

Research Article

Valorisation of Pine Cone as an Efficient Biosorbent for the Removal of Pb(II), Cd(II), Cu(II), and Cr(VI)

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Valorisation of pine cone as an efficient, low-cost, and eco-friendly biosorbent for the removal of heavy metals from aqueous solutions is evaluated. The morphology and surface chemistry of the biosorbent are characterized by scanning electron microscopy, energy-dispersive elemental analysis, and Fourier transform infrared spectroscopy, revealing the presence of carboxylic and alcoholic functional groups that interact with metal ions. The effect of the contact time, pH, amount of adsorbent, and initial metal concentration in the adsorption is studied, resulting in removal percentages for Cd(II), Cu(II), Pb(II), and Cr(VI) (metal concentration of 5 mg L^{-1}) of 82.24%, 93.71%, 94.67%, and 88.8%, respectively (pH = 5.4, 2 g L^{-1} of adsorbent), except for Cr(VI) (pH = 2, 10 g L^{-1}). The equilibrium data of Pb(II) and Cd(II) were found to follow the Langmuir-Freundlich model, with maximum adsorption capacities of 100.01 and 78.73 mg g^{-1} , respectively, whereas Cu(II) followed the Langmuir model with 33.55 mg g^{-1} . Cr(VI) adsorption data also fitted the Langmuir model, and the maximum adsorption capacity was 57.36 mg g^{-1} . Adsorption data was obtained at pH 5.4 for divalent metal ions and at pH 2 for Cr(VI) and in a range of metal concentrations ranging from 1 to 500 mg L^{-1} at 298.2 K. The presence of the three metal ions in the solution does not affect the percentage of the target metal ion adsorbed, proving the absence of competition between them and showing the pine cone to be an efficient adsorbent to treat multimetal effluents allowing water reuse.

1. Introduction

It is increasingly difficult to obtain access to clean water due to the highly contaminating effect of certain industries compounded by ever more frequent conditions of drought, and so the removal of heavy metals such as Cd(II), Cu(II), Cr(VI), and Pb(II) from industrial wastewater is a major concern for society, given that their lack of biodegradability and toxicity are especially damaging to both ecosystems and human health [1].

Different technologies, such as ion exchange, solvent extraction, chemical precipitation, electrolysis, reverse osmosis, and adsorption on activated carbon, have been applied to remove heavy metals from wastewaters. However, the applicability of all these techniques has several disadvantages, including incomplete metal removal, high investment and operational costs, energy and reagent requirements, and gen-

eration of toxic sludge and other waste products [2]. Activated carbon is the most widely used adsorbent given its large surface area and porous structure; however, the poor functionalization of its surface is a drawback for the adsorption of metal ions [3]. The large amount of functional groups on the surface and high specific surface areas of nanomaterials, such as graphene oxides, carbon nanotubes, carbon nitride (C_3N_4), chitosan materials, and covalent organic frameworks (COFs), makes them excellent adsorbents for the elimination of metal ions [4]. The preparation of magnetic COF with high adsorption capacities allows the removal of pollutants such as Cr(VI) at the same time facilitating easier separation of the adsorbent [5]. The high price of these nanomaterials, which is due to the synthesis process, together with their tendency to aggregate, which results in a reduction in the available active sites, currently restricts their real applications [6]. Biochar and biochar-supported composites

showed high sorption capacities for heavy metal ions allowing the simultaneous elimination of both organic and inorganic pollutants [7]. However, biochar preparation and modification process are costly due to the consumption of chemical reagents and energy.

Biosorption, which uses low cost and readily available dead and live biomass, is an effective treatment to eliminate heavy metals from industrial effluents through many different metal binding mechanisms, such as ion exchange, chelation/coordination, precipitation, and sorption by other physical and chemical forces [8, 9]. A wide variety of agricultural residues has been evaluated as biosorbents taking advantage of the local availability of different vegetable matter around the world and their low cost as most of them are considered waste products. These include, among others, potato and banana peels [8], waste tea leaves [10], plantain peels [11], rice husk [12], and sweetsop [13], pistachio shells [14], date palm leaves [15], mahogany leaves [16], lemon grass [17], coconut shell [18], and almond green hull [19]. One drawback of using biosorbents is their low sorption capacity in comparison with other sorbents. Although this limitation can be overcome by modifying their surface through physical and chemical treatments that improve their capacity to bind to metal ions, these treatments require the use of energy and chemical reagents, which increase the cost. Two examples are the chemical treatment applied to modify lemon peel, resulting in an improved capacity to remove Ni(II) [20], and the thermal treatment of pea peels at 600°C to adsorb Pb(II) [21]. Besides the use of lignocellulose-rich biomass for bioethanol production, this biomass has been shown to be more efficient than other biosorbents to remove metal ions. The different types of plant parts such as stems, stalks, leaves, husk, shells, roots, and barks as raw material or as agricultural residues can be used to reduce environmental pollution.

Pine cones are produced in large quantities annually all over the world. In the Western Mediterranean, Spain has a pine-cultivated area of 460,000 hectares [22], whereas in the Southern Mediterranean, 320,000 hectares of forest cover in Tunisia is made up of *Pinus halepensis* and *Pinus pinea* [23]. After the separation of the pine nuts, the remaining material is typically released into the environment as waste [24]. Pine cones are mainly composed of cellulose, hemicellulose, and lignin, which have functional groups such as carbonyl (ketone), carboxyl, sulfhydryl (thiol), sulfonate, thioether, amine, alcohols, and esters that can bind heavy metals. Moreover, the cones have excellent physicochemical properties, including water retention, swelling capacity, and mechanical strength, that make them particularly suitable for use as an adsorbent [25]. Pine cones have been used in previous studies to adsorb different metal ions including Cr(VI) [25], Cu(II) and Cd(II) [26], Cu(II) [27], Pb(II) [28], and binary solutions of Cu(II) and Pb(II) [29].

Moreover, pine cones have also been applied to the removal of textile dyes from coloured wastewater [30]. A chemical treatment using KOH was successfully applied to improve the surface properties of pine cones to adsorb Pb(II) and Cu(II) [31]. Pine cone was also used as a precursor of organic carbon and then directly applied to the removal of

Pb(II), Cu(II), Ni(II), and Cr(VI) [32] and to produce a porous carbon low-cost photocatalyst support for environmental remediation [33].

