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## GREEN GRAPE MARC BIOSORBENTS PREPARATION FOR MERCURY REMOVAL IN AQUEOUS MEDIA

### Article Highlights

- Grape marc-based biosorbents from wastes of Negroamaro wine production
- The green approach was used in biosorbent preparation with water, ethanol, and citric acid
- Biosorbent has a good adsorption capacity of Hg(II) ions in the water of 36.39 mg g<sup>-1</sup>
- A physical adsorption mechanism of Hg(II) on the biosorbent was observed
- Biosorbent selectivity compared to Cu(II) and Ni(II) was proven

### Abstract

*In this study, grape marc waste from Negroamaro (a South of Italy vine variety) winery production was used to prepare biosorbents for Hg(II) removal in aqueous media. A green approach was used to develop a proper biosorbent through two different grape marc washing procedures. In particular, the common chloridric acid and the greener citric acid were evaluated. The biosorbent prepared using citric acid as a washing agent (GM-CA) gave similar results to the biosorbent washed with HCl (GM-HCl) with a maximum adsorption capacity of 36.39 mg g<sup>-1</sup>. Isothermal studies revealed heterogeneous physical adsorption of Hg(II) on the biosorbents. Moreover, FTIR analysis of the grape marc-based biosorbent without and with Hg(II) confirmed ionic interactions in the biosorbent that fit with a pseudo-second-order kinetic model. Furthermore, no significant adsorption on the biosorbent was observed when two other heavy metals, copper(II) and nickel(II), previously studied for similar sorbents, were considered. Finally, the reusability of GM-CA biosorbent was also demonstrated over three cycles. Thus, the green preparation approach used in this work can be considered suitable for developing grape marc-based biosorbents.*

*Keywords: adsorption isotherms, citric acid, Hg(II) removal, grape marc, green waste biosorbent, kinetic study.*

Nowadays, the widespread diffusion of heavy metals in the environment, mainly released from industrial and agricultural processes, is one of the major and critical issues in the fight against pollution. The World Health Organization considered mercury one of the most hazardous pollutants for human health [1]. Mercury ions and organomercury compounds are easily solubilized in water and living tissues. As a result,

they can bioaccumulate in the human body, causing weakness, damage to the central nervous system, chromosomal mutations, etc., with lesser effects on the renal and gastrointestinal sections [2,3]. Its chemical and physical characteristics are fundamental for industrial processes such as pharmaceutical, oil refinery, electroplating, battery manufacturing, and mining activities [4]. Conventional methods for Hg(II) removal from water include solvent extraction, coagulation-flocculation, flotation, membrane filtration, ion exchange resin, and bioremediation [5–8]. However, traditional methods used to remove metal and heavy metal ions have many disadvantages, such as incomplete removal, low selectivity, the need to use chemical reagents, and high energy costs.

In the last years, the interest in materials, defined

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as biopolymers, extracted from natural matrices with a potential adsorbent capacity of metal ions, has grown considerably for the development of new treatment techniques and alternative technologies for the removal of toxic metals, especially from natural water and wastewater [9]. Biopolymers have interesting characteristics, such as easy availability, low cost, high binding capacity, biodegradability, and the possibility of reuse. Most of these materials derive from agricultural products processing, fruit, wood, and barks, as well as wastes of the textile and fish industries. It is important to underline the significance of using biopolymers since it is in line with some of the fundamental principles of the circular economy, such as the careful and efficient management of resources and their recycling and reuse. In this context, recent biosorbents, such as *Rosmarinus officinalis* leaves [10], Spanish broom plants [11], and exhausted coffee waste [12] were used for the removal of Hg(II) from water. Grape marc represents a widespread biopolymer that remains a byproduct of wine-making production. Tens of millions of tons of grapes are produced worldwide each year and are mainly used for wine production. Currently, grape marc is directly treated as fertilizer and animal feed. However, it is worth noting that some efforts are addressed in developing other more profitable grape marc utilization that point out their high potential commercial value.

Additionally, as reported by the International organization of vine and wine (OIV), Italy has been the largest wine-producing nation in the world, at least for the last four years [13]. Thus, in this work, the adsorption behavior of grape marc for mercury removal was studied. Chemical-physical characterization of grape marc has been extensively studied [14], as well as its application as a source of added-value compounds. A recent review of Muhlack *et al.* covers the value-added uses via extraction of valuable components from grape marc and thermochemical and biological treatments for energy recovery [15]. Furthermore, grape marc has been used as a potential biosorbent for the adsorption of organic compounds such as pesticides [16] and caffeine [17]. On the contrary, the application of grape marc for metal ions adsorption has been only little considered in the literature, such as the removal of Cd(II) ions [18], Cu(II), and Ni(II) ions [19] and Cr(VI), Cu(II), Ni(II) ions [20,21]. To our knowledge, the use of grape marc for mercury ion adsorption has not been considered in the literature.

The present work aims first to study the potential use of grape marc wasted from red wine production in Salento, a South of Italy area, as a biosorbent for mercury removal. A green procedure that employs green substances such as ethanol, citric acid (CA), and water during the preparation procedure, was

developed. A comparison was made between the common chloridric acid and the greener citric acid as a washing agent. Both prepared grape marc biosorbents, GM-HCl and GM-CA, were tested in batch Hg(II) adsorption experiments. The pH of Hg(II) ions solutions was considered to evaluate the performance of the biosorbent at pH 7 to minimize additional pretreatment of the water sample. A complete isotherm study was made using Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D-R) equations. Further, kinetics, FTIR characterization, comparative experiments with other metal ions, and reusability were also evaluated.

