



Vegetable lignocellulosic wastes used as biosorbent for removal of Cu(II) from aqueous media

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ABSTRACT

The use of plant waste as a biosorbent to retain chemical contaminants in wastewater is one of many approaches to plant waste recovery produced by various industries. In this context, we set out to examine the biosorption capability of some vegetable waste that was produced during the liquid–solid extraction process used to get plant extracts (used later as biopesticides) from plants like *Primula veris*, *Achillea millefolium*, *Origanum vulgare*, and *Artemisia absinthium*. This type of biosorbent was used for the biosorption of Cu(II) ions from aqueous solutions in a batch system. In order to assess their biosorptive properties, the influence of certain physical parameters such as: temperature, solution pH, amount of biosorbent, metal ion concentration, and phase contact time were investigated. The experimental data were processed on the basis of Freundlich, Langmuir and Dubinin–Radushkevich adsorption isotherm models, and the obtained results underline that the equilibrium data were best fitted by Langmuir I isotherm with a biosorption capacity of about 24.271 mg/g at 22°C.

Keywords: Aqueous medium; Biovegetal wastes; Metal ions; Biosorption

1. Introduction

With the quick growth of some industries, such as metal corrosion protection facilities, the mining industry, the mineral fertilizer and pesticide industry, tanneries, batteries, paper and pulp industry, etc., the amount of wastewater that is released into the environment directly or indirectly has increased as well. Wastewater commonly contains high concentrations of the ions zinc, copper, nickel, mercury, cadmium, lead, and chromium; these ions entering the ecosystem through soil and watercourses and eventually accumulating along the food chain [1,2].

In contrast to organic contaminants, heavy metals are not biodegradable and have a tendency to accumulate in

living things. Even at low concentrations, they can cause serious ailments like cancer, damage to the nervous system, and kidney failure, and excessive amounts can be lethal. Copper is a micronutrient that, together with a few proteins and enzymes, is essential for building bones, but in excess, it can be quite detrimental. Due to their involvement in numerous biological processes, copper(II) ions are crucial for biocenosis. Freshwater animals' osmo-regulatory systems are harmed by too many Cu(II) ions in aquatic ecosystems and freshwater resources [3,4]. Copper is also a phytotoxic substance that is employed as an algicide to prevent algal blooms.

Additionally, food can include contaminants like copper, particularly in crustaceans, liver, mushrooms, almonds, and chocolate. The human body experiences significant

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mucosal irritation, corrosion, capillary damage, gastrointestinal irritation, central nervous system irritation, and possibly necrotic changes in the liver and kidneys when copper ions are ingested in excess [5].

Numerous methods, including chemical precipitation, ion exchange, adsorption, membrane filtration, coagulation–flocculation, flotation, and electrochemical technologies, have been studied and applied over time for the removal of copper ions [6–10]. The purpose of wastewater treatment is to remove or concentrate the ions present in the wastewater in the same or separate phases. These methods were chosen because they offered advantages including high selective separation, simplicity of control, and the need for small spaces. High operational costs, high energy consumption, and high chemical prices, however, continue to be a limitation of these methods [11].

Chemical precipitation is a widely used method that can be used for both the precipitation of hydroxide and sulfides. It is a simple procedure with low operational costs. Sulfide precipitation has the advantage that its solubility is lower than that of copper hydroxide [12]. For a wide range of copper concentrations, 50–1,000 mg/L, chelating precipitants have been explored and developed due to the drawbacks of hydroxide/sulphide precipitation procedures [13]. Among these, potassium ethylxanthate stands out [14]. Another technology used is the ion exchange procedure, which has a huge treatment capacity, a high efficiency, and rapid kinetics. To nearly completely remove all heavy metals from solution, synthetic resins are commonly chosen among the materials employed in ion exchange procedures [15,16]. Copper ions in aqueous solution go through spontaneous electrochemical reduction at the interface in a heterogeneous process known as cementation, which results in the metallic copper state [3]. Cementing copper with an iron item produces metallic copper deposits that may be used in metallurgical operations, making it the simplest and most logical method of recovering copper [17]. The increased metal consumption of the method is its main disadvantage [11]. Membrane filtration has recently been intensively investigated for treating copper-contaminated industrial wastewater. Membrane filtration is particularly effective for solid organic and inorganic compounds in suspension [18,19]. However, membrane filter technology needs to be improved to limit energy consumption and thermodynamic working conditions. Electrocoagulation, electrofluorination, and electrooxidation are the three electrochemical processes that are most frequently employed to remove heavy metal ions from solutions [20–22]. The type of cell and electrode employed have been observed to have an impact on the effectiveness of metal removal [23]. Electrochemical wastewater systems have not been widely used because they require a significant upfront investment and a costly electrical supply. However, over the past two decades, electrochemical technologies have become more significant globally due to environmental rules surrounding wastewater disposal [11,12].

