Potential use of grape waste as a bioadsorbent to remove copper and cadmium from liquid effluents

Maribel Guzman 0000-0002-7954-7679; Fabrizzio Villar 0009-0003-4401-0454; Cesar Villegas 0009-0003-6364-6175; Claudia Toledo 0009-0000-8378-5496
Pontificia Universidad Católica del Peru, Peru
mguzman@pucp.edu.pe, a20230753@pucp.edu.pe, cvillegasl@pucp.edu.pe, claudia.toledo@pucp.edu.pe

Abstract*– A major source of water pollution from mining is acid mine drainage, produced by the oxidation of minerals with high sulfide content. Currently, the possibility of using bioadsorbents to remove heavy metals has become an attractive alternative. This article presents preliminary results on the removal of copper and cadmium using grape waste from the wine industry. Through batch removal trials, optimal removal conditions will be established by monitoring the amount of biosorbent, effluent volume, contact time, and temperature. The final concentration of each contaminant will be determined using atomic absorption spectroscopy (AAS). The maximum removal percentage will also be determined for each contaminant. Removal tests demonstrate that it is possible to remove up to 46% of copper and 34% of cadmium. The Langmuir model fit better than the Freundlich model for copper ($R^2 = 0.876$) and cadmium ($R^2 = 0.957$) adsorption in grape pomace. The aim is to use waste from the wine industry as an efficient, economical, and eco-friendly bio-additive, making it an attractive and competitive alternative to other contaminant removal technologies for mining effluents.

***Keywords*-- Bioadsorbents, Environment, environmental impacts, grape residues.**

I. Introduction

In recent years, the impacts of mining activities on the environment have generated great concern, particularly with regard to the management of water resources near the mining areas [1-3]. Currently, several methods exist for metal removal, with lime precipitation being the most widely used [4,5]. However, these techniques have limitations due to the high initial, operational and maintenance investments [6]. For this reason, the possibility of using bioadsorbents for heavy metal removal has become an interesting alternative [7-10].

In fact, bioadsorbents are a cost-effective and sustainable remediation technique, as they are sourced from other industries such as agriculture [11,12]. Globally, agricultural waste has proven to be a versatile solution in the development of bioadsorbents for the treatment of contaminated effluents [6,13,14]. This minimizes environmental impact and contributes to a circular economy model [11]. Special attention is paid to residual by-products from the wine industry, such as grape skins and seeds, which have shown great potential in the removal of heavy metals in mining effluents [15-19].

On the other hand, the wine industry in Peru has consolidated its position among Latin American wine producers in recent years, winning silver medals at the 2023 Concours Mondial de Bruxelles [20-22]. However, this development has also led to an increase in the amount of organic waste that is incinerated or ends up in landfills [11].

In this regard, the use of a bioadsorbent made from wine industry waste aims to offer a viable and sustainable solution for removing copper (Cu^{2+}) and cadmium (Cd^{2+}) present in mining effluents.

This research aims mitigate the environmental impacts generated by mining activities and will allow for the valorization of agro-industrial waste, promoting a beneficial alternative for both the environment and the national economy.

II. Methodology

A. Grape waste sample

The grape variety used to obtain the waste was Black Borgoña was obtained from an area south of Lima.

1) Obtaining the grape waste sample (bioadsorbent)

3.0 kilos of grape sample were used. Grape bunches consist of a woody skeleton called the rachis or stalk, to which numerous berries (the grapes) are attached by small stems (pedicels). Each individual berry contains skin, pulp, and sometimes seeds. In our case, the berries were separated from the rachis. The berries were pressed, and the residue (peel and seeds) was dried at 60°C for 72 hours. On the other hand, the branches were dried for 20 hours at 60 C.

The dried sample was ground and sieved through mesh # 40 (425 μm). Subsequent tests were performed using the sample that passed through the 40 mesh.

