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Strategic Design of Heavy Metals Removal Agents through Zeta Potential Measurements

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Abstract

Industrial wastewater generally contains significant amounts of toxic heavy metals that cause a problem of contamination to the environment. In this chapter, the use of poly-electrolytic waste as new coagulant-flocculating-chelating agents in the separation of Cu, Ni, Zn, Pb, Cd, Cr by a coagulation-flocculation process is discussed. The isoelectric point ($\zeta = 0$) of the residual water was reached with a dose of 2.5 mg chitosan and observed a clarification kinetics = 187.49% T/h, sediment kinetics = 93.96 mm/h and an efficiency of 85% in the removal of heavy metals. With the SEM-EDS analysis and the determination of heavy metals in the treated water, it is shown that the functional groups that chitosan has in its structure have the following order of affinity for the removal of heavy metals from the wastewater model: Cr = 27.64% > Ni = 21.96% > Pb = 21.28% > Zn = 14.68% > Cu = 10.96% > Cd = 3.35% > Ca = 0.12%.

Keywords: heavy metals, zeta potential, wastewater treatment, biopolyelectrolytes, coagulation-flocculation

1. Introduction

The environmental pollution problems increase, with the aim of controlling and reducing the impact of industrial activities that cause damage to the environment, and environmental regulations are increasingly demanding. One of the issues of greatest scientific and technological interest is the care of water quality, derived from the problems of scarcity and water contamination by a variety of chemical elements such as heavy metals [1]. The main sources of heavy metals include mineral processing, pulp and paper industry, printing in the graphic

industry, metallurgical, printed board manufacturing, nuclear, mining, battery manufacturing, leather tanning, smelting, petrochemicals, metal finishing and plating, semiconductor manufacturing, textile dyes, ceramic and other industries, which are those that consume significant amounts of water and therefore generate wastewater with a high content of heavy metals (>200 mg/L) that cannot be discharged to water bodies without previously carrying out a treatment process [2, 3].

The most common heavy metals that are often present in industrial wastewater include nickel, zinc, silver, lead, iron, chromium, copper, arsenic, cadmium, and uranium [1].

One of the main reasons why heavy metals should not be discharged into water receiving bodies is that they are nonbiodegradable, toxic, and easy to accumulate at low concentrations in living organisms in general, specifically in humans, and cause serious illnesses such as cancer, nervous system damage, and kidney failures and can be deadly at high concentrations [4].

Currently, there are different technologies to perform the treatment of wastewater containing heavy metals, including adsorption using various adsorbent materials (polymers, carbon, nanomaterials, clays, zeolites), electrodeposition, membrane filtration (ultrafiltration, nanofiltration and reverse osmosis), coagulation-flocculation, chemical precipitation with hydroxides, sulfides and chelating precipitations, electrocoagulation, electrodialysis, ion exchange, biological treatment, photocatalysis, and electroflotation. Each technology has certain advantages and disadvantages. Considering the most demanding environmental legislation, industries need more efficient wastewater treatments to eliminate suspended or dissolved metals [5–20].

In this context, the use of waste from the food industry and renewable sources of biopolyelectrolytes such as shrimp shell waste, nopal mucilage, nejayote, mesquite seeds, coffee, and tule residues as biodegradable coagulating-flocculating-chelating agents is proposed [21, 22]. Due to the chemical nature of the interactions that predominate at the molecular level between the functional groups of the biopolyelectrolytes (BPE) and the heavy metals present in the wastewater, in this work, the zeta potential measurements were used. The zeta potential is a key parameter to determine the surface charge density of the BPE, the isoelectric point (IEP) and define the strategy of adding the BPE to wastewater with heavy metals.

2. Experimental section

2.1. Materials and methods

2.1.1. Materials

The heavy metal wastewater model was prepared with the nitrate salts of each metal ion: $\text{Ca}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, and $\text{Cr}(\text{NO}_3)_3$. Sodium alginate (AG) with viscosity (5–40 cP) were purchased from Sigma Aldrich.