## MATERIAL AND METHODS

### Chemicals

Mercury(II) chloride (HgCl<sub>2</sub>), anhydrous CA, and Cu(NO<sub>3</sub>)<sub>2</sub>·2.5H<sub>2</sub>O were supplied from Sigma-Aldrich (Steinheim, Germany). Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was purchased from Fluka (Steinheim, Germany). Analytical grade ethanol and HCl 36-38% were obtained from J.T. Baker (Deventer, Holland). Nitric Acid (67-69%) for trace metal analysis, Ni(II), Cu(II), and Hg(II) standard solutions (1000 mg L<sup>-1</sup>) were supplied from Romil-SpA. All solutions were prepared with deionized water provided by a water purification system (Human Corporation, Korea).

### Instrumentation

Fourier transform infrared spectroscopy (FTIR) analysis was performed on a JASCO 660 plus infrared spectrometer. UV-vis analyses were performed by using a Jasco V-660 UV-visible spectrophotometer. An ultrasonic water bath from Bandelin Electronic, Sonorex RK 102H, was used (Bandelin Electronic, Berlin, Germany, Europe, [www.bandelin.com](http://www.bandelin.com)). A centrifuge PK121 multispeed of Thermo Electron Corporation was adopted (Thermo Electron Corporation, Waltham, Massachusetts, USA, [www.thermoscientific.com](http://www.thermoscientific.com)). Equilibrium batch adsorption studies and selectivity evaluations were carried out using a Thermo Scientific inductively coupled plasma mass spectrometry (ICP-MS) iCAP Q (Thermo Fisher, Scientific, Waltham, USA). pH was defined using a pH meter (Basic 20, Crison, Alella, Barcelona, Spain).

### Biosorbents collection and preparation

Grape marc of Negroamaro variety, achieved in the wine production process, were supplied by a wine manufacturer in the Salento region (Lecce, Italy). They were sun-dried for three days, milled using a grinder, and finally sieved (< 2 mm) to remove coarse particles

and fibers. After that, the biosorbents preparation process was carried out following various washing steps described below. Each washing step was made by shaking the dispersion for 15–30 min at 250 rpm, centrifugation for 15 min at 9000 rpm, and finally with the supernatant removal.

After a preliminary washing in water, grape marc was washed with ethanol to remove the most polar organic components, which could interfere with the adsorption process, until no UV-vis absorbance was observed in the 280–800 nm.

Washings with acidic aqueous solutions were carried out to eliminate most cation ions in the grape marc. Thus, different experimental conditions were adopted by using HCl (0.1 M, pH 1), similar to the pH used in the literature [19], and also with CA at milder pH conditions that were pH 3 (0.002 M) and pH 2 (0.6 M). The number of washings was defined by monitoring cation ions concentration ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , and  $\text{Na}^+$ ) using ICP-MS until a value lower than  $1 \text{ mg L}^{-1}$  was found. After, five washings with water were made to eliminate the acidic environment and chlorine or citrate ions. Finally, the biosorbents were dried in the oven at  $60 \text{ }^\circ\text{C}$  till constant weight was reached. The above-described adsorbents were tested with an aqueous solution of Hg(II) ( $100 \text{ mg L}^{-1}$ ) and washed five times with the aqueous solution of HCl (0.1 M, pH 1) or CA (0.6 M, pH 2), denoted GM-HCl and GM-CA, respectively, that were selected for further studies.

### Hg(II) adsorption experiments

Batch adsorption experiments were performed for both biosorbents GM-HCl and GM-CA by shaking the dispersion prepared by mixing 3 mg of the dry biosorbent with 3 ml of  $\text{HgCl}_2$  aqueous solution at known concentrations in the range of 23–300  $\text{mg L}^{-1}$  [18,22]. The mixture was shaken for 20 h at room temperature and 250 rpm and filtrated through a  $0.20 \text{ }\mu\text{m}$  filter to remove the sorbent. The solution was then analyzed to determine Hg(II) concentration by ICP-MS. The ion amount adsorbed on the biosorbent matrix ( $\text{mg g}^{-1}$ ) was calculated by the following equation:

$$q_e = (C_i - C_e) \frac{V}{m} \quad (1)$$

where  $C_i$  is the initial Hg(II) concentration ( $\text{mg L}^{-1}$ ) and  $C_e$  is the equilibrium metal ion concentration ( $\text{mg L}^{-1}$ ),  $V$  is the volume of Hg(II) aqueous solution (L), and  $m$  is the mass of biosorbent (g). Each experiment was carried out in triplicate.

### Isotherms studies

The adsorption data were fitted into four linearized

Langmuir, Freundlich, Temkin, and D-R isotherms [22]. Langmuir isotherm model describes the formation of a monolayer adsorbate on the outer surface of the biosorbent, and it is represented in the following linear form [12,18,22,23,24]:

$$\frac{1}{q_e} = \frac{1}{q_{\max} C_e K_L} + \frac{1}{q_{\max}} \quad (2)$$

where  $q_e$  is the amount of Hg(II) adsorbed per gram of biosorbent at equilibrium ( $\text{mg g}^{-1}$ ),  $C_e$  is the equilibrium Hg(II) concentration ( $\text{mg L}^{-1}$ ) of the incubated solution, while  $K_L$  ( $\text{L mg}^{-1}$ ) and  $q_{\max}$  ( $\text{mg g}^{-1}$ ) are the Langmuir equilibrium constant and the maximum monolayer adsorption capacity of the biosorbent respectively that are calculated from the slope and intercept of the linear plot of  $1/q_e$  versus  $1/C_e$ .

The linearized Freundlich equation [12,18,22,24] is used to describe the adsorption characteristics of the heterogeneous surface:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (3)$$

where  $q_e$  ( $\text{mg g}^{-1}$ ) and  $C_e$  ( $\text{mg L}^{-1}$ ) are defined above while  $K_f$  and  $n$  are Freundlich isotherm constant related to the apparent affinity constant and adsorption intensity related to the number of the sites, respectively  $K_f$  and  $n$  were determined respectively from the intercept and slope of the linear plot of  $\ln q_e$  versus  $\ln C_e$ .