2) Characterization of bioadsorbent

The chemical composition of the samples was determined using the Energy Dispersive Spectroscopy (EDS) technique. EDS analysis was performed in a Scanning Electron Microscopy (SEM) with a coupled Ametek EDAX TEAM system. For this, an SEM (FEI Quanta 650, The Netherlands) was used in the secondary electron mode with an accelerating voltage of 3–10 kV.

3) Determination of Point of Zero Charge (PZC)

To determine the PZC of the bioadsorbent, the mass titration method was used; employing a potassium nitrate solution [23]. Different weights of grape waste samples (0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 g) were placed in a 50 mL Erlenmeyer flask. Supplies of KNO_3 corresponding to concentrations of 1% and 6% were then added. The samples were stirred at room temperature (150 rpm for 24 hours) [23-25].

After that, the pH measurement of the samples was performed with a Hanna multiparameter meter, which was previously calibrated using standard buffer solutions of pH 4, 7, and 10.

B. *Preparation of Cu^{2+} and Cd^{2+} solutions*

Copper and cadmium solutions were prepared by dissolving $CuSO_4$ and $CdSO_4$ in MiliQ water. The concentrations studied were 10 and 50 ppm. The pH of each solution was adjusted to the PZC value. For this purpose, HNO_3 (5% and 20%) was used.

C. *Removal tests*

The adsorption experiments were performed in batch systems, using 500 mg of bioadsorbent in 50 mL of each solution of copper and cadmium dilutions (20 and 50 mg/L). Three stirring times were evaluated: 20, 40 and 60 minutes, using an orbital shaker at 170 rpm and at room temperature.

The concentrations of copper and cadmium, before and after the removal process, were obtained using atomic mass spectrometry (AAS). These results allowed the determination of the percentage of removal in each case.

III. Results

A. *Grape waste sample*

The bioadsorbent was obtained as described in the previous section. Fig. 1 shows the fresh grapes and the dried bioadsorbent before and after being crushed.

