+</sup>,  $Cr^{3+}$ , and  $Cd^{2+}$  ions from wastewater in the cassava (*Manihot esculenta*) industry using banana (*Musa paradisiaca*).

In agroindustrial waste, which is converted into activated carbon, palm kernel (*Elaeis guineensis*) shells (Baby & Hussein, 2020) have excellent activity in removing metals such as  $Cr^{6+}$ ,  $Pb^{2+}$ ,  $Zn^{2+}$ , and  $Cr^{2+}$  from water samples. The use of cocoa (*T. cacao* L.) pod shells converted into an adsorbent has been shown to be effective in removing  $Pb^{2+}$  and  $Cu^{2+}$  from water samples from a processing plant containing a mixture of metals and from a refinery and petrochemical company (Odubiyi et al., 2012; Sadheesh et al., 2021).

The reported methodologies for manufacturing activated carbon include the use of chemical activators and the limited use of cocoa pod shells as lignocellulose biomass. The metals removed did not include aluminium (Al<sup>3+</sup>), copper (Cu<sup>2+</sup>), iron (Fe<sup>2+</sup>), and zinc (Zn<sup>2+</sup>), but were oriented towards chromium (Cr<sup>6+</sup>) and cadmium (Cd<sup>2+</sup>), which have not been discussed in depth in the literature.

Therefore, if cocoa pod shells are converted by thermochemical activation, followed by carbonisation, and the thermochemical modification time is controlled, activated carbon with excellent adsorbent characteristics to remove heavy metals from the waters of the Ucayali River will be obtained. Therefore, the purpose of this study was to manufacture activated carbon from cocoa pod shells (*T. cacao* L.) and determine its adsorption efficiency and removal of heavy metals in water samples from the Ucayali River, Peru.

#### **MATERIALS AND METHODS**

#### Manufacture of activated carbon by pyrolysis: experimental and statistical design

Activated carbon was obtained, as described by Tsai et al. (2018), with adaptations comprising: reception, selection, weighed (200 g) on Ohaus-PA512 scale, repeatability 0.01 g, cut into pieces, chopped to 5 mm, thermal modification at 100, 150, and, 200 °C for 1.0, 1.5, and 2.0 h, pyrolysis and thermal activation at 400, 500, and, 600 °C, in a muffle furnace (Thermolyne brand Thermo Fisher Scientific, MA, USA; FB1414M,  $\pm 0.5$  °C at 1,000 °C) for 1 h, ground to particles of 149 µm (0.149 mm), washed with distilled water until total decolourisation, dried at 150 °C in an oven (Memmert, precision up to 99.9 °C: 0.1/from 100 °C: 0.5) for 1 h, with 6.4% humidity (ASTM, 1997), and packaging in glass jars. Obtaining activated carbon followed a 3<sup>3</sup> factorial design with three repetitions, because it is a widely used technique to optimize activation conditions to minimize the number of experiments and obtain maximum information (Grich et al., 2024). The response surface methodology was used for its optimization because it was a multi-factor experiment, which allowed us to effectively distinguish the degree and difference of the influence of each factor (Aksoy & Sagol, 2016), the variables studied being the thermal modification temperature  $(X_1)$ , thermal activation time  $(X_2)$ , and the carbonization temperature  $(X_3)$ , whose parameters are shown in Table 1.

| Variable                         | Unit | Code  | -1  | 0   | +1  |
|----------------------------------|------|-------|-----|-----|-----|
| Change temperature               | °C   | $X_1$ | 100 | 150 | 200 |
| Activation time                  | h    | $X_2$ | 1.0 | 1.5 | 2.0 |
| Pyrolysis/activation temperature | °C   | $X_3$ | 400 | 500 | 600 |

Table 1. Variables and their levels for the production of activated carbon

The weight of the activated carbon obtained was considered the response variable, as represented in Eq. 1.

$$Y_{1} = B_{0} + B_{1}X_{1} + B_{2}X_{2} + B_{3}X_{3} + B_{11}X_{1}^{2} + B_{12}X_{1}X_{2} + B_{13}X_{1}X_{3} + B_{22}X_{2}^{2} + B_{23}X_{2}X_{3} + B_{33}X_{3}^{2}$$
(1)

where  $Y_1$  – response variable (amount of activated carbon);  $B_0$  – coefficient of the constant;  $B_1$ ,  $B_2$ ,  $B_3$  – linear coefficients;  $B_{12}$ ,  $B_{13}$ ,  $B_{23}$  – binary interaction coefficients;  $B_{11}$ ,  $B_{22}$ ,  $B_{33}$  – quadratic coefficients, and  $X_1$ ,  $X_2$ ,  $X_3$  – levels of the variables for manufacturing activated carbon.