The linearized Temkin isotherm [22], considering the effect of the adsorbate interaction on adsorption, is given by the following equation:

$$q_e = B \ln A_t + B \ln C_e \quad (4)$$

$$B = RT / b_T \quad (5)$$

where  $A_t$  is the Temkin isotherm equilibrium binding constant ( $\text{L g}^{-1}$ ) and  $B$  is the constant related to the heat of adsorption ( $\text{J mol}^{-1}$ ) that can be calculated respectively from the intercept and slope plot of  $q_e$  versus  $\ln C_e$ . Moreover, in Eq. (5),  $R$  ( $\text{J mol}^{-1} \text{K}^{-1}$ ) is the universal gas constant,  $T$  (K) is the temperature, and  $b_T$  is a parameter associated with the heat of adsorption.

Finally, the D-R model [18,22], which does not assume a homogeneous surface or a constant biosorption potential, is given by Eq. (6):

$$\ln q_e = -K_{ad} \varepsilon^2 + \ln \ln q_{\max} \quad (6)$$

where  $K_{ad}$  and  $\varepsilon$  are the coefficients associated with the free energy adsorption ( $\text{mol}^2 \text{kJ}^{-2}$ ) and the Polanyi's potential ( $\text{kJ mol}^{-1}$ ), respectively, calculated from the slope and the intercept of  $\ln q_e$  versus  $\ln q_{\max}$ .

The free energy of adsorption  $E$  ( $\text{kJ mol}^{-1}$ ), used to distinguish the physical and chemical adsorption of metal ions, was determined from  $K_{ad}$  following Eq. (7):

$$E = \frac{1}{\sqrt{2K_{ad}}} \quad (7)$$

### FTIR biosorbent characterization

FTIR spectra were registered on KBr pellets through 64 scans between 4000 and 650  $\text{cm}^{-1}$ . Pellets were prepared by mixing a few dry biosorbent particles (1 mg) in 100 mg of KBr matrix and successively pressed at 10 tons. After incubation with 150  $\text{mg L}^{-1}$  Hg(II) aqueous solution, the GM-CA was filtered and dried in the oven at 60 °C for two days (enough to reach a stable sample weight) before pellet preparation.

### Kinetic adsorption

A kinetic adsorption experiment was performed, measuring Hg(II) concentration, in the incubated solution, at different times ( $t$ ) up to 20 h. First, the adsorption experiment for biosorbent GM-CA was carried out following the procedure described in (Hg(II) adsorption experiments) by using an initial concentration of Hg(II) equal to 78  $\text{mg L}^{-1}$  ( $C_i$ ). Then, using Eq. (1), the milligrams of Hg(II) adsorbed per gram of biosorbent at time  $t$ ,  $q_t$  ( $\text{mg g}^{-1}$ ), was calculated by the difference between  $C_i$  and  $C_t$ , the concentration at the adsorption time  $t$ .

Kinetic adsorption data were fitted using two commonly adopted kinetic models: pseudo-first order and pseudo-second order [23]. The pseudo-first-order Lagergren model was expressed as Eq. (8):

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303} t \quad (8)$$

where  $q_e$  is the milligram of Hg(II) adsorbed per gram of biosorbent at equilibrium, while  $q_t$  is the milligram of Hg(II) adsorbed per gram of biosorbent at time  $t$ , and  $K_1$  ( $\text{min}^{-1}$ ) is the rate constant of the first-order adsorption.

The pseudo-second-order model was given by Eq. (9):

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (9)$$

where  $K_2$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) is the rate constant of the pseudo-second-order adsorption.

### Comparative adsorption studies

The adsorption capacity of GM-CA biosorbent for other two divalent metal ions, Cu(II) and Ni(II), was measured. In particular aqueous solutions of 100  $\text{mg L}^{-1}$  of Cu(II) and Ni(II) were prepared and used for batch experiments following the same procedure described for Hg(II) adsorption experiments. Eq. (1) was used to calculate their adsorption capacity. Each experiment was carried out in triplicate.

### Reusability procedure

The reusability of GM-CA biosorbent was tested by washing the impregnated biosorbent after each batch experiment procedure. In detail, 30 mg of biosorbent was incubated with 30 mL of a Hg(II) 100  $\text{mg L}^{-1}$  aqueous solution and taken under stirring for 7 h at 250 rpm to reach the adsorption equilibrium. Then, the mixture was centrifuged for 15 min at 9000 rpm, the supernatant was filtered and analyzed using ICP-MS to measure Hg(II) concentration, and the adsorption capacity  $q_e$  was evaluated. Next, the impregnated biosorbent was treated with a 0.1 M (pH 1) solution of HCl and stirred for 30 min to release the adsorbed Hg(II). Then it was washed with water until neutral pH reached and finally dried before its reuse. The procedure herein described was repeated for three cycles. Finally, the regeneration efficiency ( $RE$ ) was determined by using the following equation:

$$RE = q_n / q_0 \quad (10)$$

where  $q_0$  is the adsorption capacity before the regeneration process ( $\text{mg g}^{-1}$ ) and  $q_n$  is the adsorption capacity ( $\text{mg g}^{-1}$ ) at the  $n$  adsorption cycle. The same reusability procedure was carried out using a 0.6 M (pH 2) solution of CA for Hg(II) release.

## RESULTS AND DISCUSSION

### Biosorbents preparation

Fermented grape marc samples were collected from a small local winemaker at the end of the red Negroamaro wine production process and adequately treated. Grape marc represents a cheap and abundant wine production waste in the Salento area, and its utilization is of great interest (Figure 1).