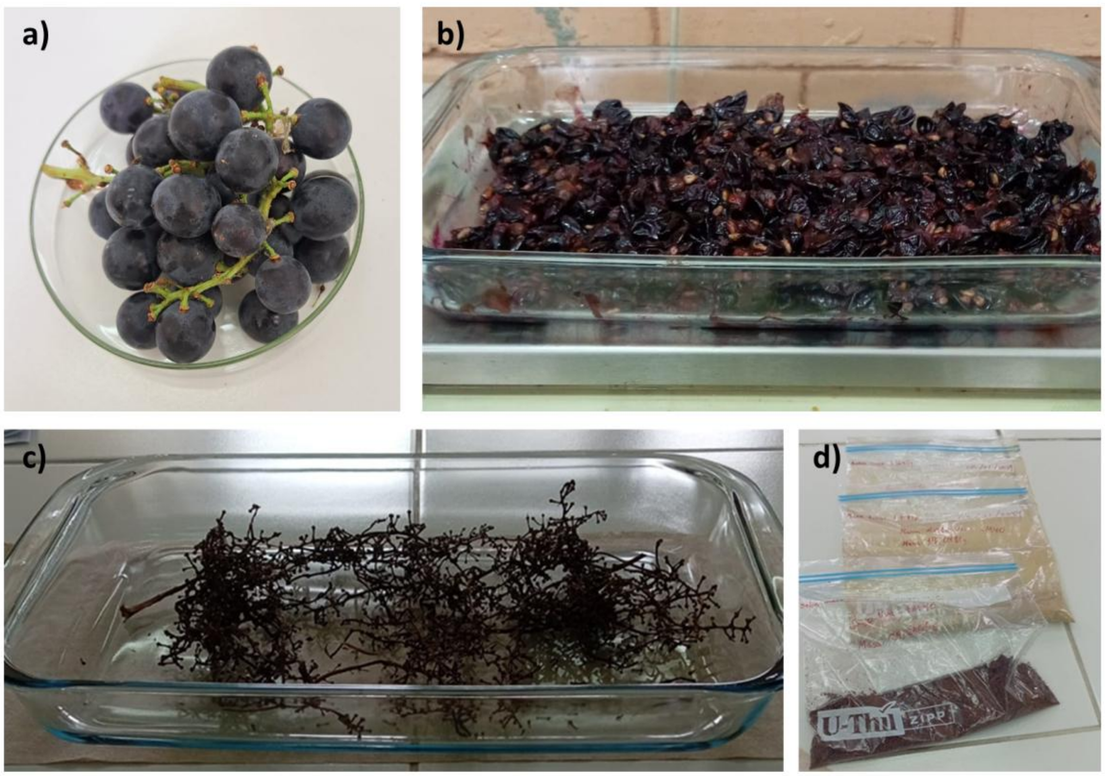


Fig. 1 a) Fresh black Borgoña grapes; b) residues of the grapes after being pressed and dried at 60°C (pomace) ; residues from the branches after being dried at 40°C; and d) ground bio-adorbents obtained.

B. *Semi-quantitative chemical composition.*

Micrographs of the bioadsorbent from peel and seeds were obtained by SEM (Fig. 2). The photographs shows that the obtained fragments are in the range of 50 to 180 µm. Fig. 2b shows a detailed view of the bioadsorbent, where certain pores can be observed.

The EDS spectrum of the bioadsorbent sample is shown in Fig. 3. The EDS spectrum shows that the sample does not contain heavy elements as contaminants. Micrographs of SEM of branches are shown in Fig. 4.

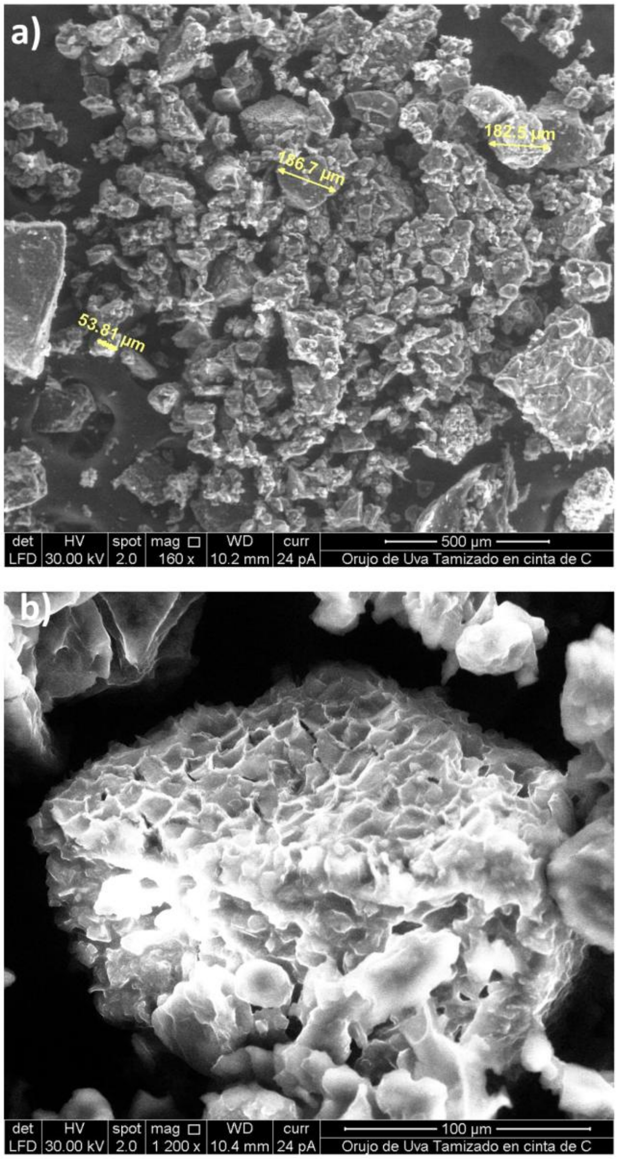


Fig. 2 SEM photo of bioadsorbent from grape pomace a) general view and b) detail.