However, milled pine cone is used in this study without performing any previous biosorbent treatment to reduce the costs and complexity of the biosorbent process. Hence, the aims of the present study are to characterize the milled pine cone and to valorise it as a biosorbent for the removal of heavy metals such as Pb(II), Cd(II), Cu(II), and Cr(VI) from water solutions.

2. Materials and Methods

Pine cones were collected from a forest in Tunisia and were washed several times with distilled water and sun-dried for two days. The dried samples were then crushed to a powder and sieved to obtain particle size < 1 mm.

The morphology of the milled pine cones was analysed by scanning electron microscopy (SEM) (Model ZEISS DSM-960A) operated at 30 kV. Samples were examined at magnification ranges of 50x, 500x, and 1000x. The SEM was equipped with an energy-dispersive X-ray spectrometer Bruker Nano XFlash Detector 5010 to determine the surface composition of the material. The particle size distribution was determined by the analysis of SEM images.

The adsorbent material was analysed by Fourier transformed infrared spectroscopy (Perkin-Elmer Paragon 2000 FTIR spectrometer) from 600 cm⁻¹ to 3600 cm⁻¹ to identify the functional groups present on the adsorbent.

The surface area of the adsorbent was determined using Brunauer-Emmett-Teller (BET) measurements. This analysis was carried out by the N₂ adsorption at 22°C using BET micromeritics ASAP 2020.

The pH at the point of zero charge (pH_{pZC}) of an adsorbent surface is the pH at which this surface has a net neutral charge. This value was calculated by adding 1 g of milled pine cones to 100 mL of distilled water and varying the pH from 2 to 11, stirring for 2 hours. The initial pH was adjusted by adding either HCl (0.1 M) or NaOH (0.1 M). The final pH of the solution was measured and the $\Delta pH = pH_f - pH_i$ was plotted against the pH of the initial solution.

Stock solutions of metals of 1000 mgL⁻¹ were prepared by dissolving appropriate quantities of Cd(NO₃)₂·4H₂O, K₂CrO₄, Cu(NO₃)₂·3H₂O, and Pb(NO₃)₂ (Panreac, Barcelona, Spain) in ultrapure water and diluted to obtain different concentrations.

2.1. Batch Experiments. The equilibrium time was studied by adding 0.04 g of milled pine cone to 20 mL of a metal solution with an initial metal concentration of 5 mgL⁻¹ at pH 5.4. After equilibrium was reached, the solutions were filtered to eliminate the adsorbent and analysed by inductively coupled plasma emission spectrometry (Varian, Liberty series ICP-AES). Calibration solutions of different concentrations were prepared by dilution of a 1000 mgL⁻¹ standard solution (Merck, Mollet del Vallès, Spain) of each individual metal. The effect of the amount of adsorbent was studied by using different concentrations ranging from 1 gL⁻¹ to 10 gL⁻¹ with an initial metal concentration of 5 mgL⁻¹ at pH = 5.5 for

Pb(II), Cu(II), and Cd(II), except for Cr(VI), which was at pH = 2.

Separate tests with initial Cd(II), Cu(II), Cr(VI), and Pb(II) concentrations ranging from 1 to 500 mg L⁻¹ were performed by adding 0.04 g of adsorbent to 20 mL of each solution for 2 hours.

The effect of pH on the metal adsorption was evaluated by adding 0.04 g of adsorbent to 20 mL of a 5 mg L⁻¹ solution at different pHs (2, 5.5, and 9), adjusted by adding HNO₃ 0.1 M and NaOH 0.1 M (Panreac, Barcelona, Spain). The pH of the solution was measured before and after adsorption.

Competition experiments between Cd(II), Cu(II), and Pb(II) were then performed using 0.04 g of adsorbent and 20 mL of metal solution containing (1, 5, and 10 mg L⁻¹) of each metal at pH 5.5 for 2 hours. All experiments were performed in triplicate at room temperature.

3. Results and Discussion

3.1. Milled Pine Cone Characterization before and after Adsorption. The FTIR spectrum of milled pine cone is presented in Figure 1(a). Five bands corresponding to the different functional groups can be seen in this figure. The broad band at 3379 cm⁻¹ proved the presence of hydroxyl groups (O-H stretching vibration), indicating strong hydrogen bonding. The peak at 2935 cm⁻¹ indicates the presence of aliphatic C-H group stretching vibrations of the -CH₃ and -CH₂ groups. The peak observed at 1635 cm⁻¹ denotes the stretching vibration of C=O of carboxylic groups, the peaks at 1386 cm⁻¹ and 1268 cm⁻¹ can be associated to carboxylic/aromatic hydroxyl (-OH) stretching of phenol group, and the peak at 1033 cm⁻¹ shows the stretching vibration of C-O of the primary alcohol group. As can be seen in Figure 1(a), there are changes in the bands at 3352 cm⁻¹, 2929 cm⁻¹, 1610 cm⁻¹, 1378 cm⁻¹, 1275 cm⁻¹, and 1027 cm⁻¹ after metal biosorption. These band shifts indicate that the hydroxyl and carboxylic groups are involved in the adsorption of the metals as have been reported for lignocellulosic substrates in which two acid sites—a low-pH (carboxylic) site and a high-pH (phenolic) site—are present [34]. Moreover, there is a decrease in the intensity after metal biosorption indicating an ion exchange or surface complexation process as the interaction with the metal ions prevents, in most of the cases, the vibration of the bonds [35]. Martín-Lara et al. [29] also reported that the carboxylic group is the main active site of pine cone, and this finding is supported by the slightly acidic value of pH_{PZC} = 5.62. However, in our study, we found a pH_{PZC} of 6.2.

The SEM images before and after adsorption show some modifications, an accumulation of metals on the cracks of the adsorbent surface (Figures 1(b) and 1(c)). The study of the chemical composition of the biosorbent is important to explain its behaviour during the sorption process. Pine cone is a lignocellulosic material with hemicellulose, lignin, cellulose, and extractive materials [36]. The surface elemental analysis of milled pine cones performed by EDX analysis (Figure 1(b)) showed a composition of 53.48% of C, 44.77% of O, and 0.17% of S which is similar to the findings of other studies [22, 29]. The characterization by EDX after adsorp-

tion (Figure 1(c)), which was performed by putting the milled pine cones into contact with a solution containing three divalent metal ions, confirms the presence of Cd, Cu, and Pb in the material with weight percentages of 0.3, 4.61, and 12.41%, respectively. Lead has the highest percentage, indicating the greater affinity of the biosorbent for this metal ion, followed by copper and cadmium. This result is in agreement with the strength of binding by the carboxylic and hydroxyl functional groups that follow the sequence Pb(II) > Cu(II) > Cd(II) [34].