2.2. Methods

2.2.1. Extraction and physicochemical characterization of biopolyelectrolytes

Chitosan is obtained from waste shrimp shells using the adapted method proposed by Goycoolea et al. [23]. Maize gum was obtained by fractional separation, using hexane, ethanol, hydrochloric acid, isopropanol, acetone, and methanol formed by the steps of desalmidonado, deproteinization, delipidation, and delignification, which are adaptations of the methods proposed [24–26]. Mesquite gum was extracted from mesquite seeds using the method reported by Sciarini et al. [27]. For the extraction of nopal mucilage (NM), the methodology was reported by Cárdenas et al. [28]. Extraction of lignin was performed by the delignification method from black liquors of coffee and tulle [29]. The process consists of precipitating the lignins by acidification from black liquors obtained from tulle and coffee residues. The FTIR spectra were recorded on a FT-IR Spectrometer (Perkin Elmer). Universal Attenuated Total Reflectance (UATR Two) attachment was employed to analyze the biopolyelectrolyte.

2.2.2. $\zeta = f(\text{pH})$ profiles of the alginate, maize gum, mesquite gum, nopal mucilage, coffee and tulle lignin and chitosan

The zeta potential of the anionic, cationic, and neutral biopolyelectrolytes was measured in a Stabino Particle Charge Mapping (Microtrac). The measurements were done at ambient temperature in teflon cuvettes. Influence of pH on the zeta potential behavior of each biopolyelectrolytes was studied within a pH range of 2–11 with 0.1 M NaOH and 0.1 M HCl to determine the isoelectric point (IEP) and the highest degree of ionization of the biopolyelectrolytes [30].

2.2.3. Evaluation of the chelating performance of the BPE

The performance of the BPE in the separation of heavy metals present in the wastewater model was evaluated using stability analysis to determine the kinetics of coagulation-flocculation, morphology and elemental composition of the formed flocs, content of metals remaining in the treated water, in each test of dosage of BPE to synthetic heavy metals wastewater. Samples of flocs obtained were examined in a SEM ZEISS EVO-MA15, equipped with an EDS (energy dispersive spectroscopy) BRUKER detector for heavy metals-relative estimations. Agilent Technologies 4200 MP-AES were used to determine metals concentration. Stability tests were carried out, performing a transmittance scan every 25 s for 30 min using Turbiscan Lab® Expert.

3. Results and discussion

3.1. Physicochemical characterization of biopolyelectrolytes

Considering that the surface functional groups of the BPE are responsible for the molecular interactions between the biopolyelectrolytes (AG, Ch, Mag, nopal mucilage, Meg, CL, and TL)