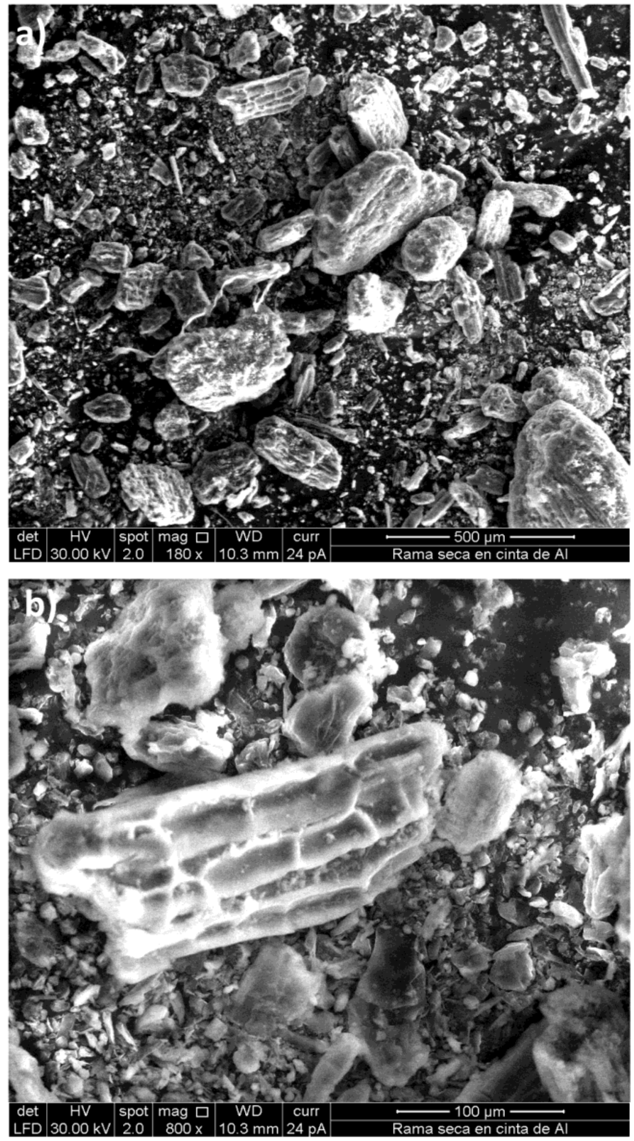
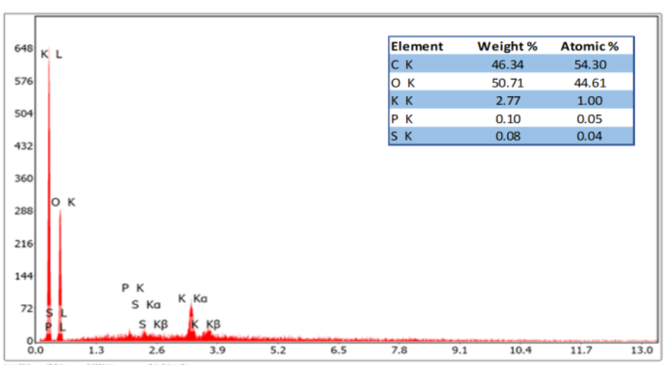


Fig. 4 SEM micrography of bioadsorbent from grape's branches a) general view and b) detail.



Element	Weight %	Atomic %
C K	46.34	54.30
O K	50.71	44.61
K K	2.77	1.00
P K	0.10	0.05
S K	0.08	0.04

Fig. 3 EDS spectrum of bioadsorbent from grape pomace.