The BET surface area, which is related to the capacity of the adsorbent, is 0.2536 m²g⁻¹, whereas the Langmuir surface area is 0.3108 m²g⁻¹. These values are smaller than those reported for pine cones and other agricultural wastes (0.5 > S_{BET} > 5 m²/g) [29]. The results obtained for the particle size distribution show that 88% of the particles of the 6376 particles analysed have a diameter of 50 μm, 8% of 100 μm, 3% of 150 μm, and 1% of 200 μm.

3.2. Batch Adsorption

3.2.1. Effect of Contact Time on Biosorption. The effect of contact time on the adsorption of metals onto the pine cones was studied. All four metals achieved equilibrium in 2 hours with removal percentages of 82.24% for Cd(II), 93.71% for Cu(II), 94.67% for Pb(II), and 75.43% for Cr(VI) (Figure 2(a)). The high adsorption percentage of Cu(II) and Pb(II) is explained by their greater affinity to the carboxylic, ketonic, and aldehyde functional groups [37].

3.2.2. Effect of pH. The influence of the pH solution is an important parameter as it affects both the protonation of the functional groups on the adsorbent surface and the metal speciation. Figure 2(b) shows the percentage removal of Cd(II), Cu(II), Pb(II), and Cr(VI) at different pHs.

At pH 2, low percentages of metals were removed. This percentage was higher when the pH was increased, reaching a maximum at pH 5.5 with percentages of 82.24%, 93.17%, and 94.67% for Cd(II), Cu(II), and Pb(II), respectively. This result is explained by the competition between protons and metal ions for the available sites of the functional groups on the adsorbent surface. At acidic pH, the presence of protons H⁺ increased in the solution, protonating the functional groups present on the adsorbent surface. At higher pHs, the percentage of H⁺ decreased in the solution resulting in the binding of a greater number of metal ions to the functional groups. This tendency continued until pH 8.8 only in the case of Cd(II) as precipitation of Cu(II) and Pb(II) hydroxides starts at pH > 6.7 in accordance with the fraction diagrams calculated with Medusa software [38]. The fraction diagrams were calculated at 5 mg L⁻¹ showing that Cu²⁺ and Pb²⁺ ions are the predominant species until pH 6 while Cd²⁺ is predominant until pH 9. Moreover, the adsorbent surface becomes deprotonated at pH > pH_{PZC}, facilitating the electrostatic interaction between Cd(II) and the negatively charged groups (OH⁻ and COO⁻) of the adsorbent, explaining the increase in the percentage of metal removal from 82.24% at pH 5.5 to 94.12% at pH 8.8.

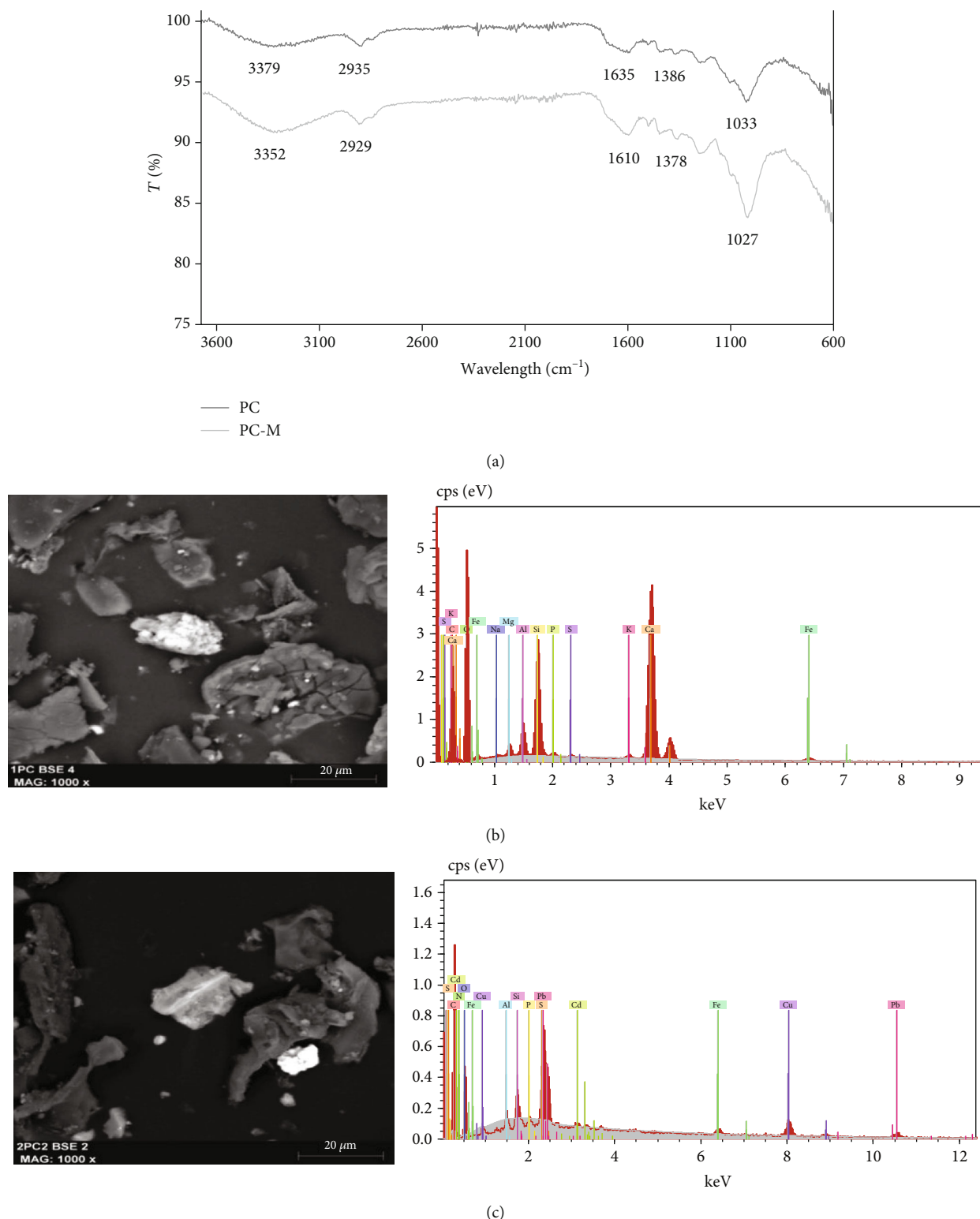


FIGURE 1: (a) FTIR spectra of pine cone (PC) and pine cone after metal adsorption (PC-M), (b) SEM micrograph and EDX spectra of pine cone, and (c) SEM micrograph and EDX spectra of pine cone after adsorbing Cu(II), Cd(II), and Pb(II).

