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Applying circular economy principles and life cycle assessment: A novel approach using vine shoots waste for cadmium removal from water

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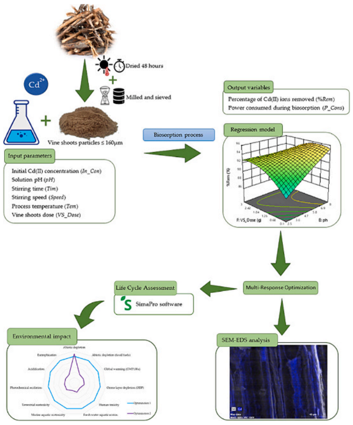
HIGHLIGHTS

- Valorization of vine shoots waste as a biosorbent for efficient Cd(II) removal
- The environmental impacts of the biosorption process were evaluated by Life Cycle Assessment.
- Effects of initial Cd(II) concentration, pH, biosorbent dose, temperature, and stirring time and speed were studied.
- The vine shoots biowaste exhibited a high adsorption performance.

GRAPHICAL ABSTRACT



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ABSTRACT

This research investigates the potential of utilizing vine shoots, a byproduct of the viticulture industry, as biosorbent for cadmium removal from aqueous solutions. The Spanish wine industry, one of the most influential sectors, produces two to three million tons of vine shoots. By using vine shoots as biosorbent, this study contributes to the circular economy paradigm, transforming waste materials into valuable resources and minimizing environmental impacts associated with waste generation and disposal. The research underscores the significance of vine shoots in biosorption due to its high lignocellulosic content. By experimental analysis, the efficacy of vine shoots in cadmium biosorption is evaluated, considering factors such as environmental impact or energy consumption. This study examines the effect of six key input parameters on cadmium removal efficiency and power consumption, identifying optimal conditions for maximum removal with minimal energy consumption. The findings suggest that vine shoots offer promising biosorption capabilities, promoting sustainability in wastewater treatment and environmental remediation efforts. By employing the response surface method alongside desirability functions, the study determined the optimal variables for two distinct optimization scenarios. Notably, in

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the second optimization scenario, a cadmium removal rate of 99.23 % was achieved while consuming 25.6 W of power. The input parameters for this achievement should be set as follows: initial cadmium concentration of 100 ppm, pH level of 8, stirring time of 75 min, stirring speed of 100 rpm, temperature of 26 °C, and a dose of vine shoots of 0.1 g.

1. Introduction

The growing development of industry has significantly increased material consumption and wastewater disposal (Chin et al., 2022). Climate change has underlined the need for humankind to adopt sustainable development. Instead of continuing to be use existing resources in a linear economy, they must be employed in a circular economy. Reducing the demand for natural resources and the waste generation while extending the useful life of resources and commodities is the goal of a circular economy. A modern, resource-efficient, and competitive economy is what the European Green Deal (EGD) seeks to achieve through economic transformation. One of the key components of the EGD is the new circular economy action plan (CEAP). Furthermore, it is necessary to stop the loss of biodiversity and meet the EU's 2050 climate neutrality goal. The efforts announced in the CEAP span the entire product life cycle. It focuses on product design, supports circular economy procedures, stimulates sustainable consumption, and seeks to guarantee that waste is avoided, and resources are used for as long as feasible within the EU economy. Using wastes more circularly is an essential tactic to drastically lessen the environmental impact of human economic activity, especially on biodiversity. Thus, the waste management industry holds a special position in the circular economy as a necessary tool for achieving these challenging climate goals (Kacprzak and Sobik-Szołtysek, 2022).

According to the IPCC's Sixth Assessment Report, the most important sources of influence on climate change are agriculture, followed by the production and use of fossil fuels (Mikulčić et al., 2022). The wine industry is one of the most influential sectors, devoting a significant amount of productive land to the agricultural sector. According to "Datos INFOVI año 2022" (n.d.), Spain is the country that has the largest vineyard area in the world, with approximately 930,080 ha of vineyards in 2022 (approximately 13 % of the world's total). Furthermore, it is the world's third largest wine producer with a production of >35 million hl in 2022. The Spanish wine industry produces two to three million tons of residues or by-products yearly, primarily during the harvest season. Vine shoots constitute the wine industry's most abundant agricultural byproduct, with a high lignocellulosic content. Vine shoots have traditionally been burnt or crushed in the vineyard for use as fertilizer due to the high expense of managing such a plentiful and low-density waste (Benito-González et al., 2020). However, burning practices generate a high carbon footprint and greenhouse gas emissions that the EGD aims to reduce. In this scenario, methods to increase the value of vine shoots are presently under investigation.

The survival and well-being of humankind depend on water. To preserve the social and economic benefits of access to high-quality water resources, the sustainability of water systems must be ensured. To achieve this, the EGD addresses the matter of protecting the environment and oceans by proposing a series of priorities. These include: (i) protecting biodiversity and ecosystems, (ii) reducing air, water, and soil pollution, (iii) transitioning to a circular economy, and (iv) improving waste management. The emission of different heavy metals into natural ecosystems has grown due to the ongoing expansion of industrial and human activities. The discharge of heavy metals into aqueous media represents a significant problem because of their toxic, non-biodegradable and bioaccumulative nature. Therefore, before releasing this effluent into the environment, it is essential to remove the dangerous metals that have contaminated it. All waste management initiatives must adhere to the following priority sequence, as mandated by European legislation: prevention, reuse, recycling, other recovery, and disposal (Zhou et al., 2020). Following the implementation of these measures, there should be a reduction in the amount of heavy metals discharged into the environment. This, in turn, should reduce the concentration of metals in surface water. Among heavy metals, cadmium (Cd(II)) is a very hazardous metal with water solubility. It is one of the most dangerous pollutants that can be found in naturally contaminated water sources (Tiwari et al., 2023). The main sources of Cd(II) contaminated wastewater are industrial discharges related to pigments, industrial fertilizers, mining activities, waste incineration, alkaline batteries, insecticides, ceramics, combustion of certain coals and oils, pesticides, and electroplating and metal plating (Kwikima et al., 2021), insecticides, or plastic and paper industry (Tran et al., 2017). Cadmium endangers the aquatic habitat and has an impact on irrigation and water intake downstream when released into water. It is possible for Cd(II) to enter crops when agricultural land is irrigated with water that contains it. Furthermore, cadmium reaches the human body through the food chain. Cadmium may interfere with calcium interactions even at low levels of exposure, resulting in bone degeneration and a greater risk of fractures (Kim et al., 2019). The adverse effects of prolonged exposure to cadmium may include reproductive issues and damage to essential organs, such as the kidneys, liver, and lungs (Suhani et al., 2021).

Consequently, heavy metal contamination of water supplies and the high expense of treating it pose particular problems for developing nations. Contamination of water bodies is a result of the ongoing quest for less expensive options that use natural resources and can cut the expense of water treatment. However, because the heavy metals cannot be reduced by traditional biological wastewater treatment, treating industrial wastewater containing heavy metal ions is a significant technological and financial problem. Some of the treatments to remove heavy metals efficiently from wastewater are chemical precipitation, ion exchange, coagulation/flotation, membrane filtration, and adsorption. These techniques have a number of serious drawbacks. They include high energy, operational cost and chemical needs, high volume of toxic sludge generation, and limited effectiveness at low initial concentrations of heavy metals creating problems of treatment and disposal (Chai et al., 2021). In addition to these methods, adsorption is a broad physiochemical phenomenon in which an adsorbent, or solid material, is used to draw other particles, such as atoms, ions, and molecules, to its surface primarily by the properties of adhesion, electrostatic attraction, and ion exchange. Due to its cheap operating costs and great efficacy in removing heavy metal ions from water effluents, bioremediation, also known as biosorption of heavy metals, has become increasingly common in the process of treating wastewater. As a result, it is employed in remediation processes to bind all contaminants to the adsorbent's surface and cleanse the sample being placed. Adsorbents can be classified as follows: microbial, lignocellulosic, waste biomass, industrial waste, and more sophisticated types, such as metal organic frames, hybrid adsorbents, and nano-adsorbents (Kumar et al., 2021). Waste from agriculture activity is a plentiful renewable resource that is produced from many plant components, including bark, stem, leaves, fruit biomass, shell, and stone, such as olive stone (Corral Bobadilla et al., 2020). They have attracted attention in the production of adsorbents as substitutes for commercial activated carbon because of their biological and chemical characteristics, as well as their low operating cost. These aspects encourage the use of adsorbents to solve the enduring environmental problems successfully and sustainably. A large number of hydroxyl groups may be found in the primary components of agricultural waste, cellulose, hemicellulose, and lignin (Othmani et al., 2022). They can attach to heavy metals with high effectiveness. These results lend credibility to the use of cellulose as a biosorbent. Vine shoots have a high lignocellulosic content which makes them a potentially useful source of cellulose. Consequently, this study intends to resolve both problems (removing heavy metals from wastewater and lowering the environmental impact of improper disposal of vineyard residues). It will do this by optimizing the use of vine shoots as biosorbent agents for cadmium removal from industrial wastewater. Other authors have studied the removal efficiency of other heavy metals, such as lead (Sabando-Fraile et al., 2023) or lead and copper (Çiftçi et al., 2023), using activated carbon from vine shoots. However, there is currently no reference in which raw vine shoot material is used for the removal of heavy metals.

Another challenge is to evaluate the life cycle assessment of this cadmium biosorption process that uses vine shoots. Throughout a product's useful life, Life Cycle Assessment (LCA) can be used to quantify emissions, raw material and power consumption, waste generation, and their effects (Moni et al., 2020). The entire environmental effect of wastewater treatment methods and infrastructure may be thoroughly evaluated using LCA. It includes indirect emissions from the manufacturing and delivery of all chemicals, energy, and infrastructure needed for treatment, as well as direct emissions from wastewater treatment plants. This makes it possible to evaluate the costs and environmental advantages of removing contaminants in order to adhere to tougher laws (Rahman et al., 2018). Several studies have investigated the LCA in cadmium removal from aqueous solutions. For example, Nishikawa et al. (2018) analyzed the environmental impact of using alginate extraction waste for Cd(II) biosorption and compared them to those of commercial activated carbon. Choudhary et al. (2023) evaluated the possible environmental impact of electrocoagulation for the simultaneous removal of chromium, cadmium, and lead. Although LCA has been used to assist in the design and selection of the wastewater treatment process, little is known about the environmental effects of the biosorption process for the removal of Cd(II) from wastewater. Moreover, studies of the life cycle and environmental effects of cadmium biosorption using vine shoots have not been conducted specifically.