C. Point of Zero Charge (PZC)

The PZC values for certain are shown in Fig. 5. The PZC for the skin and seed part is 3.2. This pHpzc value indicates that the grape surface is negatively charged at pH values> 3.2, while the biosorbent surface is positively charged at pH values < 3.2. Similar value between 2.8 and 3.5 was reported by Fiol & Villaescusa [23] and Haydar et al. [26] in plant materials subjected to thermal processes.

In the case of the branch, its PZC value was greater than 4. Therefore, in this case, it is preferable to work with the bio-adherent obtained from grape pomace.

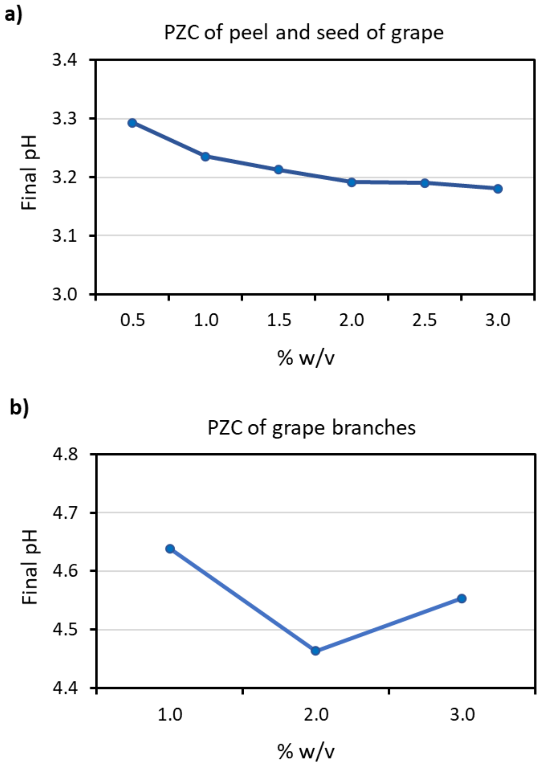


Fig. 5 EDS spectrum of bioadsorbent from a) peel and seeds of grape. b) grape's branches.

D. Removal tests

In the case of the branch, its PZC value was greater than 4. Therefore, in this case, it is preferable to work with the bio-adherent obtained from grape pomace. Removal tests were performed in an orbital shaker at 20, 40 and 60 minutes and at room temperature (Fig. 6).

Fig. 6 EDS Copper and cadmium removal tests using grape pomace waste.

The copper and cadmium removal results are shown in Fig. 7 and Fig. 8, respectively. Table I shows that the highest removal rate (46%) is obtained when the most dilute copper solution is used. If the metal (mg)/bioadorbent (g) ratio increases from 2.0 to 3.8, then the removal percentage decreases to 32% (Fig. 7). A similar behavior is observed for cadmium, where the maximum removal is 34% when the metal (mg)/ biosorbent (g) ratio is 1:1, and when this ratio is 5:1 the removal only reaches 21% (Fig. 8 and Table III).

When comparing the removal of both metals, copper is removed more effectively than cadmium (Table II).