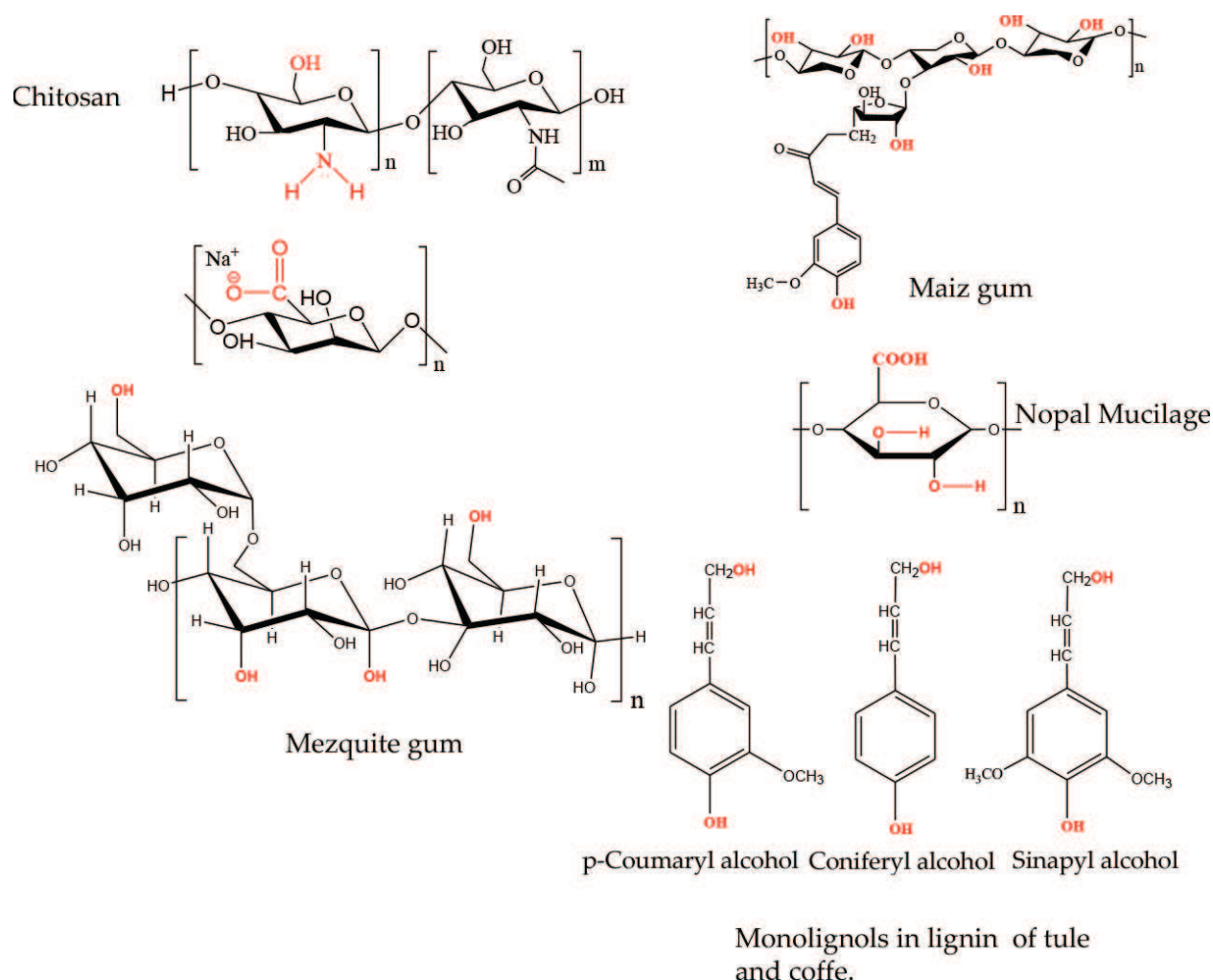


Figure 1. Chemical structure of the BPE.

(see **Figure 1**) and the heavy metals contained in the wastewater, they were studied by FTIR [31]. The most common BPE functional groups are carbonyl, phenolic, acetamido, alcoholic, amido, amino, and sulfhydryl, which have an affinity for heavy metal ions to form complexes or metal chelates [32].

In **Figure 2**, the FTIR spectra corresponding to the anionic biopolyelectrolytes that have higher density of negative surface charge are shown. In **Figure 2a** and **c**, the characteristic signals are shown to the three main compounds present in the coffee and tulle lignin: p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. Assignment bands shown at the wavelength $3500\text{--}3100\text{ cm}^{-1}$ are attributed to the stretching vibrations of the OH, the stretching vibrations at $2910\text{--}2835\text{ cm}^{-1}$ are attributed to the CH group, and the stretching vibrations at $1700\text{--}1550\text{ cm}^{-1}$ are attributed to the C—C group. There are also other signals at 1230 cm^{-1} and 1012 cm^{-1} , corresponding to the vibration bands of the C—O.

Figure 2b shows the FTIR spectrum of the anionic biopolyelectrolyte (maize gum) obtained from nejayote. The signal observed at 2923 cm^{-1} corresponds to the vibrations of the CH bonds of the methyl groups and the wide band that appears at 3421 cm^{-1} is due to the stretches of the HO bonds of the hydroxyl groups present in the macromolecule of the maize gum.