## Evaluation of the adsorbent activity of activated carbon and statistical analysis

Water samples from the Ucayali River were taken 30 m from the shore at the Reloj Público port, using 1 L glass bottles, which were immediately insulated and stored under refrigeration using thermal boxes.

The effectiveness of the adsorbent was evaluated using atomic absorption spectroscopy, as recommended by Sibal & Espino (2018). For this purpose, 250 mL water samples were collected from the Ucayali River, with Fe<sup>+2</sup>, Al<sup>+3</sup>, Cu<sup>+2</sup>, and Zn<sup>+2</sup> of 1.37, 0.25, 0.041, and 0.011 mg L<sup>-1</sup>, respectively. Water samples were spiked with 1, 3, or 5 g of washed and dried activated carbon, shaken at 300 rpm for 30, 60, or 90 min, filtered, packed in glass jars, hermetically sealed, coded, and stored under refrigeration. The adsorption of Fe<sup>+2</sup>, Al<sup>+3</sup>, Cu<sup>+2</sup>, and Zn<sup>+2</sup> on the water samples by activated carbon was measured by atomic absorption using a spectrophotometer (Labtron, model LAAS-A11, precision  $\lambda \leq \pm 0.5$  nm), and a calibration curve was made with five concentrations and a reagent blank in the linear range for each element measured. To evaluate the adsorptive effectiveness of activated carbon in the adsorption of metals from water samples from the Ucayali River, a factorial 3<sup>2</sup> design with three replicates was used, and the adsorption was optimised using response surface methodology, considering the amount of activated carbon (X<sub>1</sub>) and agitation time (X<sub>2</sub>) as variables, as shown in Table 2.

**Table 2.** Factors, codes, and values determined in the adsorption of metals from water samples with activated carbon

| Factors                    | Unit | Code           | -1 | 0  | +1 |  |
|----------------------------|------|----------------|----|----|----|--|
| Amount of activated carbon | g    | $X_1$          | 1  | 3  | 5  |  |
| Stirring time              | min  | $\mathbf{X}_2$ | 30 | 60 | 90 |  |

Statistical analysis of the generated data was performed using the Statgraphics CENTURION XIX software, version 19.1.2 (StatPoint, 2020).

The response variables ( $Y_{Fe, Al, Cu, Zn}$ ), show the adsorption of the metals (Eq. 2).

$$Y_{\text{Fe,Al,Cu,Zn}} = B_0 + B_1 X_1 + B_2 X_2 + B_{11} X_1^2 + B_{12} X_1 X_2 + B_{22} X_2^2$$
(2)

where  $Y_{Fe,Al,Cu,Zn}$  – response variable (adsorption of Fe<sup>+2</sup>, Al<sup>+3</sup>, Cu<sup>+2</sup>, Al<sup>+2</sup>); B<sub>0</sub> – coefficient of the constant; B<sub>1</sub> and B<sub>2</sub> – linear coefficients; B<sub>12</sub> – binary interaction coefficient; B<sub>11</sub> and B<sub>22</sub> – quadratic coefficients, and X<sub>1</sub> and X<sub>2</sub> – coded values of the variables responsible for the adsorbed metal.

## **RESULTS AND DISCUSSION**

# Characterization of the raw material, production of activated carbon, pyrolysis, and ANOVA

The analysis of variance (ANOVA) of the data obtained for the amount of activated carbon as a function of the modification temperature, activation time, and pyrolysis and activation temperatures is reported in Table 3.

