Heliyon 10 (2024) e36811

Contents lists available at ScienceDirect

Heliyon

journal homepage: www.cell.com/heliyon

Research article

Insights into the environmental benefits of using apple pomace for biosorption of lead from contaminated water

Gabriela Ungureanu [a], Iuliana-Maria Enache [a], Irina Gabriela Cara [b], Iuliana Motrescu [a,b], Antoanela Patras [a,*]

[a] "Ion Ionescu de la Brad" Iasi University of Life Sciences, Faculty of Horticulture, 3 Mihail Sadoveanu Alley, 700490, Iasi, Romania
[b] "Ion Ionescu de la Brad" Iasi University of Life Sciences, Research Institute for Agriculture and Environment, 9 Mihail Sadoveanu Alley, 700490, Iasi, Romania

ARTICLE INFO

Keywords:
Apple juice
Food waste
Lead removal
Biosorption
Low-cost adsorbents

ABSTRACT

The apple processing industry generates large quantities of organic waste, presenting a major source of organic contamination. Consequently, finding an effective solution for valorizing this waste has become a pressing issue. This study aims to address two key concerns: (i) solving an agricultural problem by efficiently using agri-food residue, and (ii) removing lead, an extremely toxic element, from contaminated waters to mitigate environmental pollution. Two biosorbents were tested: raw apple waste (RA), obtained from a mixture of apple varieties, and the same material after extracting valuable bioactive and reusable components, extracted apple (EA). The study evaluated the influence of pH, initial biosorbent mass, adsorption kinetics, and equilibrium isotherms. The results are very promising, showing a lead removal efficiency of 82 % for RA and 100 % for EA at a low initial concentration of the solution of 20 mg Pb^{2+}/L and an optimal pH of 5 ± 0.5. The Langmuir model predicted a maximum adsorption capacity of 44.6 mg/g for RA and 48.6 mg/g for EA. These findings demonstrate that apple waste, even after selective extraction of valuable bioactive components, can be effectively used for environmental remediation on a practical scale.

1. Introduction

Organic wastes represent an increasing challenge, and their reuse arises as an imperative necessity, as a mandatory economically and ecological alternative. An important amount of organic waste outcomes from the fruit processing industry. The apple ranks as one of the most widely consumed fruits worldwide, with an annual production of around 86 million tons - a number expected to rise in the coming years due to the growing global population. the growing recognition of the benefits of apple consumption, as well as the food sector development. The apple processing industry alone generates between 6 and 12 million tons of apple pomace annually. After apple products are processed, around 25–30 % of the material becomes solid waste [1]. It is a significant fraction that requires finding appropriate and effective solutions. The management of these agri-food wastes could become a major problem, especially since certain legal regulations must also be fulfilled. These legislative fences have led to the development of a sustainable management regarding the disposal of organic waste. In the European Union, the Landfill Directive prohibits, starting from May 2005, the disposal of organic

* Corresponding author.
E-mail addresses: ing.gabriela.ungureanu@gmail.com (G. Ungureanu), iuliana.enache@iuls.ro (I.-M. Enache), irina.cara@iuls.ro (I.G. Cara), iuliana.motrescu@iuls.ro (I. Motrescu), antoanela.patras@iuls.ro (A. Patras).

https://doi.org/10.1016/j.heliyon.2024.e36811
Received 21 May 2024; Received in revised form 19 August 2024; Accepted 22 August 2024
Available online 23 August 2024
2405-8440/© 2024 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC license (http://creativecommons.org/licenses/by-nc/4.0/).

waste without a preceding treatment [2]. Biorefining represents an extremely promising perspective for a sustainable apple pomace recovery. By this way, it is possible to benefit from the rich biochemical composition of apple waste in order to subsequently obtain added-value products. But also, biorefinery by extraction of the valuable components from the apple waste is an excellent option to fulfil the legislative requirements. The recovery of fibres and bioactive constituents such as for example oils, polyphenols, vitamins, carotenoids or enzymes as well as starch, pectin and lignin, components that can constitute raw materials for other industries (pharmaceuticals, cosmetics, innovative foods, fertilizers) has been widely studied and a considerable number of papers presents very efficient methods for a complete extraction of these phytochemicals [3–7]. The question that arises is what is the best solution for the remaining material? Landfilling or incineration are alternatives however, these depleted residues have the potential for further valorization. The fruit wastes, after going through a biorefinery process, can be converted into biosorbents and utilized to dispose heavy metals from contaminated water effluents. Adsorption is regarded as a straightforward and likely cost-effective process, well-suited for removing low levels of contaminants and ideal for point-of-use treatment. The application of biomass adsorption for retaining heavy metals from wastewater has been extensively studied in numerous research works, and the results were very encouraging. In particular, fruits wastes were tested for lead sequestration from liquid solutions and the obtained adsorption capacities have a wide range of results. Banana peels show an adsorption capacity of 0.19 mg/g [8]. Hamimelon, avocado and dragon fruit peels were tested after saponification with NaOH. The pretreatment was applied to generate additional hydroxyl functional groups on the biosorbent's surface, enhancing its sorption properties. A starting concentration of Pb(II) of 100 mg/L, using 10 g/L of Hamimelon, avocado, and dragon fruit as adsorbents, resulted in retention capacities of 7.89 mg/g, 4.93 mg/g, and 4.60 mg/g, correspondingly. Peanut husk was also considered for lead removal. In this study also, the adsorbent [9] was previously subjected to an improvement treatment by washing with diluted HCl and also NaOH. The biosorbent was applied at a dose of 5 g/L, with a stirring time of 6 h, and an initial lead concentration of 100 mg/L. The study determined the maximum adsorption capacity for Pb(II) to be 27.03 mg/g [10]. Adsorption capacity of Carica papaya peel waste was 6.25 mg/g, using untreated biosorbent with a dosage of 14.6 g/L, and initial lead solution of 96.5 mg/L in pH 4 aqueous solution and 3 h contact time [11]. Dragon fruit, rambutan and passion fruit were considered to be potential biosorbents for lead uptake from a laboratory-prepared solution with an preliminary concentration of 100 mg/L, at pH 4 and 2.5 g/L of sorbent. The adsorbents preparation includes a pretreatment with a solution of 4 mol/L H_2SO_4 for 30 min. Very good results were attained, the tested biosorbents revealing maximum removal capacities of 97.08 mg/g, 114,94 mg/g and 103,09 mg/g [12]. Consequently, the scientific literature includes numerous studies utilizing adsorbents derived from various vegetal materials to remove lead from contaminated aqueous solutions. These adsorbents may or may not undergo pre-treatments to enhance their adsorption capacity. The primary scientific contribution of this work is twofold: first, it involves the use of a food industry waste that has been minimally studied and has not undergone pre-treatments, which would otherwise increase its production cost and reduce its economic attractiveness; second, this waste was subjected to a biorefining process before testing, process involving selective extraction, during which valuable bioactive components with practical applications in other industries were separated. Also, the majority of carried out studies, use high initial lead concentrations, around 100 mg/L Pb(II), far above the values found in real wastewater, fact that could eventually favor getting results that are difficult to translate into practice. This study aims to evaluate lead concentrations similar to those found in industrial effluents. In the production of lead-acid batteries, wastewater typically contains lead concentrations ranging from 5 to 15 mg/L [13]. Metal mining also introduces important quantities of lead into the environment, around 6 mg/L. Additionally, industries such as paints, pigments, glass, chemicals, and electroplating contribute lead concentrations ranging from 0.7 to 25 mg/L [14]. In aqueous solutions, lead predominantly exists as a cation, and its specific chemical form, or speciation, is influenced by the pH (acidity or basicity) and pE (redox potential) conditions of the solution. Lead and its inorganic compounds are classified by the International Agency for Research on Cancer (IARC) as Group 2A - *probably carcinogenic to humans,* indicating their potential to cause cancer in humans [15]. Children are especially vulnerable to the toxic effects of lead on the central nervous system, which can lead to permanent neurological and cognitive damage, blindness, deafness, encephalopathy, convulsions, coma, and even death. In adults, lead exposure can lead to peripheral neuropathy, renal dysfunction, deafness, and hypertension [16]. Consequently, eliminating lead from contaminated environments, particularly wastewater, remains a crucial objective and an urgent priority for both environmental protection and public health.