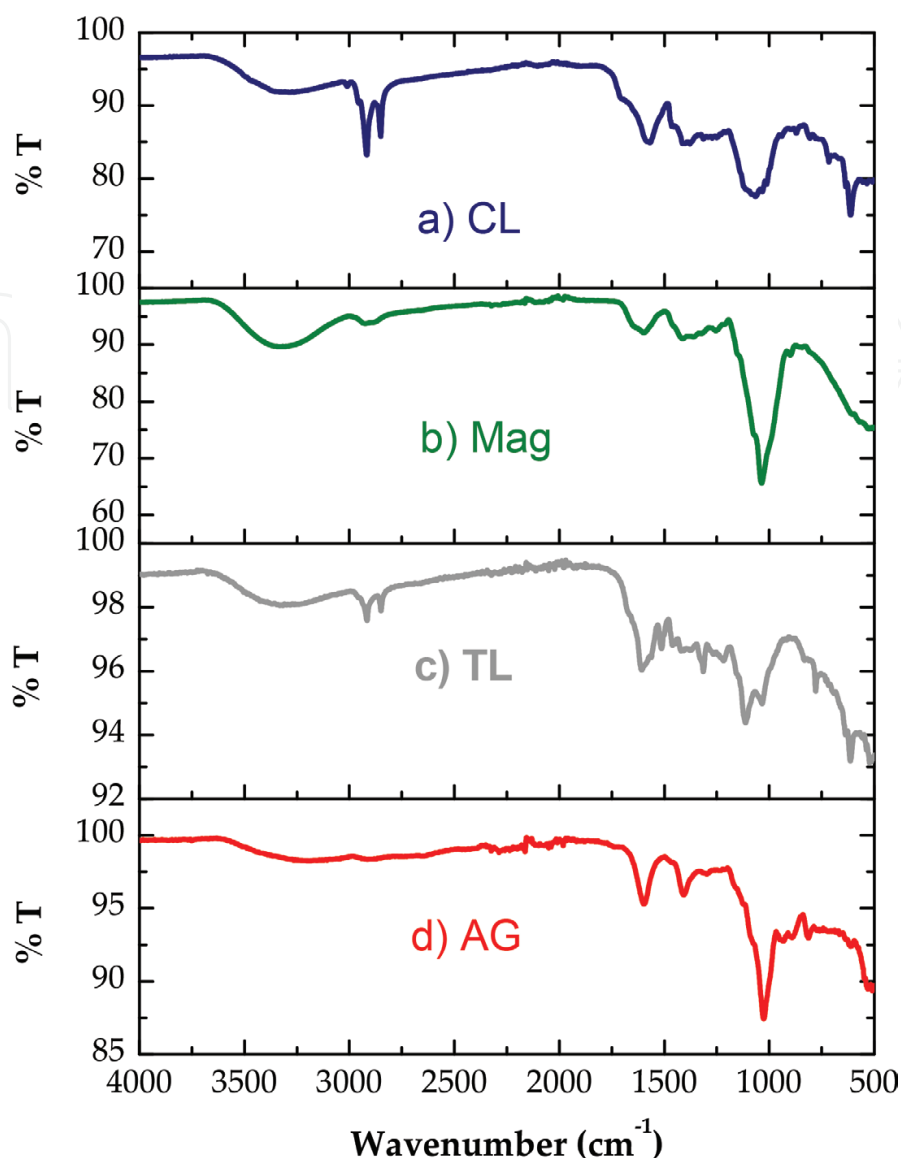


Figure 2. FTIR spectra of biopolyelectrolytes with higher density of negative surface charge: a) Coffe lignin, b) Maize gum, c) Tule lignin, d) Alginate.

The OH groups are those that give anionic character to this biopolyelectrolyte and that favors its interaction with metal ions present in the wastewater.

Figure 2d shows the characteristic signals of the alginate macromolecule, in which the band at the $3500\text{--}3200\text{ cm}^{-1}$ region is attributed to the hydroxyl groups and the signal at 1500 cm^{-1} corresponds to the carboxyl groups found distributed along the anionic biopolyelectrolyte chain.

Figure 3 shows the FTIR spectra of the BPE of cationic, non-ionic and slightly anionic character, considering the zeta potential values.

In the spectrum of Ch (**Figure 3a**), the characteristic bands at 3450 cm^{-1} (--OH group), at 3292 cm^{-1} (NH group), at 2919 and 2862 cm^{-1} (CH group), at 1655 cm^{-1} (amide I), at 1580 cm^{-1} (double group --NH_2), at 1313 cm^{-1} (amide III), at 1154 cm^{-1} (antisymmetric stress of the COC bridge), at 1082 and 1032 cm^{-1} (skeletal vibrations characteristic of the pyranotic structure) and 896 cm^{-1} (CH tension of the anomeric groups) are shown.