The experimental framework for this cadmium biosorption investigation utilizing vine shoots integrates the Box-Behnken Design (BBD) method. Furthermore, the Response Surface Methodology (RSM) is applied to align the model equation with empirical data and generate response plots. RSM is a strong statistical mathematical technique that may be used to create regression models, enhance process efficiency, reduce the number of variables, and lower the time and cost for experiments (Myers et al., 2016). To enhance the efficiency of the process, the following input variables are identified for optimization: initial cadmium concentration (*In_Con*), vine shoot dose (*VS_Dose*), solution pH

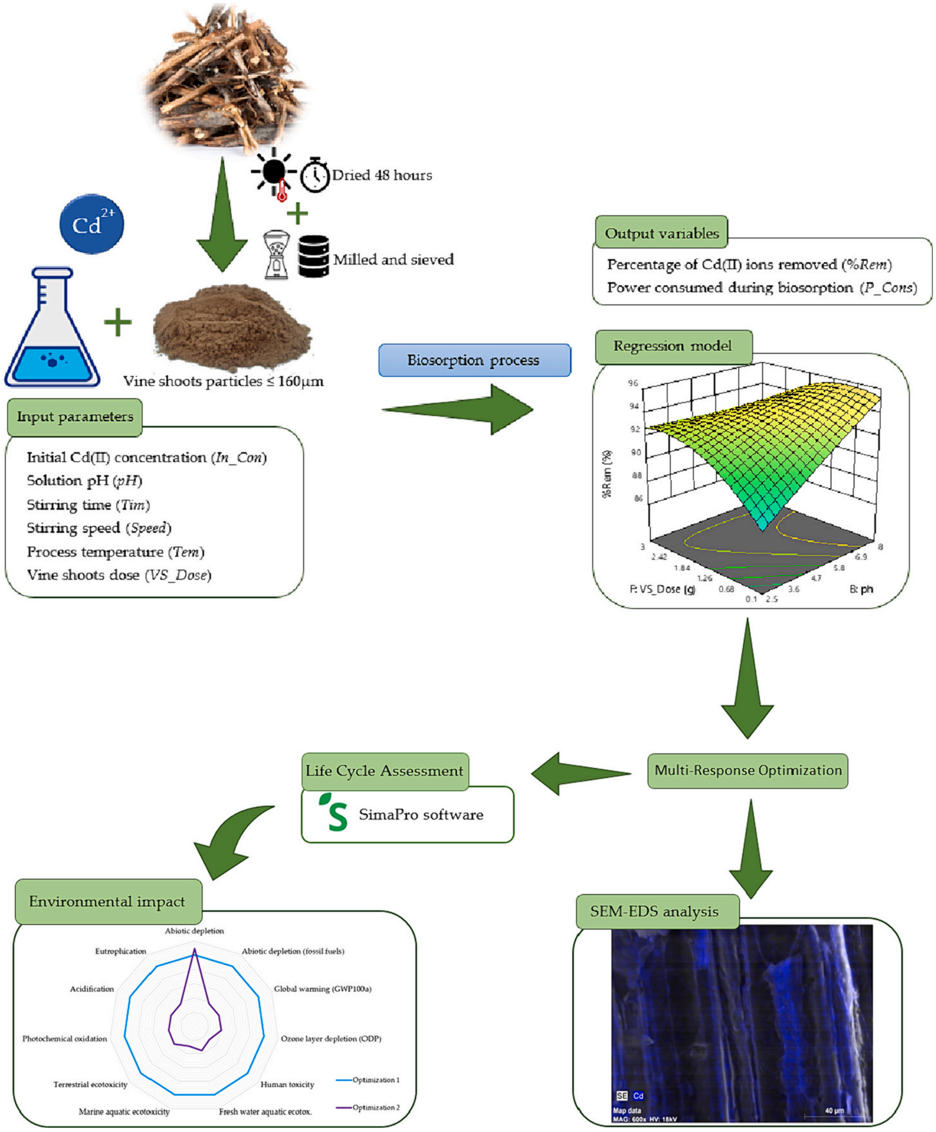


Fig. 1. Methodological workflow of cadmium biosorption by vine shoots.

(*pH*), process temperature (*Tem*), stirring speed (*Speed*), and stirring time (*Tim*). The output variables of significance are the percentage of cadmium ions within the treated wastewater (*%Rem*) and the power consumed during the cadmium biosorption process using vine shoots (*P_Cons*). The primary goal is to optimize the cadmium biosorption process, focusing on the input variables that contribute to maximum efficiency.

In summary, this research seeks to utilize waste materials from the wine industry, specifically vine shoots, as a biosorbent for cadmium removal from industrial wastewater, without incurring additional processing costs. To achieve this, an RSM study is used with a BBD design to optimize the process. Additionally, an LCA is conducted to evaluate its environmental impact through a 'gate-to-gate' analysis. This research is novel as it examines thoroughly the use of vine shoots to remove cadmium and promoting the circular economy. Fig. 1 illustrates the methodological workflow that was adopted in this cadmium biosorption process using vine shoots.

2. Materials and methods

2.1. Raw vine shoots

The vine shoots were provided by the "Bodega Castillantico", located in Cárdenas (La Rioja, Spain). The vine shoots are obtained after the harvest, typically in late November. They are the new branches that are born each year and from which the leaves and, finally, the clusters of grape emerge. Every year, the plant produces new buds from which vine shoots sprout. Winter pruning is carried out on the vine shoots to limit their growth and improve vine production, but generating waste. After being cleaned three times using deionized water, the vine shoots were sun-dried for 48 h, ground using an IKA M20 mill (IKA-Werke GmbH&Co, Staufen, Germany), and sieved to remove particles smaller than, or equal to, 160 μm.

Then, elemental analysis of the vine shoots was conducted using a Vario EL instrument (Elementar, Germany) following the ASTM D5373–16 standard (ASTM, Standard D5373-16, 2016). The experiments were carried out in triplicate to ensure repeatability and minimize discrepancies in the experimental results of the analysis. The relative deviation was maintained within the order of ±0.13 %, and the average results were reported. The percentages of carbon, hydrogen, nitrogen, and oxygen in the biosorbent appear in Table 1. The elemental analysis revealed that the vine shoots used in the biosorption method were composed mostly of carbon (45.61 %) and oxygen (48.05 %), as was expected for most lignocellulosic material.

The TAPPI T222 om-6 method was used to calculate the Klason lignin content. First, 300 mg of dry vine shoots were thoroughly mixed with 3 ml of H_2SO_4 (72 % extrapure, CAS, 7664-93-9) in glass tubes. Next, the tubes were immersed in a water bath at 30 °C for one hour, with a vortex every ten minutes. Each tube was then filled with 84 ml of deionized water and stirred. After being autoclaved for one hour at 121 °C, the resulting material was chilled with ice until room temperature was reached. After filtering the tube contents, the solid material was dried for overnight at 105 °C in an oven. The lignin content was determined using gravimetric methods. Three separate sets of determinations were made. The result of the lignin content was obtained by averaging the three outcomes. Thus, it was found that vine shoots have a lignocellulosic content of 36.5 %. Similar results have been obtained in other studies; for example, Scurtu et al. (2023) confirmed the presence of cellulose (35 %), hemicellulose (26 %) and lignin (30 %) in comparable amounts. Additionally, Garita-Cambronero et al. (2021) determined that cellulose is the largest component of vine shoots 34 %, followed by lignin at 27 % and hemicellulose at 19 %. Similarly, Benito-González et al. (2020) documented comparable findings, with their study reporting a lignin content of around 30 % from tempranillo and verdejo vine shoots. Because of this composition, vine shoots have the ability to sequester carbon, thus reducing greenhouse gas emissions by retaining the carbon within the biomass (Bastos and Fleischer, 2021).

Table 1
Elemental analysis of vine shoots.

Carbon	Hydrogen	Nitrogen	Oxygen
%	%	%	%
45.61	5.88	0.46	48.05

2.2. Chemical solutions

It was essential for the purpose of this research that the presence of other metals in the aqueous solutions had no effect on the vine shoots' effectiveness of cadmium biosorption. Consequently, different concentrations of cadmium(II) chloride hemipentahydrate ($CdCl_2{\cdot}2.5H_2O$) were dissolved in distilled water to create synthetic metal solutions. The cadmium levels that were used ranged from 0.5 to 100 mg/l. The first range of cadmium content was selected in accordance with the laws governing wastewater sanitation and purification in La Rioja, Spain (Comunidad Autónoma de La Rioja, 2000). For instance, preparation of the solution of 50 mg/l of Cd(II) required dissolving 0.10157 g of $CdCl_2{\cdot}2.5H_2O$ (CAS: 77990–78-5) in one liter of distilled water. Flame atomic absorption spectroscopy (FAAS) was used to detect the concentration of metal using a PinAAcle 500 atomic absorption spectrophotometer (PerkinElmer Inc., Waltham, USA). Background correction by deuterium lamp was employed to minimize the background absorption of samples in the flame. Table 2 presents the instrumental parameters that were used in this analysis.

When using an external standard and standard additions quantification methodologies, there were no significant differences noted between the two approaches. Several analytical performance characteristics of the determination by FAAS and external standard quantification methodology are shown in are shown in Table 3.

To adjust the pH of the solution to the desired value, hydrochloric acid (HCl, 37 % pure, CAS: 7647-01-0) and sodium hydroxide (NaOH, 98 % extra-pure, CAS: 1310-73-2) were used. In compliance with ASTM D1293–18 (*"Standard Test Methods for pH of Water,"* 2018), a Violab DHS pH meter model XS PH50+ (Giorgio Bormac s.r.l, Carpi, Italy) was utilized for the pH adjustment technique. Merck & Company supplied all of the analytical grade chemicals and reagents used in this investigation.