Present research contributes to solving an agricultural and environmental problem by testing two biosorbents obtained from apple waste resulted from juice preparation, for the mitigation of lead from water bodies. To keep their price as low as possible, none of the biosorbents underwent prior physical or chemical treatments with the aim of improving their adsorption capacity. Moreover, one of the tested sorbents was passed through a biorefining process by a selective extraction and the water-soluble and lipid-soluble compounds were separated for further efficient applications economically profitable. This study offers (i) a structural characterization of two biosorbents and (ii) a critical comparative analysis on lead adsorption capacity of these agri-food wastes. Additionally, it explores a potential mechanism for lead removal in relation to the chemical structure of the sorbents. The research was carried out using a mono-

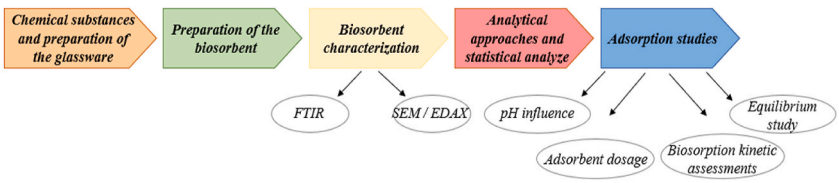

Fig. 1. Diagram of methodological steps.

component synthetic lead solution. Additionally, the initial concentration of the pollutant solution is intentionally chosen to reflect the levels commonly found in industrial wastewater pollution. As far as we know, there is no other study presents the application of biorefined apple waste for lead aqueous remediation, considering relatively small concentrations, hard to remove.

2. Experimental methods

The research methodology for this study follows a series of steps, which are schematically presented in Fig. 1.

2.1. Chemical substances and preparation of the glassware

A precise amount of $Pb(NO_3)_2$ (Merck, analytical grade) was dissolved in distilled water to obtain a stock solution of 1000 ppm Pb (II). This solution was diluted to obtain the less concentrated solutions used for the subsequent stages of the experiment. Diluted solutions of NaOH (analytical grade NaOH pellets, purity $\geq$99.0 %, Merck) or HNO_3 (prepared from HNO_3 65 % p. a., Sigma Aldrich) were utilized for adjustments of the pH of the lead solutions as needed. After each test, the plastic materials and glassware were immersed in a 20 % HNO_3 solution for 24 h, cleaned carefully in distilled water, and finally dried at room temperature.

2.2. Preparation of the biosorbent

Apple pomace, generated as waste during juice preparation, was collected immediately after the cold pressing of apples. To stabilize it, the pomace was dried at 60 °C until reaching a constant mass, using Biobase BOV-T30C convective laboratory oven (Shandong, China). Subsequently, it was ground and sieved through a 1 mm mesh, then stored in a cool, dry place. This sample was labelled as RA.

To obtain the depleted apple pomace (EA) and thoroughly eliminate both water-soluble and lipid-soluble compounds, a novel procedure was experimented for the first time.

(1) Precisely 7.5 g of dried RA were weighed and placed in an Erlenmeyer flask containing 150 mL of distilled water. The extraction process was carried out for 20 min at 50 ± 0.2 °C using an ultrasonic bath (MRC, model AC-120H, Essex, UK) with the ultrasonic frequency of 40 KHz. Afterward, the erlenmeyer containing the extract was transferred to a water bath with rotary stirring (100 rpm) at 80 ± 2 °C for 30 min, followed by filtration. The recovered solid fraction was then dried at 45 °C in the convective laboratory oven;
(2) 75 mL of a solvent mixture containing chloroform/methanol (1/2, v/v) was added to the solid fraction obtained at (1) and introduced in the ultrasonic bath at 50 ± 0.2 °C for 20 min and then, in the water-bath with rotary stirring (100 rpm) at 50 ± 0.2 °C for 30 min, followed by decantation;
(3) the solid fraction obtained at (2) was washed with 100 mL of ethanol 96 %, by keeping the mixture for 20 min on the water-bath at 50 ± 0.2 °C, under stirring at 100 rpm and followed by decantation. The procedure was repeated one more time;
(4) the solid fraction obtained at (3) was rinsed twice with 200 mL of distilled water, followed by decantation and the washing water was thrown away immediately. Then the solid fraction was washed with same amount of water, by keeping the mixture for 10 min on the water-bath at 50 ± 0.2 °C, under stirring at 100 rpm and followed by decantation. The procedure was repeated one more time;
(5) 150 mL of distilled water has been added to the solid fraction obtained at (4) and introduced in the ultrasonic bath at 50 °C for 20 min, followed by decantation;
(6) 150 mL of distilled water has been added to the solid fraction obtained at (5) and introduced for 20 min in the water-bath at 50 ± 0.2 °C, under stirring at 100 rpm and followed by decantation. Afterward, the solid fraction was dried up at 45 °C to steady weight, using the convective laboratory oven. This sample was noted as EA (extracted/depleted apple pomace).

2.3. Biosorbent characterization

2.3.1. Infrared spectroscopy

FTIR spectra (Fourier transform infrared) were recorded between 4000 and 400 cm^{-1} using a Nicolet iS50 FT-IR spectrometer (USA) by diamond reflection attenuated total reflectance (ATR) module. The raw and extracted apple were dried, grounded and the readings of spectra was performed directly on ATR device. The crystal was cautiously cleaned before each measurement with ultrapure water and isopropanol. This analysis was conducted to qualitatively characterize the functional groups presents on the surfaces of RA, Pb-loaded RA, EA, and Pb-loaded EA.

2.3.2. EDAX (elemental chemical analysis) and SEM (scanning electron microscopy)

The surface morphology of the biosorbent before and after lead adsorption was analyzed using scanning electron microscopy (SEM) with a Quanta 450 (FEI, Thermo Fisher Scientific, Hillsboro, OR, USA) and an energy dispersive X-ray detector (EDS) (EDAX, AMETEK Inc., Berwyn, PA, USA). The EDS spectra were processed using the TEAM V4.1 software. The elemental analysis was performed by a Vanta M series portable X-ray fluorescence (XRF) Analyzer, Olympus Scientific Solutions Americas, Waltham, MA, USA. The samples were glued on aluminium stubs using carbon double tape and the analyses were made for the samples without any other preparation. Quanta 450 works in the environmental mode, thus not needing to cover the samples with a conductive layer. The measurements were

carried out in high vacuum (HV) at a pressure of around 10^{-3} Pa using an Everhart-Thorley detector (ETD) with the samples placed at 10 mm and an acceleration voltage of 15 kV. Elemental analysis of the samples was conducted directly without any prior preparation and was performed using a Vanta portable X-ray fluorescence (XRF) analyzer from Olympus Scientific Solutions Americas (Waltham, MA, USA).

2.4. Analytical approaches and statistical analyze

The concentrations of metal in solutions were measured using atomic absorption spectrometry (AAS) with a ContrAA 700 spectrophotometer (Analytik Jena, Germany). When needed, dilutions were made to ensure concentrations within the instrument's linear range. The analysis was conducted with an air/acetylene flame (99.95 % purity), with triplicate readings at 217 nm wavelength, and background correction performed automatically by the software. Before each analysis, calibration curves were generated, with a minimum acceptable determination coefficient of $R^2 > 0.995$. Prior to AAS-flame analysis, samples were filtered through cellulose acetate membrane filters with 45 μm porosity. Sorption experiments were carried out in a batch system using Erlenmeyer flasks with 25 mL lead solution, stirred continuously at 120 rpm and maintained at constant temperature (23 ± 1 °C). The concentration of lead solutions used for the experiments was 20 mg/L Pb^{2+} for pH assessments, adsorbent dosage and kinetic studies. For sorption isotherms, lead concentrations were 7.5, 25, 50, 70, 80, and 100 mg/L Pb^{2+}. All assessments were completed in duplicate.

The experimental data resulting from the tests were mathematically modeled by CurveExpert Professional software by non-linear regression fitting, The well-known Lagergren model by pseudo-first-order and pseudo-second-order equations were plotted for kinetic experiments, while for equilibrium assessments, the Langmuir and Freundlich models were employed.

