

Obtaining cashew bark extract and its application for removal of metallic species in aqueous matrix

Thaíse da Silva Borges (✉ thaisesb@yahoo.com.br)

Federal University of Bahia

Luciano Matos Queiroz

Federal University of Bahia

Sérgio Luís Costa Ferreira

Federal University of Bahia

Nádia Mamede José

Federal University of Bahia

Research Article

Keywords: Anacardium occidentale L., aqueous extract obtained from cashew tree bark, removing metals, green chemistry

Posted Date: January 1st, 2024

DOI: <https://doi.org/10.21203/rs.3.rs-3813617/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.
[Read Full License](#)

Additional Declarations: No competing interests reported.

Abstract

This work presents the preparation and characterization of the powder from the bark of the cashew tree *Anacardium occidentale L.* and the aqueous extract obtained from the bark of the cashew tree and studies the use of this extract for removing metals in acid solution. The experiments were carried out on a laboratory scale using contaminated water with a concentration of 4.0 mol/L of the metals Ba, Cd, Cr, Cu, Mn, Pb, Sn, Zn and different volumes of the extract obtained from the bark of the cashew tree. The coagulation process between the extract and the metal species led to a decrease in the metal concentration in solution due to precipitation. Removal of up to 25% was obtained for all analyzed metals. Using the principles of green chemistry, the process was evaluated with a very good green approach.

1. Introduction

Heavy metal ions are among the most released contaminants, and this is one reason why they are of particular concern [1]. Heavy metals and metalloids are elements that have an atomic density greater than 4 g/cm³; therefore, they include copper (Cu), cadmium (Cd), zinc (Zn), lead (Pb), mercury (Hg), arsenic (As), silver (Ag), chromium (Cr), iron (Fe), and platinum (Pt). These toxic metallic elements are released daily into water from various natural and anthropogenic sources [2].

Heavy metals are not biodegradable; therefore, they tend to bioaccumulate, leading to an increase in the concentration of these metals in living organisms over time [3]. They are also persistent and can directly or indirectly affect multiple organisms due to biomagnification. Many heavy metal ions are toxic or carcinogenic. Even at very low concentrations, they can induce damage to multiple organs, affecting the lungs, kidneys, liver, prostate, esophagus, stomach and skin, and may also cause neurodegenerative disorders and diseases, such as Alzheimer's and Parkinson's disease. Metals can also affect aquatic organisms (phytoplankton, zooplankton and fish), accumulating in various organs and causing oxidative damage, endocrine disruption and depression of the immune system, which can also affect survival and growth. These effects, as well as the potential ecological impacts of heavy metals, require the development of technologies to efficiently remove them from water [2].

Wastewater treatment technologies to remove heavy metals include chemical precipitation, photocatalysis, flotation, ion exchange, remediation, electrochemical treatment, adsorption, membrane technologies and coagulation/flocculation. These processes are technologies with industrial efficiency and practical feasibility. In general, the key factors in selecting the most suitable process for wastewater treatment are cost, wastewater characteristics and applicability in the process [4]. Most treatment technologies are used in combination for the effective remediation of water or effluent pollution [5].

Wastewater treatment technologies can be classified into primary, secondary and tertiary treatments. Primary treatment focuses on removing organic matter and suspended solids from wastewater through physical and chemical processes. Microfiltration, chemical filtration, coagulation and flocculation are key

technologies important when dealing with high concentrations of heavy metals [6]. Secondary treatments (anaerobic or aerobic) are based on natural microorganisms capable of converting organic and inorganic contaminants into simpler and safer substances, which allow for greater removal efficiency. The microbial effectiveness to eliminate metals is still under study, but the results showed high removal rates [7]. Tertiary treatments include chemical oxidation, electrochemical precipitation, crystallization, distillation and photocatalysis, adsorption, membrane technologies and ion exchange technologies. At this stage, wastewater is converted into good quality water. Removal efficiencies as high as 99% can be achieved when tertiary treatments are properly combined with primary and secondary treatments [8].

Chemical precipitation is the most common technology for removing dissolved metals from industrial wastewater. The most used chemical precipitation process is hydroxide precipitation, in which metallic hydroxides are formed with the help of calcium hydroxide Ca(OH)_2 [9]. This method is very attractive because it results in a high degree of metal removal at low cost and almost all metals precipitate under suitable pH conditions [10]. Most metal hydroxides are amphoteric. Therefore, when a process effluent contains mixed metals, the ideal pH for precipitation of one metal may cause the solubilization of another metal [11]. Furthermore, chelating agents, sequestering agents, bath additives, cleaning products and formulations will interfere with the hydroxide precipitation reaction [12, 13].

As an alternative to hydroxide precipitation, coagulation-flocculation is a highly efficient physical-chemical method to remove heavy metals [14]. In this process, fine particles and colloids agglomerate into larger particles, which reduces turbidity, natural organic matter and other wastewater pollutants. In the first step, a coagulant added to water encourages the coalescence of the colloidal material into small aggregates known as flakes. In the second stage, the flakes are agglomerated under light agitation, sedimented and then discarded as sludge. This process is used as a pre-treatment, post-treatment or main treatment of wastewater due to its versatility [15].

Coagulation-flocculation has been widely applied in the treatment of water and effluents. Tannins, are natural water-soluble polyphenols that are present in most plant cells that have been widely accepted and applied as a coagulant. The application of a tannin-based coagulant in water and wastewater treatment around the world has been shown to successfully remove pollutants including turbidity, dyes, suspended solids, chemical oxygen demand, algae and heavy metals. The level of effectiveness of tannins as a coagulant is associated with their chemical structure and the degree of modification of the tannins, which are linked to the plant source from which they are extracted [16]. The use of tannin-based flocculants stands out when compared to aluminum flocculants due to their natural origin, which makes it more accessible and more available than aluminum, and can be synthesized directly in situ; there is no need to adjust the pH, saving reagents; and preventing people from having contact with aluminum, already related to Alzheimer's disease [17].

Common methods to remove heavy metals from water, including membrane filtration, activated carbon adsorption, and electrocoagulation, are not feasible for developing countries [18]. Difficulties associated with capital and technical requirements for installation, operation and maintenance can result in

inadequate application of technologies, particularly in decentralized contexts and developing countries [2]. As a result, significant research has been carried out on low-cost materials to evaluate their ability to remove heavy metals.

Brazil has accumulated over the centuries the losses of mineral exploration and processing, being of great importance the development of effective methodologies for the removal of metallic pollutants from water. In this context, in a developing country with real problems of effluent contamination with toxic metals and seeking to expand the scenario of low-cost, easy-to-apply and efficient technologies for metal decontamination in an aqueous matrix, we investigated the applicability of the extract obtained from cashew tree bark for the removal of metallic pollutants in acid solution.

The cashew tree is a plant native to Brazil and characteristic of the fields and coastal regions of the north and northeast of the country. It was introduced in Africa and India by the Portuguese in the 16th century and today it is spread throughout all tropical regions of the globe. The cashew crop has great economic and social importance for Brazil. Its main product, cashew kernels, participates in a billion-dollar world market, with transactions exceeding US\$ 2.4 billion per year, in addition to directly employing 1.2 million people. The choice of cashew bark as raw material for this work took into account the aforementioned aspects and also the tannin potential of the cashew tree bark, which is approximately 20%.

This work presents the preparation and characterization of powder from the bark of the cashew tree *Anacardium occidentale* L. and the aqueous extract obtained from the bark of the cashew tree, and studies the use of this extract for removal of metals in acid solution. Additionally, we employ the principles of green chemistry to assess how green the process is.