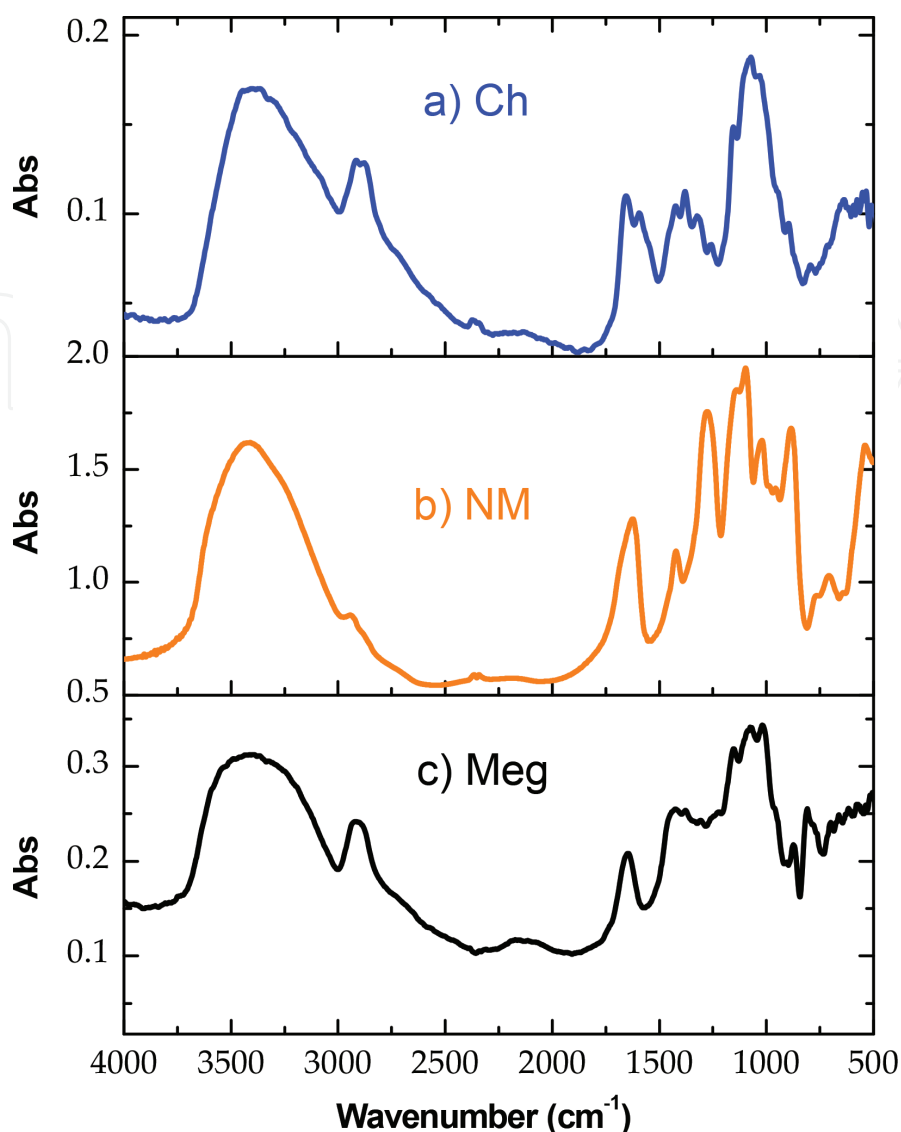


Figure 3. FTIR spectra of the BPE of cationic, non-ionic, and slightly anionic character: a) Chitosan, b) Nopal mucilage, c) Mezquite gum.

The absorption bands that are common for mesquite gum (**Figure 3b**) correspond to the OH-group centered around 3400 cm^{-1} and the C—H found in the band at 2900 cm^{-1} . Other characteristic absorption bands are observed in the bands at $1150\text{--}950\text{ cm}^{-1}$, which are associated with the signals of C—O and carbohydrates (C—O—H). Also, in the bands at 870 cm^{-1} and 813 cm^{-1} indicate the presence of units of β -D mannopyranose and units of α -D galactopyranose.

The nopal mucilage spectrum is shown in **Figure 3c**, and the spectral region at 1350 cm^{-1} to 1750 cm^{-1} assigned to the vibrations of the bands of the nonionized COOH carboxylic groups is observed. Likewise, ionization leads to its disappearance and to the appearance of new bands associated with the symmetric and asymmetric vibrations of the COO— groups, centered approximately between at $1600\text{--}1650\text{ cm}^{-1}$ and at $1400\text{--}1450\text{ cm}^{-1}$.