2.5. Adsorption studies

2.5.1. pH influence

The pH in the initial stages of an adsorption study is crucial as it significantly affects the biosorbent's removal efficiency. Since most real lead-contaminated wastewaters have an acidic pH [13,17,18], preliminary adsorption experiments were conducted within this pH range. The tested pH values were 2, 3.5, and 5.5, using Erlenmeyer flagons with 25 mL of an initial 20 mg/L Pb^{2+} solution and a precisely weighed 0.5 g/L biosorbent. During 4 h of stirring, the pH was repeatedly measured and returned to the initially proposed setting to maintain a constant pH (maximum variation ± 0.5). Adjustments were made with diluted solutions of HNO_3 or NaOH. Upon completion of the test, the concentration of Pb(II) in the solution was determined by AAS after filtration of the samples. The amount of lead removed was then calculated using the mass balance equation (q, mg/g) (Eq. (1)):

$$q = \frac{C_{in} - C_f}{m} V \tag{1}$$

where C_{in} means the lead initial concentration in liquid phase (mg/L), C_f signify the lead concentration subsequent to adsorption process (mg/L), m represents the biosorbent mass (g) and V is volume of the solution (L).

The uptake efficiency was calculated using the equation (Eq. (2)):

$$\%\ removal = \frac{C_{in} - C_f}{C_{in}} 100 \tag{2}$$

2.5.2. Adsorbent dosage

In similar conditions were carried out the biosorbent dosage experiments. The tests were conducted using a metal solution with an initial concentration of 20 mg/L at a pH of 5 ± 0.5. Biosorbent dosages that have been assessed were 0.25, 0.5, 1.0, 2.0, 4.0, and 10.0 g/L. The total dissolved Pb^{2+} in the solution was quantified, and the quantity of lead adsorbed per gram of biosorbent material was calculated using Eq. (1). The removal efficiency was determined using Eq. (2).

2.5.3. Biosorption kinetic assessments

Based on the results obtained from previous tests, the dynamic kinetic studies were performed to evaluate the time required for the biosorption process to reach equilibrium. Therefore, a starting concentration (C_{in}) of 20 mg/L Pb (II), 0.5 g/L dose of sorbent and pH 5 ± 0.5, were the reaction conditions to test several pre-established reaction times (5, 15, 30, 60, 120, 240, 360, 480 min) to accomplish the lead concentration decrease for each contact time.

Two highly employed mathematical models were utilized to adjust the experimental findings, viz Lagergren (1898) pseudo-first-order and pseudo-second-order models [19] expressed by Eq. (3), respectively Eq. (4).

$$q = q_e \left(1 - e^{-k_1 t}\right) \tag{3}$$

$$q = q_e \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{4}$$

where, q *(mg/g)* represent the biosorbed amount for a contact time t *(min)*, q_e *(mg/g)* signify the biosorbed quantity at equilibrium, and k_1 *(min^{-1})* and k_2 *(g mg^{-1} min^{-1})* are the models kinetic constants.

Eq. (1) was initially applied to calculate the concentration of lead in the solution as a function of the time of reaction. The resulting data were then utilized to construct linear models based on pseudo-first-order and pseudo-second-order kinetics. The data derived from these linear representations were subsequently employed to develop non-linear models.

2.5.4. Equilibrium study

The sorption isotherms for lead removal using biobased materials were conducted at pH 5 ± 0.5. An accurately weighed biosorbent concentration of 0.5 g/L (for each sample) was used with 25 mL of lead solution. The initial concentration of Pb(II) solutions used to build the equilibrium curve begins from a low value, increasing to a value that is relatively high, but reasonable for the possible lead concentrations found in real effluents contaminated with lead [13,14], respectively 7.5, 25, 50, 70, 80 and 100 ppm. The results of this experiment will confirm the maximum adsorption capacity predictable for the adsorbent, this resulting from the compatibility between the bio-based sorbent tested and the adsorbate. The considered reaction time was 4 h, as a consequence of the results previously obtained in kinetic tests which showed that this period is enough for the system to attain the equilibrium. Eq. (1) was utilized to determine the quantity of Pb(II) adsorbed per biosorbent mass unit (q). In this specific instance, C_f coincides to the concentration of lead on equilibrium (C_e) and q matches to the quantity absorbed on equilibrium (q_e).

The renowned equilibrium models Langmuir (1918) and Freicundlh (1906) [20] were plotted to experimental parameters by nonlinear regression. The Langmuir model is represented by Eq. (5), where q_e (mg/g) denotes the solute concentration on equilibrium in solid phase, Q_{max} (mg/g) represents the highest adsorption capacity, C_e (mg/L) is the lead concentration on equilibrium, and K_L (mg/L) is the constant of Langmuir.

$$q_e = \frac{K_L Q_{max} C_e}{1 + K_L C_e} \tag{5}$$

Eq. (6) illustrate the Freundlich model, and the significance of the symbols are: K_F (mg/g(mg/L)$^{-1/nF}$) represents a constant of the adsorption system which is correlated to the removal capability and n_F signify a constant which expresses the acuity of adsorption process ($n_F > 1$, favourable isotherm; $n_F \leq 1$, unfavourable isotherm).

$$q_e = K_F C_e^{\frac{1}{n_F}} \tag{6}$$

3. Results and discussions

3.1. Biosorbents characterization

3.1.1. FTIR spectroscopy

The surface of apple pomace exhibits a variety of functional groups due to its highly complex structure. FTIR spectroscopy was conducted to qualitatively recognize the functional groups existing on the studied sorbents surface. Spectra for both biosorbents were obtained before their interaction with lead, and any changes in their vibrational frequencies following biosorption were also recorded. This approach allows for the identification of the functional groups that are crucial in the pollutant removal mechanisms. The attained spectra are presented in Fig. 2.

Some differences are observed between the spectra of the two initial biosorbents, RA and EA. The peaks that identify certain functional groups are present at the same wavenumber for both raw and extracted apple, but are more accentuated for RA, which suggests that the functional groups in EA were quantitatively diminished most probably following the extraction procedure. The band about 3340 cm^{-1} is due to -OH stretching frequencies [21]. The band between 3050 and 3500 cm^{-1} is very broad and is formed due to -OH stretching, possibly coming from primary, secondary and tertiary alcohols, as well as from phenols [22–24]. The same aspect is also observed around 1050 cm^{-1}, where is noticeable a reduction of the peak that could correspond to the deformation vibrations -OH

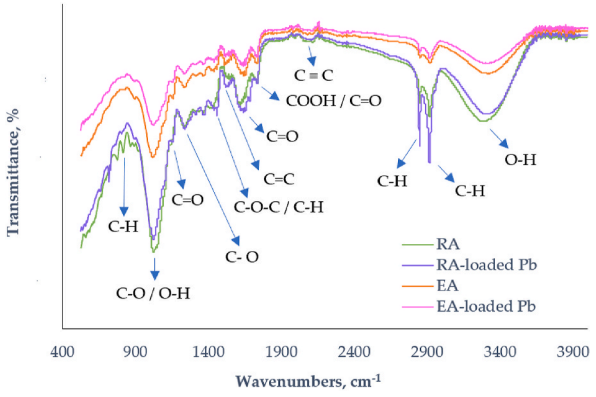

Fig. 2. FTIR spectra of studied biosorbents (ahead and afterward Pb-loading).

coming from alcohols. The peaks among 2950 to 2750 cm^{-1} are extremely characteristic for aliphatic compounds C-H stretching vibrations, but also could be from methyl or methylene groups [24–27]. Between 2200 and 2050 cm^{-1} the most probably are C ≡ C stretches from alkynes and the small peaks at 1690 and 1740 cm^{-1} could indicate C(O)-OH functional groups derived from carboxylic acids or C=O stretching vibrations resulting from esters [28]. The group of peaks around 1640 cm^{-1} could be represented by carbonyl stretch C=O from amides (primary, secondary and tertiary) or from aliphatic groups that are distinctive spectra of polysaccharides, cellulose and also of hemicellulose [28,29]. The peak from approx. 1515 cm^{-1} is assigned to C=C aromatic stretch from lignin [21]. At 1460 - 1380 cm^{-1} are found C-H asymmetric deformation vibrations of CH_3 from aliphatic hydrocarbons or C-O-C stretching of ester groups [28]. At aprox.1250 cm^{-1} are present C-O stretches from esters or alcohols [28].