In the case of chromium, the lower the pH, the greater the adsorption percentage, with values of 76% at pH = 2, 70% at pH = 5.5, and 5.8% at pH = 9. The pH of the aqueous solution influences chromium speciation and the acid-based

properties of active functional groups ($-\text{OH}$, $-\text{COOH}$) of the lignocellulosic material, which are protonated at low pHs. Negatively charged HCrO_4^- and CrO_4^{2-} species predominate in the aqueous solution at pH values between 2.0

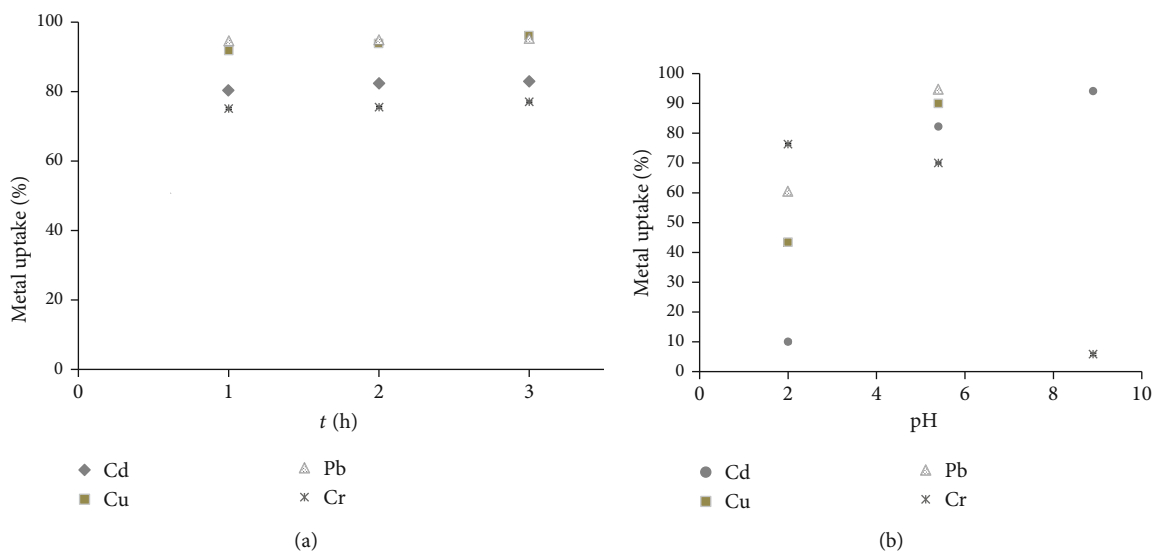


FIGURE 2: (a) Effect of the time on the metal uptake percentage of Cd(II), Cu(II), Pb(II), and Cr(VI) ($pH = 2$, $C_i = 5 \text{ mg L}^{-1}$, $pH = 5.4$, and adsorbent concentration = 2 g L^{-1} ($n = 3$)). (b) Effect of the pH on the metal uptake percentage of Cd(II), Cu(II), Pb(II), and Cr(VI), $C_i = 5 \text{ mg L}^{-1}$, adsorbent concentration = 2 g L^{-1} , and $t = 2 \text{ h}$ ($n = 3$)).

and 6.0 for concentrations less than 500 mg L^{-1} . These negatively charged species can interact with the protonated functional groups at the adsorbent surface. At $pH > 6$, the competition of the anionic CrO_4^{2-} with the OH^- for the active sites of the adsorbent and the fact that at $pHs > pH_{PZC}$ most of these active sites are negatively charged led to a dramatic reduction of the Cr(VI) adsorption [28]. Similar results were reported in other studies [39, 40, 37], which found the maximum Cr(VI) removal at low pH. Nowadays, the adsorption-coupled reduction reaction is the most accepted mechanism to explain Cr(VI) biosorption by natural materials [29, 41, 42]. In this mechanism, the removal of Cr(VI) involved two processes: biosorption and reduction to Cr(III) [43]. Different biomaterials, including pine cone, were used to demonstrate this coupled mechanism by verifying the oxidation state of chromium by X-ray photoelectron spectroscopy and measuring the pH variation during the adsorption process at low pHs. Protons and electrons, supplied by electron-donor groups of the biomaterial such as carboxylic groups, are required for the reduction of Cr(VI) to Cr(III), resulting in an increase in the pH of the metal solution [41]. In our study, an increase of 0.3 units of pH of the solution after the adsorption of chromium proved the reduction of one part of Cr(VI) to Cr(III), showing that adsorption of Cr(VI) may take place through this coupled mechanism.

In the case of the divalent metals, Pb(II), Cu(II), and Cd(II), the removal was through surface complexation by their association with carboxylic or OH groups as is indicated by the band shifts of these functional groups in the FTIR spectra after the adsorption of the metal ions (Figure 1(a)). As the pH of the solution is increased, the presence of ligands and the deprotonation of functional groups such as hydroxyl ($-\text{OH}$) and carboxyl ($-\text{COOH}$) on the surface of the biosorbent facilitate the formation of complexes with the metal ions, leading to further adsorption.

3.2.3. Effect of the Adsorbent Concentration. Figure 3(a) shows that higher removal percentages of Cd(II) and Cr(VI) were obtained by increasing the amount of biosorbent, while for Pb(II) and Cu(II), the removal percentages did not change when the amount was increased. As can be deduced from this figure, 2 g L^{-1} is the optimum dosage of milled pine cone at $pH 5.5$ to remove Cu(II) and Pb(II) with percentages of 93.71% and 94.97%, respectively. In the case of Cd(II), the best results (89%) were obtained with a dose of 5 g L^{-1} at $pH 5.5$, whereas for Cr(VI), this percentage was achieved with a dose of 10 g L^{-1} at $pH 2$.