2. Materials and methods

2.1 OBTAINING AND PREPARING THE RAW MATERIAL

The raw material for carrying out this study is the bark of the stem of the cashew tree *Anacardium occidentale* L. collected in *Barra do Jacuípe*, a small village located in the municipality of *Camaçari*, north coast of Bahia state, Brazil, under the geographic coordinates – 12.697968, -38.128461 of latitude and longitude, respectively.

Chips were removed from the bark of the cashew tree stem between 25 cm from the base and up to 1.30 m in height of the tree, taking care not to reach the vascular cambium. The cashew tree barks were washed to remove sand, dust and other possible unwanted materials. They were dried in an oven at 70 °C for 24 hours. Subsequently, the shells were reduced to smaller fragments with the aid of a Quimis analytical mill model Q298A21. The milling process was carried out with regular stops to avoid overheating the mill knives, which could cause changes in the chemical composition of the material. The ground material was sieved and the fraction that passed through the 1.00 mm sieve (16 mesh) and was retained on the 0.25 mm sieve (60 mesh) was selected. The cashew bark powder (CBP) was stored in a desiccator and protected from light.

It is important to highlight that the chips removed from the bark of the cashew tree's stem apparently did not cause harm to the tree, as we observed that it continued to grow and develop in the following years. Considering a possible interest in scaling the process for large-scale production, it is worth noting that cashew tree stem peels could be obtained from existing plantations whose purpose is to sell cashew nuts and cashew pulp.

2.2 RAW MATERIAL CHARACTERIZATION

The characterizations of the raw material were carried out according to the availability of materials and equipment and with the aim of understanding the physical-chemical characteristics of the material.

The morphological analysis of the CBP surface was obtained through scanning electron microscopy (SEM), performed in a Jeol equipment, model JSM-6610LV, with gold deposition on the surface of the sample performed in a Denton Vacuum DeskV metallizer.

The content of hemicellulose, cellulose and lignin present in three CBP samples was determined using a methodology based on the determination of insoluble fibers in neutral detergent [19].

The thermogravimetric behavior of the CBP was determined through thermogravimetric analysis (TG), carried out in a Shimadzu model TGA-50 equipment, in a nitrogen atmosphere (N_2) and a heating rate of 10 °C per minute in a temperature range of 30 to 1000 °C.

The thermal behavior of the material was observed using the differential scanning calorimetry (DSC) technique, performed in a Shimadzu model DSC-50 equipment, in a nitrogen atmosphere (N_2) and a heating rate of 10 °C per minute in a range of 30 to 600 °C.

Infrared spectra with Fourier transform were obtained in an IRPrestige-21 Shimadzu instrument, using scanning in the spectral range of 4000 to 400 cm^{-1} , for the analysis of the functional groups contained in the CBP.

Acid digestion was carried out followed by the quantification of the metals through the reading of the samples using optical emission spectrometry for the determination of the metallic concentration present in the CBP. Three CBP samples were submitted to the acid digestion procedure using a cold finger as a reflux system for the decomposition of the cashew bark powder. The samples were weighed directly into the digestion tubes where, then, concentrated HNO_3 was added. The samples were placed in the digester block heated to 140 °C where two additions of 30% H_2O_2 were performed, the first addition was performed 60 minutes after the start of digestion and the second after 90 minutes. It was waited 30 minutes after the last addition of H_2O_2 until completing 2 hours of digestion to remove the tubes from the digester block. After cooling the samples, the digestate was transferred to polyethylene bottles and swelled with ultrapure water to 10 mL. The analytical blanks consisted of the same mixture of nitric acid and hydrogen peroxide used in the digestion, without the presence of the sample. Quantitative

determination of metallic species was performed using the inductively coupled argon plasma optical emission spectrometer (ICP-OES), Shimadzu ICPE-9820.

2.3 OBTAINING AND CHARACTERIZING THE CASHEW BARK EXTRACT

In order to obtain the cashew bark extract, CBP was added to a volumetric flask, together with ultrapure water. The flask was connected to a reflux condenser and covered with aluminum foil to protect from light. The system was maintained under heating at 100 °C and stirring for 2 hours. The extracted liquid was centrifuged in a Quimis Q222T204 centrifuge, stored in a plastic container and kept in a refrigerator and protected from light to avoid degradation of the material.

Each CBP sample was subjected to two extractions. Thus, a shell:water ratio of 1:20 p/v (g/mL) was used. At the end, each 2 g of CBP produced 25 mL of cashew bark extract (CBE).

The characterizations of the aqueous extract of the cashew tree bark were carried out according to the availability of materials and equipment and with the objective of knowing the physicochemical characteristics of the extract.

In order to determine the CBE density in the range of 10 to 50 °C, an Anton Paar densimeter DSA5000 was used.

Infrared spectra with Fourier transform were obtained in an IRPrestige-21 Shimadzu instrument, using scanning in the spectral range of 4000 to 400 cm^{-1} for the analysis of the functional groups contained in CBE.

The charge and stability of the extract were determined by means of zeta potential analysis, performed in a Malvern Zetasizer Nano ZS equipment using a 1 mL cuvette for zeta reading.

In order to determine the metal concentration present in CBE, its acid digestion was performed followed by the quantification of metals by reading the samples using optical emission spectrometry. Wet digestion of three CBE samples was used using a cold finger as a reflux system. The samples were weighed directly into the digestion tubes where, then, concentrated HNO_3 was added. The samples were placed in the digester block heated to 140 °C where two additions of 30% H_2O_2 were performed, the first addition was performed 60 minutes after the start of digestion and the second after 90 minutes. It was waited 30 minutes after the last addition of H_2O_2 until completing 2 hours of digestion to remove the tubes from the digester block. After cooling the samples, the digestate was transferred to polyethylene bottles and swelled with ultrapure water to 10 mL. The analytical blanks consisted of the same mixture of nitric acid and hydrogen peroxide used in the digestion, without the presence of the sample. Quantitative determination of metallic species was performed using the inductively coupled argon plasma optical emission spectrometer (ICP-OES), Shimadzu ICPE-9820.

2.4 METAL REMOVAL EVALUATION

A synthetic contaminated water with known amounts of the metallic species was prepared using analytical grade reagents (Merck) and ultrapure water with a specific resistivity of 18.2 MΩcm from an Elga LabWater® purification system (Option-Q, UK). Artificially contaminated water has a pH of 1.0 and a concentration of metallic species of 4.0 mol/L. The tests were carried out in the *Nova Ética* equipment, where water contaminated with metallic species and CBE was used. After 1 hour of stirring at 50 sec⁻¹, the system was allowed to stand for 24 hours. The supernatant was collected and the concentration of metal species Ba, Cd, Cr, Cu, Mn, Pb, Sn and Zn was determined. This procedure was performed using volumes of 0.5; 1.0; 2.0; 3.0; 4.0 and 5.0 mL of CBE for a volume of 500 mL of contaminated water. The experiments were performed in duplicate.

Quantitative determination of metallic species was performed using the inductively coupled argon plasma optical emission spectrometer (ICP-OES), Shimadzu ICPE-9820.

The concentration of each metal was determined in samples of contaminated water, in the blank and in the collected supernatant. Thus, the metallic removal was given by Eq. 2:

$$MR = \left(1 - \left(\frac{[M]_s - [M]_b}{[M]_c} \right) \right) \times 100\%$$

2
MR indicates metal removal, [M]_s represents the metal concentration in the supernatant, [M]_b expresses the metal concentration in the blank, [M]_c reveals the initial metal concentration in the contaminated water.