C=O stretch from aliphatic ether, respectively C-O and -OH deformation vibrations from alcohols could be the peaks founded at 1160 cm^{-1} and the pecks at 1030 cm^{-1} are specific for the occurrence of phenolic complexes (C-O-H) [22]. All the signals positioned under 900 cm^{-1} correspond to aromatic C-H stretch vibration [25] or hydrocarbon (-C-H) with a strong sensitivity for capturing heavy metal ions [27]. The spectral analysis of RA and EA beforehand and following to the removal of lead ions, indicates that some peaks also decrease in intensity or even disappear as a result of the interaction of Pb(II) with the functional groups [28–30]. The C-H peaks at 2920 cm^{-1} and also at 2850 cm^{-1} undergo a noticeable transformation after loaded Pb, which clearly leads to the conclusion that these functional groups have an active character in the adsorption of Pb^{2+} by apple biosorbents. It is also noticed that the bands from 3280 cm^{-1} (in case of RA) correlated to OH functional groups pass to 3300 cm^{-1} (for RA-loaded Pb), those from 1640 cm^{-1} (for RA) associated with C=O functional groups were moved subsequently to biosorption to 1620 cm^{-1} (for RA-loaded Pb) and, the pecks at 1515 cm^{-1} associated with C=C disappear after contact with lead. Correspondently, similar changes are observed for EA. These transformations indicate the involvement of functional groups of type O-H, C=O and C=C in the adsorption lead mechanism. The FTIR spectra confirm the occurrence of carboxyl, hydroxyl and ester groups on the surface of both biosorbents studied. This suggests that the biosorption mechanism of Pb^{2+} onto RA and EA involves the attraction/chelation of positively charged Pb^{2+} ions to negatively charged ($-COO^-$)/($-OH^-$) groups, which become deprotonated at pH levels above 4. The literature confirms that lead has a predisposition to form coordinate bonds [31,32].

3.1.2. SEM/EDAX

Fig. 3 reveals SEM images of the surface of both biosorbents tested, RA and EA, as well as images of RA-loaded Pb and EA-loaded Pb. The surface morphology of the materials shows a porous structure, with a slightly lamellar assembly in the case of the raw apple [Fig. 3 (a and b)], and a more organized hierarchical porous structure in the case of the apple after biorefining process [Fig. 3 (c and d)]. Most likely, this porous structure creates binding-sites where lead can be retained improving in this way the lead ions distribution on the adsorbent surface.

Elemental relative concentrations of the biosorbents were acquired through X-ray microanalysis, and semi-qualitative outcomes are depicted in Fig. 4. Random samples of the tested biosorbents were analyzed, so it should be taken into account that the information

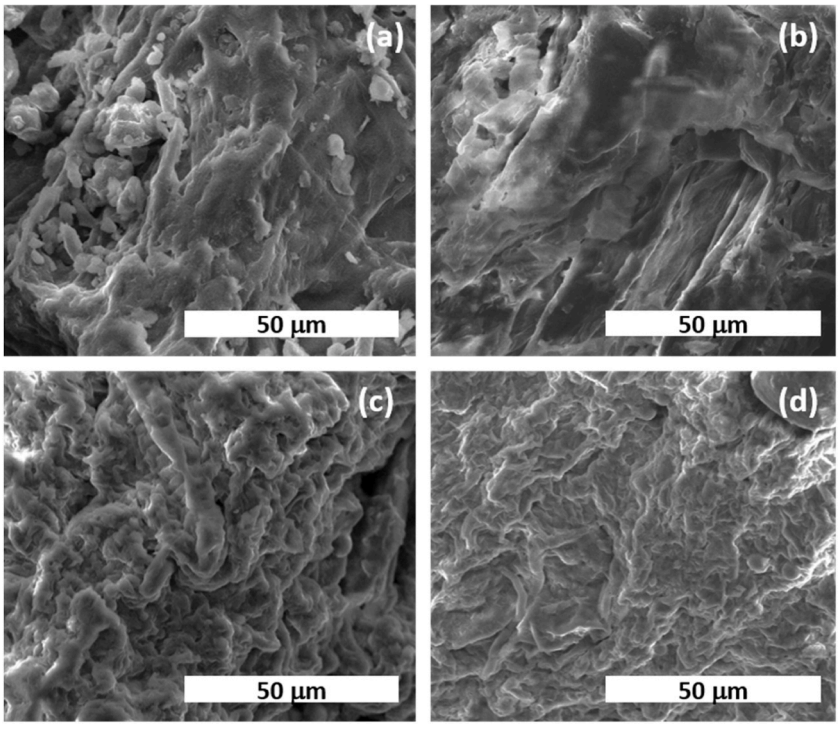

Fig. 3. SEM pictures for: (a) RA; (b) RA-loaded Pb; (c) EA; (d) EA-loaded Pb.

provided may not fully reflect the average elemental configuration of apple varieties mixture, but should be used only for comparative purposes.

As predictable, it is visible in Fig. 4 the main occurrence of carbon (around 42–45 %), oxygen (around 45–49 %) and nitrogen (between 6 and almost 10 %), compared to other components with much lower percentages: Ca, K, Ni, P, Mg, Al, Na, Fe. As noticeable, comparing Fig. 4 (a) with Fig. 4 (c), the characteristic emission lines of the most elements (Ca, P, K, Na, Mg) practically disappeared

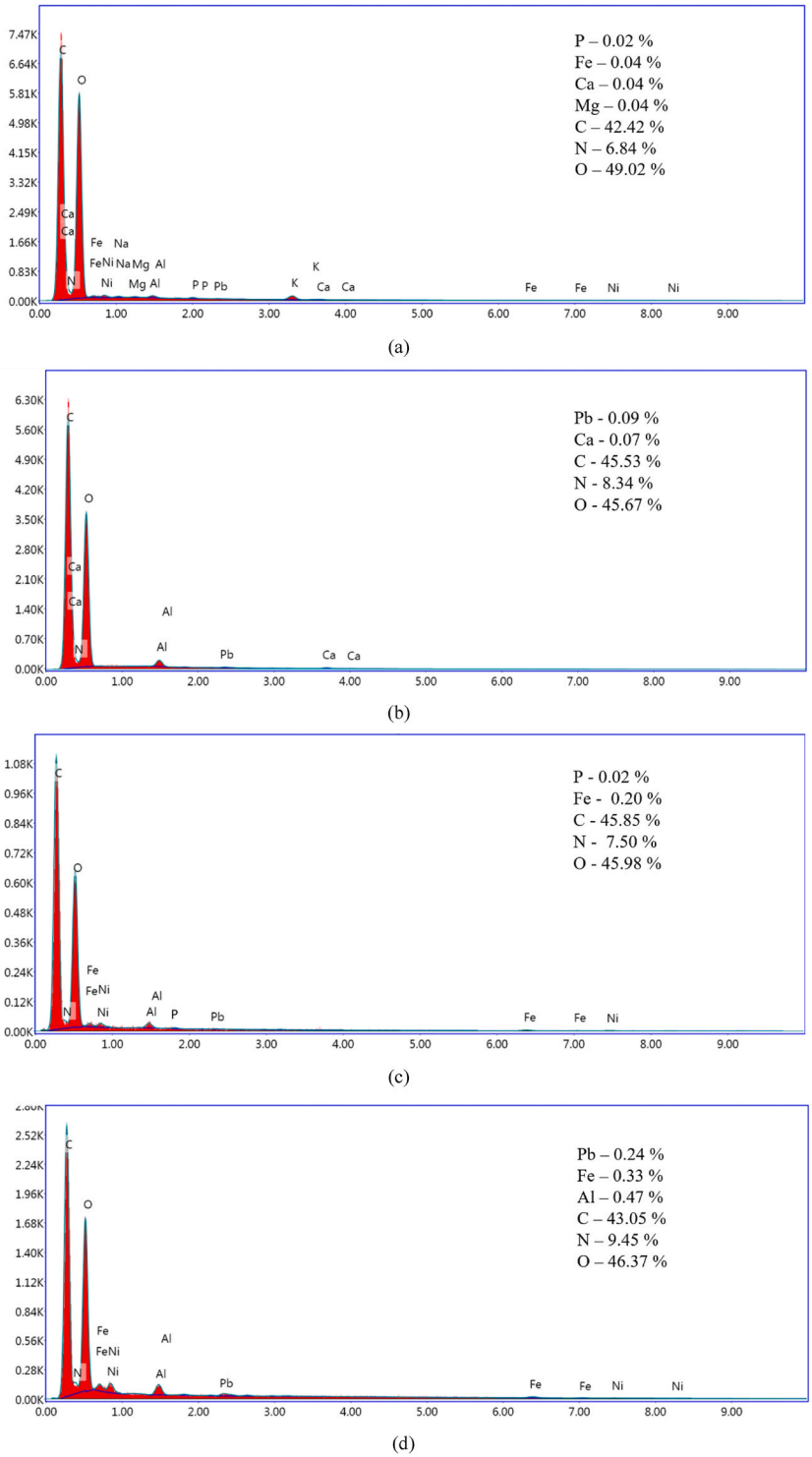

Fig. 4. Elemental chemical analysis by EDAX: (a) RA; (b) RA-loaded Pb; (c) EA; (d) EA-loaded Pb.

which aligns with the expected effect of extracting the main valuable components. Also, associating in Fig. 4 the spectra (a) with (b) and respectively (c) with (d) it is easy to observe that a significant proportion of lead appears in the analyzed biosorbents after the lead elimination from the water solution, which proves an important lead sorption on both studied materials. The results were confirmed by XRF qualitative assessment of the lead content in the samples, which indicated a value of (6 ± 1) ppm for RA and (4 ± 1) ppm for EA, while for the loaded samples the values were (1077 ± 4) ppm in the case of RA-loaded Pb, and (7169 ± 22) ppm for the EA-loaded Pb, respectively (supplementary material).