To remove copper ions and other metal ions from industrial effluent, the adsorption technique is still often utilized [2,24–28]. It also has a number of benefits due to its simple design and low initial cost in comparison to other treatment options [29]. Numerous low-cost adsorbents have been developed as a result of the removal of copper ions

from contaminated wastewater. Natural materials, modified biopolymers, biological waste, residual industrial materials, and nanomaterials were all used to create these adsorbents [30–35].

In order to provide access to clean water, new environmentally friendly and inexpensive solutions must currently be developed. The development of biomaterials with the ability to adsorb harmful substances is one of the many strategies for recovering contaminants from wastewater. Due to their availability and high cellulose content, biosorbents are among the most sustainable solutions for treating water, prompting a boom in research in recent years.

Due to their high biodegradability, fruit and vegetable wastes generated in large amounts by the food industry and agriculture industries frequently create annoyance in municipal landfills [36]. They mostly consist of lignocellulosic polymers that are found in nature. Toxic heavy metals and organic contaminants can be removed from wastewater using biosorption by these waste-based biosorbents in an economical and effective manner [37–39]. The biosorbents made from organic waste are considered to be both economically and environmentally viable decontamination solutions due to their high absorption capacity, quick kinetics and availability.

Our current study was set out to test the biosorption potential of plant waste resulting from liquid–solid extraction (using 96% ethanol – extracts used as biopesticides) from plants such as: *Primula veris*, *Achillea millefolium*, *Origanum vulgare* and *Artemisia absinthium*. This was accomplished by first characterizing the vegetal wastes physically before introducing them as a biosorbent in the process of removing Cu(II) ions from aqueous media. The biosorption process was researched in a batch system, and the effects of various physical factors on the procedure were observed. The biosorption equilibrium was tested at three temperatures (5°, 22°, and 50°C) once the optimum experimental conditions have been identified. The data were processed using the Langmuir, Freundlich, and Dubinin–Radushkevich models from the literature.

2. Materials and methods

2.1. Materials

2.1.1. Biosorbent

The material used as biosorbent is represented by a mixture of vegetal waste (*Primula veris*, *Origanum vulgare*, *Artemisia absinthium*, *Achillea millefolium*) resulting from the process of obtaining plant extracts with biopesticidal potential, through different liquid–solid extraction variants, where the extractant was 96% ethyl alcohol [40–42].

2.1.2. Adsorbate

Cu(II) was selected as an emerging chemical pollutant of aqueous environments. $\text{CuSO}_4 \cdot x\text{H}_2\text{O}$ salt (MW = 159.609) was dissolved in double-distilled water to prepare a stock solution with a concentration of 635.76 mg of CuSO_4/L . The working solutions, with the established concentration, were obtained by the corresponding dilution of the stock solution.