After preliminary drying, grinding, and sieving steps to remove coarse particles and fibers, a progressive extraction process of polar organic compounds and ions was made by using ethanol, acidified water, and water. It is worth noting that a green approach was also adopted to set up the biosorbent preparation process. To this aim, only green solvents, water and ethanol, were used. Grape marc was firstly washed with ethanol to remove the polar organic compounds to avoid contamination of the analyzed solutions during the adsorption process. Moreover, it is interesting to note that the ethanol washing procedure could be helpful for successive value-added uses since the recovered supernatants contain polar organic extractives that could also be isolated as valuable products. Grape marc includes skin, seeds, and stalks with a variety of polar organic compounds that could be used by the food, cosmetic, and pharmaceutical industries. Thus, it can be considered a promising source of phytochemicals, phenolic compounds,

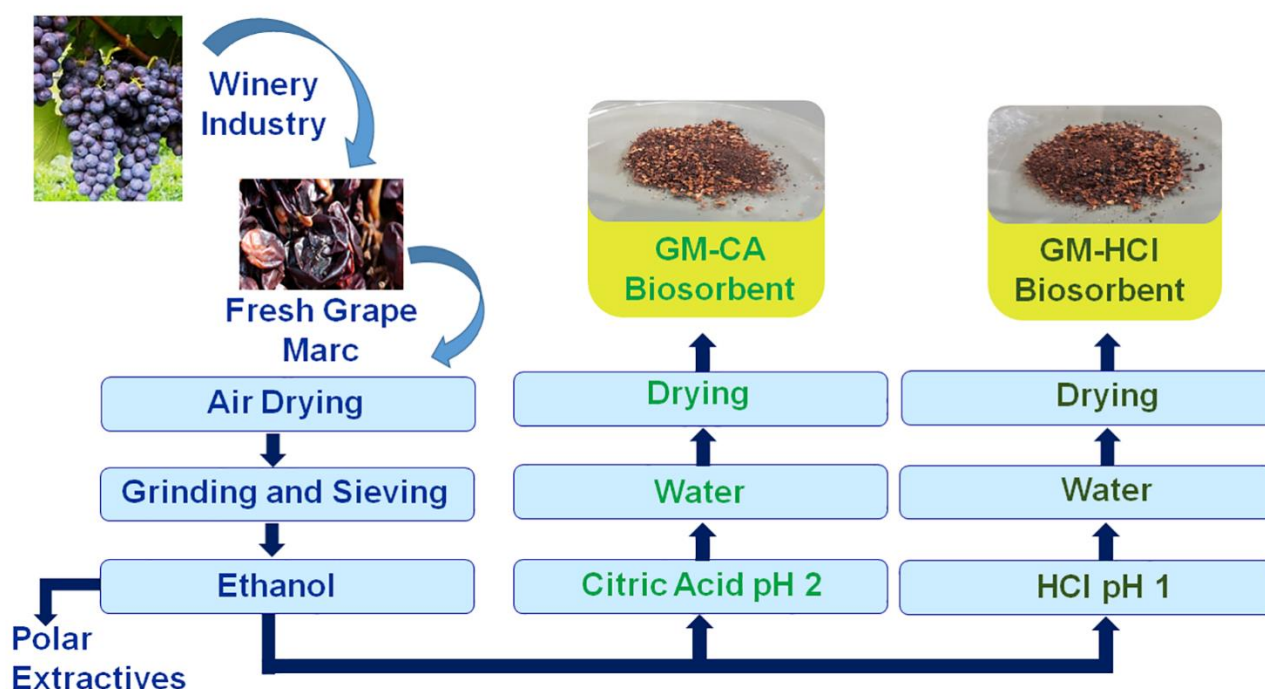


Figure 1. The experimental schematic preparation process of grape marc-based biosorbents.

pigments, and antioxidants [15]. Since phenolic compounds, pigments and antioxidants show absorption in the range of 280–800 nm; each ethanol washing solution was monitored using UV-vis analysis until almost no absorption was observed. Successively, a treatment with diluted acid was defined to remove some cations trapped inside it, leaving free coordination sites available for mercury cation uptake during the adsorption stage. It is known, in fact, the presence of some cations in grape marc matrices. Villaescusa *et al.* measured Ca(II), Mg(II), K(I), and Na(I) cations concentration from diluted HCl washing of grape marc waste and found mainly Ca(II) and K(I) ions released in solution [19]. In this study, this step was carried out by using a common and cheap acid HCl and also, as an alternative, a greener and inexpensive CA. Following Villaescusa *et al.* procedure, a preliminary washing with the 0.1 M (pH 1) HCl aqueous solution was used. Moreover, two other CA procedures at milder pH conditions (pH 3 and 2) were also tested. The washings were done till the concentration of cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , and  $\text{Na}^+$ ) was lower than  $1 \text{ mg L}^{-1}$ . The adsorption capacity of biosorbents treated with each washing procedure was evaluated and biosorbent washed with CA at pH 3 gave lower adsorption capacity than grape marc treated with CA at pH 2. Thus, it was not considered for further studies.

Citric acid is an interesting alternative washing agent since it is also the main acidic compound of lemon fruit. Thus, the results of this research might be helpful as preliminary data for future studies that use

lemon juice for the acidic washing steps of the grape marc, which is interesting from a green point of view. For the above consideration, a CA concentration with a pH close to lemon juice (close to pH 2) was used. Both biosorbents prepared with the different acids will be successfully tested as Hg(II) adsorption materials to verify the efficiency of the greener biosorbent GM-CA compared to GM-HCl.

#### Hg(II) adsorption isotherms

The adsorption behavior of both biosorbents was evaluated by batch experiments. The data were processed by Langmuir, Freundlich, Temkin, and D-R equations to assess their adsorption properties. This work aims to obtain a specific green biosorbent able to bind Hg(II) in a water solution with neutral pH, such as drinking water or tap water, to avoid additional pretreatments of the water sample before incubation. It is well known in the literature that the adsorption performances of similar matrices increase proportionally with the pH. Indeed, to obtain good adsorption results, pH in the range of 5–7 was required. In fact, under these conditions, the deprotonation of the acidic functional groups present in the modified biosorbent, such as lignin, increases the availability of active sites, favoring the electrostatic interactions between the metal ions and the surface of the biosorbent [11,12,19]. For this reason,  $\text{HgCl}_2$  was directly dissolved in water with a pH of 7.