2.5 ASSESSMENT OF HOW GREEN THE PROCESS IS

In order to measure how green the process under study is, we used the methodological tool where the color code and numerical scale, shown in Table 1, classifies each step of the process in relation to the 12 principles of green chemistry [20]. In other words, the study was separated into four stages and for each stage of the process it was indicated which principles of green chemistry were applied and, in parentheses, the classification of each one, on a numerical scale from 1 to 10. At the end, we added up all the numbers used in the classification and the total value was divided by the number of principles analyzed.

Table 1 Analysis and evaluation scale of how green a process is [20]

	(10)	Totally green
	(9)	Great green approach
	(8)	Very good green approach
	(7)	Good green approach
	(6)	Take a green approach
	(5)	Transition from coffee to green
	(4)	Slightly coffee
	(3)	Moderately coffee
	(2)	Too much coffee
	(1)	Totally coffee

3. Results and Discussion

3.1 RAW MATERIAL CHARACTERIZATION

3.1.1 Scanning Electron Microscopy

Scanning electron microscopy of CBP revealed a surface with roughness, but without porosity, making physisorption phenomena unfeasible (Fig. 1).

3.1.2 Content of Hemicellulose, Cellulose and Lignin

Determination of the chemical composition of CBP revealed a mass percentage of 43.10% lignin, 27.23% cellulose and 9.55% hemicellulose. Therefore, lignin is the majority component of CBP, followed by cellulose and, with a lower content, hemicellulose.

3.1.3 Thermogravimetric Analysis and Differential Scanning Calorimetry

Figure 2 (a) shows the thermogravimetric (TG) curve of CBP. The first stage of mass loss occurred between 20 and 124 °C with a loss of 11% of mass. The second stage, between 200 and 386 °C, with a mass loss of 42%. In the third stage, observed from 386 to 986 °C, a mass loss of 26%. The total mass loss observed in the studied temperature range was 79%.

The pyrolysis of the three main components of biomass: hemicellulose, cellulose and lignin is reported in the literature. Hemicellulose shows mass loss mainly between 220–315 °C and cellulose between 315–400 °C. However, lignin decomposition is more difficult, with mass loss occurring at a very low rate and over a wide temperature range, from 160 to 900 °C [21].

Comparing the thermogravimetric analysis obtained in this work with the results reported in the literature [21], it is possible to notice that the results are similar. Thus, we can attribute the first stage of mass loss of cashew bark powder to the loss of moisture and volatile substances present in the material. The second stage of mass loss verified occurs in a range that encompasses that reported for the decomposition of hemicellulose and cellulose. The final stage of mass loss, called the third stage, can be attributed to the decomposition of the by-products formed in the second stage and the continuity of lignin decomposition [21]. It is important to point out that in the study used as a reference [21] the constituents were analyzed separately, allowing the identification of weight loss intervals without interference or overlapping. In the present study, the material was analyzed in its *in natura* form, that is, with the full presence of its constituents.

Figure 2 (b) presents the CBP DSC curve, indicating an endothermic peak at 83 °C that can be attributed to the evaporation of water and volatile substances adsorbed in the material.

Thermogravimetric analysis and differential scanning calorimetry proved the thermal stability of the material at the temperatures used for drying, grinding and storage.

3.1.5 Fourier Transform Infrared Spectroscopy

Figure 3 shows the FTIR spectrum of PCCAJ. It is possible to observe a broad band around 3426 cm^{-1} that can be attributed to the axial deformation of the intermolecular O-H bond, the smaller band at 2356 cm^{-1} is commonly associated with the symmetric stretching of carbon dioxide $\text{C}=\text{O}$, present in the atmosphere at the measurement location. The band at 1624 cm^{-1} is related to the axial deformation of the $\text{C}=\text{O}$ bond, the band at 1450 cm^{-1} is associated with the deformation of the resonant C-C bond of the ring, the band at 1340 cm^{-1} can be attributed to the C-H deformation of the CH_2 , as well as the bands at 1239 cm^{-1} and 1040 cm^{-1} are associated with the C-O axial deformation vibration of C-O-(H) alcohols and phenols.

The main components of biomass (lignin, cellulose and hemicellulose) are composed of alkenes, esters, aromatics, ketone and alcohol, with different functional groups containing oxygen, such as OH ($3400 - 3200\text{ cm}^{-1}$), $\text{C}=\text{O}$ ($1765 - 1715\text{ cm}^{-1}$), C-O-C (1270 cm^{-1}) and C-O-(H) ($\sim 1050\text{ cm}^{-1}$), etc. Although each component presents different structures in the infrared [22].

3.1.6 Determination of metallic concentration

Table 2 shows the average concentration of metals found in CBP after acid digestion followed by their respective standard deviation.

3.2 CHARACTERIZATION OF THE CASHEW BARK EXTRACT

3.2.1 Density

The CBE density was determined in the range of 10 to 50 °C, as can be seen in Fig. 4. At the room temperature at which the experiments were carried out (~ 25 °C) the CBE density is 0.99970 g/cm³ and can be considered equal to 1.0000 g/cm³ by rounding. Thus, 1 g of extract is equivalent to 1 mL, facilitating the correlation between mass and volume.

3.2.2 Fourier Transform Infrared Spectroscopy

Figure 5 shows the CBE FTIR spectrum. It is possible to observe an intense band between 3343 – 3252 cm⁻¹, a band around 2356 cm⁻¹, another at 2136 cm⁻¹, a well-defined band at 1633 cm⁻¹ and smaller bands at 1321 cm⁻¹ and 1212 cm⁻¹.

The band around 3300 cm⁻¹ can be attributed to the stretching of the OH group, due to the inter and intramolecular hydrogen bonds of the compound. The band at 1212 cm⁻¹ can be attributed to the axial deformation of the C–O bond and is one of the characteristic bands of tannins.

Hydrolysable and condensable tannins show the following bands: 1615 – 1606 cm⁻¹ and 1452 – 1446 cm⁻¹ attributed to aromatic ring stretching vibrations, 1211 – 1196 cm⁻¹ and 1043 – 1030 cm⁻¹ attributed to C-O bond stretching vibrations and 1518 – 1507 cm⁻¹ due to aromatic ring skeleton vibration.

Condensed tannins are clearly identified by the presence of three strong bands at 1288 – 1283 cm⁻¹, 1160 – 1155 cm⁻¹ and 1116 – 1110 cm⁻¹ and two weak bands at 976 and 844 – 842 cm⁻¹ [23].

The bands between 1288 – 1283 cm⁻¹ are characteristic for tannins from the flavonoid group. These bands can be attributed to C-O bonds by the asymmetric stretching vibrations resulting from the ring structure of pyran derivatives of this class of tannins [24].

Comparison between the FTIR spectrum of CBE and the bands associated with tannins that are reported in the literature indicated the presence of some bands of CBE that can be attributed to tannins, although other bands characteristic of tannins were not found in the FTIR spectrum of the CBE.

3.2.3 Zeta potential

The average zeta potential measured was – 24.3 mV. The negative value of the zeta potential indicates that the extract particles have a negative surface charge, which can be generated due to the existence of strong polar groups, such as hydroxyls, present in structures such as tannins. We can attribute to this potential the electrostatic behavior of the extract of attracting metallic species, which are dissociated in solution in the form of metallic cations of the M^{x+} type. It is this electrostatic attraction between the charges of the extract and the metallic species that causes the formation of agglomerates that are decanted, resulting in the removal of metals from the solution.