2.2. Biosorption methodology

All the biosorption experiments were performed in triplicate by batch techniques. The amount of 0.075 g (3 g/L) biosorbent was contacted with metal ion solutions with an initial concentration in the range 25.43–203.44 mg/L in 50 mL Erlenmeyer flasks. The desired pH values of the solutions were achieved using a 1 N H₂SO₄ solution. Equilibrium studies were performed at established temperatures 5°, 22°, and 50°C using thermostated systems, applying intermittent agitation on the studied system. After reaching the equilibrium times, the metallic ions concentration in solution was spectrophotometrically determined using a Shimadzu UV-1280 UV-VIS Spectrophotometer (Shimadzu Corporation, Kyoto, Japan). Determination of equilibrium concentrations were performed at the maximum wavelength ($\lambda = 378$ nm) of the complex formed by Cu ions with 0.05% rubenic acid in acetate buffer (pH = 4.6) solution.

The biosorption capacity (q , mg of Cu(II)/g of biosorbent) was calculated using Eq. (1) and the removal percent (R , %) with Eq. (2).

$$q = \frac{C_0 - C}{G} \times V \quad (1)$$

$$R\% = \left[\frac{(C_0 - C)}{C_0} \right] \times 100 \quad (2)$$

where C_0 and C are the initial and the equilibrium (residual) concentration of Cu(II) ions in solution (mg/L), G is the amount of vegetal waste powder (g) and V is the volume of initial Cu(II) ions solution (L).

The equilibrium data were analyzed using three of the most known adsorption equilibrium models: Freundlich (3) with their linearized Eq. (4); Langmuir [Eq. (5)] with their two linearized forms of Eq. (6) and Dubinin–Radushkevich [Eqs. (7) and (8)] [43,44], and are presented:

- Freundlich

$$q = K_F \times C^{1/n} \quad (3)$$

$$\log q = \log K_F + \frac{1}{n} \log C \quad (4)$$

where K_F and $1/n$ – constants related to the adsorption capacity and intensity (efficiency), respectively; a favorable adsorption corresponds to a value of $1 < n < 10$.

- Langmuir

$$q = \frac{K_L \times C \times q_0}{1 + K_L C} \quad (5)$$

$$L1: \frac{1}{q} = \frac{1}{q_0} + \frac{1}{K_L \times q_0} \frac{1}{C}; \quad L2: \frac{C}{q} = \frac{1}{q_0 \times K_L} + \frac{C}{q_0} \quad (6)$$

where q_0 is the maximum amount of adsorbed solute (mg/g) and K_L is the constant related to the binding energy of adsorbate (L/mg).

- Dubinin–Radushkevich

$$q = q_0 \exp(-B \times \varepsilon^2); \quad \ln q = \ln q_0 - B\varepsilon^2 \quad (7)$$

$$\varepsilon = RT \ln \left(1 + \frac{1}{C} \right); \quad E = \frac{1}{\sqrt{2B}} \quad (8)$$

where q_0 is the maximum adsorption capacity (mg/g); B is the activity coefficient related to mean adsorption energy; ε is the Polanyi potential; E is the mean free energy of adsorption (kJ/mol).

2.3. Thermodynamic of biosorption process

For the studied biosorption process, the thermodynamic parameters were calculated using the Langmuir equilibrium constant and Eqs. (9) and (10) [44,45]:

$$\Delta G = -RT \ln K_L \quad (9)$$

$$\ln K_L = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (10)$$

where ΔG° is the free energy (kJ/mol), ΔH° – the enthalpy (kJ/mol), ΔS° – the entropy changes (kJ/mol·K), R – the universal gas constant (8.314 J/mol·K), T – the absolute temperature (K), K_L is the value of Langmuir constant (L/mol).

2.4. Analytical methods for physico-chemical characterization

Fourier-transform infrared spectroscopy (FTIR) was applied for the lignocellulosic vegetal material studied and for the biosorbent loaded with ionic metal of Cu(II). A Digilab FTS-2000 FTIR spectrophotometer was used to record the FTIR spectra in duplicate, in the 400–4,000 cm⁻¹ range according to KBr pellet method.