3.2.4. Effect of the Initial Metal Concentration. The initial metal concentration is an important parameter that affects the efficiency of biosorption. It was studied at different values ranging from 1 to 500 mg L^{-1} . Figure 3(b) shows the removal percentage of metals as a function of the initial metal concentration. As can be seen, the removal efficiency of milled pine cone decreases as the initial metal concentration increases. This effect is higher for Cu(II), Cd(II), and Cr(VI) than for Pb(II), more than 60% of which is removed at an initial concentration of 300 mg L^{-1} . This decrease is explained by the fact that at higher concentrations, the saturation of the adsorbent surface is faster given the competition for the available binding sites resulting in more ions without there being more sites to attach to. However, in the case of Pb(II), the adsorption capacity increases when the initial concentration was increased from 1 to 20 mg L^{-1} indicating that the presence of more metal ions generates a driving force that overcomes the mass transfer resistance between the aqueous and the solid phases. The biosorption capacity for Pb(II) remains practically constant from 20 to 100 mg L^{-1} , showing that there were available binding sites on the pine cone surface. The greater affinity of pine cone to Pb(II) can be explained by its longer ionic radius (119 pm) in comparison with Cd(II)

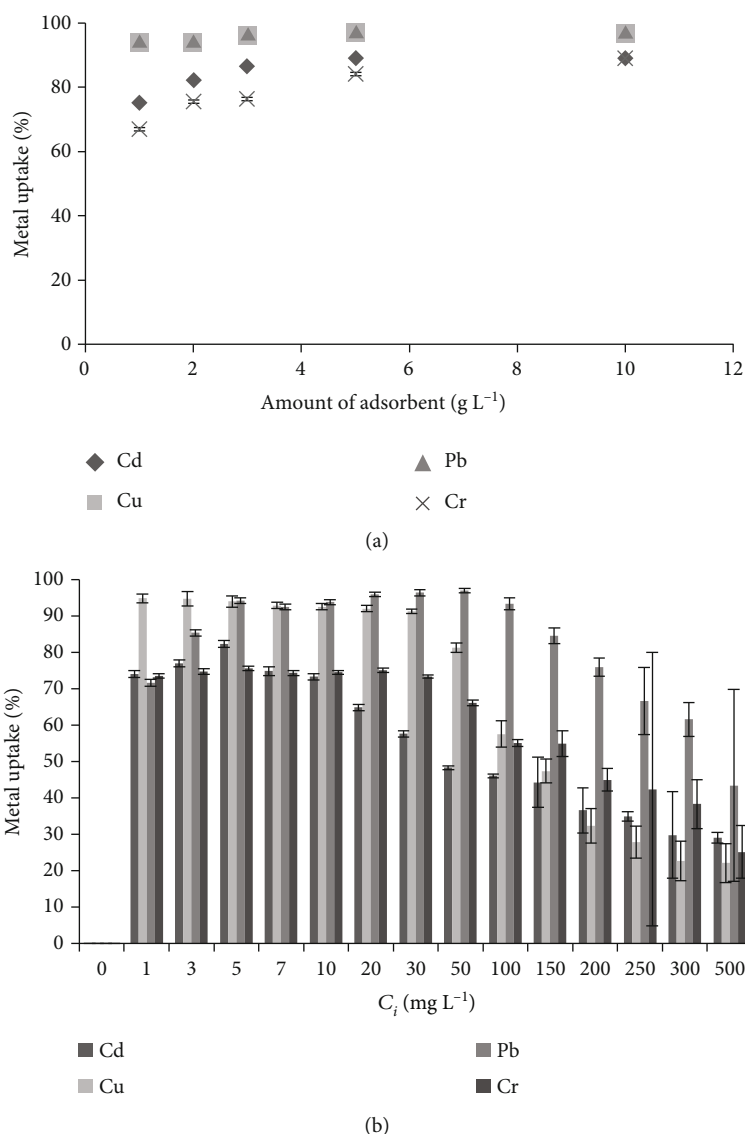


FIGURE 3: (a) Effect of the adsorbent concentration on the metal uptake percentage of Pb(II), Cu(II), Cd(II), and Cr(VI) (pH = 2), $C_i = 5 \text{ mg L}^{-1}$, pH 5.4, and $t = 2 \text{ h}$ ($n = 3$). (b) Effect of the initial metal concentration on the metal uptake percentage of Cd(II), Cu(II), Pb(II), and Cr(VI) (pH = 2), adsorbent concentration = 2 g L^{-1} , $t = 2 \text{ h}$, and pH = 5.4 ($n = 3$).

(95 pm) and Cu(II) (73 pm) as well as by the fact that it has the lowest hydration ion radius and the highest covalent index [29]. The covalent index is a function of the ionic radius (r) and the electronegativity (X_m) and is defined by the following: $CI = X_m^2(r + 0.85)$. The greater the covalent index of the metal ion, the greater the potential of this metal ion to form covalent bonds with the functional groups of the biosorbent. Lead has a covalent index of 11.1 whereas copper and cadmium have covalent indexes of 5.56 and 5.14, respectively [44].

Moreover, the metal removal efficiencies at low concentrations such as 1 and 3 mg L^{-1} are greater for Cu(II) than for the other metals, whereas at concentrations ranging from 5 to 30 mg L^{-1} , removal rates of more than 90% were obtained for Cu(II) and Pb(II). At higher concentrations, the removal percentages of Cu(II), Cd(II), and Cr(VI) fell. The removal

efficiencies for the divalent metals follow the order $\text{Pb(II)} > \text{Cu(II)} > \text{Cd(II)}$, which corresponds to the order of their affinity towards OH from phenolic groups [34].