2.3. Experimental design of the cadmium biosorption process

The Response Surface Methodology (RSM) comprises an array of experimental techniques intended to evaluate the correlation between many controlled experimental variables and the responses based on one or more predetermined criteria (Ba Mohammed et al., 2020). Regression analysis and experiment design are used in RSM to optimize a process's predicted values. RSM not only improves operating conditions, but also saves time by reducing the number of experimental runs, as evaluating all practical elements one at a time would be a lengthy process. The Box-Behnken design (BBD) based on RSM was created to anticipate precisely the ideal conditions for cadmium biosorption by vine shoots and reduce the number of experiments required (Gasemloo et al., 2019). This is an

Table 2
Instrumental parameters of spectrophotometer.

PinAAcle 500 Perkin Elmer Spectrophotometer	
Atomization system	Air-acetylene flame: 10.0 l/min of air and 2.5 l/min of C_2H_2
Lamp	Lumina hollow cathode lamp of Cd. $I = 4$ mA
Wavelength	228.80 nm
Monochromator slit	0.7 nm
Background correction	Yes

Table 3
Analytical features of the determination method.

Linearity	Sensitivity	Limit of detection	Repeatability	Limit of quantification	Correlation coefficient
mg Cd/l	l/mg Cd	mg Cd/l	s_r (%)	mg Cd/l	–
0.080–5	0.164 ± 0.006	0.023	0.8	0.080	0.9995

effective way to enhance and optimize the process of biosorption. Additionally, RSM based BBD is a potent technique that is used frequently to improve the key operational elements that affect the biosorption process in order to ascertain the ideal circumstances for maximal removal capability. The optimal parameter choices that yielded the greatest response value were found by fitting a quadratic model to the experimental data by using the Design-Expert software version 23.1.0 (Stat-Ease Inc., Minneapolis, MN, USA). Enhancing process efficiency may be achieved using the design of experiments (DoE) approach. It entails varying every significant parameter at the same time in a series. The findings from these trials are then integrated to the outcomes using a mathematical model (Montgomery, 2017).

To construct the DoE in this instance, 53 experiments were required. The input variables chosen to create the DoE were: initial cadmium concentration (*In_Con*), solution pH (*pH*), stirring time (*Tim*) and speed (*Speed*), process temperature (*Tem*), and vine shoots dose (*VS_Dose*). The factors that were selected for optimization appear in Table 4, along with the corresponding ranges and levels.

The outputs considered in this biosorption process were: the percentage of cadmium ions within treated wastewater (*%Rem*) and the power consumed during the cadmium biosorption process using vine shoots (*P_Cons*). The relationship between each input variable and the associated outputs is represented by the *p*-value. The lower the parameter is, the stronger is the effect on the output variable. If the experiment findings are significant, the *p*-value can be found using an analysis of variance (ANOVA).

2.4. Studies on Cd(II) biosorption

The Box-Behnken design matrix was used to conduct the studies in a lab setting. The effectiveness of Cd(II) removal was evaluated by measuring the final cadmium concentration (*Fin_Con*) in each experiment following the biosorption procedure. The biosorbent was separated using 0.25 μm filters. After being collected, the samples were placed in glass containers and examined with an atomic adsorption spectrophotometer (PinAAcle 500; PerkinElmer Inc., Waltham, USA) to check for any remaining Cd(II) ions. To determine the removal efficiency (*%Rem*) from *Fin_Con* and *In_Con*, Eq. (1) was used.

$$\%\text{Rem} = \frac{\text{In\_Con} - \mathit{Fin\_Con}}{\text{In\_Con}} \cdot 100 \tag{1}$$

A PCE-GPA 50 power analyzer (PCE Iberica S.L., Spain) was used to measure the amount of power consumed during the laboratory trials. Key operational parameters, including temperature, stirring time and speed of the biosorption process were considered to assess their impact on the overall power consumption. Consequently, it was possible to calculate the total power used (*Power_C*) in the trials.

Table 4
Levels of input variables for cadmium biosorption.

Input	Notation	Magnitude	Levels		
			−1	0	1
Initial Cd(II) concentration	*In_Con*	mg/l	0.5	50	100
pH	*pH*	–	2.5	4	8
Stirring time	*Tim*	min	10	95	180
Stirring speed	*Speed*	rpm	100	250	400
Temperature	*Tem*	°C	15	35	55
Biosorbent dose	*VS_Dose*	g	0.1	1.55	3

2.5. Life cycle assessment

An appropriate technique to evaluate environmental performance of a product or service is life cycle assessment (LCA) (Wolf et al., 2011). The life cycle evaluation of this cadmium biosorption by vine shoots was conducted in accordance with the International Organization for Standardization Standard 14,040/14044 (ISO, 2006). There are four stages in the life cycle evaluation (LCA) process. These consist of (1) defining the objective and scope, (2) carrying out a life cycle inventory, (3) evaluating the life cycle's impact, and (4) analyzing the results.

LCA in the removal of cadmium from aqueous solutions has been the subject of several investigations. However, there are no references to any particular research conducted on the life cycle and environmental impacts of cadmium biosorption using shoots. The ISO standard defines LCA as the process of gathering and analyzing data on the inputs, outputs, and possible environmental effects of a product system over the course of its life cycle. In particular, LCA can serve as a scientific foundation for policies on product design, consumer information, public procurement, waste management, energy, and food supply. It also provides valuable, comprehensive quantitative data on the environmental impact of products and services.

Since the strategy employed for the next steps in the LCA approach depends on the goals of the study, the first step is essential (Habibi et al., 2023). In the next step, it is necessary to gather all inputs and outputs of the system. This is the most expensive and time-consuming phase in an LCA study. The two categories of data that should normally be provided in this stage are foreground and background data. Foreground data refers to the kind and volume of all inputs and outputs into and out of the system (Hu et al., 2020). Background data is usually obtained from reputable sources and related to the environmental impacts of the system's transportation and material and energy production. For this inquiry, background data was used from the EcoInvent 3 database. Depending on the objectives of the investigation, several baselines may be utilized during the third step of assessing life cycle effect. The specific baselines used in life cycle inventory are midpoint and endpoint. The endpoint method is less reliable than the midpoint. It requires more data integrality, weighting, modeling, and value decisions to carry out a thorough environmental evaluation (Ding et al., 2021). According to Reap et al. (2008), endpoint indicators normalize and combine influences from several categories to streamline findings. In contrast, midpoint indicators restrict ambiguity. Endpoint indicators and lead to increased uncertainty and less transparency. The reason for this is that additional environmental and impact models need to be connected in order to provide a conclusion. Midpoint indicators are generally chosen for wastewater systems. However, endpoint indicators that incorporate normalization, grouping, and weighting (according to ISO 14044 criteria) should not be considered if they do not offer enough clarity for decision-making (Corominas et al., 2020). Thus, in this research, CML-IA database has been utilized for the midpoint indicator.

2.6. Scanning electron microscopy and energy-dispersive X-ray spectroscopy characterization

The surface characteristics of the vine shoots before and after the cadmium biosorption process were investigated using a COXEM EM-30 N (Daejeon, Korea) scanning electron microscope (SEM). An operating voltage of 10 kV was utilized to examine the surface properties of the vine shoots both before to and during the cadmium biosorption procedure, using a COXEM EM-30 N scanning electron microscope (SEM) from Daejeon, Korea. Before the SEM analysis, the sample surfaces were made conductive by sputtering a thin coating of gold onto them using a COXEM SPT − 20 ion coater. Energy-dispersive X-ray spectroscopy (EDS) was utilized for the qualitative investigation of the elemental composition of the biosorbent. The instrument used included an Oxford Instruments Xplore Compact 30 EDS detector and the AZtecOne 6.0 program (Oxford Instruments, Pasadena, USA).

3. Results and discussion

3.1. Experimental results

After defining the DoE input parameters using Design-Expert 23.1.0 software, a series of experimental tests were conducted. As previously mentioned, 53 experiments were completed to formulate the DoE. The resulting data is detailed in Table 5. The examined output variables encompassed (i) the percentage removal of Cd(II) ions (*%Rem*) that were determined by Eq. (1), and (ii) the power consumption (*P_Cons*) in each biosorption experiment by vine shoots.

3.2. Analysis of variance for the cadmium biosorption process

By using Analysis of Variance (ANOVA), connections between a single answer and the controlled factors in an experiment can be investigated. Specifically, ANOVA has the capacity to distinguish between the varying responses among the several samples and their respective contributions to the design of the experiment (Bertinetto et al., 2020). Tables 6 and 7 show the ANOVA results for the percentage of cadmium removal (*%Rem*) and power consumed (*P_Cons*) in this biosorption process by vine shoots.

As can be seen in Table 6, the Model F-value of 5.47 implies that the

Table 5

BBD design matrix for cadmium biosorption and output values.