3. Results and discussion

3.1. Preparation of vegetal waste and their physical–chemical characterization

The used vegetal waste material is represented by Yarrow (*Achillea millefolium*), Wormwood (*Artemisia absinthium*), Oregano (*Origanum vulgare*) and Primrose (*Primula veris*) plants collected from Tomesti (Iasi, Romania) location results from a liquid–solid extraction process with 96% ethyl alcohol. After extraction, the plant material was washed with ethyl alcohol, dried and kept in closed containers in cool and dark places until use. The characterization of vegetable waste was done according to a protocol presented in our previous work [47], followed the determination humidity, ash, holocellulose, lignin and cellulose content in accordance with the ASTM standard [48], and the results obtained are systematized in Table 1.

3.2. Characterization of biosorbent before and after Cu(II) ions biosorption

The FTIR spectrum of vegetal wastes (Fig. 1, black line) evidenced numerous peaks allocated to different functional

groups, some which are able to interact with copper ions species. For both of the spectra the main absorption bands may be allocated as follows: the ~3,420 cm⁻¹ results from O–H stretch in both alcoholic and phenolic components. The ~2,920 and ~2,850 cm⁻¹ result from the presence of methyl and methylene moieties. The presence of the ~1,730 cm⁻¹ is assigned to C=O stretch in saturated aldehydes with possible overlapping of C=O in esters and acids groups. The water present in samples as moisture is evidenced by the peak at 1,649 cm⁻¹ overlapping with the presence ketones and carboxyl groups. The presence of the aromatic rings (band at 1,510 cm⁻¹) is visible only in the blue spectrum. The ~1,375 cm⁻¹ was assigned to O–H bending. The absorption bands between 1,150 and 1,350 cm⁻¹ and 1,000 and 1,260 cm⁻¹ are to be assigned to C–O vibrations in acyl moieties (ethers) and to alkoxy moieties, respectively.

3.3. Effect of the some physical–chemical operating parameters on Cu(II) ions biosorption

The biosorption process of Cu(II) ions on studied biosorbents is influenced by some physical parameters, such as [48]: pH 1.5–5.0 (adjusted with 1 N H₂SO₄ solution), the biosorbent dose 0.2–2.0 g/L, temperature 5°C, 22°C, and 50°C and the initial Cu(II) ions concentration in the aqueous solution (25.824–206.59 mg/L). The study of their influence finally allows establishing the optimal conditions for obtaining the highest possible biosorption capacity.

The analysis of experimental data from Fig. 2 corroborated with previous conclusions [48] leads to the following observations: the maximum biosorption capacity is achieved in a strong acidic environment (pH = 2). The increase of the

biosorbent amount has a negative impact on the biosorption process, while the temperature raises and increasing the initial concentration of Cu(II) ions solution are increasing the process efficiency, based on remove percentage, R.