Adsorption experiments were done by shaking

3 mg of GM-HCl or GM-CA biosorbent with 3 mL of aqueous solutions of Hg(II) at known concentrations, from 23 to 300 mg L<sup>-1</sup>. Adsorption equilibrium isotherms of GM-HCl and GM-CA are shown in Figure 2. Moreover, the concentrations of Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, and Na<sup>+</sup> were monitored before and after mercury adsorption giving values lower than 0.5 mg L<sup>-1</sup>, and no release can be assumed.

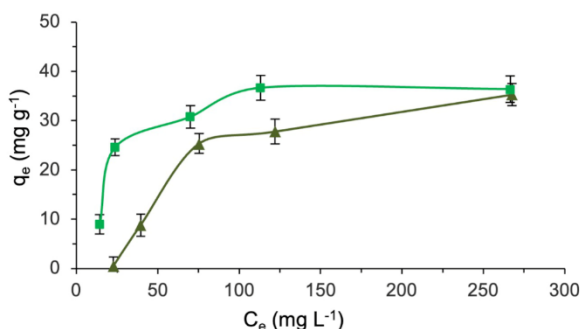


Figure 2. Adsorption capacity isotherm of Hg(II) using grape marc biosorbents GM-HCl (▲) and GM-CA (■).

As it can be seen, the graphics clearly show that the adsorption capacity increases with the increase of the analyte concentration until a saturation point is reached for both biosorbents. An experimental maximum adsorption capacity of 35.30 mg g<sup>-1</sup> and 36.39 mg g<sup>-1</sup> was obtained for the GM-HCl and GM-CA, respectively. Furthermore, it can be observed that the GM-CA curve has a sharper slope with  $q_e$  values slightly higher than the corresponding  $q_e$  values in the GM-HCl curve, with a plateau reached already at 150 mg L<sup>-1</sup> of  $C_e$ . These results show that the acidic treatment helps obtain an efficient biosorbent for mercury removal by using CA under mild conditions, with a pH of around 2, similar to the pH of lemon juice. In Table S1 (supplementary materials), a comparison between the adsorption performances of GM-CA and GM-HCl against Hg(II) with other biosorbents from literature was reported.

In an attempt to verify the adsorption process starting from the experimental adsorption data, four different isotherms were used: Langmuir, Freundlich, Temkin, and D-R. Figures 3 and 4 show the isotherm linear regression curves obtained for GM-HCl and GM-CA biosorbents, respectively, while the significant isotherm parameters were summarized in Table S2.

Langmuir model describes homogeneous binding sites with a monolayer adsorption process only on the outer surface of the sorbent. This model assumes that the adsorption of each metal ion on the active sites takes place with uniform energies with no transmigration process of the adsorbates on the surface. In Figures 3a and 4a, the parameters  $1/q_e$  versus  $1/C_e$  were plotted. The obtained linear curves

showed  $R^2$  values of 0.78 and 0.84, which are unsuitable for describing the adsorption process studied in this work.

On the contrary, the Freundlich isotherm adequately describes the adsorption on heterogeneous surface energy when monolayer adsorption occurs as in the Langmuir model but with a heterogeneous energetic distribution of the active sites and predicting interactions between the adsorbates metal ions. In Figures 3b and 4b,  $\ln q_e$  versus  $\ln C_e$  was plotted, and a bad agreement with the experimental data was found for both grape marc sorbents since regression coefficients lower than 0.73 were obtained.

The Temkin isotherm is generally suitable for a heterogeneous liquid and solid interface. This model assumes a linear decrease of heat adsorption of coverage rather than a logarithmic one predicted in the Freundlich model when the extremely low and high value of concentrations are excluded [22]. Temkin isotherm is characterized by a uniform binding energy distribution up to a maximum value. For this model,  $q_e$  versus  $\ln C_e$  was plotted (Figures 3c and 4c), and the Langmuir, Freundlich, and Temkin parameters are compared in Table S2. The Temkin equation shows the highest regression coefficients, suggesting that this model best fits the adsorption curves for the applied biosorbents. Indeed, the corresponding B constants equal to 17.5 J mol<sup>-1</sup> for the GM-HCl and 11.74 J mol<sup>-1</sup> for the GM-CA are typical of physical adsorption.

Finally, the D-R model, which assumes a heterogeneous surface, was also used to test the experimental data to determine the mechanism of the adsorption process, plotting  $\ln q_e$  versus  $\varepsilon^2$ . The model is generally successfully used with high solute activities and an intermediate range of concentrations. Linear curves with  $R^2$  higher than 0.98 confirm the validity of this model. Moreover, a  $q_{max}$  of about 36 mg g<sup>-1</sup>, very close to the experimental data, was obtained with energies  $E$  lower than 8 kJ mol<sup>-1</sup>, typical of the physical adsorption mechanism [24]. In conclusion, the validity of the D-R model suggests a physical adsorption mechanism for both grape marc sorbents studied, following the results found in the previous Temkin isotherm model. The maximum adsorption capacities, calculated from DR-isotherm, were 35.71 mg g<sup>-1</sup> and 36.41 mg g<sup>-1</sup> for the GM-HCl and GM-CA, respectively, comparable to the values found in other similar biosorbents [12]. Therefore, it can be assumed that by using a greener citric acid instead of a common HCl (generally used for grape marc treatment) for acidic washing steps, biosorbents with similar adsorption performance were also obtained. Thus, from the adsorption isotherm studies, it can be concluded that citric acid is an attractive green alternative washing agent. Furthermore, the biosorbent prepared in this