	Input variables						Output variables	
	In_Con (mg/l)	*pH* (–)	*Tim* (min)	*Speed* (rpm)	*Tem* (°C)	*VS_Dose* (g)	*%Rem* (%)	*P_Cons* (W)
01	100	4.0	180	250	35	0.10	95.04	26.42
02	100	8.0	95	100	35	1.55	98.02	26.23
03	50	2.5	10	250	15	1.55	91.27	31.63
04	50	4.0	95	250	35	1.55	92.96	26.23
05	50	2.5	95	250	15	3.00	92.12	29.02
06	50	4.0	180	100	35	0.10	95.10	25.29
07	0.5	4.0	95	400	15	1.55	93.81	34.64
08	100	4.0	95	400	55	1.55	83.57	30.85
09	100	4.0	95	100	15	1.55	94.37	26.09
10	50	8.0	95	250	15	0.10	95.16	26.99
11	0.5	4.0	95	400	55	1.55	86.32	29.72
12	100	4.0	10	250	35	3.00	95.01	34.96
13	50	8.0	10	250	15	1.55	95.09	31.86
14	50	4.0	10	100	35	3.00	95.26	34.51
15	50	4.0	10	400	35	0.10	90.15	41.71
16	100	4.0	95	100	55	1.55	93.98	26.35
17	50	2.5	95	250	15	0.10	85.63	27.22
18	0.5	8.0	95	400	35	1.55	89.69	29.15
19	50	4.0	180	400	35	0.10	89.62	30.24
20	50	2.5	180	250	15	1.55	95.26	27.91
21	50	4.0	95	250	35	1.55	92.91	25.55
22	50	2.5	10	250	55	1.55	93.14	47.56
23	50	8.0	10	250	55	1.55	93.81	51.38
24	50	8.0	180	250	55	1.55	92.69	25.84
25	50	4.0	95	250	35	1.55	95.16	26.90
26	50	4.0	180	400	35	3.00	92.94	30.02
27	0.5	4.0	95	100	15	1.55	82.96	26.32
28	50	2.5	95	250	55	3.00	91.85	28.15
29	100	4.0	95	400	15	1.55	96.09	31.72
30	50	8.0	95	250	15	3.00	93.10	27.89
31	100	2.5	95	400	35	1.55	85.99	30.28
32	50	4.0	10	400	35	3.00	92.95	41.49
33	100	8.0	95	400	35	1.55	93.66	30.05
34	0.5	4.0	95	100	55	1.55	94.68	26.57
35	50	4.0	95	250	35	1.55	91.04	26.23
36	0.5	2.5	95	400	35	1.55	92.56	29.83
37	0.5	2.5	95	100	35	1.55	92.37	25.33
38	0.5	4.0	180	250	35	3.00	90.00	28.67
39	50	4.0	10	100	35	0.10	88.26	34.74
40	0.5	4.0	10	250	35	3.00	91.68	35.41
41	100	4.0	10	250	35	0.10	94.14	35.41
42	50	2.5	95	250	55	0.10	83.80	27.25
43	50	8.0	95	250	55	0.10	93.50	27.25
44	50	4.0	95	250	35	1.55	93.28	27.80
45	50	8.0	180	250	15	1.55	98.33	29.03
46	0.5	4.0	10	250	35	0.10	87.64	34.51
47	100	2.5	95	100	35	1.55	85.56	26.23
48	100	4.0	180	250	35	3.00	94.26	28.22
49	50	2.5	180	250	55	1.55	92.15	27.19
50	50	4.0	180	100	35	3.00	92.80	25.29
51	0.5	8.0	95	100	35	1.55	94.56	26.23
52	50	8.0	95	250	55	3.00	90.15	27.25
53	0.5	4.0	180	250	35	0.10	90.90	27.09

Table 6
ANOVA results for *%Rem*.

Source	Sum of squares	Df	Mean square	F-value	p-Value (Pr (>F))
Model	500.54	27	18.54	5.47	<0.0001
A-In_Con	44.98	1	44.98	13.26	0.0012
B-pH	62.89	1	62.89	18.54	0.0002
C-Tim	4.36	1	4.36	1.29	0.2675
D-Speed	29.14	1	29.14	8.59	0.0071
E-Tem	26.00	1	26.00	7.67	0.0104
F-VS_Dose	2.47	1	2.47	0.7276	0.4018
AB	10.47	1	10.47	3.09	0.0913
AC	0.0242	1	0.0242	0.0071	0.9334
AD	7.96	1	7.96	2.35	0.1381
AE	36.76	1	36.76	10.84	0.0030
AF	0.5490	1	0.5490	0.1618	0.6909
BC	0.0118	1	0.0118	0.0035	0.9535
BD	11.05	1	11.05	3.26	0.0832
BE	3.59	1	3.59	1.06	0.3133
BF	41.67	1	41.67	12.28	0.0017
CD	3.03	1	3.03	0.8920	0.3540
CE	10.88	1	10.88	3.21	0.0855
CF	16.73	1	16.73	4.93	0.0356
DE	122.78	1	122.78	36.20	<0.0001
DF	0.2490	1	0.2490	0.0734	0.7887
EF	0.0096	1	0.0096	0.0028	0.9580
A^2	3.09	1	3.09	0.9105	0.3491
B^2	0.2479	1	0.2479	0.0731	0.7891
C^2	22.22	1	22.22	6.55	0.0169
D^2	3.88	1	3.88	1.15	0.2948
E^2	13.49	1	13.49	3.98	0.0572
F^2	32.25	1	32.25	9.51	0.0049
Residual	84.80	25	3.39		
Lack of fit	76.24	21	3.63	1.69	0.3265
Pure error	8.57	4	2.14		
Cor total	585.34	52			

Table 7
ANOVA results for *P_Cons*.

Source	Sum of squares	Df	Mean square	F-value	p-Value (Pr (>F))
Model	1400.68	27	51.88	9.08	<0.0001
A-In_Con	0.0006	1	0.0006	0.0001	0.9917
B-pH	0.1041	1	0.1041	0.0182	0.8937
C-Tim	579.62	1	579.62	101.47	<0.0001
D-Speed	110.19	1	110.19	19.29	0.0002
E-Tem	28.84	1	28.84	5.05	0.0337
F-VS_Dose	1.12	1	1.12	0.1969	0.6611
AB	0.0497	1	0.0497	0.0087	0.9264
AC	0.2903	1	0.2903	0.0508	0.8235
AD	0.0523	1	0.0523	0.0092	0.9245
AE	1.99	1	1.99	0.3479	0.5606
AF	0.1562	1	0.1562	0.0273	0.8700
BC	9.58	1	9.58	1.68	0.2071
BD	1.77	1	1.77	0.3102	0.5825
BE	3.53	1	3.53	0.6187	0.4389
BF	0.1549	1	0.1549	0.0271	0.8705
CD	2.28	1	2.28	0.3999	0.5329
CE	193.61	1	193.61	33.90	< 0.0001
CF	0.6202	1	0.6202	0.1086	0.7445
DE	4.96	1	4.96	0.8686	0.3603
DF	0.0063	1	0.0063	0.0011	0.9737
EF	0.4050	1	0.4050	0.0709	0.7922
A^2	0.6893	1	0.6893	0.1207	0.7312
B^2	0.7971	1	0.7971	0.1395	0.7119
C^2	326.75	1	326.75	57.20	<0.0001
D^2	17.03	1	17.03	2.98	0.0966
E^2	20.57	1	20.57	3.60	0.0693
F^2	4.64	1	4.64	0.8126	0.3760
Residual	142.80	25	5.71		
Lack of fit	139.90	21	6.66	9.20	0.0218
Pure error	2.90	4	0.7239		
Cor total	1543.48	52			

model is significant. There is only a 0.01 % chance that an F-value that is this large could occur due to noise. *P*-values <0.0500 indicate that the model terms are significant. In this case *In_Con*, *pH*, *Speed*, *Tem*, *In_Con·Tem*, *pH·VS_Dose*, *Tim·VS_Dose*, *Speed·Tem*, *Tim*^{2}, and *VS_Dose*^{2} are significant model terms. Values >0.1000 indicate that the model terms are not significant. Specifically, the input parameter that has the greatest effect on *%Rem* is *pH* (*p*-value = 0.0002) followed by *In_Con* (p-value = 0.0012). These outcomes are comparable to those of research where fish scale (Jaafar et al., 2021) *Shewanella putrefaciens* (Yuan et al., 2019) or *Chlorella coloniales* (Jaafari and Yaghmaeian, 2019) were used to remove cadmium. The Lack of Fit F-value of 1.69 implies the Lack of Fit is not significant relative to the pure error. There is a 32.65 % chance that a Lack of Fit F-value that is this large could occur due to noise. Non-significant lack of fit is good because we want the model to fit.

Table 7 shows that the Model F-value of 9.08 implies that the model is significant. In this case *Tim*, *Speed*, *Tem*, *Tim·Tem*, and *Tim*^{2} are significant model terms. Specifically, the input parameter that has the greatest effect on *P_Cons* is *Tim* (*p*-value <0.0001) followed by *Speed* (p-value = 0.0002) and *Tem* (p-value = 0.0337). Logically, the greatest energy consumption is incurred during the heating and stirring of the aqueous solution. This suggests that *Tim*, *Speed*, and *Tem* are intricately linked to power consumption. In this context, the dynamic interplay between heating and agitation directly influences the temporal and velocity aspects, establishing a clear correlation with the overall power consumption. The Lack of Fit F-value of 9.20 implies that the Lack of Fit is significant. There is only a 2.18 % chance that a Lack of Fit F-value that is this large could occur due to noise.

According to the model summary statistics, the quadratic model's regression coefficient was the best one for this particular biosorption process and was statistically significant (p-value <0.0001). The second-order polynomial model was the one that best describes the relationship between the variables and responses, according to an ANOVA study that verified the models' sufficiency. As a result, Eqs. (2) and (3) present the response variable and the test variables, respectively, linked by the following second-order polynomial equation derived by multiple regression analysis on the experimental data:

$$
\begin{gathered}
\%Rem = 56.9462 + 0.11809 \cdot A + 2.2889 \cdot B + 0.0166 \cdot C \\
+ 0.0735 \cdot D + 0.6931 \cdot E + 6.4499 \cdot F + 0.0078 \cdot A \cdot B - 1.3008\mathrm{E} \\
-05 \cdot A \cdot C - 9.4511\mathrm{E} - 05 \cdot A \cdot D - 0.0021 \cdot A \cdot E - 0.0036 \cdot A \cdot F - 0.0002 \cdot B \cdot C - 0.0027 \cdot B \cdot D - 0.0083 \cdot B \cdot E - 0.5366 \cdot B \cdot F \\
-4.8235\mathrm{E} - 05 \cdot C \cdot D - 0.0007 \cdot C \cdot E - 0.0083 \cdot C \cdot F - 0.0013 \cdot D \cdot E + 0.0008 \cdot D \cdot F + 0.0012 \cdot E \cdot F - 0.0002 \cdot A^2 - 0.0275 \cdot B^2 \\
+ 0.00021 \cdot C^2 - 2.7827\mathrm{E} - 05 \cdot D^2 - 0.00292 \cdot E^2 - 0.8581 \cdot F^2
\end{gathered} \tag{2}
$$