3.3. Adsorption Isotherm. In the adsorption isotherm graph, the amount of adsorbate per mass unit of adsorbent is represented as a function of the equilibrium concentration in the solution at a constant temperature. The shape of the line depends on the adsorbent and adsorbate characteristics and on the type of interaction between them. This shape is used to classify the adsorption isotherms in different types following the Giles classification [45]. As can be seen in Figure 4, the sorption isotherms for Pb(II), Cu(II), and Cr(VI) are type I (convex shape), corresponding to an L-type isotherm where the slopes remain constant at a maximum sorption value. The L type is associated to a monolayer adsorption of

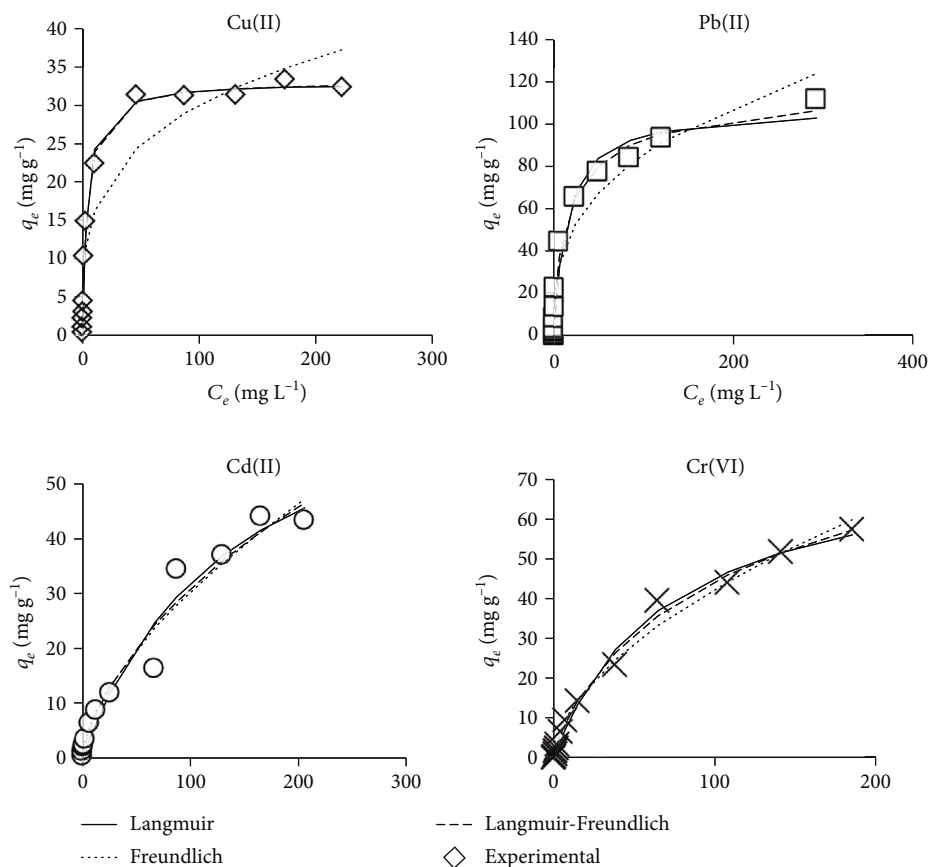


FIGURE 4: Adsorption isotherms of Cd(II), Cu(II), and Pb(II) at pH = 5.4 and Cr(VI) (pH = 2).

nonporous or microporous adsorbent, which is the type of adsorption isotherm most typically found in the case of agricultural wastes. The sorption isotherm of Cd(II) is type IV, which is characterized by the presence of two plateaus separated by an inflection due to the change from the first plateau to a concave shape until the second plateau is reached.

The Langmuir, Freundlich, and Langmuir-Freundlich models (Table 1) can be used to characterize the experimental data of the metal adsorption isotherm.

The Langmuir isotherm is characterized by the separation factor R_L , which can measure the facility for adsorption. The expression of R_L is defined as follows:

$$R_L = \frac{1}{1 + C_i b}, \quad (1)$$

where b is the Langmuir constant ($L\ mg^{-1}$) and $R_L = 0$ means that an irreversible adsorption process is taking place, whereas if $R_L = 1$, the adsorption is linear, and if $0 < R_L < 1$, it is considered that the adsorption is favoured.

The R_L values obtained, which varied between 0 and 1, indicate that biosorption onto the milled pine cones was favoured. When the initial metal concentration was increased, the separation factor R_L decreased at a constant rate for all metals, indicating the high affinity of these metals to the biosorbent even with high metal concentrations. In the case of the lowest initial metal concentration of $1\ mg\ L^{-1}$, the

R_L values were close to 1 (linear adsorption) for Cd(II), Pb(II), Cu(II), and Cr(VI), whereas in the case of the highest initial concentration of $300\ mg\ L^{-1}$, R_L values were lower and varied between 0.02 and 0.13. Moreover, Cu(II) and Pb(II) had the lowest separation factor R_L values at an initial concentration of $20\ mg\ L^{-1}$ (0.25 and 0.56, respectively) indicating the greater affinity of both metal ions to the biosorbent.

The fit of the experimental data to Langmuir, Freundlich, and Langmuir-Freundlich isotherm models was determined by using both nonlinearized and linearized equations. In the case of the nonlinearized equations, both the experimental points and the calculated models are depicted in Figure 4. As can be seen in this figure, there is good agreement between the experimental points in the case of Cu(II) and Pb(II) and the curves corresponding to the Langmuir and Langmuir-Freundlich isotherm models, while in the case of Cd(II) and Cr(VI), the curves of the three models agree with the experimental points. In order to find out the best adsorption isotherm model, we employed linearized equations, as have most published papers [46], despite the inherent bias created by linearization. The results obtained by applying the linearized Langmuir, Freundlich, and Langmuir-Freundlich equations are recorded in Table 1. The degree of agreement was assessed by comparing the determination coefficient (R^2) of each model and by applying the Akaike criterion (AIC), and the F test as R^2 is insufficient to perform the comparison of the models.

TABLE 1: Results obtained from the linearized Langmuir, Freundlich, and Langmuir-Freundlich isotherms.