The statistical significance was observed in factors C and B<sup>2</sup> ( $p \le 0.05$ ), which corresponds to the activation time and the quadratic effect of the pyrolysis and activation temperature.

| Source of variation                 | Sum of squares | gl | Mean square | F-ratio | P-value              |
|-------------------------------------|----------------|----|-------------|---------|----------------------|
| A: Modification temperature         | 0.1701         | 1  | 0.1701      | 0.05    | 0.8257 <sup>ns</sup> |
| B: Pyrolysis/activation temperature | 5.4891         | 1  | 5.4891      | 1.61    | 0.2212 <sup>ns</sup> |
| C: Activation time                  | 85.4996        | 1  | 85.4996     | 25.12   | 0.0001*              |
| $A^2$                               | 2.4876         | 1  | 2.4876      | 0.73    | $0.4045^{ns}$        |
| AB                                  | 2.1168         | 1  | 2.1168      | 0.62    | 0.4412 <sup>ns</sup> |
| AC                                  | 1.2936         | 1  | 1.2936      | 0.38    | 0.5457 <sup>ns</sup> |
| $B^2$                               | 62.1675        | 1  | 62.1675     | 18.27   | 0.0005*              |
| BC                                  | 0.3571         | 1  | 0.3571      | 0.10    | 0.7500 <sup>ns</sup> |
| $C^2$                               | 0.2576         | 1  | 0.2576      | 0.08    | 0.7865 <sup>ns</sup> |
| Error                               | 57.8564        | 17 | 3.4033      |         |                      |
| CV (%)                              | 16.7000        |    |             |         |                      |
| <u>R<sup>2</sup></u>                | 0.7342         |    |             |         |                      |

Table 3. ANOVA for the fitted quadratic polynomial model for activated carbon manufacture

ns and \*, not significant and significant, respectively,  $p \le 0.05$  using the *F* test; CV: coefficient of variation;  $R^2$ : coefficient of determination.

After optimising the variables used in the production of activated carbon, 18.41 g was determined as the optimum quantity, obtained at 100 °C modification temperature, 400 °C pyrolysis and activation temperature, and 1 h of activation time. Eq. 3 shows the optimal variables generated by the software:

$$\hat{y}_1 = 115.74 - 10.5406^* X_3 + 0.00032189^* X_2^2$$
 (3)

The graph of the optimisation of obtaining activated carbon from cocoa pod husks (in g) is shown in Fig. 1, A, which corresponds to the response surface, while Fig. 1, B shows the analysis of the main effects. At lower modification and pyrolysis temperatures, there was a higher yield of activated carbon. The activation time had a negative effect because increasing its value decreased the production of activated carbon.



**Figure 1.** Effect of modification temperature, pyrolysis and activation temperature (A), and activation time (B) on obtaining activated carbon from cocoa pod husks.

MT – Modification Temperature; PT – Pyrolysis and Activation Temperature; AC – Activated Carbon; Mt – Modification Time.

Using lignocellulose materials from forestry and food industries as raw materials to manufacture activated carbon using pyrolysis, to be used as an adsorbent (Martelo et al., 2022), reduces costs, revaluates and minimises industrial waste, and becomes a viable alternative for carbon capture, thereby optimising environmental management and taking advantage of the benefits of its chemical composition.

Cocoa pods, depending on the variety, and according to Díaz-Oviedo et al. (2022) and Lara et al. (2016), have 43.6 and 12.66% lignin, 34.4 and 19.82% cellulose, and 11.75 and 9.45% hemicellulose, respectively, the latter two being carbohydrates, which decompose independently during pyrolysis (Kim et al., 2022), because hemicellulose is the first component to degrade between 220 and 315 °C (Yang et al., 2007). In contrast, at temperatures between 300 and 400 °C, cellulose undergoes decarbonisation, ring-opening polymerisation, and aromatisation (Hoang et al., 2021) to form aromatic groups (Lara et al., 2016). According to Ma et al. (2016), the pyrolysis of lignin leads to the transformation of methoxyl groups (-O-CH<sub>3</sub>), and total phenol groups and G-type phenols (guaiacol) increase at 500 °C; however, from 400 to 700 °C, S-type phenols (syringol) decrease, while P-type phenols (phenol) and C-type phenols (catechol) increase, which are important for giving activated carbon its adsorbent characteristics.

Rincón et al. (2015) reported that the production of activated carbon typically involves two stages: the carbonisation (pyrolysis) of the raw material, and the activation of the carbonised material at temperatures of  $\geq 500$  °C. In the current study, it was carbonised and activated at 400, 500, and 600 °C. The high carbonisation and activation temperatures (700 °C) give the activated carbon larger pores (mesopores), making it suitable for water treatment (Rincón et al., 2015). Wang et al. (2021) stated that the production of activated carbon from lignocellulosic biomass comprises two main processes, activation and pyrolysis, which were applied in this study.