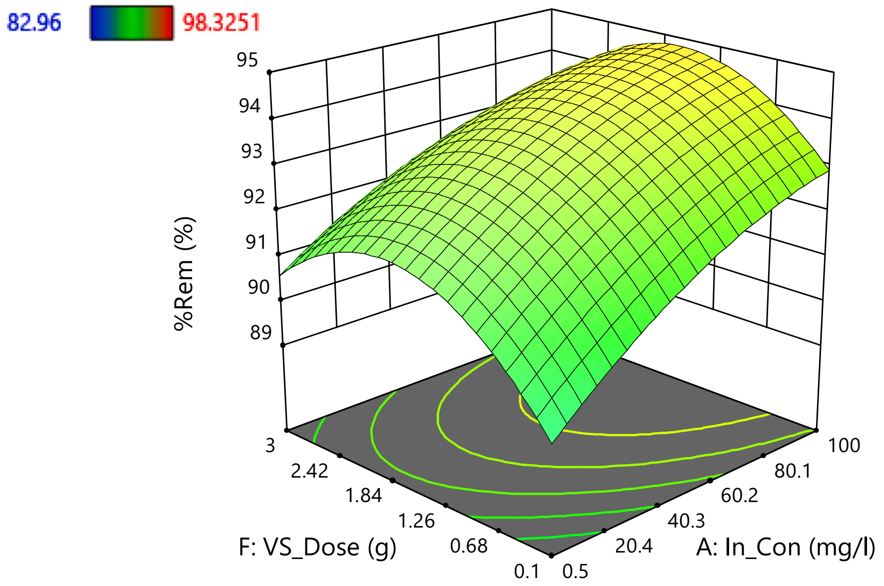


Fig. 2. 3D surface plot illustrating how *VS_Dose* and *In_Con* interact to influence the Cd(II) removal percentage.

$$P\_Cons = 26.9144 - 0.0006{\cdot}A - 0.0745{\cdot}B - 0.0809{\cdot}C + 0.0061{\cdot}D + 0.0875{\cdot}E + 1.5967161829575020615{\cdot}F + 0.0005{\cdot}A{\cdot}B \\ -4.5044\mathrm{E}-05{\cdot}A{\cdot}C - 7.6603\mathrm{E}-06{\cdot}A{\cdot}D + 0.0005{\cdot}A{\cdot}E - 0.0019{\cdot}A{\cdot}F - 0.0044{\cdot}B{\cdot}C - 0.0011{\cdot}B{\cdot}D + 0.0083{\cdot}B{\cdot}E \\ -0.0327{\cdot}B{\cdot}F - 4.1912\mathrm{E}-05{\cdot}C{\cdot}D - 0.0029{\cdot}C{\cdot}E + 0.0016{\cdot}C{\cdot}F - 0.0003{\cdot}D{\cdot}E - 0.0002{\cdot}D{\cdot}F - 0.0077{\cdot}E{\cdot}F - 0.0001{\cdot}A^2 \\ +0.0492{\cdot}B^2 + 0.0008{\cdot}C^2 + 5.8268\mathrm{E}-05{\cdot}D^2 + 0.0036{\cdot}E^2 - 0.3255{\cdot}F^2 \quad (3)$$

3.3. Effect of input parameters on removal efficiency

Understanding the impact of input parameters (*In_Con*, *pH*, *Tim*, *Speed*, *Tem*, and *VS_Dose*) on the percentage of cadmium removal (*%Rem*) is essential to enhance the efficiency of this biosorption process. By analyzing these parameters, conditions can be optimized to maximize cadmium removal by vine shoots and improve overall process effectiveness. Adjusting these inputs enables one to fine-tune the biosorption process and achieve a more efficient removal of cadmium contaminants from wastewater. To analyze the effect of input parameters on *%Rem*, 3D surface plots were constructed. Regression equations are graphically represented by the 3D surface plots that display two parameters while

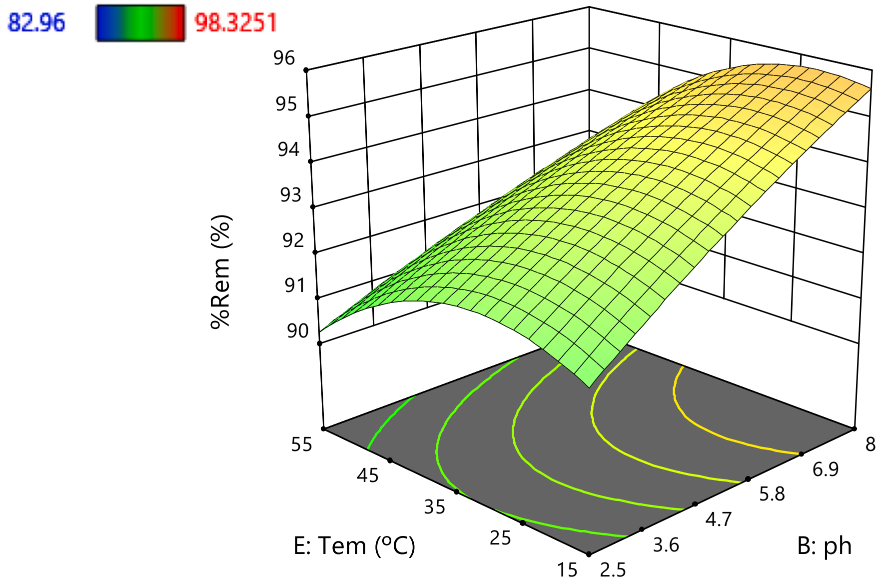


Fig. 3. 3D surface plot illustrating how *Tem* and *pH* interact to influence the Cd(II) removal percentage.

holding the other elements constant. Understanding the main and interaction impacts of factors can be improved with the use of these graphs (Hadiani et al., 2018).

3.3.1. *Effect of initial Cd(II) concentration*

In this Cd(II) biosorption process by vine shoots, the initial cadmium concentration was established in 0.5, 50 and 100 mg/l following the DoE. Fig. 2 shows the interaction between the percentage of Cd(II) removal (*%Rem*) and the initial cadmium concentration (In_Con). The *% Rem* reached approximately 92 % at 0.5 mg/l to a maximum of 95 % at an initial cadmium concentration of 100 mg/l. The initial concentration acts as a significant incentive to get beyond the Cd(II) mass transfer resistances (Aksu, 2001). Thus, a greater Cd(II) initial concentration will promote the adsorption process, as observed. Although there are no references in which cadmium removal by vine shoots is studied, similar results have been reached by other authors using other biosorbents. For example, Afraz et al. (2020) used the bacteria *Lactobacillus acidophilus* to remove Cd(II) and Pb(II) from water, showing that as metal ion concentrations increased, their removal efficiencies progressively improved. Hiew et al. (2021) concluded that, at a constant temperature, when the initial Cd(II) concentration increased, so did the biosorption capacity of okara-based waste. In this instance, the mass transfer barrier at the solid-liquid interface was largely overcome by the difference in concentration. Because of the greater impetus at higher initial concentrations that enabled more cadmium to be adsorbed onto the biosorbent, the mass transfer resistance was reduced (Chen et al., 2023).

3.3.2. *Effect of pH and temperature of the solution*

One of the environmental elements that has a significant impact on the removal of heavy metals using biosorption procedures is the pH of the solution (Esposito et al., 2001) (Ba Mohammed et al., 2020). The effect of biosorption yield of the solution's pH and temperature in the current research may be anticipated based on the 3D surface plots shown in Fig. 3. The initial pH of the cadmium solution was adjusted to 2.5, 4.0, and 8.0 in order to examine the effect of various pH values on the cadmium biosorption by vine shoots. As can be seen in the figure, the removal cadmium percentage reached from *%Rem* = 92 % at pH 2.5 to *%Rem* = 95 % at pH 8. Thus, the highest removal efficiency was reached at pH 8. The reason for this might be that, at low pH levels, the H in solution affects the adsorbent's surface proton release, preventing cadmium ions in solution from exchanging with the adsorbent's surface protons and leading to an undesired adsorption capacity for cadmium (Chen et al., 2023). Similar results can be found for cadmium removal by magnetic olive wood (El-Sheikh and Alshamaly, 2020). Similar results were also obtained by Zhang et al. (2023), who used humic acid prepared from waste biomass (rice straw) for the cadmium removal from water.

Fig. 3 also illustrates the relationship between temperature of the solution (Tem) and *%Rem*. The data indicates that *%Rem* peaks at 94 % when the temperature is 26 °C. Additionally, there is a discernible trend as the temperature ranges from 15 °C to 55 °C, with *%Rem* showing a decrease from approximately 93.7 % to 92 %. This indicates a noteworthy sensitivity of the removal efficiency to temperature variations within this range. In other studies, as the one conducted by (Li et al., 2021) temperature also played a significant role in the interaction between metal ions and biomass, primarily by impacting the stability of the sorbent-metal complex and the ionization of cell wall moieties. Furthermore, (Sun et al., 2018) reported that, due to the endothermic nature of the adsorption process, a higher temperature increases the cadmium ion diffusion rate, resulting in a higher percentage of removal of this heavy metal.

3.3.3. *Effect of stirring time*

Fig. 4 shows the impact of agitation time (*Tim*) on cadmium removal by vine shoots. The data reveals a rapid increase in *%Rem* from 77 min, where the minimum value (*%Rem* = 93.8 %) is observed, to 180 min, achieving the peak *%Rem* at 95.9 %. Moreover, *%Rem* reaches 94.9 % within the first 10 min.

In other studies, such as the one conducted by Li et al. (2021) in which as the incubation period extended from 0 to 270 min, the adsorption ability rose and then stayed nearly constant. Extended incubation times increase the length of time that the bacterial active sites have in which to adsorb cadmium. The cadmium was adsorbed quickly during the first half of time. Similarly, Yuan et al. (2019) observed that initially, the effectiveness of removing cadmium increased quickly.