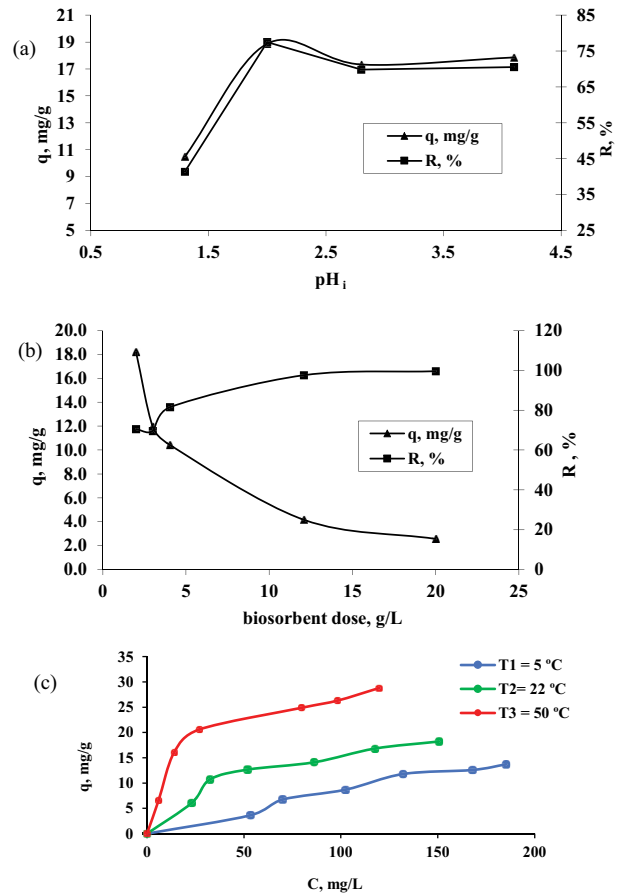


Fig. 2. Physical operating parameters influencing the Cu(II) ions biosorption onto vegetal waste: (a) the influence of pH (C₀ = 127.152 mg/L; 0.4 g/L biosorbent dose; T = 22°C), (b) the influence of biosorbent dose (C₀ = 105.96 mg/L; pH = 4.5; T = 22°C) and (c) the influence of temperature and initial concentration of Cu(II) ions solution (pH = 2; 0.4 g/L biosorbent dose).

Table 1
Physical–chemical characterization of vegetal waste

Humidity of raw material, %	9.124
Ash, %	8.94
Holocellulose, %	51.26
Lignin, %	24.49
Cellulose, %	29.7

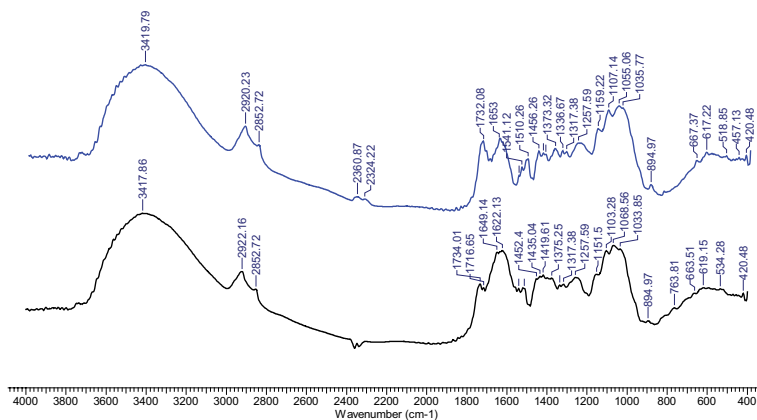


Fig. 1. FTIR spectra of vegetal wastes before (black line) and after Cu(II) ions (blue line) biosorption.

3.4. Study of biosorption equilibrium

The amount of metal ions retained by the biosorbent unit (q , mg/g) depending on the concentration of metal ions at equilibrium in the liquid phase (C , mg/L) represents the biosorption isotherm and is represented graphically in Fig. 2C. These isotherms could be described and modeled by a lot of isotherm models in order to evaluate the quantitative characteristic parameters and to acquire preliminary information about the involved mechanism.

The graphic representation of the linearized equations of the studied models (Fig. 3) allowed the calculation of the characteristic quantitative parameters for each selected adsorption model (Freundlich, Langmuir I and II and Dubinin–Radushkevich), these being systematized in Table 2. To establish which model describes to better study the biosorption process, the values of the correlation coefficients, R^2 , were used.

The following conclusions may be drawn after analyzing the information in Table 2:

- The values of Freundlich parameters, K_F and n increase with temperature increment, showing that the biosorption process could be favorable at relative high temperature;
- The values of the correlation coefficients (R^2) higher than 0.99 show that the Langmuir model was more suitable to describe the biosorption process. Taking into account the values of the correlation coefficient R^2 at all

three temperatures, model II ($1/g = f(1/C)$) is more suitable than model I for describing the studied biosorption process.

- The values for the maximal biosorption capacity from the Langmuir II model (q_0 , mg/g) rise as the temperature rises, indicating that the biosorption process may be endothermic and is aided by rather high temperatures.
- The mean free biosorption energy, E , obtained using Dubinin–Radushkevich equation, can be used for a preliminary estimation of the biosorption process mechanism (physical or chemical) [49]. The obtained values in range (5.892–11.323) kJ/mol indicate a potential physical mechanism involved in Cu(II) ions biosorption onto biosorbent based on vegetal wastes.
- The values of the biosorption capacity in the Dubinin–Radushkevich equation, q_0 (represents the total specific meso- and macropore volume of the biosorbent, mg/g), are higher than q_0 value resulted from Langmuir II isotherm model, for all three temperatures. The explanation would be that in the case of the Dubinin–Radushkevich equation, the porous structure of the biosorbent was taken into account when calculating the capacity.