3.2. pH variation influence

pH significantly influences lead speciation in liquid environments. This aspect is largely recognized and deliberate in literature, the overwhelming majority of published works, having this issue as the starting point of any study on lead. Distribution of lead species in water is shown in Fig. 5.

The diagram shows that approximately below the neutral pH value, the most common specie of lead mainly present is cationic elementary Pb^{2+} (see Fig. 5). For pH values in basic range, lead forms aqueous complexes and the hydrolyzed species $PbOH^{+}$, $Pb(OH)_2$ and $Pb(OH)_3$ are more abundant than Pb^{2+}. Also, precipitation of the lead solutions in basic environments, particularly for higher concentrations of lead, occurs [33]. So, due to the fact that, overall, the real effluents contaminated with lead have a pH in acidic range, correlated with the fact that up to a neutral pH, lead is predominantly present as Pb^{2+}, the interval chosen to study lead adsorption in this work was between 2 and 5 (±0.5).

Fig. 6 (a, b) depicted the outcomes of pH tests. As is readily apparent, both bio-based materials are effective for Pb^{2+} removal and the influence of the pH is really significant. RA proves a lead retention capacity of over 80 %, while for EA it reaches up to 98 %.

Both the raw apple and the biorefined apple demonstrate an increase in lead retention efficiency as pH rises. The negative surface charges of biosorbents increase on acidic pH, which further conducts to the creation of active centers where positive lead ions can be retained [34]. Also, da Silva et al. (2020) [35] confirms in the published work that, simultaneously with the rise in the pH value, the functional groups are deprotonated, especially the carboxylic ones and particularly for the pH range 3–5. This reduces the repulsive forces between H_3O^{+} and Pb^{2+}, thereby intensify the affinity of Pb(II) ions for the active sites on the biosorbent's surface. The results of the pH tests, corroborated with the aspects discussed in the literature on the same topic, led to the decision to perform the following assessments in this study at pH 5 ± 0.5.

3.3. Effect of adsorbent dosage

The effect of the starting biosorbent dosage on Pb(II) uptake was tested and the outcomes are depicted in Fig. 7 (a and b) as a percentage of removal effectiveness and biosorption capacity. The sorbent concentrations under study were 0.25, 0.5, 1, 2, 4, and 10 g/L for both RA and EA. Both materials exhibited high retention percentages, particularly at preliminary adsorbent concentrations above 1 g/L, reaching up to 80 % for RA and 100 % for EA. These numbers are superimposed on adsorption capacities since 24.41 mg/g for solid/liquid proportion of 0.25 g/L until 1.60 mg/g for 10 g/L for RA and 29.72 mg/g for solid/liquid proportion of 0.25 g/L to 2.40 mg/g for 10 g/L for EA, correspondingly.

This work aims to test the affinity of the studied material for lead using the smallest possible amount of biosorbent, but which does not generate possible errors and at the same time offers promising results. Conversely, using a large amount of biosorbent may result in less efficient utilization of the material's surface area, leading to a lower amount of lead adsorbed at equilibrium. Taking into account the experimental results, as well as the discussed theoretical considerations, the solid/liquid proportion of 0.5 g/L was chosen carrying out further kinetics and equilibrium assessments.

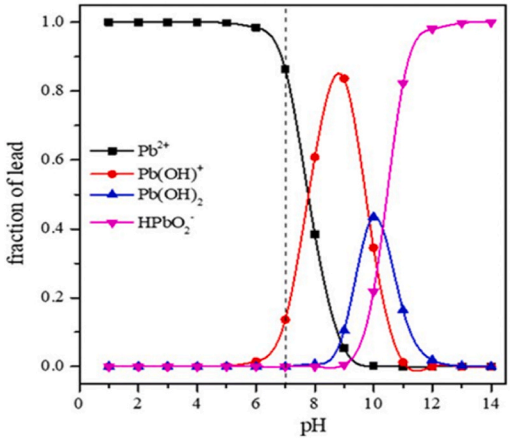

Fig. 5. Lead species distribution in water at 25 °C (33).

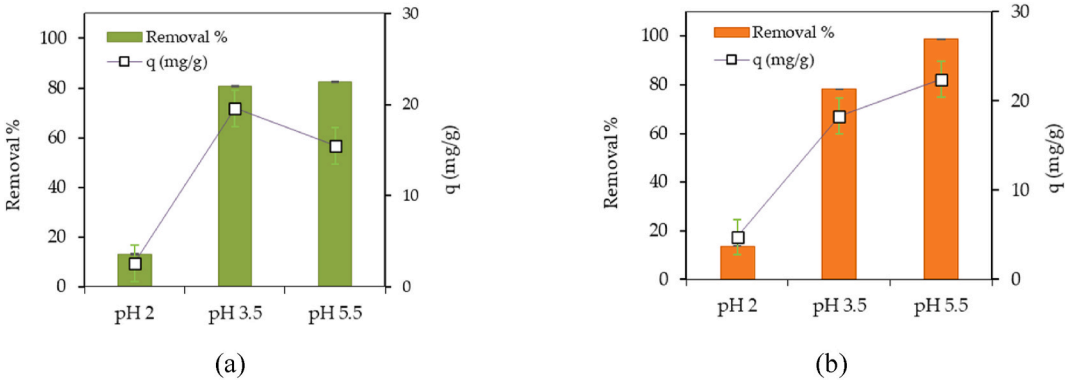

Fig. 6. pH effect on lead adsorption, C_0 = 20 mg/L Pb(II), T = 23 ± 1 °C, 4 h contact time, C_s = 0.5 g/L (a) RA and (b) EA.

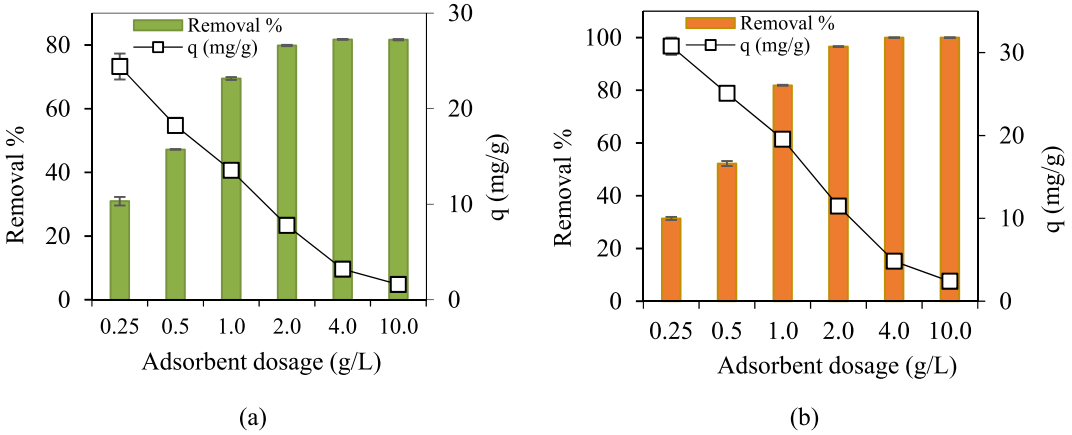

Fig. 7. Removal effectiveness and adsorbed amount by (a) RA and (b) EA, at various biosorbent concentrations, C_0 = 20 mg/L Pb(II), pH 5 ± 0.5, T = 23 ± 1 °C, 4 h reaction time.