3.3.4. *Effect of stirring speed and vine shoots dosage*

Fig. 5 illustrates the interaction effects of vine shoots dosage (*VS_Dose*) and stirring speed (*Speed*) on cadmium removal efficiency. Initially, it is evident that *%Rem* varies from 91.7 % for *VS_Dose* = 0.1 g to *%Rem* = 92.4 % for *VS_Dose* = 3 g, reaching a maximum *%Rem* = 94 % for a *VS_Dose* of approximately 1.7 g. While the surface area of the vine

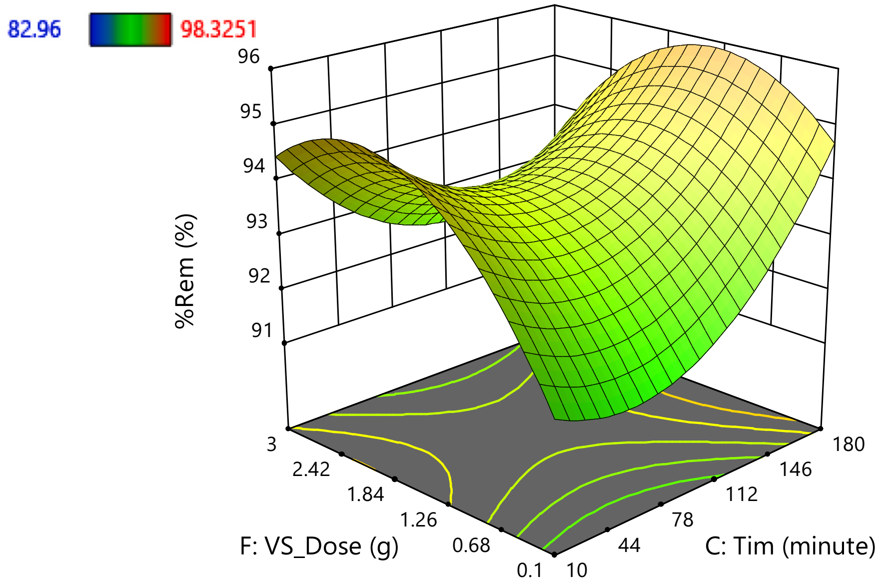


Fig. 4. 3D surface plot illustrating how *VS_Dose* and *Tim* interact to influence the Cd(II) removal percentage.

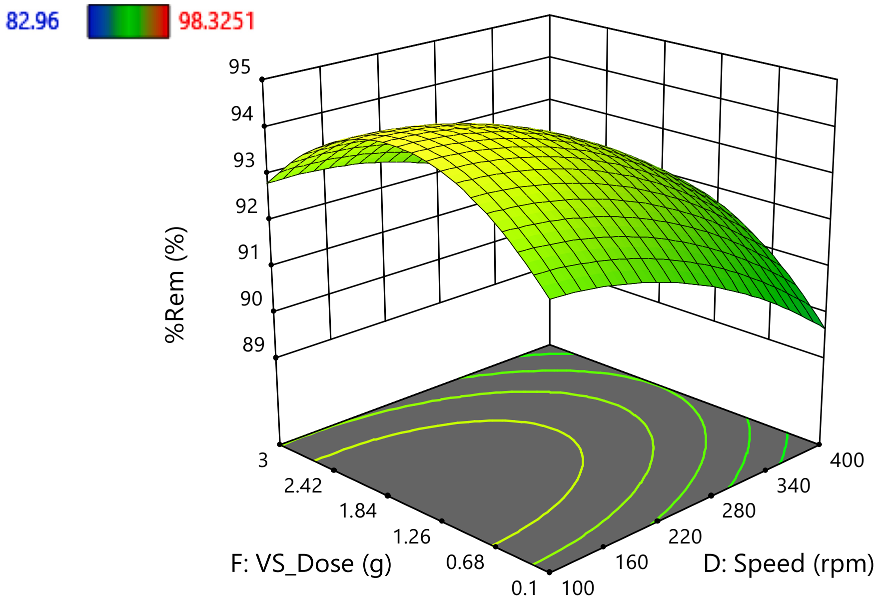


Fig. 5. 3D surface plot illustrating how *VS_Dose* and *Speed* interact to influence the Cd(II) removal percentage.

shoots grows and more adsorption sites become accessible as the biomass dosage is increased, the results shown that the metal adsorption shrinks when the biosorbent dosage is increased. The fact that more sites are accessible for biosorption even when the biomass dose is increased may help to explain this, as these sites could be unsaturated throughout the biosorption process. These findings, which are corroborated by references in the literature, show that a decrease in biomass enhanced the removal of metals. The reason is that metal ions in the biosorption media were exhausted or that metal ion binding sites interacted with one another (Hadiani et al., 2018). According to Yuan et al. (2019), high adsorbent concentrations caused cell aggregation, which, in turn, reduced the intercellular distance. They suggested in their results that there was a shielding effect between the thick cell layer and the metal ion binding sites. The stronger the metal adsorption at low biomass dosages, the farther distant the cell space was, resulting in ideal electrostatic contact between cells with a sizable biosorption factor. Similar results were noticed by Chen et al. (2023), who also reached the highest removal rate when the biosorbent dosage was 1.5 g, and by Zhang et al. (2023) who found 1 g as the highest quantity.

In regard to the agitation speed (*Speed*), the results obtained indicate that, as the input parameter Speed increases, the output %Rem decreases gradually. Consequently, the highest *%Rem* value observed is 94.6 % at *Speed* = 100 rpm, whereas the lowest *%Rem* recorded is 92 % at *Speed* = 400 rpm.

3.4. *Effect of input parameters on power consumed during the biosorption process*

In the analysis of the power consumption of the biosorption process (*P_Cons*), a selective approach is warranted to discern the significant variables. By means of rigorous analysis, it has been determined that *Tim*, *Tem*, and *Speed* are the principal input parameters influencing *P_Cons* as corroborated by ANOVA and logical deduction. This determination is based on the recognition that power consumption occurs during the stirring and heating phase, wherein energy is expended to maintain agitation and facilitate the interaction between vine shoots and the Cd(II) solution. Notably, the other input parameters (*pH*, *In_Con*, and *VS_Dose*) show minimal impact on *P_Cons*. Although these variables are necessary for overall process efficiency, they do not contribute directly to the energy expended by magnetic stirring. Therefore, by concentrating the analysis on *Tim*, *Tem*, and *Speed*, the intention is to elucidate the nuanced relationship between these parameters and *P_Cons*, thus refining the understanding of energy dynamics inherent in the biosorption process. By a greater exploration of the interaction between these variables, valuable insights can be gained to optimize power usage while maintaining or improving cadmium removal efficiency. This approach not only enhances comprehension of the biosorption process, but also sets the stage for the development of more sustainable and energy-efficient methodologies for treating cadmium-contaminated wastewater.

Fig. 6 shows the influence of input parameters *Tim*, *Speed*, and *Tem* on *P_Cons*. Fig. 6a concerns the influence of *Tim* on *P_Cons* during the biosorption process by vine shoots. It shows that, when the duration of the biosorption process is set to *Tim* = 10 min, the power consumed reaches *P_Cons* = 38 W. Conversely, with an increase in the process time to *Tim* = 180 min, the power consumption falls to *P_Cons* = 27 W. The minimum power consumption of *P_Cons* = 26 W is observed when *Tim* = 136 min, indicating an optimal duration for minimizing energy usage during the biosorption process. This variation could be attributed to the possibility that, when the magnetic stirrer is initially switched on, there could be a spike in power consumption as a surge of energy is required to overcome initial resistance and establish stirring within the solution (Sardeshpande et al., 2016). This surge might be more pronounced during shorter durations of the biosorption process, where the frequency of turning the magnetic stirrer on and off is highest. As the duration of the biosorption process lengthens, the frequency of turning the magnetic stirrer on and off declines. This might result in a more stabilized power consumption rate over time. Consequently, at longer durations, the system may reach a more steady-state condition, in which the power consumed to maintain stirring becomes relatively constant.

Fig. 6b shows the effect of *Speed* on *P_Cons* during the biosorption process by vine shoots. The 3D surface plot reveals a rise in power consumption with increasing stirring speed. Specifically, when the biosorption process operates at the minimum speed (*Speed* = 100 rpm), the power consumption measures *P_Cons* = 25.4 W, but at the maximum speed (*Speed* = 400 rpm), *P_Cons* increases to 30.2 W. Similar results were found by Ascanio et al. (2004). The reason for this increase in *P_Cons* could be that, as the speed of the magnetic stirrer increases, there is greater friction and turbulence within the solution. Thus, more energy would be required in order to maintain agitation.

Fig. 6c indicates the influence of *Tem* on *P_Cons* during the biosorption process by vine shoots. It is apparent that, as the temperature