Metal	Langmuir (L)		Freundlich (F)		Langmuir-Freundlich (L-F)			Akaike criterion*		F test*	
	q_{\max}	$q_c = q_{\max} b C_e / (1 + b C_e)$	R^2	K_F	$q_c = K_F C_e^{1/n}$	$q_e = q_{L-F} (K_{L-F} C_e)^{M_{L-F}} / (1 + (K_{L-F} C_e)^{M_{L-F}})$	R^2	R^2	AICC	L and L-F	F and L-F
	(mg g^{-1})	(L mg^{-1})			$\frac{1}{n}$	$q_{L-F} (\text{mg g}^{-1})$	K_{L-F}	M_{L-F}	AICC	$P < 0.05$	$P < 0.05$
Cu(II)	33.04 ± 0.75	0.26 ± 0.01	0.99	8.67 ± 0.05	0.27 ± 0.15	33.21 ± 0.08	0.25 ± 0.03	0.97 ± 0.04	$50.69(\text{F}) > 16.34(\text{L-F}) > 10.92(\text{L})$	$F = 0.12$ $P < 0.0001$	$F = 186.32$ $P < 0.0001$ L-F
Cd(II)	77.12 ± 0.41	0.007 ± 0.01	0.90	1.81 ± 0.75	0.61 ± 0.007	78.73 ± 0.06	0.009 ± 0.005	0.72 ± 0.07	$48.27(\text{F}) > 44.02(\text{L}) > 14.98(\text{L-F})$	$F = 104.22$ $P < 0.0001$ L-F	$F = 144.72$ $P < 0.0001$ L-F
Cr(VI)	57.36 ± 0.70	0.014 ± 0.004	0.96	3.21 ± 0.90	0.55 ± 0.10	56.31 ± 0.05	0.018 ± 0.007	0.79 ± 0.10	$32.86(\text{F}) > 29.14(\text{L-F}) > 28.53(\text{L})$	$F = 4.19$ $P = 0.0709$ L	$F = 133.19$ $P < 0.0001$ L-F
Pb(II)	108.05 ± 0.77	0.07 ± 0.02	0.8	17.75 ± 0.02	0.34 ± 0.09	100.01 ± 0.04	0.05 ± 0.03	0.71 ± 0.02	$72.04(\text{F}) > 63.58(\text{L}) > 58.31(\text{L-F})$	$F = 10.92$ $P = 0.008$ L-F	$F = 104.48$ $P < 0.0001$ L-F

*AICC: the lowest value corresponds to the best model. * F test: the null hypothesis is that the simpler model (Langmuir or Freundlich) is correct and alternative model L-F is better than L or F when $P < 0.05$.

TABLE 2: Comparison of the adsorption capacity of milled pine cone for Pb(II), Cu(II), Cd(II), and Cr(VI) with the other biosorbents.

Biosorbents	Metals	Particle size	pH	Concentration (mg L ⁻¹)	Dose (g L ⁻¹)	q_m (mg g ⁻¹)	References
Custard apple	Cd(II)	—	5	50-200	1.5	71	Isaac and Sivakumar [13]
	Pb(II)	—	5	5-200	1.5	90.93	
Ulva lactuca	Cr(VI)	≤0.063 mm	1	5-50	2	10.61	El-Sikaily et al. [48]
Olive stone	Cu(II)	<0.250-1 mm	5	10-300	10	1.97	Blázquez et al. [40]
Pine bark	Cu(II)	—	5	10-300	10	11.94	
Maize husk	Cu(II)	1.8 mm	6	—	—	1.21	Duru et al. [9]
Pine sawdust	Pb(II)	0.6-1.2 mm	5	1-50	10	13.48	Semerjian [49]
	Cu(II)		7	1-50	10	9.59	
Rice husk	Cd(II)	<0.125 mm	—	—	—	5.54	Jabbar et al. [12]
Pine cone	Cd(II)	—	7	20-200	2	14.7	Izanloo and Nasserri [50]
Pine cone	Cr(VI)	—	1	10-120	2	65.36	Najim and Yasin [37]
Pine cone	Cu(II)	—	5	50-250	3	18.69	Değirmen et al. [46]
	Pb(II)		7	50-250	3	23.2	
Pine cone	Cu(II)	4-8 mm	5	5-100	10	6.52	Martín-Lara et al. [29]
	Pb(II)		5	5-100	10	17.41	
Pine cone (<i>P. resinosa</i>)	Cu(II)	<0.15 mm	5	10-300	10	9.68	Awad and Erkurt [51]
	Pb(II)		5	10-300	10	17.24	
Olive stone	Pb(II)	—	6	1-10	5	0.581	Amar et al. [44]
	Cu(II)		6	1-10	5	0.557	
	Cd(II)		6	1-10	5	0.3	
	Cr(VI)		2	1-10	10	2.345	
Pine cone	Pb(II)	—	5.4	1-500	2	95	Present study
	Cu(II)		5.4	1-500	2	33.55	
	Cd(II)		5.4	1-500	2	50	
	Cr(VI)		2	1-500	2	68.03	

In the case of the Akaike criterion, the model for which corrected AIC (AICc) has the lowest value is selected as the best model [47]. The F test, based on traditional statistical hypothesis testing, compares the least-square regression fits of the linearized Langmuir or Freundlich equations with those of the linearized Langmuir-Freundlich model. As can be seen in Table 1, when the F test was used to compare Freundlich and Langmuir-Freundlich, the latter was the best model for all the metal ions; however, in comparing the Langmuir and Langmuir-Freundlich models, Langmuir was the selected model for Cr(VI) and Cu(II) and the Langmuir-Freundlich model for Pb(II) and Cd(II). These results are in agreement with those obtained by applying the Akaike criterion (Table 1).

The experimental data of Cu(II) fitted the Langmuir model with a maximum adsorption capacity of 33.04 mg g⁻¹. Consequently, this metal ion was adsorbed onto the surface of the pine cone, forming a monolayer, which provides a single site to attach each metal ion. A similar result was obtained by Blázquez et al. [27], who proposed a surface complexation model for the adsorption of Cu(II) by pine cone shell. The Langmuir model was also the best suited to describe the experimental data for Cr(VI) adsorption with a maximum adsorption capacity of 57.36 mg g⁻¹. In the case of Pb(II) and Cd(II), the best model is the Langmuir-Freundlich isotherm with maximum adsorption capacities of 100.01 and 78.73 mg g⁻¹, respectively. This model is suitable for predicting adsorption on heterogeneous surfaces, thereby avoiding the

limitation of increased adsorbate concentrations associated with the Freundlich model, but at a high concentration of adsorbate, it predicts the Langmuir model (monolayer adsorption); hence, the Langmuir-Freundlich isotherm is a concentration-dependent model.

The differences between the adsorption isotherm models for Cu(II) and Pb(II) can explain the differences in the metal removal percentages when the initial metal concentration was varied from 1 to 5 mg L⁻¹. As has been discussed earlier in the case of Cu(II), at these low initial concentrations, the metal uptake percentage remained constant (~94%), whereas for Pb(II), it increased from 73.5 to 94%.