The value obtained for the biosorption capacity (at 22°C) was compared with other values obtained on lignocellulosic biosorbents studies (Table 3).

The data presented in Table 3 show that the plant material studied – plant waste resulting from a liquid–solid

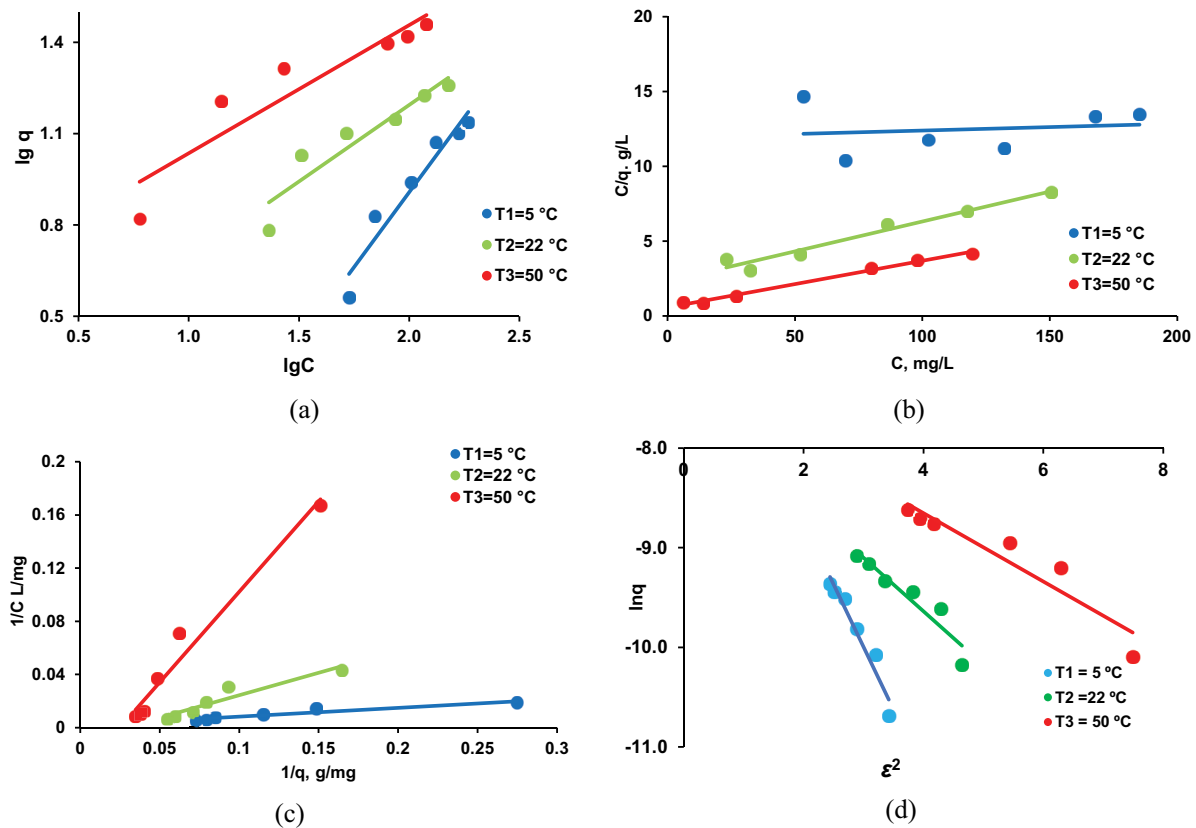


Fig. 3. Linearized form of Freundlich (a), Langmuir I (b), Langmuir II (c), and Dubinin–Radushkevich (d) plots for the Cu(II) ions biosorption on vegetal waste. Conditions: pH = 2.0; contact time = 24 h; biosorbent dose = 0.4 g/L.