According to ASTM Standard D4187-82, the stability of the particle can be related to the zeta potential. Considering the average zeta potential of -24.3 mV obtained for the extract, the particles can be classified as slightly unstable. This result is consistent with the instability of tannins mentioned in the literature [25].

3.2.4 Determination of metallic concentration

The determination of the metallic concentration present in the CBE aims to define if there is a significant increase of metals in the investigated system due to the addition of the extract in the metallic removal study stage. Table 2 presents the average metallic concentration found in the cashew tree bark powder and in the extract.

Table 2
Metallic concentration found in CBP and CBE after acid digestion

Analyte	Metallic concentration (mg/L) in CBP	Metallic concentration (mg/L) in CBE
Ba	0.065 +/- 0.002	< LQ of the equipment
Cd	0.006 +/- 0.005	< LQ of the equipment
Cr	0.003 +/- 0.003	< LQ of the equipment
Cu	0.8 +/- 0.2	0.045 +/- 0.008
Mn	0.441 +/- 0.007	0.0209 +/- 0.0002
Pb	0.140 +/- 0.005	0.014 +/- 0.004
Sn	0.39 +/- 0.03	0.07 +/- 0.01
Zn	0.22 +/- 0.03	0.010 +/- 0.005

The concentration of all metals analyzed in the CBP was low, on the order of parts per million (ppm).

At CBE, the concentration of barium, cadmium and chromium is below the quantification limit (LQ) achieved by the equipment used. The concentration of the other metals analyzed was low, on the order of parts per billion (ppb). Thus, it is possible to state that CBE does not provide a significant amount of metals to the solution. That is, CBE does not add metals to the investigated synthetic water.

3.3 METAL REMOVAL EVALUATION

The efficiency of the different volumes of CBE in removing the metallic species Ba, Cd, Cr, Cu, Mn, Pb, Sn and Zn are presented in Table 3.

Table 3
Mean percentage removed from metallic species using CBE

Used volume of cashew bark extract (mL)						
Analyte	0.5	1.0	2.0	3.0	4.0	5.0
Ba	22.69502	7.89035	12.41126	11.40665	5.42058	5.98594
Cd	22.98471	7.86686	13.12832	11.97619	5.57571	6.22748
Cr	22.11209	7.55862	13.21984	11.92116	6.56547	7.55352
Cu	25.11503	9.63437	14.15330	13.15662	6.64360	7.24580
Mn	24.44381	9.10274	14.03784	12.82563	6.31144	7.13051
Pb	24.72052	9.49654	14.09879	13.31480	6.94106	7.66886
Sn	23.22051	2.00842	6.30619	10.49235	5.18866	5.71693
Zn	24.61423	9.62137	14.54708	13.43506	7.06049	7.81799

Metal removals varied between 2 and 25%. It is possible to perceive a similar behavior for all metallic species analyzed, with the smallest volume of CBE showing the highest percentages of metallic removal from the solution. The results indicated that the volume of 0.5 mL of CBE presented removals between 22 and 25% for all tested metals.

Among the investigated metals, the one that presented the smallest removals was Sn, indicating that this element possibly has the lowest affinity in the interaction with CBE.

The individual behavior of each metal can be better observed in Fig. 6, where the average metallic percentage removed for each volume of CBE used and the standard deviation of each measurement are presented.

The process can be explained as a coagulation that occurs mainly through the formation of chemical bridges between CBE and metallic species in solution.

The use of a small volume of aqueous extract obtained from the bark of the cashew tree was able to reduce the metallic concentration in the effluent by up to 25%. It is important to emphasize that the studied process concomitantly removes the eight metals present in the metallic solution.

Generally, coagulation-flocculation is not able to completely treat toxic metals in effluents [3]. However, the results observed in metallic removal indicate that CBE can be used in a pre-treatment step in order to reduce the metallic concentration in the effluent.

3.4 ASSESSMENT OF HOW GREEN THE PROCESS IS

Figure 7 presents the analysis of the entire process of obtaining the cashew tree bark extract and its application for the removal of metallic contaminants from the perspective of the twelve principles of green chemistry.

The final evaluation is determined through the sum of all the evaluations carried out (131), which is divided between the total of events analyzed (16), thus obtaining the corresponding evaluation for the process, which is considered with a very good green approach (8.2).

Comparing CBE with the main commercial products used for metallic precipitation, we can say that the cashew tree bark extract presents itself as a promising option from an environmental perspective.

4. Conclusions

It is an almost universal consensus among scientists the concern with environmental preservation. But often this care is not carried out due to financial and technological limitations. Thinking about contributing to the reduction of these limitations, the present work described the obtaining and characterization of the cashew bark powder and the aqueous extract obtained from it, in addition to applying the extract for the concomitant removal of eight polluting metallic species.

The characterization of the cashew bark powder revealed a surface with roughness, but without porosity, making physisorption phenomena unfeasible. The Fourier transform infrared spectroscopy revealed bands that can be attributed to the main components of the biomass (lignin, cellulose and hemicellulose), in addition, the analysis of the chemical composition revealed that the major component is lignin with 43.10% of the mass. Thermogravimetric analysis and the differential scanning calorimetry proved the thermal stability of the material at the temperatures used for drying, grinding and storage. The digestion of cashew bark powder followed by the determination of the metallic concentration revealed low metallic concentrations, in the order of parts per million (ppm), indicating that the raw material does not add significant metallic concentrations to the process.

The characterization of extract obtained from the bark of the cashew tree revealed that the liquid has a density of 0.99970 g/cm^3 , facilitating the correlation between mass and volume, since 1 g of the extract is approximately equivalent to 1 mL. Fourier transform infrared spectroscopy indicated the presence of some bands that can be attributed to tannins. The zeta potential classified the particles present in the liquid as slightly unstable, which favors coagulation/flocculation processes. The determination of metallic concentration revealed very low concentrations of the analyzed metals, in the order of parts per billion (ppb), indicating that the use of the extract does not add significant metallic concentrations to the investigated process.

The experiments of application of the natural extract, without chemical modifications, in the removal of toxic metals present in aqueous medium revealed that the volume of 0.5 mL of the extract obtained from the bark of the cashew tree promoted removals between 22 and 25% for all eight metals tested, presenting itself as a new option for a natural, renewable and biodegradable source that can be used to

reduce the concentration of toxic metals in effluents. Finally, the process was classified as a very good green approach, from the perspective of green chemistry.

Declarations

Acknowledgments

The authors would like to thank the Bahia State Research Support Foundation (FAPESB) for the scholarship.

Funding

Not applicable.

Conflicts of interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

Availability of data and material

Data will be made available on reasonable request.

Code availability

Not applicable.

Author's contributions

All authors listed have contributed sufficiently to the project to be included as authors.

References

1. A. Azimi, A. Azari, M. Rezakazemi, M. Ansarpour, Removal of heavy metals from industrial wastewaters: A review, *ChemBioEng., Rev.* 4 (2017) 37–59.
<http://dx.doi.org/10.1002/cben.201600010>.
2. C. Zamora-Ledezma, D. Negrete-Bolagay, F. Figueroa, E. Zamora-Ledezma, M. Ni, F. Alexis, V.H. Guerrero, Heavy metal water pollution: A fresh look about hazards, novel and conventional remediation methods, *Environmental Technology & Innovation*, 22 (2021) 101504.
3. F. Fu, Q. Wang, Removal of heavy metal ions from wastewaters: A review, *J. Environ. Manage.*, 92 (2011) 407–418.
4. T.A. Saleh, M. Mustaqeem, M. Khaled, Water treatment technologies in removing heavy metal ions from wastewater: A review, *Environmental Nanotechnology, Monitoring & Management*, 17 (2022) 100617.