As can be in Table 1, the values of the maximum adsorption capacities calculated from the Langmuir and Langmuir-Freundlich models are similar in the case of Cd(II) and Pb(II) and the same, considering the standard deviation, in the case of Cr(VI) and Cu(II). With regard to R^2 , the highest values correspond to the Langmuir model for Cu(II) and Cr(VI) and to the Langmuir-Freundlich model for Cd(II) and Pb(II). This statistic is in agreement with the results of the application of the Akaike criterion and F test to compare the Langmuir and Langmuir-Freundlich models for each metal ion.

Table 2 summarizes the comparison of the adsorption capacity of milled pine cones for Cu(II), Cd(II), Pb(II), and Cr(VI) with other nontreated biosorbents. It is seen in these results that the milled pine cone has the highest adsorption capacity for all metals. Pine cone was a more effective

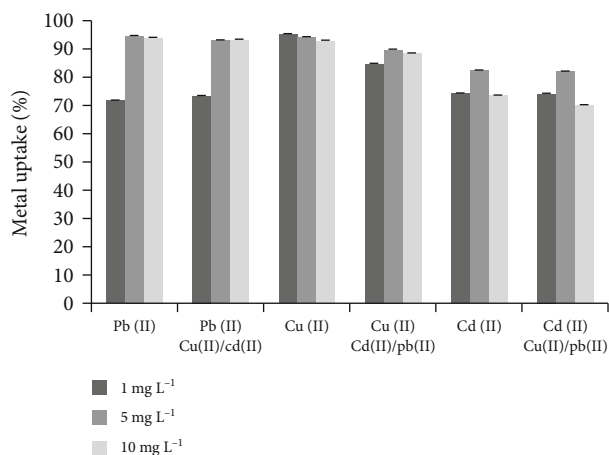


FIGURE 5: Comparison of the removal percentage of Pb(II), Cu(II), and Cd(II) between single metal and multimetal solutions at different initial concentrations: pH = 5.4, adsorbent concentration = 2 g L⁻¹, and $t = 2$ h ($n = 3$).

biosorbent for Pb(II) than custard apple [13], *Ulva lactuca* [45], and olive stones [41]. Moreover, milled pine cone presents a higher adsorption capacity for Cd(II) and Cr(VI) than that obtained by rice husk [12, 36] and olive stones [44]. In the case of Cu(II), pine cone is also more efficient than maize husk [9] and olive stones [40]. Therefore, milled pine cone has been demonstrated to be more efficient than milled olive stone in the removal of Pb(II), Cu(II), Cd(II), and Cr(VI). However, the maximum adsorption capacities for these ions differ depending on the experimental conditions used (initial metal concentrations, particle size, dosage of adsorbent, and pH and the type of pine biomass: pine bark or pine cone, *Pinus halepensis*, or *Pinus resinosa*).

3.4. Competition between Cu(II), Pb(II), and Cd(II). The competition of different metals to occupy the binding sites of the adsorbent was investigated using three multimetal solutions containing Pb(II), Cd(II), and Cu(II) at different initial concentrations of 1 mg L⁻¹, 5 mg L⁻¹, and 10 mg L⁻¹ at pH 5.4 using 2 g L⁻¹ of adsorbent for 2 h. Figure 5 compares the adsorption efficiency of milled pine cones towards a solution containing a single metal ion and three metal ions. In the case of Pb(II), the removal percentage increased from 71.6% to 94% when the initial concentration was increased from 1 to 5 mg L⁻¹, and the same results were obtained when Cu(II) and Cd(II) were present at the same concentration levels, showing that the presence of these metal ions did not affect Pb(II) removal. A similar trend was observed in the case of Cd(II), whose removal percentages were the same for both the single and multimetal solutions, except in the case of the highest concentration (10 mg L⁻¹). Cu(II) was the only metal ion affected by the competition with the other ones, and its removal percentage decreased by around 10% in the presence of Pb(II) and Cd(II) at all the concentrations tested, confirming the higher affinity of pine cone by Pb(II). The biosorption of the binary Cu(II)–Pb(II) system by pine cone was investigated in a batch reactor and in a fixed-bed column. The results obtained in both operational modes confirmed a

slight suppression of copper biosorption due to the presence of lead when both metal ions are present in the solution [29]. Recently, a review on the dominance of Pb during competitive biosorption from multimetal systems has concluded that most biosorbents can effectively remove Pb(II) even in the presence of other heavy metals, but the adsorption of Cu(II), Cd(II), Zn(II), Ni(II), and Cr(III) decreases significantly due to the presence of Pb(II) [52].

4. Conclusions

In this study, milled pine cone was used to remove metal ions such as Pb(II), Cu(II), Cd(II), and Cr(VI). The effect of different parameters such as the contact time, pH, amount of adsorbent, and initial metal concentration on the removal efficiency was studied. Milled pine cone is seen to be an effective biosorbent for the removal of divalent metal ions due to the high affinity of these ions for the carboxylic and hydroxyl groups, which are present on the adsorbent surface, as well as for its availability and low cost. The efficiency of milled pine cone to remove trace concentration levels of Pb(II), Cd(II), and Cu(II) has been demonstrated, resulting in capacities of 100.01 mg g⁻¹, 78.73 mg g⁻¹, and 33.04 mg g⁻¹ at pH 5.5, respectively. These capacities are higher than those reported for other biosorbents with similar characteristics. Moreover, an adsorption capacity of 57.36 mg g⁻¹ was obtained for Cr(VI) at pH 2, and its maximum removal percentage (88.8%) was obtained at pH 2 with 10 g L⁻¹, showing that this toxic anion can be removed via an ion-exchange mechanism. The experimental adsorption data correlated well with the Langmuir model for Cu(II) and Cr(VI), whereas for Pb(II) and Cd(II), the best correlations were obtained with the Langmuir-Freundlich model. In the case of the divalent ions (Pb(II), Cu(II), and Cd(II)), there is no competition between them towards the adsorbent sites at low metal concentration levels (1–10 mg L⁻¹), given that the presence of other metal ions did not reduce the removal efficiencies.

The prolific production of pine cones around the Mediterranean rim results in the abundant availability of waste residue that can be successfully valorised for the creation of the environmentally valuable process developed in this study to remove heavy metals from industrial effluents such as the highly toxic multimetal-containing wastewaters released by electroplating industries.

Data Availability

The data that support the findings of this study are available from the corresponding author (VS) upon reasonable request.

Conflicts of Interest

The authors do not declare any conflict of interest.

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