In the production of activated carbon, the pyrolysis temperature a considerable influence on its texture, which in turn influences its adsorbent properties depending on its pore type. Rodríguez-Sánchez et al. (2019), when processing chestnut (*Castanea sativa Mill*) waste activated carbon at low-temperature (220 °C) carbonisation, obtained BET areas (specific surface areas) of  $3 \text{ m}^2 \text{ g}^{-1}$ , whereas at 800 °C, the BET area was 568 m<sup>2</sup> g<sup>-1</sup>, and the micropore and mesopore volumes were 0.133 cm<sup>3</sup> g<sup>-1</sup> and 0.033 cm<sup>3</sup> g<sup>-1</sup>, respectively. Notably, the temperature, residence time, and heating rate have a substantial impact on pyrolysis (Yogalakshmi et al., 2022).

In this regard, Chen et al. (2022) indicated that during pyrolysis, lignocellulosic components were degraded, generating the first volatile hemicellulose compounds, followed by cellulose, and then volatile lignin.

The pyrolysis of lignocellulose feedstocks leads to the formation of carbon, depolymerisation, and fragmentation of molecules via various mechanisms. In this regard, Chen et al. (2022) indicated that during pyrolysis, lignocellulosic components were degraded, generating the first volatile hemicellulose compounds, followed by cellulose, and then volatile lignin. Pyrolysis of lignin generates hydrocarbons due to aromatic rings and methoxy groups. With increasing temperature, the carboxy-C and O-alkyl-C structures in biochar decrease, whereas aryl-C increases due to deoxygenation reactions such as dehydroxylation, decarboxylation, decarbonylation, and demethoxylation, which reduce the amount of oxygen-containing functional groups (such as -OH, -C=O, -COOH, and -OCH<sub>3</sub>), and polycondensation reactions, leading to the formation of more polycyclic aromatic hydrocarbon units during pyrolysis. According to Nyirenda et al. (2022), the heat treatment produced by pyrolysis develops oxide compounds on the surface of activated carbon, which directly influences its ability to remove metals from water samples.

# Adsorbent activity, metal adsorption mechanisms of activated carbon, and ANOVA

The results of the statistical analysis of the data generated by the adsorptive action of the activated in removing  $Fe^{2+}$ ,  $Al^{3+}$ ,  $Cu^{2+}$ , and  $Zn^{2+}$  as water pollutants, as well as their significance, are presented in Table 4.

| Sources of variation          | <i>P</i> -value      |           |                      |                      |  |  |
|-------------------------------|----------------------|-----------|----------------------|----------------------|--|--|
|                               | Fe <sup>2+</sup>     | $Al^{3+}$ | $Cu^{2+}$            | $Zn^{2+}$            |  |  |
| A: Amount of activated carbon | 0.0000*              | 0.0000*   | 0.0000*              | 0.0000*              |  |  |
| B: Stirring time              | 0.0000*              | 0.0001*   | 0.0000*              | 0.0000*              |  |  |
| AA                            | 0.0002*              | 0.0000*   | 0.2014 <sup>ns</sup> | 0.6955 <sup>ns</sup> |  |  |
| AB                            | 0.0000*              | 0.0048*   | 0.0020*              | 0.5082 <sup>ns</sup> |  |  |
| BB                            | 0.9912 <sup>ns</sup> | 0.0001*   | 0.6326 <sup>ns</sup> | $0.8754^{ns}$        |  |  |
| CV (%)                        | 37.52                | 36.95     | 32.28                | 38.34                |  |  |

Table 4. Summary of removal of Fe<sup>+2</sup>, Al<sup>+3</sup>, Cu<sup>+2</sup>, and Zn<sup>+2</sup> according to ANOVA

ns and \*, not significant and significant, respectively,  $p \le 0.05$  using the F test; CV: coefficient of variation.