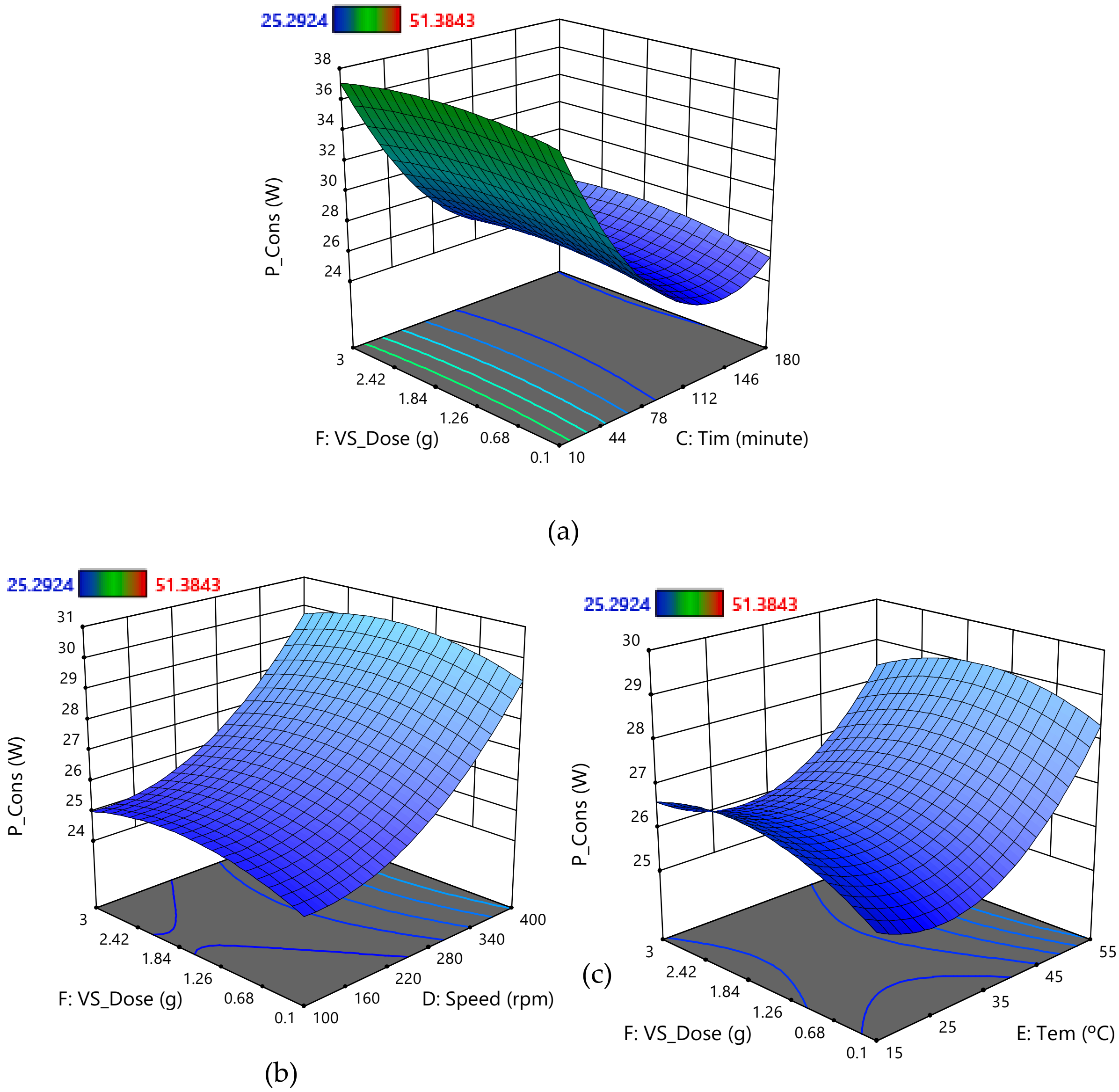


Fig. 6. 3D surface plot illustrating how *VS_Dose* and (a) *Tim* (b) *Speed*, and (c) *Tem* interact to influence the power consumed during the biosorption process.

Table 8
First Cd(II) biosorption by vine shoots optimization scenario.

	Goal	Min	Max	Opt
In_Con	inRange	0.5	100	94
pH	inRange	2.5	8	8
Tim	inRange	10	180	165
Speed	inRange	100	400	300
Tem	inRange	15	55	18
VS_Dose	inRange	0.1	3	1.4
%Rem	max	82.96	98.33	99.9
P_Cons	inRange	25.3	51.4	29.6

Table 9
Second Cd(II) biosorption by vine shoots optimization scenario.

	Goal	Min	Max	Opt
In_Con	inRange	0.5	100	100
pH	inRange	2.5	8	8
Tim	min	10	180	75
Speed	min	100	400	100
Tem	min	15	55	26
VS_Dose	min	0.1	3	0.1
%Rem	max	82.96	98.32	99.23
P_Cons	min	25.3	51.4	25.6

increases, there is a corresponding rise in power consumption. Thus, at the minimum temperature of *Tem* = 15 °C, *P_Cons* = 26.8 W, whereas at the maximum temperature of *Tem* = 55 °C, *P_Cons* rises to 29 W. Calorimetric measurements provide another method for determining the power demand in a stirred vessel. However, they require an energy balance (Ascanio et al., 2004). This energy balance is affected directly by temperature. With rising temperatures, both the biosorbent material and the solution experience thermal expansion. This may increase resistance

Table 10
Experimental %Rem for the two optimization scenarios.

Optimization	Experimental values *%Rem*	Percent error *%Rem*
1	98.9	0.98
2	98.3	0.99

to stirring as the distance between internal particles becomes greater (Honorio et al., 2021). As a result, more power would be needed. Additionally, higher temperatures lead to a reduction in the viscosity of the solution, thereby promoting better fluidity and dispersion of the biosorbent (Cornelissen and Waterman, 1955). However, this increased fluidity may necessitate a greater energy input to maintain uniform stirring throughout the biosorption process.

3.5. Optimization of Cd(II) biosorption by vine shoots

Reaching the ideal values of input parameters for Cd(II) removal from aqueous solution is the goal of the experimental design and optimization. By using Design-Expert v.23.1.0 software to analyze the aforementioned experimental data, the ideal conditions for the biosorption of cadmium by vine shoots were found. Response optimization in numerical optimization enables researchers to select the desired goal for every input parameter and output variable. Tables 8 and 9 provide the optimal results for the Cd(II) biosorption process in wastewater using vine shoots for two different optimization scenarios. The first optimization scenario is shown in Table 8. The objective of this scenario is to achieve the highest percentage of Cd(II) removal. Consequently, the output variable *%Rem* was maximized, but the remaining input and output parameters were maintained in their specified ranges. The second optimization scenario is shown in Table 9. The objective of this scenario is to achieve the highest percentage of Cd(II) removal while minimizing expense. To minimize expense, the power consumed by the biosorption process and the dosage of biosorbent were considered. Thus, the goal is to minimize the parameters of *Tim*, *Speed*, *Tem*, *VS_Dose*, and *P_Cons*, while maximizing *%Rem*, *In_Con* and *pH* were set in range.

In order to validate the two possible optimization processes aimed at maximizing the removal of final Cd(II) concentration and minimizing energy consumption, using MRS with desirability functions, two new experiments with the optimal biosorption factors identified in Tables 8 and 9 were conducted. Table 10 presents the experimental values obtained from these experiments, including the optimal removal of final Cd (II) and the percent errors for the biosorption response. The results indicate that this combination effectively achieves the highest possible removal of final Cd(II) concentration while minimizing energy consumption, using vine shoots waste as biosorbent.

3.6. Life cycle assessment of Cd(II) biosorption by vine shoots

3.6.1. Defining the goal and scope

Defining the goal and scope are the starting point in the LCA method. Therefore, it is necessary to clearly define these two issues. The main goal of this research is to employ vine shoots waste as a biosorbent in Cd (II) removal. The functional unit chosen for this was the treatment of 1000 ml of distilled water contaminated with cadmium. In this Life Cycle Assessment (LCA), the results of the two optimization scenarios determined in the previous section were compared.

The scope of the LCA in this biosorption process using vine shoots has been conducted from a "gate-to-gate" perspective. In the laboratory studies of cadmium biosorption by vine shoots, this research accounts for the use of resources and the environmental impact of emissions. Thus, the study specifically focuses on activities from the initial gate (use of resources and raw materials) to the final gate (completion of the biosorption process). Thus provides a comprehensive analysis within this defined scope. This process determines the elements that are most likely to have an impact on the environment using scaled-up inventory data. The laboratory produced the wastewater sample sets. In order to conduct the LCA quantitatively, each training test considered the beginning and final cadmium concentration, the dose of vine shoots, and the power used in the biosorption process. Vine shoots are typically left on the ground and are not the main objective of the production process. This fact could produce additional negative effects on the ecosystem. However, for this study, the residue was considered to be just a raw material with no intrinsic worth or significance. Thus, allocation factors were overlooked. The energy requirements of the magnetic stirrer in the lab, which is employed in the cadmium biosorption process, were measured and computed. The sieving step was not taken into consideration because of the size of this study and the challenges that resulted from the inability to distinguish between the variations in sieving procedures. The process's losses in biosorbent mass and the biosorbent regeneration were not considered. Finally, as this was a lab-scale gate-to-gate investigation, regeneration of the biosorbent was not taken into consideration due to insufficient data.

3.6.2. Midpoint indicator assessment

The data was processed using SimaPro v.9.2.0.2 software to enhance comprehension of the environmental effect. The CML-IA baseline v3.06 served as the foundation for this study's LCA and midpoint indicator, as it is generally chosen for wastewater systems (Corominas et al., 2020). The method of impact evaluation is restricted to the initial stages of the cause-and-effect chain by using this baseline methodology. It provides excellent transparency and easy handling (Khanali et al., 2022). The inventory data for the inputs came from the Ecoinvent 3 database, whereas the data on the materials and energy used came from the process simulations. Every economic activity for every human activity involved in the process of cadmium biosorption is included in this life cycle inventory.

Eleven categories of impacts were identified by the midpoint indicator assessment. These include: abiotic depletion (fossil fuels), fresh water aquatic ecotoxicity, marine aquatic ecotoxicity, terrestrial ecotoxicity, eutrophication, acidification, global warming, ozone layer depletion, human toxicity, and photochemical oxidation. Eutrophication is caused by an overabundance of nutrients being released. The features of the environment that are exposed to acidifying compounds determine how much of an acidifying influence there is, and the variation is substantial. The global warming potential, which is based on greenhouse gas emissions and is calculated over a 100-year period, is one of the main environmental indicators (Ghasemi-Mobtaker et al., 2022). The lifetime of ozone layer depletion is forty years. The main determinants of human toxicity are halides, a measurement based on exposure to, and interactions between, the body and the hazardous material. Photochemical oxidation is the process *via* which active chemicals that are harmful to ecosystems and public health are released. The exploitation of fossil fuels is linked to their abiotic depletion. In this biosorption process, the release of acidifying chemicals into the environment and the damage done to freshwater and groundwater sources are considered when assessing environmental toxicity. It is divided into three primary categories: fresh water aquatic ecotoxicity, marine aquatic ecotoxicity, and terrestrial ecotoxicity.