Table 2
Characteristic parameters for the Cu(II) ions biosorption on vegetal waste

Isotherms	Temperatures		
	$T_1 = 5^\circ\text{C}$	$T_2 = 22^\circ\text{C}$	$T_3 = 50^\circ\text{C}$
Freundlich			
K_f	9.493e-5	1.544	4.115
n	1.017	1.988	1.627
R^2	0.9322	0.8789	0.8635
Langmuir I, $C = f(C/q)$			
K_L , L/mg	0.0544	0.01736	0.00312
q , mg/g	32.051	25.00	37.594
R^2	0.9907	0.9596	0.8511
Langmuir II, $1/q = f(1/c)$			
K_L , L/mg	0.003	0.0315	0.0369
q , mg/g	38.61	20.79	38.168
R^2	0.9821	0.95	0.9668
Dubinin–Radushkevich			
B	0.0144	0.0069	0.0039
q_D , mg/g	201.179	71.70	91.103
E , kJ/mol	5.892	8.512	11.323
R^2	0.9424	0.8937	0.8933

extraction process, can be considered a promising biosorbent for the retention of metal ions. Also, given its low cost and availability, a series of industrially deficient metal ions can be easily recovered either by elution with appropriate solvents or by controlled incineration of plant material.

4. Conclusions

The results of this research reveal that the residual biomass, a mixture of vegetable waste (*Primula veris*, *Origanum vulgare*, *Artemisia absinthium* and *Achillea millefolium*) resulted from the biopesticide manufacturing, through different liquid–solid extraction techniques, using as an extraction agent 96% ethyl alcohol, could be taken into consideration as a potential biosorbent for the removal of Cu(II) ions from synthetic aqueous solutions.

Equilibrium biosorption data were analyzed by the Freundlich, Langmuir, and Dubinin–Radushkevich isotherm adsorption models and were better described by the Langmuir I model. The main values obtained are the biosorption capacity of about 20.79 mg/g at 22°C and the biosorption free energy (E , kJ/mol) with values ranging from 5.892 to 11.323 kJ/mol, This indicates the possibility of a functional mechanism for the biosorption of Cu(II) ions to plant waste.

The results obtained in this work indicate a potential new direction for the valorization of vegetable waste resulting from extraction processes of some active principles.

Table 3
Values of biosorption capacity of Cu(II) obtained on lignocellulosic biosorbents

Biosorbent	Pollutant	Biosorption capacity, mg/g	References
Pretreated rice straw and rice husk	Cu(II)	Rice husk – Cu(II): 8.89	[50]
	Cd(II)	Rice husk – Cd(II): 1.58 Rice straw – Cu(II): 12.22 Rice straw – Cd(II): 9.09	
Olive pomace and walnut shell	Cu(II)	Walnut shell: 8.3 Olive pomace: 12.9	[51]
Sawdust	Cu(II)	71.20	[52]
Newspaper pulp	Cu(II)	10.94	[53]
Teak (<i>Tectona grandis</i> L.f) leaves	Cu(II)	166.71	[54]
Spent coffee ground	Cu(II)	0.214 mmol/g	[55]
	Cu(II)	Olive stone – Cu(II): 1.34	[56]
Olive stone and pine bark		Olive stone – Pb(II): 2.12	
		Pine bark – Cu(II): 6.05	
		Pine bark – Pb(II): 10.04	
Almond shells	Cu(II)	9.44	[57]
Sour orange residue	Cu(II)	52.08	[58]
Dehydrated wheat bran	Cu(II)	51.51	[59]
	Zn(II)	Zn(II): 7.58	[60]
Tree fern	Cu(II)	Cu(II): 10.6	
	Pb(II)	Pb(II): 39.8	
Papaya wood	Cu(II)	Cu(II): 19.88	[61]
	Cd(II)	Cd(II): 17.22	
	Zn(II)	Zn(II): 13.45	
Vegetal wastes	Cu(II)	20.79	This study

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