3.4. Biosorption kinetic assessments

Adsorption kinetic studies offer insights into the time needed for the adsorbent-adsorbate system to achieve equilibrium. Fig. 8 (a, b) illustrates the experimental data on the impact of contact time (t) on the normalized concentration (C/C_{in}) decrease of lead in solution, along with the corresponding mathematical models.

The lead adsorption by bio-based sorbents assessed in present study is a fast process. In the first 60 min the reaction is steep and

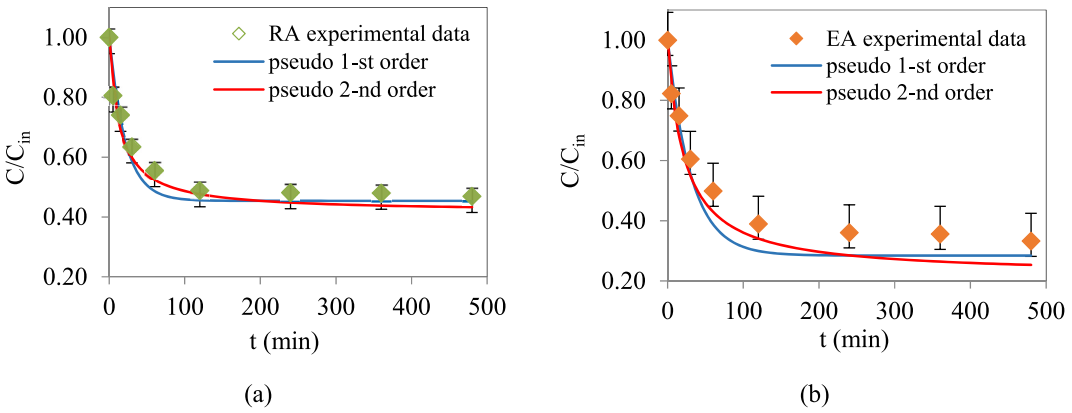

Fig. 8. Kinetics for Pb (II) biosorption on (a) RA and (b) EA at C_0 = 20 mg/L Pb(II), C_s = 0.5 g/L biosorbent dosage, T = 23 ± 1 °C: experimental points and pseudo-first (1st) and pseudo-second (2nd) order model.

around 80 % of the maximum Pb(II) removed amount was already attained for both biosorbents. After 60 min, until 120 min, the reaction gets slower and approximately 95 % of the lead is now uptake from liquid phase. These findings align with those reported in the literature for the removal of lead with various biosorbents obtained from various raw materials [36–38].

Table 1 presents the results obtained from fitting the mathematical models to the experimental data using nonlinear regression adjustments.

As shown in the table above, both mathematical models predict equilibrium adsorption capacities (q_e) that are close to the experimental values. However, the pseudo-second-order model offers a rather better fit, as indicated by its higher coefficient of determination (R^2). An R^2 value greater than 0.95 is considered indicative of a linear relationship. The pseudo-1st order model is among the earliest models applied to explain physisorption-based adsorption processes. This model establishes a direct relationship between the adsorption capacity at equilibrium and the uptake capacity at any given time during the reaction [39]. The pseudo-2nd-order model presumes that the uptake ability is directly related to the number of occupied active positions on the adsorbent [40]. The kinetic model provides insights into the mechanism of ion binding during the adsorption process. Specifically, the pseudo-first-order model suggests physisorption, involving weak electrostatic forces, while the pseudo-second-order model point to chemisorption mechanism [41]. As mentioned above, both mathematical models adapt very well to the obtained experimental data, which may indicate that both mechanisms, physisorption and chemisorption, can occur at the same time [41]. Still, as the pseudo-2nd order model shows a marginally higher coefficient of determination (R^2) compared to the one resulting from the application of the pseudo-1st order model, it suggests a higher probability that the lead retention mechanism is through chemisorption involving attraction/chelation [39].

3.5. Equilibrium studies

Adsorption equilibrium studies offer information about the maximum removal capacity, surface properties and compatibility with an adsorbate of the biosorbent. Isotherms define the correlation between the solute concentration in the liquid phase and the equilibrium concentration of the biosorbent at a given temperature. The biosorption isotherms for Pb(II) uptake on RA and EA are represented in Fig. 9 (a and b).

Langmuir model starts from the assumption that the active sites are homogeneously dispersed on the adsorbate surface, in a single layer, with constant adsorption energy and similar affinity. Also, the model assumes that there are no interactions between the adsorbed species in neighbouring centers.

This model is empirical and is based on the concept that the adsorbent's surface is heterogeneous, with active centers possessing different energies.

Table 2 displays the parameters for both models. The coefficient of determination (R^2) is a statistical parameter that measures how well the mathematical model fits the experimentally obtained data. The Freundlich model clearly provides a better description of the equilibrium data for both biosorbents studied, as indicated by its superior values for the coefficient of determination. Moreover, the value of the constant n_F is significantly higher than 1, confirming the favourable isotherm. An adsorption reaction is considered favourable if n_F constant has a value between 1 and 10 [12]. Moreover, if the "n" value of the Freundlich isotherm is bigger than 1, it points to a physisorption process. The kinetics study showed that the reaction mechanism could be binary, physical and chemisorption, but adsorption equilibrium studies indicate, through the results of the Freundlich model with $n = 3.4$ (for RA), respectively $n = 3.8$ (for EA), that physisorption is the most likely reaction mechanism present [42]. Q_{max} predicted by Langmuir model has very encouraging values, 44.6 mg/g in case of RA, respectively 48.6 mg/g for EA and proves that an apple waste, even depleted of bioactive components, can be effectively used for the remediation of lead from water. The extraction protocol proposed in this work is quite complex, including steps for the extraction of water-soluble and steps for the fat-soluble compounds. However, the main objective was to thoroughly remove all bioactive compounds present in apple pomace, which contains valuable substances such as antioxidants, pigments, glucids, aroma compounds, pectin, etc. These compounds can be utilized to produce profitable products in the food industry, cosmetics, and the extraction costs will be generously covered by the benefits gained from the commercialization of the new products. Additionally, the study aimed to determine if the remaining material (EA) is still suitable for wastewater remediation. The subsequent experiments conducted during this study yielded positive results for both tested materials (EA and RA). Both sorbents are effective for lead removal, regardless of whether only the drying step (RA) or all steps of the biorefinery process are applied (EA). The differences between the two materials are insignificant from the perspective of the adsorption process.

4. Conclusions

Two bio-based materials derived from apple waste were studied in batch mode to assess their capability to remove lead ions from a synthetic liquid solution. The FTIR spectra show that O-H, C=O, C=C, C-H are the principal functional groups on the sorbent's surface. The tests were completed with 20 mg/L Pb(II) initial lead concentration, value that falls within the lead concentrations found in real effluents. The assessments shows that biosorption of lead on apple waste is highly dependent on pH. Adsorption equilibrium studies demonstrate a better fitting for Freundlich mechanism, and Langmuir model reveals a maximum removal capacity of 44.6 mg/g for RA, respectively 48.6 mg/g for EA, at pH 5 ± 0.5 and 23 °C. This very small difference between the retention capacities of the two adsorbents proves that, even if we extract as many of the valuable components from what is already an apple waste, it can later be successfully converted from a useless material into an effective biosorbent for the bioremediation of contaminated water. Biosorption kinetic data better fit the pseudo-second order model, indicating a higher likelihood that the lead retention mechanism involves chemisorption through electron exchange. The goal of this study was to investigate an alternative approach for transitioning from a

Table 1
Parameters derived from kinetic model adjustments (value ± standard error of the coefficient).