Table 11 and Fig. 7 provide the results by environmental impact category in the cadmium biosorption process using vine shoots, based on the CML-IA baseline of midpoint indicator. The results in Table 11 show the environmental impact of the two studied optimization scenarios. In the first scenario (Optimization 1), the objective is to maximize the

Table 11
Impact analysis results for optimizations 1 and 2.

Impact category	Unit	Optimization 1	Optimization 2
Abiotic depletion	kg Sb eq	−2.61E−06	−2.85E−06
Abiotic depletion (fossil fuels)	MJ	3.87E−01	1.47E−01
Global warming (GWP100a)	kg CO_2 eq	3.38E−02	1.28E−02
Ozone layer depletion (ODP)	kg CFC-11 eq	4.32E−09	1.66E−09
Human toxicity	kg 1,4-DB eq	2.59E−02	7.30E−03
Fresh water aquatic ecotox.	kg 1,4-DB eq	3.78E−02	1.34E−02
Marine aquatic ecotoxicity	kg 1,4-DB eq	6.27E+01	1.80E+01
Terrestrial ecotoxicity	kg 1,4-DB eq	2.90E−04	1.11E−04
Photochemical oxidation	kg C_2H_4 eq	6.68E−06	2.49E−06
Acidification	kg SO_2 eq	1.67E−04	6.14E−05
Eutrophication	kg PO_4^{-3} eq	1.19E−04	4.41E−05

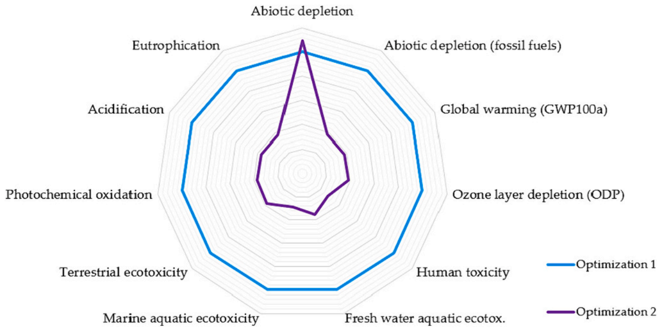


Fig. 7. Comparison of impact categories of optimizations 1 and 2.

percentage of cadmium removal without considering the values of the other parameters. In the second one (Optimization 2), in addition to achieving maximum cadmium removal, the goal is to minimize energy consumption and costs. It can be seen that the greatest environmental impact occurs in Optimization 1. This suggests that, by prioritizing exclusively the maximization of the cadmium removal percentage, there may be greater environmental repercussions than in to the approach of Optimization 2, although the latter also considers energy efficiency and economy. By focusing solely on maximizing cadmium removal, the process uses more resources and emit more pollutants, which result in higher environmental burdens. In contrast to other cadmium removal methods like electrocoagulation, Choudhary et al. (2023) investigated the environmental impact associated with cadmium elimination by electrocoagulation. Their findings revealed a significantly higher environmental impact than produced by the cadmium biosorption by vine shoots approach. In the research by Nishikawa et al. (2018), the environmental impact of cadmium biosorption employing both alginate extraction waste and activated carbon were analyzed and compared. Their results led to a preference for alginate extraction waste. However, when comparing the outcomes of alginate biosorption with those derived from Optimization 1 in this study, it became evident that the environmental impact of cadmium biosorption using vine shoots was slightly lower. Comparing the most unfavorable case in terms of environmental impacts of this research (Optimization 1) with the use of activated carbon, significant differences emerge. In terms of acidification, vine shoots exhibit a significantly lower impact with 1.67E-04 kg SO_2 eq compared to activated carbon's 1.21E-03 kg SO_2 eq. Regarding climate change, vine shoots also demonstrate a notably reduced impact with 3.38E-02 kg CO_2 eq, contrasting with activated carbon's 3.03E-01 kg CO_2 eq. While human toxicity values are comparable between the two biosorbents, with vine shoots slightly lower at 2.59E-02 kg 1,4-DB eq compared to activated carbon's 2.63.E-02 kg1,4-DB eq. Eutrophication impacts remain similar, with vine shoots in at 1.19E-04 kg PO_4^{-3} eq and activated carbon at 1.21E-04 kg PO_4^{-3} eq. Finally, vine shoots in demonstrate a significantly lower impact on photochemical oxidation with 6.68E-06 kg C_2H_4 eq compared to activated carbon's 4.76.E-05 kg C_2H_4 eq.

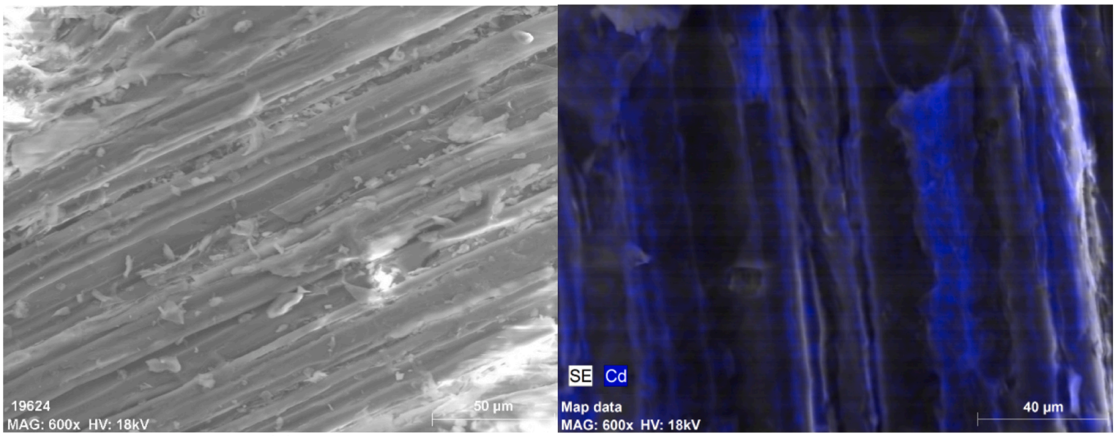
This observation suggests that vine shoots emerge as a more environmentally sustainable sorbent option than alternatives such as alginate extract or activated carbon. The findings underscore the potential of vine shoots to mitigate environmental impacts while effectively removing cadmium from aqueous solutions. Moreover, it positions biosorption by vine shoots favorably over other cadmium removal methods, such as electrocoagulation, highlighting the former's broader environmental benefits in wastewater treatment processes.

3.7. SEM-EDS analysis of Cd(II) biosorption by vine shoots

Using a scanning electron microscope, the surface of the biosorbent was examined to ensure that the raw vine shoot retained Cd(II) ions during the biosorption process. As a result, the second optimization scenario, which had the lowest environmental effect while optimizing cadmium removal and reducing power consumption and expense, was examined using the sample of raw vine shoots. The surface morphology of the vine shoots at 600× magnification appears in Fig. 8a. A linear structure can be seen. This is typical of woody fibers in which woody parenchyma can be observed. The Cd(II) ion retention capacity of this biosorbent is shown in Fig. 8b. It was further verified by EDS elemental mapping (visible in blue). This demonstrates the effectiveness of using vine shoots as sorbents for the removal of cadmium from aqueous solutions.

4. Conclusions

This study concludes that waste generated by the viticulture industry, such as vine shoots, holds potential within a circular economy framework by contributing to the enhancement of water resources. Vine shoots, considered agricultural waste, offer an opportunity for resource efficiency by repurposing a byproduct that would otherwise be discarded. This utilization presents potential cost savings for industries involved in wastewater treatment due to their abundance and low cost. Integrating vine shoots into industrial processes also opens up new market opportunities for agricultural producers. Wineries could potentially generate additional revenue streams by selling vine shoots to industries engaged in wastewater treatment. Furthermore, incorporating vine shoots into a biosorption process contributes to waste reduction by diverting agricultural residues from landfills or incineration, aligning



(a) (b)

Fig. 8. SEM image and EDS spectra of vine shoots: (a) non-adsorbed Cd(II), (b) Cd(II) adsorbed in blue color.

with circular economy principles. This promotes the reuse and recycling of materials, minimizing environmental pollution and conserving natural resources. Additionally, vine shoots, primarily composed of cellulose, hemicellulose, and lignin, are organic materials capable of sequestering carbon. Using vine shoots in biosorption processes retains carbon stored within the biomass, potentially mitigating greenhouse gas emissions, and contributing to carbon sequestration efforts. The findings also show that vine shoots serve as effective biosorbent for cadmium elimination, due to their high lignocellulose content. As a result of a comprehensive life cycle evaluation of the environmental impact, including an analysis of energy consumption during the biosorption process, it is evident that vine shoots produce lower environmental footprints than activated carbon, and at a lower cost.

Moreover, the study delves into the influence of six input parameters (*In_Con, pH, Tim, Speed, Tem*, and *VS_Dose*) on the outputs of *%Rem* (percentage of cadmium removal) and *P_Cons* (power consumption), subsequently exploring two optimization scenarios. The objective of the second scenario is to achieve maximum cadmium removal while minimizing energy consumption and expense. By this optimization, it was determined that, to achieve $\%Rem = 99.23\ \%$ and $P\_Cons = 25.6$ W, the input parameters should be set as follows: $In\_Con = 100$ ppm, $pH = 8$, $Tim = 75$ min, $Speed = 100$ rpm, $Tem = 26\ ^\circ\mathrm{C}$, and $VS\_Dose = 0.1$ g.

Future research could involve conducting similar studies using real industrial wastewater, exploring different heavy metals, or even evaluating the combined effects of two or more heavy metals to elucidate the factors under investigation in each scenario. Additionally, investigating how the particle size of vine shoots affects the removal of heavy metals could offer valuable insights into optimizing biosorption processes for enhanced efficiency and environmental sustainability.

CRediT authorship contribution statement

Celia Sabando-Fraile: Writing – original draft, Validation, Software, Methodology, Investigation, Formal analysis, Data curation. **Marina Corral-Bobadilla:** Writing – review & editing, Writing – original draft, Validation, Supervision, Investigation, Formal analysis, Data curation. **Rubén Lostado-Lorza:** Writing – review & editing, Supervision, Methodology. **Félix Gallarta-González:** Writing – review & editing, Validation, Investigation, Formal analysis, Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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