5. A. Saravanan, P.S. Kumar, S. Jeevanantham, S. Karishma, B. Tajsabreen, P.R. Yaashikaa, B. Reshma, Effective water/wastewater treatment methodologies for toxic pollutants removal: Processes and applications towards sustainable development, *Chemosphere*, 280 (2021) 130595.
6. K.M. Yenkie, S. Burnham, J. Dailey, H. Cabezas, F. Friedler, Generating efficient wastewater treatment networks: an integrated approach comprising of contaminant properties, technology suitability, plant design, and process optimization, *Comput. Aided Chem. Eng.*, 46 (2019) 1603–1608.
7. S. Bolisetty, M. Peydayesh, R. Mezzenga, Sustainable technologies for water purification from heavy metals: review and analysis, *Chem. Soc. Rev.*, 48 (2019) 463–487.
8. M. Ince, O. Kaplan Ince, Heavy metal removal techniques using response surface methodology: Water/wastewater treatment, *Biochem. Toxicol. - Heavy Met. Nanomater*, (2020) 1–19.
9. A. Du Pont, Lime treatment of liquid waste containing heavy metals, *Pollut. Eng.*, 4 (1987) 84–88.
10. S. Mauchauffée, E. Meux, Use of sodium decanoate for selective precipitation of metals contained in industrial wastewater, *Chemosphere*, 69 (2007) 763–768.
11. K.A. Baltpurvins, R.C. Burns, G.A. Lawrance, Use of the solubility domain approach for the modeling of the hydroxide precipitation of heavy metals from wastewater, *Environ. Sci. Technol.*, 30, (1996) 1493–1499.
12. K.A. Baltpurvins, R.C. Burns, G.A. Lawrance, A.D. Stuart, Effect of electrolyte composition on zinc hydroxide precipitation by lime, *Water Res.*, 31 (1997) 973–980.
13. X. Lin, R.C. Burns, G.A. Lawrance, Effect of electrolyte composition, and of added iron (III) in the presence of selected organic complexing agents, on nickel (II) precipitation by lime, *Water Res.*, 32 (1998) 3637–3645.
14. D. Xu, B. Zhou, R. Yuan, Optimization of coagulation-flocculation treatment of wastewater containing zn(II) and cr(VI). *IOP Conf. Ser. Earth Environ. Sci.* 227, 2019.
15. C.Y. Teh, P.M. Budiman, K. Pui, Y. Shak, T.Y. Wu, Recent advancement of coagulation-flocculation and its application in wastewater treatment recent advancement of coagulation-flocculation and its application in wastewater treatment, *Ind. Eng. Chem. Res.*, 55 (2016) 4363–4389.
16. A. Ibrahim, A.Z. Yaser, J. Lamaming, Synthesising tannin-based coagulants for water and wastewater application: A review, *Journal of Environmental Chemical Engineering*, 9 (2021) 105007.
17. J.B. Heredia, J.S. Martín, Municipal wastewater treatment by modified tannin flocculant agent, *Desalination*, 249 (2009) 353–358.
18. L. Joseph, B.M. Jun, J.R.V. Flora, C.M. Park, Removal of heavy metals from water sources in the developing world using low-cost materials: A review, *Chemosphere*, 229 (2019) 142–159.
19. P.J. Van Soest, R.H. Wine, Use of detergents in the analysis of fibrous feeds. IV. Determination of plant cell-wall constituents, *J. AOAC Int.*, 50 (1967) 50–55.
20. M.L.M. Galicia, J.O. Martínez, L.B.R. Sánchez, O.M. Hernández, G.A.A. Razo, A. O. Valdivia, R.M. Ruvalcaba. Qué tan verde es un experimento?, *Educ. Quim.*, 22 (2011) 240–248.

21. H. Yang, R. Yan, H. Chen, D.H. Lee, C. Zheng, Characteristics of hemicellulose, cellulose and lignin pyrolysis, *Fuel*, 86 (2007) 1781–1788.
22. S. Gupta, S.P. Singh, R.C. Gupta, Studies on tannin from Indian Wattle (*Acacia mearnsii*) bark, *Indian J. for Eng.*, 4 (1981) 18–21.
23. L. Falcão, M.E.M. Araújo, Tannins characterization in historic leathers by complementary analytical techniques ATR-FTIR, UV and chemical tests, *J. Cult. Herit.*, 14 (2013) 499–508.
24. K. Fernandez, X. Labarca, E. Bordeu, A. Guesalaga, E. Agosin, Comparative study of wine tannin classification using Fourier Transform Mid-Infrared Spectrometry and sensory analysis, *Appl. Spectrosc.*, 61 (2007) 1163–1167.
25. R.B. Broadhurst, W.T. Jones, Analysis of condensed tannins using acidified vanillin, *Journal of the Science of Food and Agriculture*, 29 (1978) 788–794.