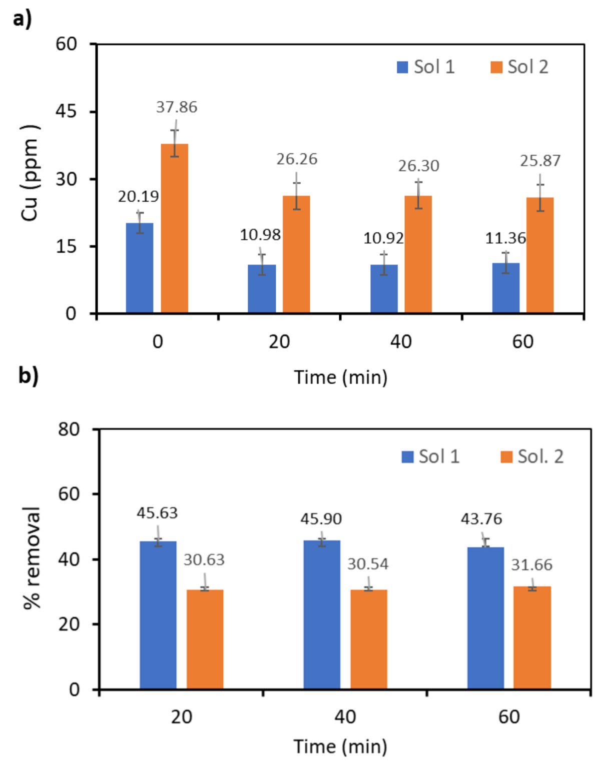


Fig. 7 a) Final copper concentrations and b) removal percentages when using grape pomace waste as a bioadsorbent.

TABLE I
FINAL COPPER CONCENTRATIONS (MG.L^{-1}) AND REMOVAL PERCENTAGES WHEN USING GRAPE POMACE WASTE AS A BIOADSORBENT.

Time (min)	Sol. 1	% removal	Sol. 2	% removal
0	20.19	---	37.86	---
20	10.98	45.63 ± 0.58	26.26	30.63 ± 1.42
40	10.92	45.90 ± 0.13	26.30	30.54 ± 0.67
60	11.36	43.76 ± 0.01	25.87	31.66 ± 1.14

TABLE II
FINAL CADMIUM CONCENTRATIONS (MG.L-1) AND REMOVAL PERCENTAGES WHEN USING GRAPE POMACE WASTE AS A BIOADSORBENT.

Time (min)	Sol. 1	% removal	Sol. 2	% removal
0	9.80	----	49.80	----
20	6.42	34.46 ± 3.50	39.11	21.46 ± 0.18
40	6.51	33.62 ± 3.75	39.55	20.58 ± 0.43
60	6.49	33.83 ± 3.97	39.44	20.81 ± 2.66

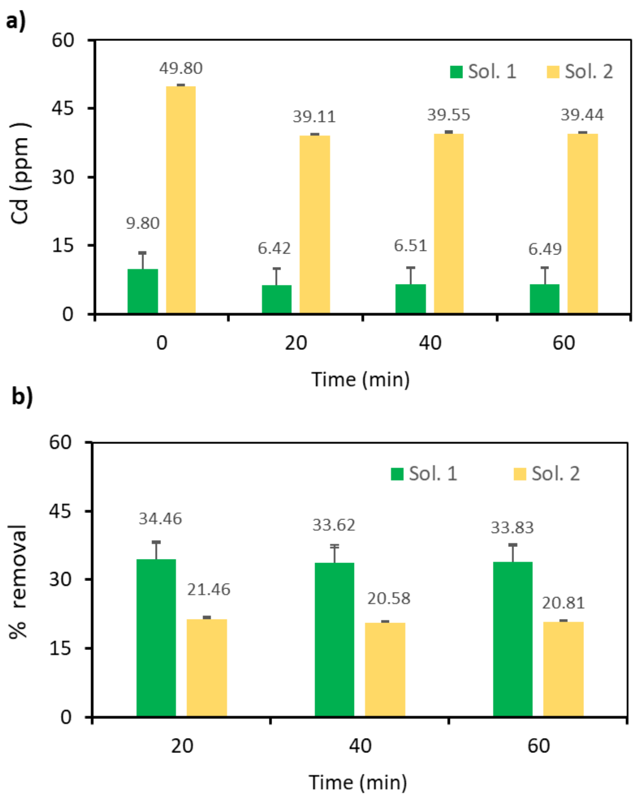


Fig. 8 a) Final cadmium concentrations and b) removal percentages when using grape pomace waste as a bioadsorbent.