3.2. $\zeta = f(\text{pH})$ profiles of the BPE

In **Figure 4**, the $\zeta = f(\text{pH})$ plot shows the charge density variation for AG, NM, Meg, CL, TL, Mag and Ch with respect to pH. The change in pH had a distinct effect with each biopolyelectrolyte because of the difference between the functional groups present in the chains of the macromolecules. Sodium alginate is a strong anionic biopolyelectrolyte and maintains negative zeta potential values ($\zeta = -480.0 \text{ mV}$) between pH 3.5 and 10, attributed to the carboxylate group ($-\text{COO}^-\text{Na}^+$) and was not observed their IEP.

Chitosan has a cationic character at $\text{pH} < 6.0$, reaching a maximum value in zeta potential $\zeta = 55 \text{ mV}$ at $\text{pH} 3.0$. This behavior is attributed to the amine groups that are protonated at $\text{pH} < \text{pKa} = 6.3$. At $\text{pH} = 6.5$, the isoelectric point of the chitosan was reached and at $\text{pH} > \text{IEP}$, the values of zeta potential remained close to neutrality ($\zeta = 0$), and this corresponds to the hydrophobic character acquired by the chitosan macromolecule due to the deprotonation of the amine groups.

The zeta potential values of the NM indicate the acid-base behavior of the carboxyl groups present in the macromolecule. The NM has its isoelectric point at $\text{pH} = 4.0$, observing the formation of NM aggregates at $\text{pH} < \text{IEP}$. At $\text{pH} > \text{IEP}$, it had an anionic character, and this derived that the carboxyl groups are ionized at $\text{pH} > \text{pKa} = 3.5$. The behavior zeta potential vs. pH of anionic BPE obtained of nejayote is shown in **Figure 4**, which has a high negative charge density ($\zeta = -35 \text{ mV}$) in the pH range 6–12, having the isoelectric point close to $\text{pH} = 2.0$.