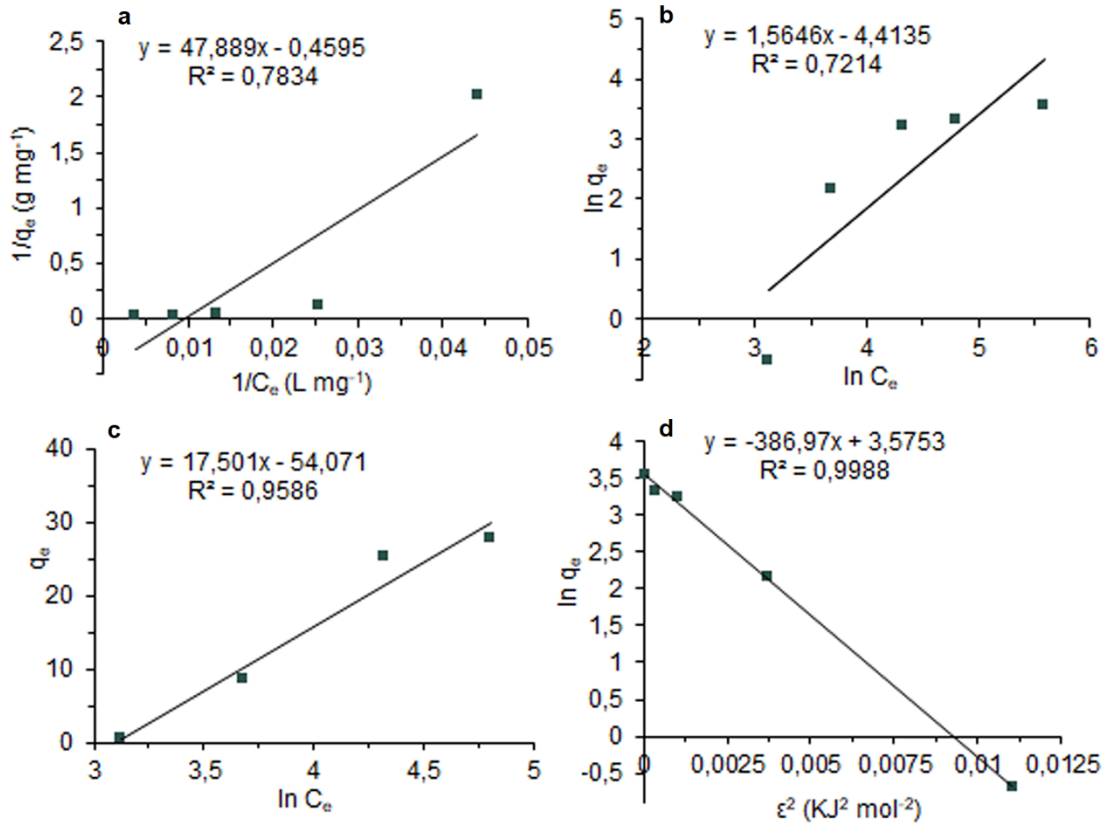


Figure 3. Langmuir (a), Freundlich (b), Temkin (c) and D-R (d) isotherms for adsorption of Hg(II) ions on GM-HCl.

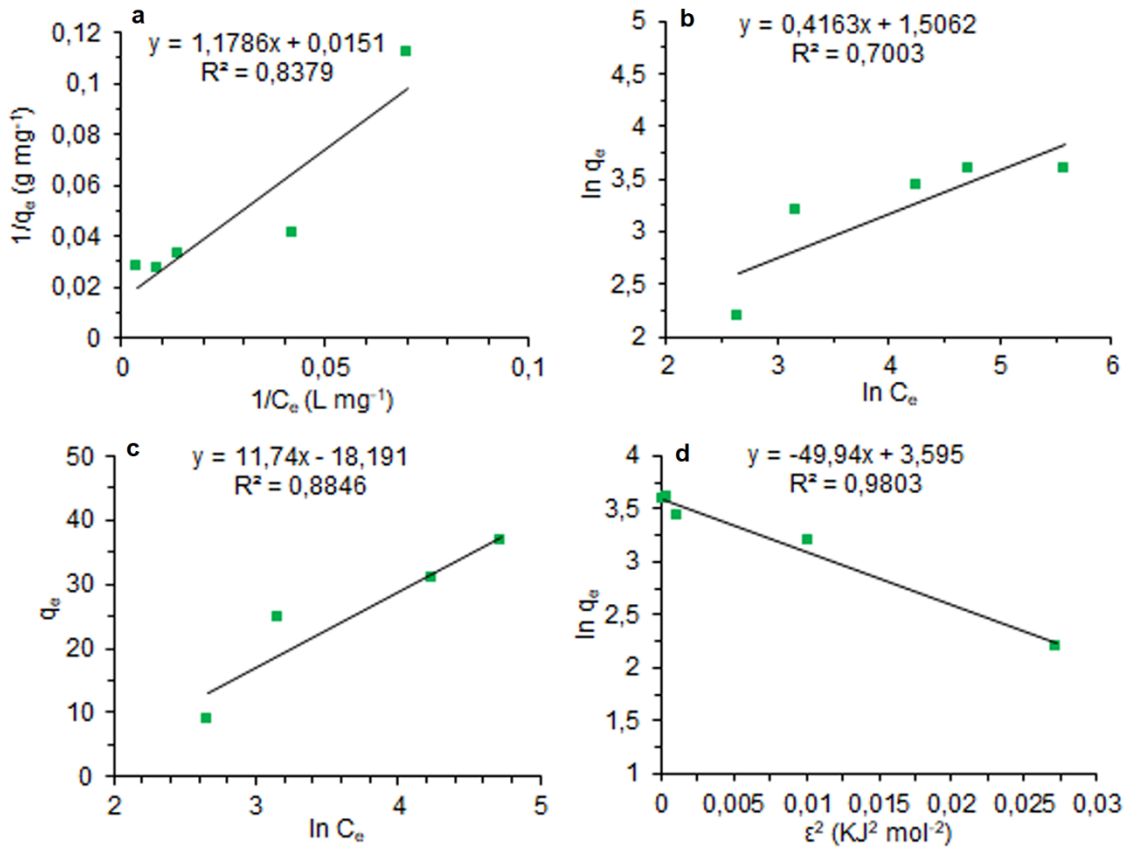


Figure 4. Langmuir (a), Freundlich (b), Temkin (c) and D-R (d) isotherms for adsorption of Hg(II) ions on GM-CA.

work using this solvent has interesting Hg(II) adsorption behavior with a physical adsorption mechanism. Therefore, only the biosorbent prepared with citric acid, GM-CA, was considered for further studies.