Figures

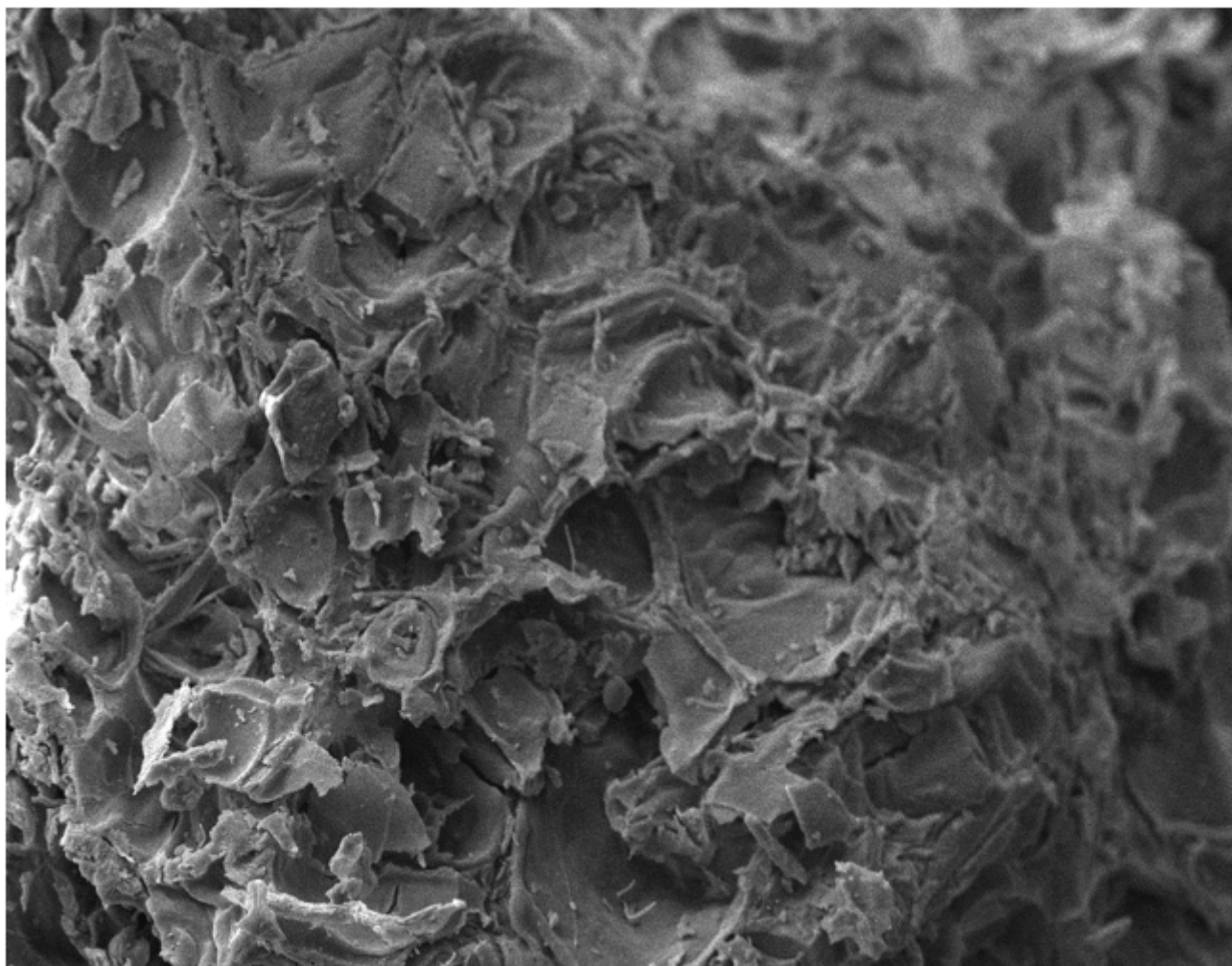


Figure 1

SEM of CBP at 500x magnification

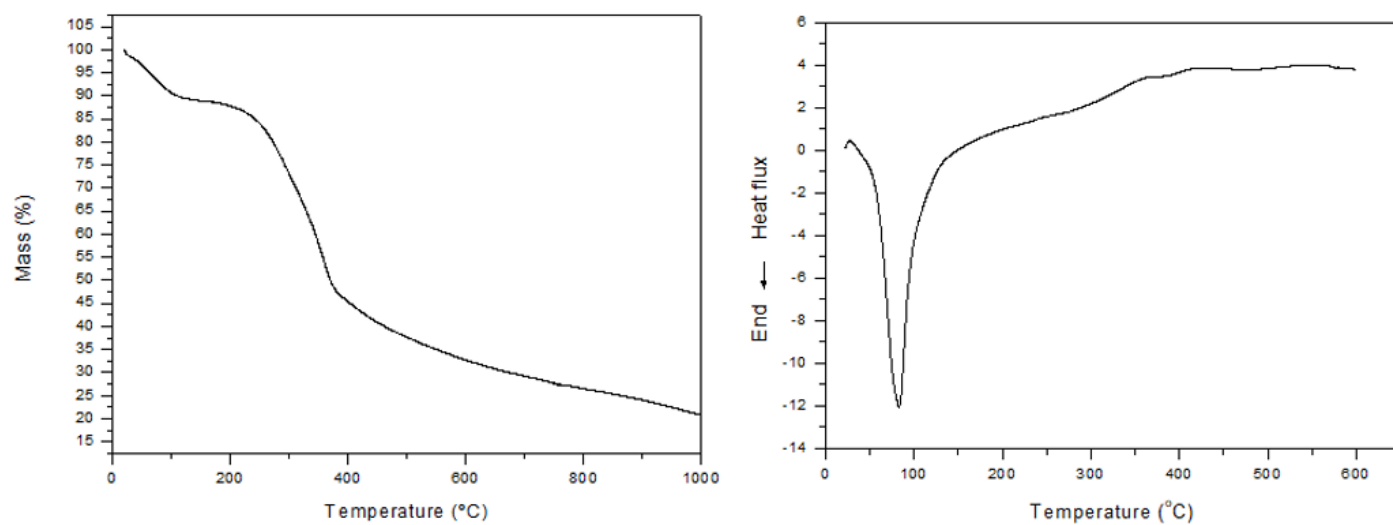


Figure 2

(a) TG CBP (b) DSC CBP

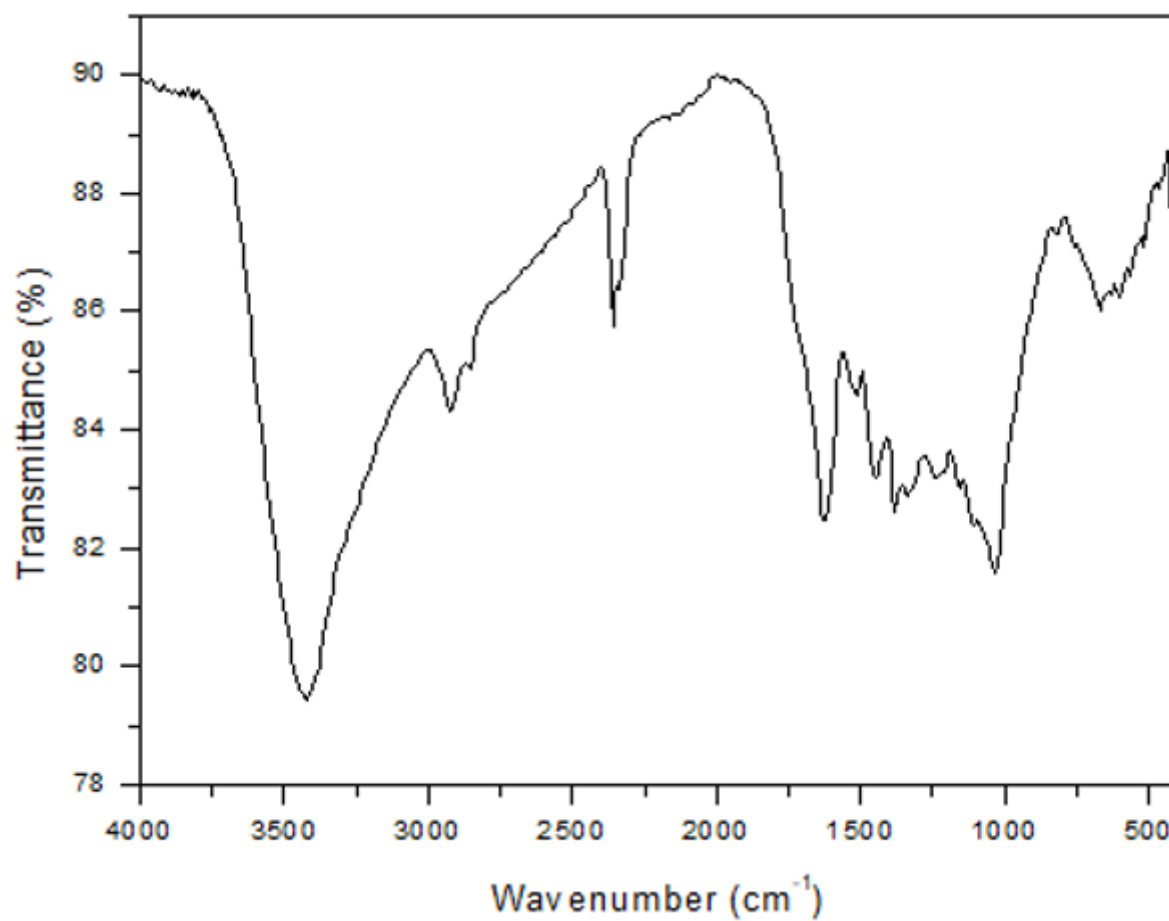


Figure 3