TABLE III
COPPER AND CADMIUM REMOVAL AS A FUNCTION OF THE METAL(MG) / ADSORBENT (G) RATIO

metal (mg) / bioadorbent (g)	% Removal	
	Cu	Cd
1 : 1	---	34%
2 : 1	46%	---
3.8 : 1	32%	---
5 : 1	---	21%

As can be seen from the results obtained (Table III), the removal of cadmium and copper is different compared to those reported by other authors using carbon as a bioadsorbent (Table IV). In the case of cadmium removal, our results are similar to those reported by Rao et al. [27]. For copper, our results are within the removal range reported by García-Díaz [28]. This may be due to the different mechanisms developed during removal.

Copper and cadmium could be removed from solutions using grape waste primarily through biosorption, involving ion exchange, surface complexation, or electrostatic interactions. Grape waste, as an organic material, contain functional groups like hydroxyl, carboxyl, and amine within their cellulose and lignin structures that bind metal ions, with maximum removal occurring at pH 4–6.

The following details the proposed mechanisms for the removal of heavy metals:

- Ion Exchange: The metal ions Cu^{2+} and Cd^{2+} are adsorbed onto the surface of the grape waste, releasing previously bound alkaline or alkaline earth metal ions like K^{+}, Mg^{+2}, and Ca^{2+}, or protons H^{+}.

$$\approx S - M_{(s)} + Me^{2+}_{(aq)} \Leftrightarrow \approx S - Me_{(s)} + M^{2+}_{(aq)} \ldots . (1)$$

- Surface Complexation: Functional groups (specifically carboxyl and hydroxyl) present in the polyphenolic compounds of the grape waste form complexes with heavy metal ions, holding them securely.
- Electrostatic Interaction: Positively charged metal ions are attracted to the negatively charged surface of the modified grape waste material, a process accelerated at higher pH levels

On the other hand, the removal of metals using the biosorbent depends on several factors such as:

- Optimal pH: Metal sorption is highly dependent on pH, with maximum uptake generally occurring between pH 4.0 and 6.5 [29-31].
- Modification: Treatment of grape waste with chemicals, such as sulfuric acid or base, significantly increases its efficiency, with some modified materials showing over 95% removal efficiency for cadmium and lead.
- Rapid Kinetics: Studies show that the adsorption process is fast, often reaching equilibrium within one hour.
- Biosorbent Type: Grape stalks have shown superior performance in column studies for removing copper and nickel, while grape pomace is also highly effective.

TABLE IV
COMPARISON OF COPPER AND CADMIUM REMOVAL USING A DIFFERENT TYPE OF BIOADSORBENT.

Metal	Dosage of absorbent ($g.L^{-1}$)	% removal	Reference
Copper	0.15	20	[32]
	1	22-99	[28]
	2	99.4	[33]
	10	90	[27]
	50	85	[34]
	10	32-46	Present study
Cadmium	0.15	60	[32]
	2.5	33-94	[35]
	10	88	[27]
	10	21-34	Present study

Using the data obtained from the copper and cadmium removal tests, the Langmuir and Freundlich isotherms were obtained (Fig. 9 and Fig. 10).

The Langmuir isotherm describes monolayer adsorption on a homogeneous surface, with equivalent adsorption sites and saturation, while Freundlich describes multilayer adsorption on heterogeneous sites, as an empirical relationship that does not reach a saturation limit and is better for low concentrations, indicating greater variability in adsorption energy [36].

The Langmuir model ($R^2 = 0.876$) had a better fit than the Freundlich model ($R^2 = 0.324$) to the copper adsorption data in grape pomace. The Langmuir model ($R^2 = 0.957$) had a better fit than the Freundlich model ($R^2 = 0.003$) to the cadmium adsorption data in grape pomace (Table IV).