### FTIR and kinetic study of GM-CA biosorbent

The FTIR spectrum of grape marc biosorbent treated with citric acid was analyzed to confirm Hg(II) adsorption on the matrix and assess the functional groups of the biomaterial involved in the uptake process. In Figure 5, the FTIR spectra of GM-CA before Hg(II) loading (Figure 5a) and after Hg(II) loading (Figure 5b) are shown. As can be seen in Figure 5a, some characteristic peaks of grape marc are due mainly to the lignocellulosic component [11]. In addition, the spectrum displays some absorption peaks, indicating the complex nature of the material analyzed. In detail, there is a broad band at  $3419\text{ cm}^{-1}$  of the O-H stretching, the aliphatic C-H stretching peaks at  $2918\text{ cm}^{-1}$  and  $2850\text{ cm}^{-1}$ , and a peak at  $1733\text{ cm}^{-1}$  for C=O stretching, typical of unconjugated carbonyl groups. Moreover, the peaks of the C=N ( $1623\text{ cm}^{-1}$ ), C=C stretching of aromatic rings ( $1556\text{ cm}^{-1}$  and  $1518\text{ cm}^{-1}$ ), and aliphatic C-H bending ( $1456\text{ cm}^{-1}$  and  $1436\text{ cm}^{-1}$ ) are also observed [12,25,26]. In Figure 5b, some of the signals present in Figure 5a are slightly modified in terms of shape, intensity, or wavenumber due to mercury interaction. In detail, as can be observed in Figure 5b, the modified signals (highlighted in the circles) after the Hg(II) uptake are related to the O-H stretching ( $3410\text{ cm}^{-1}$ ), C=N stretching (between  $1658\text{ cm}^{-1}$  and  $1611\text{ cm}^{-1}$ ), C=C stretching (between  $1546\text{ cm}^{-1}$  and  $1513\text{ cm}^{-1}$ ), and aliphatic C-H bending (around  $1452\text{ cm}^{-1}$ ). Thus, we suppose that the interaction of the Hg(II) involves mainly the lignocellulosic part, which is the main component of the biosorbent.

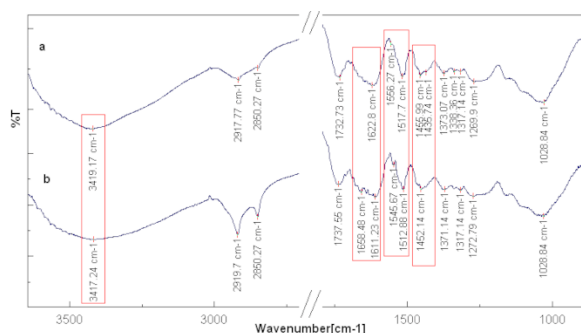


Figure 5. FTIR spectra of biosorbent GM-CA before Hg(II) ions loading (a) and after Hg(II) loading (b).

Further, the GM-CA biosorbent was evaluated by studying the Hg(II) adsorption kinetics. First, a Hg(II) solution of  $78\text{ mg L}^{-1}$  was used to incubate the GM-CA biosorbent. Then, ICP measurements of the Hg(II) concentration at different times were registered, and

the corresponding Hg(II) amount adsorbed at time  $t$ ,  $q_t$  ( $\text{mg g}^{-1}$ ), was plotted against the time in Figure 6. The plateau phase was reached within 7 h of incubation. However, it is worth noting that in the first 60 min, almost 50% of the equilibrium Hg(II) amount is adsorbed ( $10.81\text{ mg g}^{-1}$ , 48%).

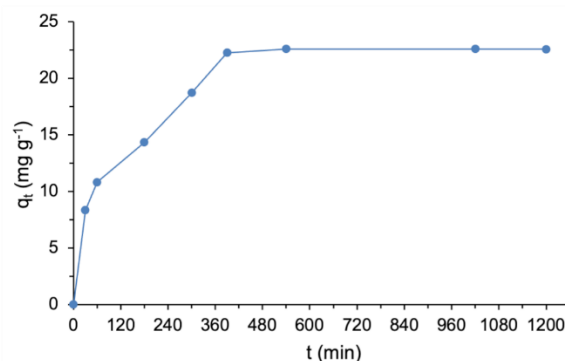


Figure 6. Adsorption kinetic curve of GM-CA with Hg(II) ions aqueous solution ( $78\text{ mg L}^{-1}$ ).

Pseudo-first order and pseudo-second-order models were considered to fit the kinetic data (Figure 7). The corresponding kinetic parameters are summarized in Table S3. The pseudo-first-order equation assumes that one adsorbate ion adsorbs within one active site of the biosorbent. On the contrary, the pseudo-second-order model assumes that one adsorbate ion is linked with two active sites of the biosorbent [27]. Based on the correlation coefficient value of ( $R^2 = 0.994$ ), the experimental data followed the second order kinetics (Figure 7b), with an adsorption rate constant  $K_2$  of  $7.67 \times 10^{-4}$  ( $\text{g mg}^{-1} \text{ min}^{-1}$ ). The theoretical  $q_e$  value estimated from the pseudo-second-order kinetic model was  $23.75\text{ mg g}^{-1}$ , similar to the experimental value obtained at an initial Hg(II) concentration of about  $78\text{ mg L}^{-1}$ . On the contrary, the pseudo-first-order kinetic equation (Figure 7a) showed a correlation coefficient of 0.9300 with an estimated  $q_e$  value of  $3.852\text{ mg g}^{-1}$ , significantly lower than the experimental one, resulting in a bad model to define the kinetics of the adsorption on the sorbent.