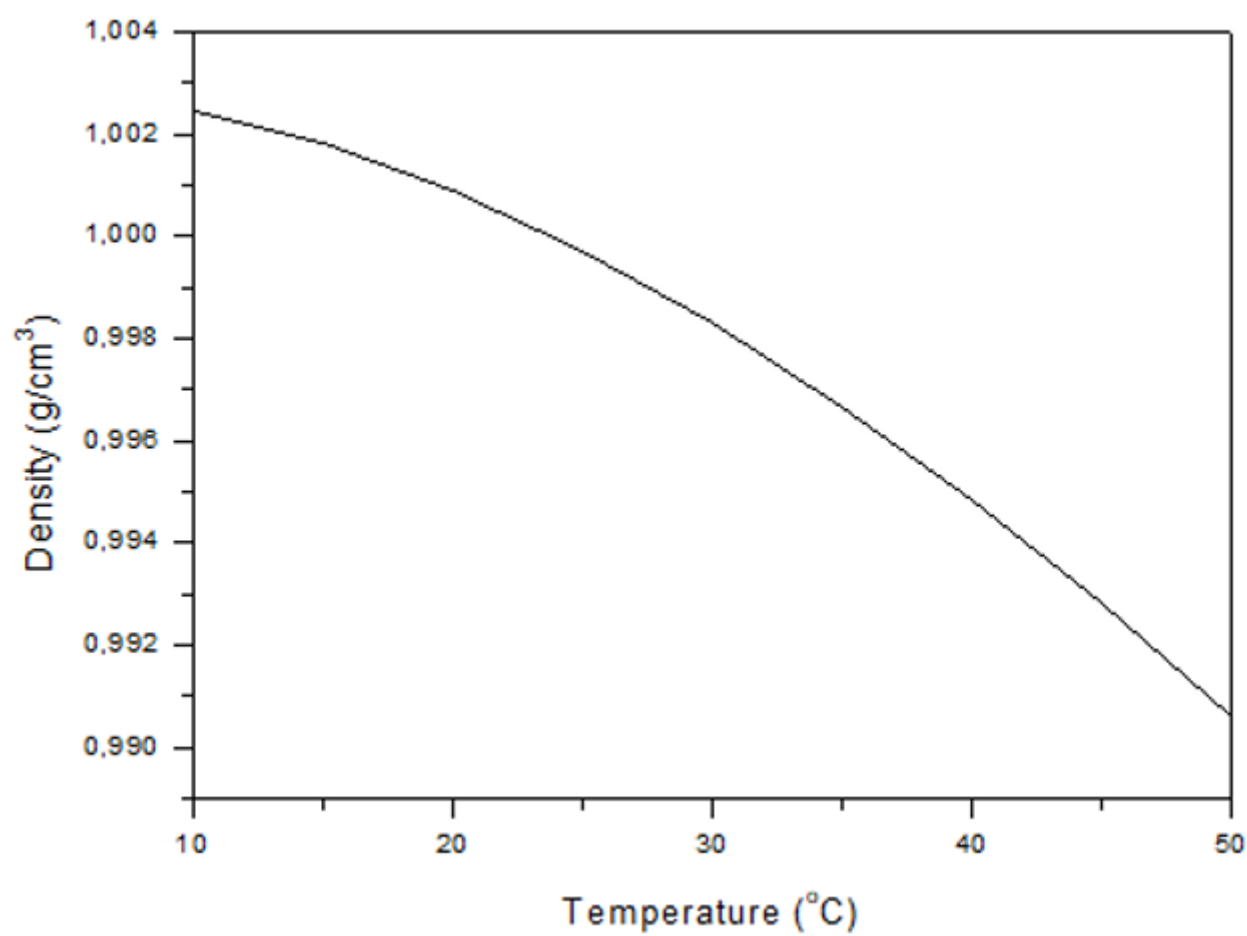


Figure 4

CBE density curve between 10 and 50 °C

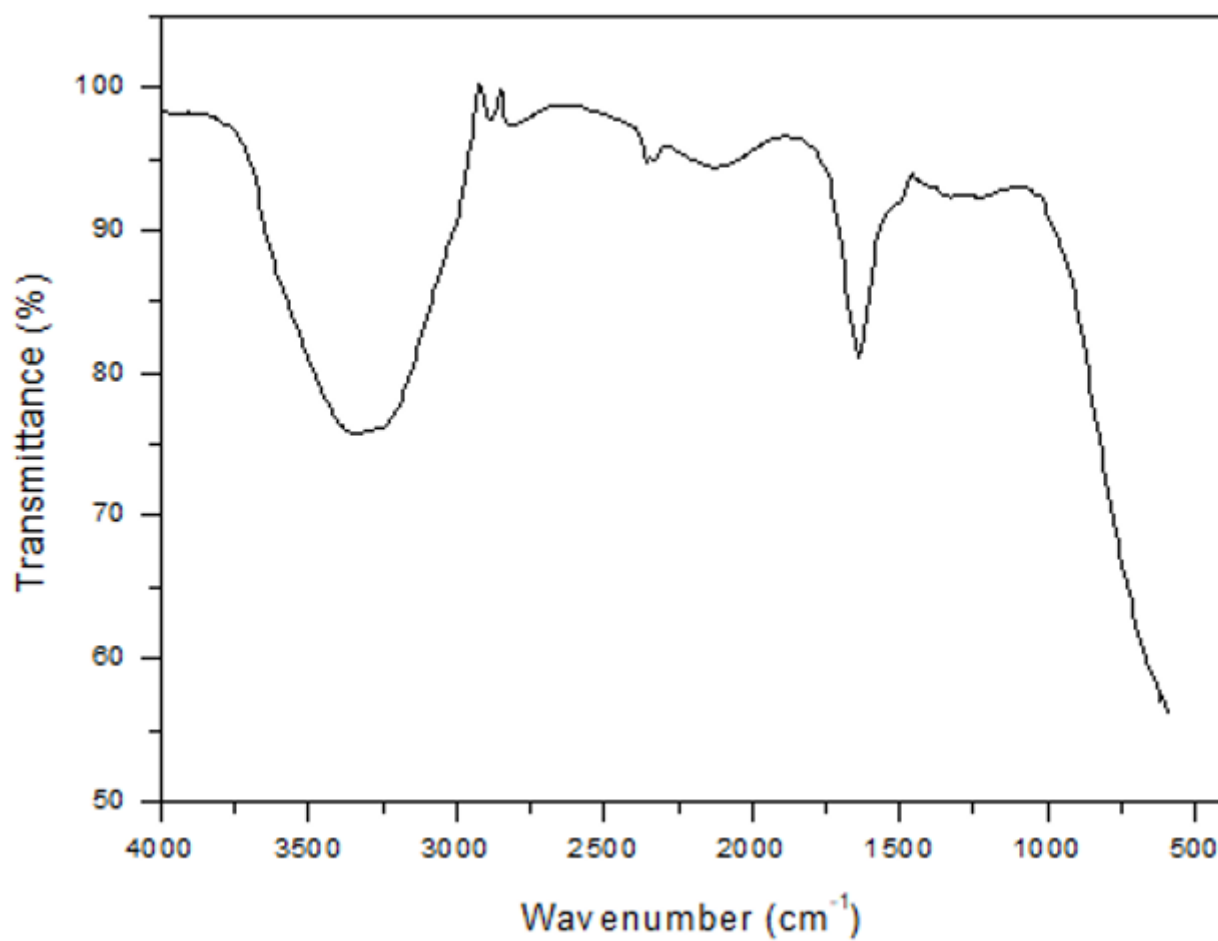


Figure 5

CBE FTIR spectrum

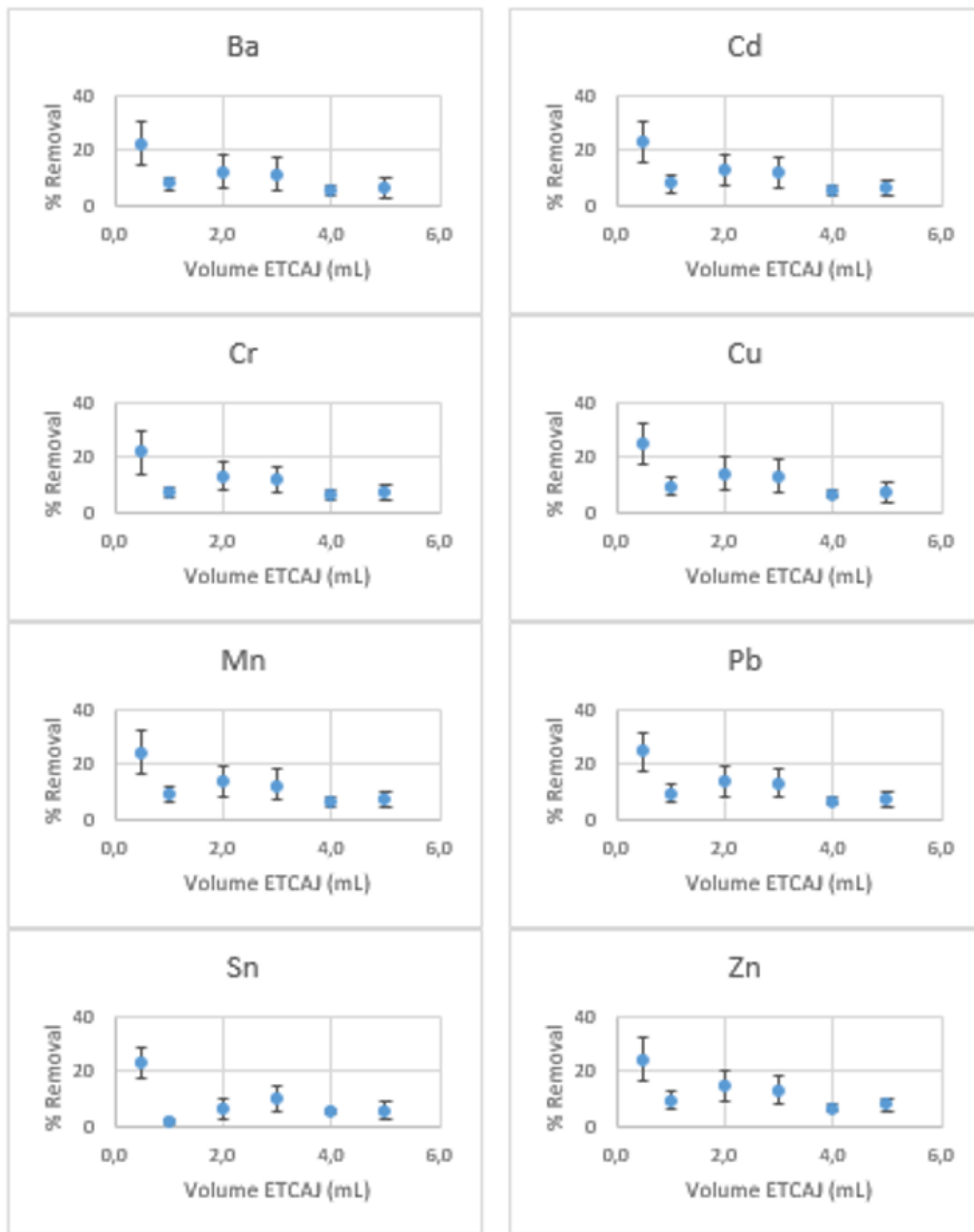


Figure 6