A 5% significance level was set for the removal of Fe<sup>2+</sup>, Al<sup>3+</sup>, Cu<sup>2+</sup>, and Zn<sup>2+</sup> as the amount of activated carbon used correlated with the stirring time at  $p \le 0.05$ . Table 5 lists the adjusted metal removal models.

| Metal<br>removed | $R^2$  | Adjusted<br>R <sup>2</sup> | Equation  |     |
|------------------|--------|----------------------------|---|-----|
| Fe <sup>2+</sup> | 0.9787 | 0.9711                     | $\begin{split} \hat{y}_{Fe^{2+}} &= 1.06911 - 0.090333^*X_1 - 0.0067889^*X_2 \\ & - 0.002425^*X_1X_2 - 0.000167^*X_1^2 \end{split}$                         | (4) |
| Al <sup>3+</sup> | 0.9937 | 0.9913                     | $\begin{split} \hat{y}_{Al^{3+}} &= 0.1560 - 0.035^* X_1 + 0.002478^* X_2 \\ & - 0.0001417^* X_1 X_2 + 0.0095^* X_1^2 \\ & - 0.0000339^* X_2^2 \end{split}$ | (5) |
| $Cu^{2+}$        | 0.9224 | 0.8938                     | $ \hat{y}_{Cu^{2+}} = 0.033889 + 0.001733^*X_1 - 0.000233^*X_2 \\ - 0.00008417^*X_1X_2 $  | (6) |
| $Zn^{2+}$        | 0.9266 | 0.8996                     | $\hat{y}_{Zn^{2+}} = 0.0084556 - 0.0007333^*X_1 \\ - 0.00005389^*X_2$   | (7) |

 Table 5. Coefficient of determination and fitted models of metal removal

\* denotes significance at  $p \le 0.05$  using the F test;  $R^2$ : coefficient of determination.

It is considered that there was a good fit in the models because the coefficients of determination ( $R^2$ ), including the adjusted  $R^2$ , ranged from 0.9224 to 0.9937 and 0.8938 to 0.9913, respectively (Table 5), in all the tests performed at the laboratory level, owing to the type of experimental design, which allowed us to determine the influence of the independent variables on the removal of metals from the water samples of the Ucayali River (Fig. 2).

The optimum removal value, according to the fitted model, was 0.778 ppm for Fe<sup>2+</sup>, with 1.0 g of activated carbon and a stirring time of 90.0 min (Eq. 4); 0.171 ppm for Al<sup>3+</sup>, with 1.0 g of activated carbon and a stirring time of 34.5 min (Eq. 5); 0.027 ppm for Cu<sup>2+</sup>, with 1.0 g of activated carbon and a stirring time of 30.0 min (Eq. 6);



and 0.0061 ppm for  $Zn^{2+}$ , with 1.0 g of activated carbon and a stirring time of 30.0 min (Eq. 6; Fig. 2).

**Figure 2.** Effect of the amount of activated carbon and the agitation time on the removal of  $Fe^{2+}$ ,  $Al^{3+}$ ,  $Cu^{2+}$ , and  $Zn^{2+}$  from water samples from the Ucayali River, Peru. ST - Stirring Time; AC - Activated Carbon.

The adsorptive effect of activated carbon on the removal of metals from water samples from the Ucayali River was obtained from the optimization of the models, which were developed under ideal conditions, and 1 g of activated carbon was established as the effective amount to remove  $Fe^{2+}$ ,

 $Al^{3+}$ ,  $Cu^{2+}$ , y, and  $Zn^{2+}$  (Table 6).

The adsorptive effectiveness of activated carbon depends on the carbonisation temperature and the activation method. Narvekar et al. (2021) obtained activated carbon with a pore volume of  $0.08 \text{ m}^3 \text{ g}^{-1}$  and a surface area of 425 m<sup>2</sup> g<sup>-1</sup> at 800 °C in the presence of N<sub>2</sub>. These

**Table 6.** Percentage of metals removed from water samples with 1 g of activated carbon from cocoa pod shells

|                 | Metal concentration (ppm) |           |                  |           |  |
|-----------------|---------------------------|-----------|------------------|-----------|--|
|                 | Fe <sup>2+</sup>          | $Al^{3+}$ | Cu <sup>2+</sup> | $Al^{2+}$ |  |
| Initial content | 1.370                     | 0.250     | 0.041            | 0.0110    |  |
| Amount adsorbed | 0.778                     | 0.171     | 0.027            | 0.0061    |  |
| % removed       | 56.8                      | 68.4      | 65.9             | 55.5      |  |

are fundamental factors to guarantee the adsorptive power of biochar, whose functionality is provided by C=C bonds (alkene group) and the -SO<sub>3</sub>H group (sulphone). The sulfone group has surfactant properties and is used for the removal of metals from wastewater by chemisorption, for example, of  $Cd^{2+}$  and  $Pb^{2+}$  (Gul et al., 2022).