	Pseudo – 1st order model			Pseudo – 2nd order model		
	k_1 (min^{-1})	q_e (mg/g)	R^2	$k_2\ 10^3$ (g mg^{-1} min^{-1})	q_e (mg/g)	R^2
RA	0.047 ± 0.008	20.8 ± 0.8	0.92	0.0033 ± 0.0005	22.2 ± 0.6	0.97
EA	0.032 ± 0.004	27.2 ± 0.9	0.96	0.0015 ± 0.0005	29.7 ± 0.8	0.98

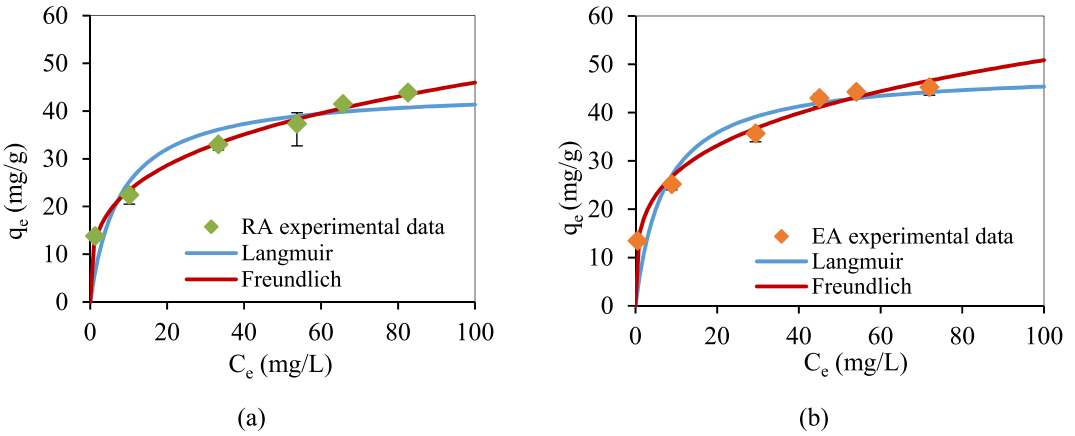

Fig. 9. Pb (II) biosorption isotherms for (a) RA and (b) EA, at different C_0 of Pb(II), C_s = 0.5 g/L dosage, T = 23 ± 1 °C, 5 h contact time: experimental points and Langmuir and Freundlich models.

Table 2
Parameters for fitting equilibrium models (value ± standard error of the coefficient).

	Langmuir model			Freundlich model		
	Q_{max} (mg/g)	K_L (L/mg)	R^2	n_F	K_F (mg/g(mg/L)$^{-1/nF}$)	R^2
RA	44.6 ± 4.5	0.12 ± 0.07	0.87	3.4 ± 0.2	11.8 ± 0.7	0.99
EA	48.6 ± 5.8	0.14 ± 0.09	0.84	3.8 ± 0.3	14.9 ± 1.2	0.99

linear economy to a sustainable circular economy. Consumption, in a linear economy, generates waste that harms the environment, while in a circular economy, waste produced by human activities or consumption is reused and integrated into an ecological cycle. The aim of this research is to find another possible solution to this problem.

Funding

This research was supported by the project AUF-DRECO-7863_SER-ECO_USVIIBI_DECHETJUS.

Data availability statement

Data included in article/supp. material/referenced in article.

CRediT authorship contribution statement

Gabriela Ungureanu: Writing – original draft, Visualization, Validation, Supervision, Methodology, Formal analysis, Data curation, Conceptualization. **Iuliana-Maria Enache:** Visualization, Investigation, Data curation. **Irina Gabriela Cara:** Software, Methodology, Investigation. **Iuliana Motrescu:** Methodology, Investigation, Formal analysis. **Antoanela Patras:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization.

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.

Acknowledgements

The authors are grateful for receiving support from the Central and Eastern Europe Francophone University Agency (AUF DRECO) and also from "Ion Ionescu de la Brad" Iași University of Life Sciences, Romania (IULS): the Research Institute for Agriculture and Environment, the Horticultural Research Center and the Laboratory for Bioactive Compounds Analysis.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.heliyon.2024.e36811.

References

[1] M.K. Awasthi, J.A. Ferreira, R. Sirohi, S. Sarsaiya, B. Khoshnevisan, S. Baladi, R. Sindhu, P. Binod, A. Pandey, A. Juneja, D. Kumar, Z. Zhang, M.J. Taherzadeh, A critical review on the development stage of biorefinery systems towards the management of apple processing-derived waste, Renew. Sustain. Energy Rev. 143 (2021) 110972, https://doi.org/10.1016/j.rser.2021.110972.
[2] P. Joshi, Fruit and vegetable processing waste management – an overview, Int. J. Food Ferment. Technol. (2020) 10, https://doi.org/10.30954/2277-9396.02.2020.4.
[3] S. Wang, Y. Fang, Y. Xu, B. Zhu, J. Piao, L. Zhu, L. Yao, K. Liu, S. Wang, Q. Zhang, L. Qin, J. Wu, The effects of different extraction methods on physicochemical, functional and physiological properties of soluble and insoluble dietary fiber from Rubus chingiiHu. fruits, J. Funct.Foods 93 (2022) 105081, https://doi.org/10.1016/j.jff.2022.105081.
[4] B. Sik, Z. Ajtony, E. Lakatos, R. Székelyhidi, The effects of extraction conditions on the antioxidant activities, total polyphenol and monomer anthocyanin contents of six edible fruits growing wild in Hungary, Heliyon 8 (2022) e12048, https://doi.org/10.1016/j.heliyon.2022.e12048.
[5] S.O. Tebbi, N. Debbache-Benaida, N. Kadri, R. Kadi, S. Zaidi, A novel strategy to improve the recovery of phenolic compounds from Pistacia lentiscus L. fruits using design-based statistical modeling for ultrasound-deep eutectic solvents extraction and the evaluation of their antioxidant potential, Sustainable Chemistry and Pharmacy 31 (2023) 100933, https://doi.org/10.1016/j.scp.2022.100933.
[6] A. Weremfo, F. Adulley, K. Dabie, S. Abassah-Oppong, E. Peprah-Yamoah, Optimization of ultrasound-assisted extraction of phenolic antioxidants from Turkey berry (Solanum torvum Sw) fruits using response surface methodology, Journal of Applied Research on Medicinal and Aromatic Plants 30 (2022) 100387, https://doi.org/10.1016/j.jarmap.2022.100387.
[7] P. Kewlani, L. Singh, T. Belwal, I.D. Bhatt, Optimization of ultrasonic-assisted extraction for bioactive compounds in Rubus ellipticus fruits: an important source for nutraceutical and functional foods, Sustainable Chemistry and Pharmacy 25 (2022) 100603, https://doi.org/10.1016/j.scp.2022.100603.
[8] A.A. Baldovi, A.P. Ayvazian, L.H.G. Coelho, T.A. de Jesus, Biosorption of Pb(II) by unmodified banana peel in batch and column experiments: a potential green and low-cost technology for industrial effluent treatment, Water, Air, Soil Pollut. 233 (2022) 490, https://doi.org/10.1007/s11270-022-05969-z.
[9] R. Mallampati, L. Xuanjun, A. Adin, S. Valiyaveettil, Fruit peels as efficient renewable adsorbents for removal of dissolved heavy metals and dyes from water, ACS Sustain. Chem. Eng. 3 (2015) 1117–1124, https://doi.org/10.1021/acssuschemeng.5b00207.
[10] I. Abdelfattah, A.A. Ismail, F.A. Sayed, A. Almedolab, K.M. Aboelghait, Biosorption of heavy metals ions in real industrial wastewater using peanut husk as efficient and cost effective adsorbent, Environ. Nanotechnol. Monit. Manag. 6 (2016) 176–183, https://doi.org/10.1016/j.enmm.2016.10.007.
[11] W. Jaihan, V. Mohdee, S. Sanongraj, U. Pancharoen, K. Nootong, Biosorption of lead (II) from aqueous solution using Cellulose-based Bio-adsorbents prepared from unripe papaya (Carica papaya) peel waste: removal Efficiency, Thermodynamics, kinetics and isotherm analysis, Arab. J. Chem. 15 (2022) 103883, https://doi.org/10.1016/j.arabjc.2022.103883.
[12] A. Wattanakornsiri, P. Rattanawan, T. Sanmueng, S. Satchawan, T. Jamnongkan, P. Phuengphai, Local fruit peel biosorbents for lead(II) and cadmium(II) ion removal from waste aqueous solution: a kinetic and equilibrium study, S. Afr. J. Chem. Eng. 42 (2022) 306–317, https://doi.org/10.1016/j.sajce.2022.09.008.
[13] D. Konstantinos, E. Valsamidou, D. Marmanis, Simultaneous removal of acidity and lead from acid lead battery wastewater by aluminum and iron electrocoagulation, Journal of Engineering Science and Technology Review 5 (2012) 1–5, https://doi.org/10.25103/jestr.052.01.
[14] M. Mondal, Removal of Pb(II) from industrial wastewater by using various natural materials - a review, International Journal of Sustainable Development and Planning - Int J Sustain Dev Plann 3 (2008) 377–393, https://doi.org/10.2495/SDP-V3-N4-377-393.
[15] IARC, Agents classifed by the IARC monographs of webpage. https://monographs.iarc.who.int/agents-classified-by-the-iarc/2024. (Accessed 7 April 2024).
[16] O. Agboola, D.E. Babatunde, O.S. Isaac Fayomi, E.R. Sadiku, P. Popoola, L. Moropeng, A. Yahaya, O.A. Mamudu, A review on the impact of mining operation: monitoring, assessment and management, Results in Engineering 8 (2020) 100181, https://doi.org/10.1016/j.rineng.2020.100181.
[17] G. Ungureanu, S.C.R. Santos, I. Volf, R.A.R. Boaventura, C.M.S. Botelho, Biosorption of antimony oxyanions by brown seaweeds: batch and column studies, J. Environ. Chem. Eng. 5 (2017) 3463–3471, https://doi.org/10.1016/j.jece.2017.07.005.
[18] H.J. Mansoorian, A.H. Mahvi, A.J. Jafari, Removal of lead and zinc from battery industry wastewater using electrocoagulation process: influence of direct and alternating current by using iron and stainless steel rod electrodes, Separ. Purif. Technol. 135 (2014) 165–175, https://doi.org/10.1016/j.seppur.2014.08.012.
[19] Y.S. Ho, D.A.J. Wase, C.F. Forster, Kinetic studies of competitive heavy metal adsorption by sphagnum moss peat, Environ. Technol. 17 (1996) 71–77, https://doi.org/10.1080/09593331708616362.
[20] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1403, https://doi.org/10.1021/ja02242a004.
[21] E. Heraldy, W.W. Lestari, D. Permatasari, D.D. Arimurti, Biosorbent from tomato waste and apple juice residue for lead removal, J. Environ. Chem. Eng. 6 (2018) 1201–1208, https://doi.org/10.1016/j.jece.2017.12.026.
[22] T. Garrido, M. Gizdavic-Nikolaidis, I. Leceta, M. Urdanpilleta, P. Guerrero, K. de la Caba, P.A. Kilmartin, Optimizing the extraction process of natural antioxidants from chardonnay grape marc using microwave-assisted extraction, Waste Manag. 88 (2019) 110–117, https://doi.org/10.1016/j.wasman.2019.03.031.
[23] O. Anjos, A.J.A. Santos, L.M. Estevinho, I. Caldeira, FTIR–ATR spectroscopy applied to quality control of grape-derived spirits, Food Chem. 205 (2016) 28–35, https://doi.org/10.1016/j.foodchem.2016.02.128.
[24] A.R. Abdul Rahim, H.M. Mohsin, M. Thanabalan, N.E. Rabat, N. Saman, H. Mat, K. Johari, Effective carbonaceous desiccated coconut waste adsorbent for application of heavy metal uptakes by adsorption: equilibrium, kinetic and thermodynamics analysis, Biomass Bioenergy 142 (2020) 105805, https://doi.org/10.1016/j.biombioe.2020.105805.
[25] R. Md Salim, J. Asik, M.S. Sarjadi, Chemical functional groups of extractives, cellulose and lignin extracted from native Leucaena leucocephala bark, Wood Sci. Technol. 55 (2021) 295–313, https://doi.org/10.1007/s00226-020-01258-2.
[26] S. Pap, T. Šolević Knudsen, J. Radonić, S. Maletić, S.M. Igić, M. Turk Sekulić, Utilization of fruit processing industry waste as green activated carbon for the treatment of heavy metals and chlorophenols contaminated water, J. Clean. Prod. 162 (2017) 958–972, https://doi.org/10.1016/j.jclepro.2017.06.083.
[27] S. Pap, V. Bezanovic, J. Radonic, A. Babic, S. Saric, D. Adamovic, M. Turk Sekulic, Synthesis of highly-efficient functionalized biochars from fruit industry waste biomass for the removal of chromium and lead, J. Mol. Liq. 268 (2018) 315–325, https://doi.org/10.1016/j.molliq.2018.07.072.