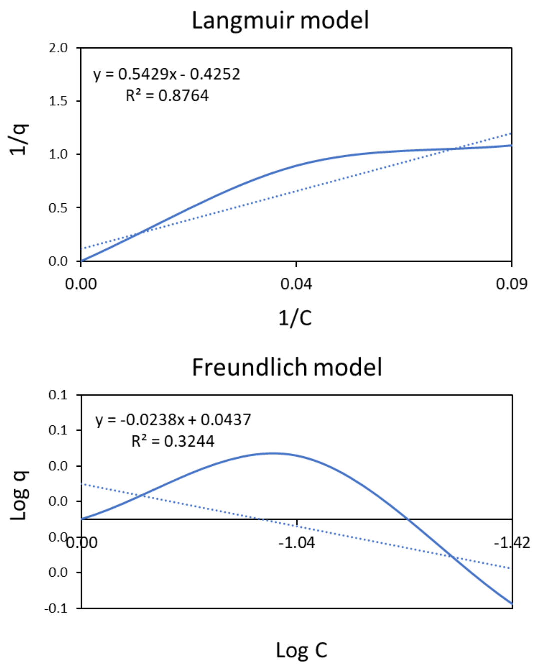


Fig. 9 Langmuir and Freundlich isotherms for copper adsorption.

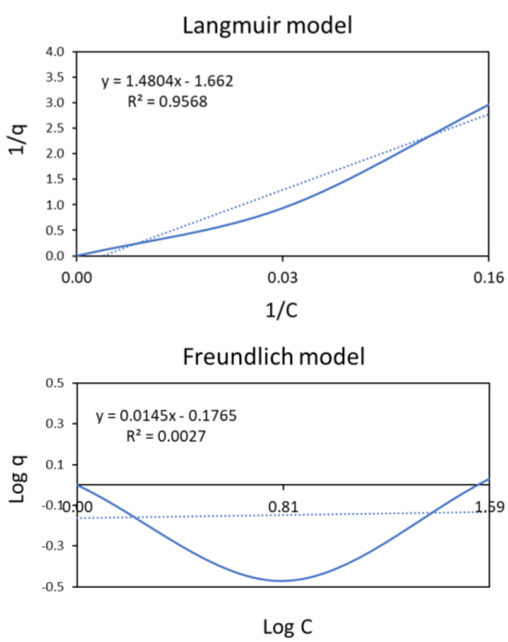


Fig. 10 Langmuir and Freundlich isotherms for cadmium adsorption.

TABLE IV

FINAL COPPER CONCENTRATIONS AND REMOVAL PERCENTAGES WHEN USING GRAPE POMACE WASTE AS A BIOADSORBENT.

Metal	Langmuir model			Freundlich model		
	q_{max} (mg/g)	K_L	R^2	K_F	n	R^2
Copper	1.277	2.352	0.876	1.045	42	0.324
Cadmium	0.891	0.602	0.957	0.838	69	0.003

E. Continuation of the research (next steps):

To obtain complete research results, it will be necessary to:

- perform copper and cadmium removal tests by varying the metal (mg)/adsorbent (g) ratio and pH values.
- determine the porosity of the bioadsorbent.
- activate the surface of the bioadsorbent in order to improve its adsorption capacity.
- removal tests will need to be performed using the bioadsorbent obtained from grape stems.
- a kinetic/thermodynamic analysis of the removal process
- a scalability analysis and the associated costs of the process.
- adsorption/desorption kinetics studies.
- evaluate the regeneration of the bioadsorbent and the maximum use cycle.
- conduct removal tests using an actual AMD.
- compare the results with other bioadsorbents such as activated carbon, zeolites, etc.

IV. CONCLUSIONS

Based on our results, we can conclude that the pomace has a copper and cadmium removal rate of approximately 46% and 34%, respectively. Copper removal is highest when the metal-to-bioadsorbent ratio is 2:1. For cadmium, removal improves when the metal-to-bioadsorbent ratio is 1:1. Langmuir isotherms best fit the adsorption of copper and cadmium. The time studied does not influence the copper and cadmium removal process.

We conclude that grape pomace waste can potentially be used for copper and cadmium removal.

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