Ahmad et al. (2018) manufactured activated carbon from banana peels (*Musa paradisiaca*) and cauliflower leaves (*Brassica oleracea* var. botrytis) by thermal modification in an oven at 200 °C for 1 h, then by pyrolysis and activation at 600 °C for 2 h. Subsequently, they were crushed to particles of 0. 452–1 mm, with which they removed metals from water by adsorption. The banana peels had the highest adsorption efficiency, being in the order of removal of  $Pb^{2+} > Cu^{2+} > Cd^{2+}$ , with the electrostatic attraction being the predominant mechanism governing the sorption process.

Lara et al. (2016) used washed, dehydrated, and ground cocoa shells as a bioadsorbent to remove Pb<sup>2+</sup> (91.32%) and Cd<sup>2+</sup> (87.80%) from wastewater samples, attributing the bioadsorption to the action of aromatic groups, specifically C-H and C=C.

Valdés-Rodríguez et al. (2022) obtained activated carbon from jacaranda (*Jacaranda mimosifolia*) and guava (*Psidium guajava*) seed residues and grape pomace (*Vitis vinifera*) and sugar cane bagasse (*Saccharum officinarum*), resulting in the jacaranda seed biochar being the most efficient for adsorbing  $Hg^{2+}$  and  $Pb^{2+}$  from wastewater samples at pyrolysis at 800 °C for 4 h, attributing the adsorption mechanism to the oxygenated functional groups present in the activated carbon.

Namasivayam et al. (2007) used activated carbon from pine nut (*Jatropha curcas*) shells, pyrolysed at 700 °C in a muffle furnace for 1 h, with particles of 250–500  $\mu$ , and successfully removed Cr<sup>6+</sup>, V<sup>5+</sup>, and Ni<sup>2+</sup> from water samples, attributing the adsorption capacity to its large surface area, its microporous characteristic, and the chemical nature of its surface.

Using plant-derived activated carbon with additives to improve adsorption capacity has been demonstrated by Nyirenda et al. (2022), who employed a silver-silica nanocomposite using activated carbon as a support, with which they were able to adsorb 84.75, 81.30, 87.72, and 81.97 mg g<sup>-1</sup> for Cu<sup>2+</sup>, Pb<sup>2+</sup>, Cd<sup>2+</sup>, and Zn<sup>2+</sup>, respectively. The removal of these metals by activated carbon adsorption occurs via electrostatic interactions between the dissolved cations and negatively charged silanolate surface sites; however, ion exchange is the main adsorption mechanism (Ahmad et al., 2017).

New alternatives to improve the adsorption capacity of activated carbon from cellulose are being experimented to maximise its capacity to remove metals present in water. Mubarak et al. (2022) experimented with activated carbon and a nanocomposite of carborundum and microcrystalline cellulose, which acted as an exceptional active adsorbent for the adsorption of  $As^{3+}$  and  $Cu^{2+}$  ions for water treatment. The main mechanism of adsorption of the ions by the nanocomposite was electrostatic interaction at moderate pH values (above 6), while at high acidity conditions (pH 2–6), the dominant mechanism was chemical complexation.

#### CONCLUSION

The production of activated carbon from cocoa pod husks by pyrolysis can be applied to various lignocellulose raw materials because the activation and modification of cellulose, hemicellulose, and lignin provides a large surface area, suitable surface functional groups, and appropriate pore diameters that confer adsorbent potential. The adsorption and heavy metal removal efficiencies of the activated carbon was a function of the parameters used for its production, such as a modified temperature of 100 °C, activation time of 1 h, and pyrolysis and activation temperatures of 400 °C, with which 18.41 g of activated carbon was obtained from cocoa husks. Moreover, 56.8%, 68.4%,

65.9%, and 55.5% of iron, aluminium, copper, and zinc was removed, verifying its use in the manufacture of filters to decontaminate water with heavy metals.

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