[28] P. Chand, Y.B. Pakade, Removal of Pb from water by adsorption on apple pomace: equilibrium, kinetics, and thermodynamics studies, J. Chem. 2013 (2013) 164575, https://doi.org/10.1155/2013/164575.
[29] A.A. Casazza, B. Aliakbarian, A. Lagazzo, G. Garbarino, M.M. Carnasciali, P. Perego, G. Busca, Pyrolysis of grape marc before and after the recovery of polyphenol fraction, Fuel Process. Technol. 153 (2016) 121–128, https://doi.org/10.1016/j.fuproc.2016.07.014.
[30] Y. Nuhoglu, E. Malkoc, Thermodynamic and kinetic studies for environmentaly friendly Ni(II) biosorption using waste pomace of olive oil factory, Bioresour. Technol. 100 (2009) 2375–2380, https://doi.org/10.1016/j.biortech.2008.11.016.
[31] A. Bauzá, S.K. Seth, A. Frontera, Tetrel bonding interactions at work: impact on tin and lead coordination compounds, Coord. Chem. Rev. 384 (2019) 107–125, https://doi.org/10.1016/j.ccr.2019.01.003.
[32] A. Ahmad, A. Khatoon, S.-H. Mohd-Setapar, R. Kumar, M. Rafatullah, Chemically oxidized pineapple fruit peel for the biosorption of heavy metals from aqueous solutions, Desalination Water Treat. 57 (2016) 6432–6442, https://doi.org/10.1080/19443994.2015.1005150.
[33] L.C. Oliveira, W.G. Botero, T.S. Farias, J.C.C. Santos, G.V.M. Gabriel, D. Goveia, T.A. Cacuro, W.R. Waldman, Application of natural organic residues as adsorbents to remove lead from waters, water, Air, & Soil Pollution 230 (2019) 191, https://doi.org/10.1007/s11270-019-4240-8.
[34] L. Ramteke, P. Gogate, Removal of copper and hexavalent chromium using immobilized modified sludge biomass based adsorbent, Clean: Soil, Air, Water 44 (2016), https://doi.org/10.1002/clen.201500371.
[35] P.A.d.S. Veiga, J. Schultz, T.T.d.S. Matos, M.R. Fornari, T.G. Costa, L. Meurer, A.S. Mangrich, Production of high-performance biochar using a simple and low-cost method: optimization of pyrolysis parameters and evaluation for water treatment, J. Anal. Appl. Pyrol. 148 (2020) 104823, https://doi.org/10.1016/j.jaap.2020.104823.
[36] C. Filote, I. Volf, S.C.R. Santos, C.M.S. Botelho, Bioadsorptive removal of Pb(II) from aqueous solution by the biorefinery waste of Fucus spiralis, Sci. Total Environ. 648 (2019) 1201–1209, https://doi.org/10.1016/j.scitotenv.2018.08.210.
[37] G. Ungureanu, A. Patras, I.G. Cara, R. Sturza, A. Ghendov-Mosanu, Innovative recovery of winemaking waste for effective lead removal from wastewater, Agronomy 12 (3) (2022) 604, https://doi.org/10.3390/agronomy12030604.
[38] I. Volf, N.G. Rakoto, L. Bulgariu, Valorization of Pistia stratiotes biomass as biosorbent for lead(II) ions removal from aqueous media, Separ. Sci. Technol. 50 (2015) 1577–1586, https://doi.org/10.1080/01496395.2014.978018.
[39] Y.S. Ho, G. McKay, A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents, Process Saf. Environ. Protect. 76 (1998) 332–340, https://doi.org/10.1205/095758298529696.
[40] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem. 34 (1999) 451–465, https://doi.org/10.1016/S0032-9592(98)00112-5.
[41] R. Nathan, D. Barr, R. Rosengren, Six fruit and vegetable peel beads for the simultaneous removal of heavy metals by biosorption, Environ. Technol. 43 (2020) 1–18, https://doi.org/10.1080/09593330.2020.1858183.
[42] J. Jose, M. Dharsana, Adsorption of lead from contaminated water using biosorbent, Materiali in tehnologije 56 (2022), https://doi.org/10.17222/mit.2021.352.