### Comparative adsorption study and reusability

Finally, the behavior of the GM-CA biosorbent was tested by evaluating its adsorption capacity for two other divalent metal ions and its reusability. In previous works, the Cu(II) and Ni(II) adsorption capacities of about  $10\text{ mg g}^{-1}$  have been found for similar biosorbents have been studied [19,20]. The adsorption experiments using Cu(II) and Ni(II) salts showed an adsorption capacity of  $100\text{ mg L}^{-1}$ . For Cu(II) and Ni(II), the differences in the concentrations measured before and after incubation were statistically insignificant. It is worth noting that different behavior is found in the



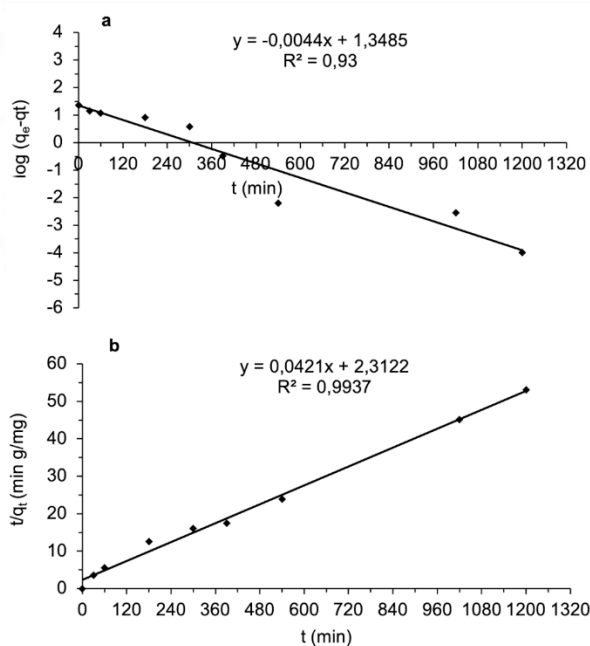


Figure 7. Adsorption kinetics of Hg(II) ions on the GM-CA grape marc-based biosorbent evaluated by the pseudo-first-order model (a) and pseudo-second-order model (b).

literature for similar matrices [20]. These results can be justified by considering the complex structure typical of the grape biomaterial and the different compositions of each grape variety, in addition to the modification of its structure during the biosorbent preparation steps.

After an adsorption experiment using the GM-CA and a Hg(II) aqueous solution of  $100 \text{ mg L}^{-1}$ , the mixture was centrifuged to separate the grape-marc-based biomaterial, which was then treated with an acidic aqueous solution to desorb Hg(II) ions. For this purpose, a solution of HCl or citric acid was used at the same concentration for biosorbent regeneration and reuse. The regenerated biomaterial was reused for another adsorption experiment. The regeneration efficiency for three successive adsorption/desorption experiments was higher than 93% for both treatments. Thus, the regenerated biomaterial showed similar adsorption capacities at least for three cycles.

## CONCLUSION

In this work, two green grape marc-based biosorbents obtained from wastes of Negroamaro wine production were prepared and successfully used for the adsorption of Hg(II) ions in neutral aqueous solutions. A green approach adopted in the biosorbents preparation process allowed the positive evaluation of green chemicals, such as water, ethanol, and citric acid. In fact, from the adsorption isotherm study, the GM-CA biosorbent, prepared using citric acid, showed a maximum adsorption capacity of  $36.39 \text{ mg g}^{-1}$  with a

physical adsorption mechanism of Hg(II) on the matrix. Further, GM-CA was chemically characterized by FTIR, demonstrating the interactions of the Hg(II) with the lignocellulosic component of the grape marc.

Herein for the first time, the adsorption capacity of Hg(II) was demonstrated for a green and cheap grape marc-based biosorbent, and its selectivity, compared to other bivalent ions Cu(II) and Ni(II), was proven as well. Furthermore, the biosorbent developed in this study shows a specific adsorption behavior characteristic of the grape variety and the preparation process. Finally, it is worth noting that these results can help promise future studies to prepare innovative green adsorbents to remove Hg(II) ions from drinking water.

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## DOBIJANJE BIOSORBENTA OD KOMINE GROŽĐA ZA UKLANJANJE ŽIVE IZ VODENIH MEDIJIMA

*Otpadna komina iz vinarije Negroamaro (sorta vinove loze južne Italije) korišćen je za pripremu biosorbenata za uklanjanje Hg(II) u vodenoj sredini. Za razvoj odgovarajućeg biosorbenta korišćena su dva različita "zelena" postupka ispiranja komine grožđa. Posebno su procenjene obična hlorovodonična kiselina i "zelenija" limunska kiselina. Biosorbent pripremljen korišćenjem limunske kiseline kao sredstva za ispiranje (GM-CA) dao je slične rezultate kao biosorbent ispran sa hlorovodoničnom kiselinom (GM-HCl) sa maksimalnim kapacitetom adsorpcije od 36,39 mg g<sup>-1</sup>. Na osnovu izoterme otkrivena je heterogena fizička adsorpcija Hg(II) na biosorbentima. Štaviše, FTIR analiza biosorbenta na bazi komine grožđa bez i sa adsorbovanom Hg(II) potvrdila je jonske interakcije u biosorbentu koje se uklapaju u kinetički model pseudo-drugog reda. Takođe, nije primećena značajna adsorpcija na biosorbentu kada su razmatrana dva druga teška metala, bakar(II) i nikel(II), koji su prethodno adsorbovani na sličnim sorbentima. Konačno, ponovna upotreba GM-CA biosorbenta je, takođe, demonstrirana tokom tri ciklusa. Dakle, korišćeni pristup "zelene" pripreme može se smatrati pogodnim za razvoj biosorbenata na bazi komine grožđa.*

*Ključne reči: adsorpcione izoterme, limunska kiselina, uklanjanje Hg(II), komina grožđa, zeleni biosorbent od otpada, kinetička studija.*