Metal removal from the solution

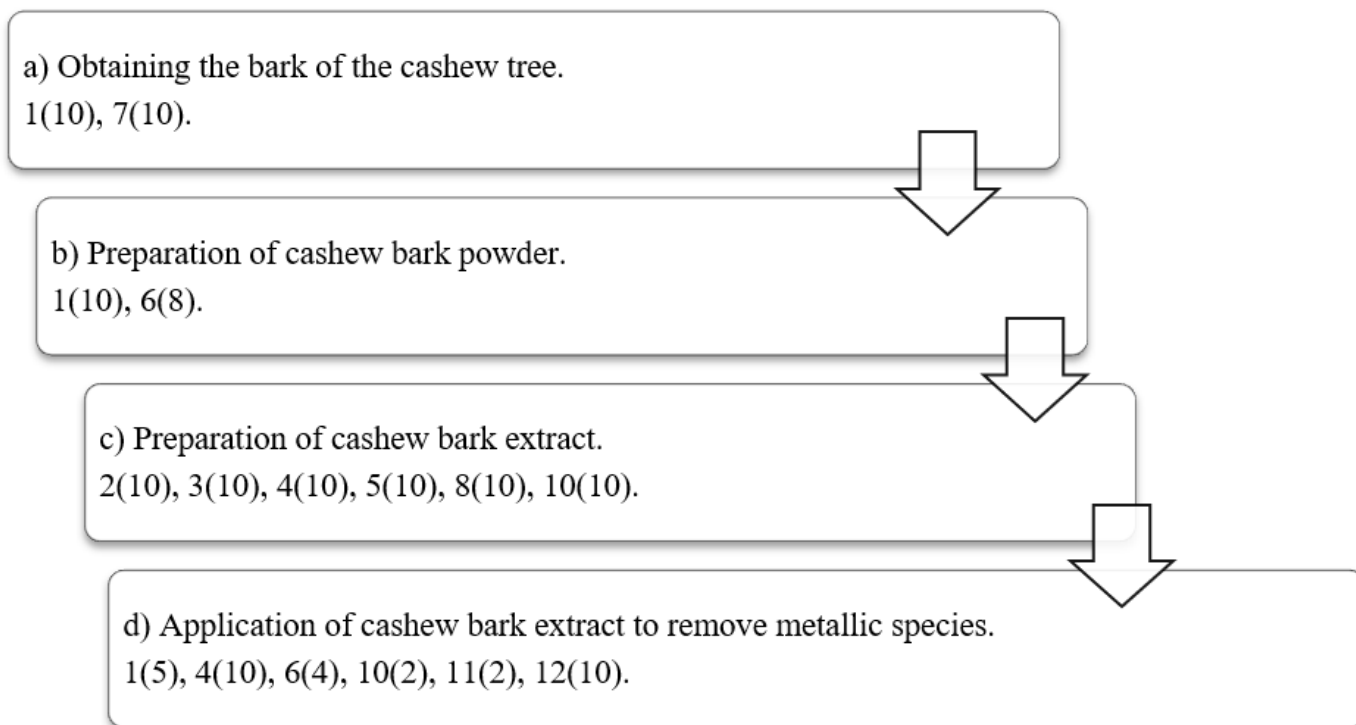


Figure 7

Process analysis from the perspective of green chemistry

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [GraphicalAbstract.docx](#)