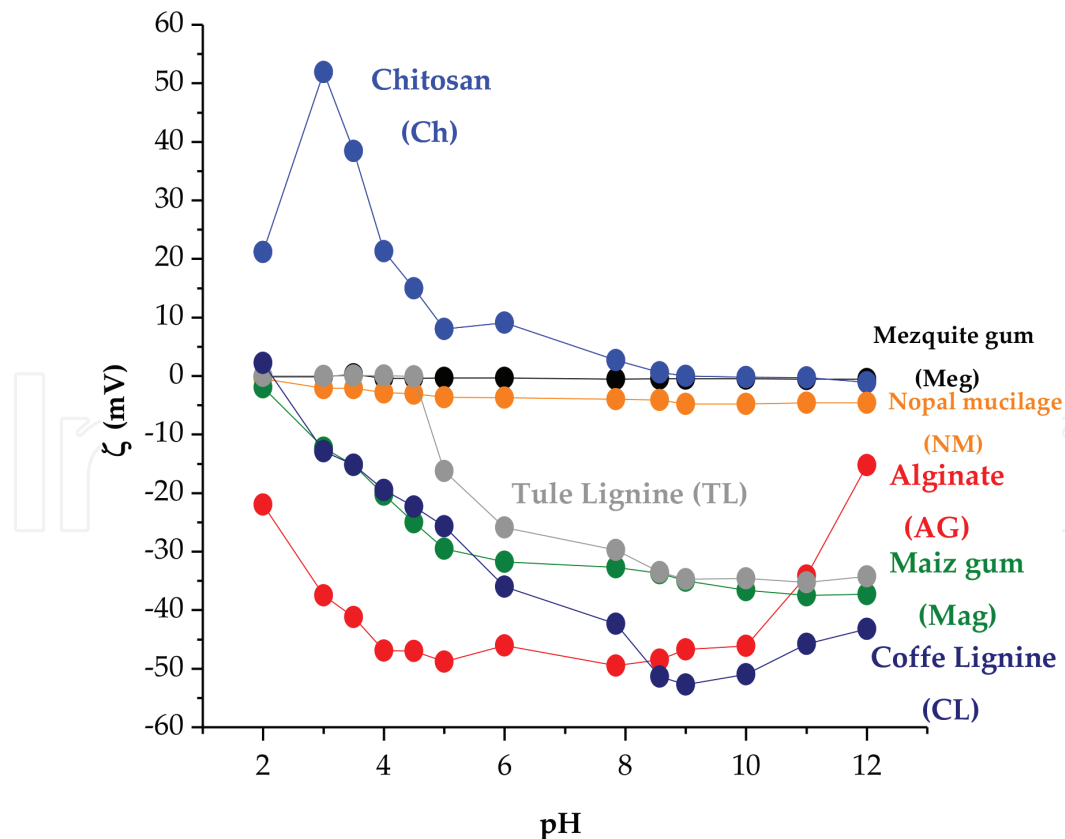


Figure 4. $\zeta = f(\text{pH})$ profiles of the BPE.

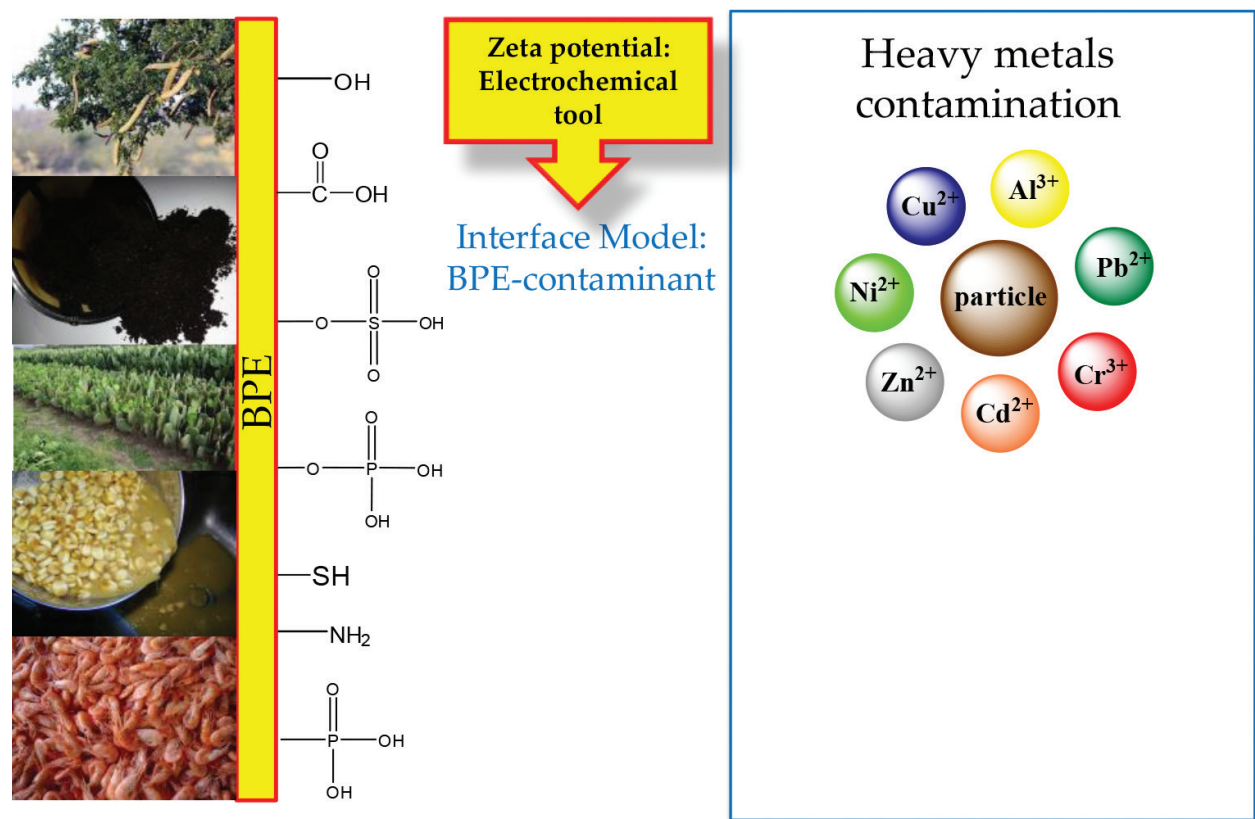


Figure 5. Outline of BPE-contaminant interface model.

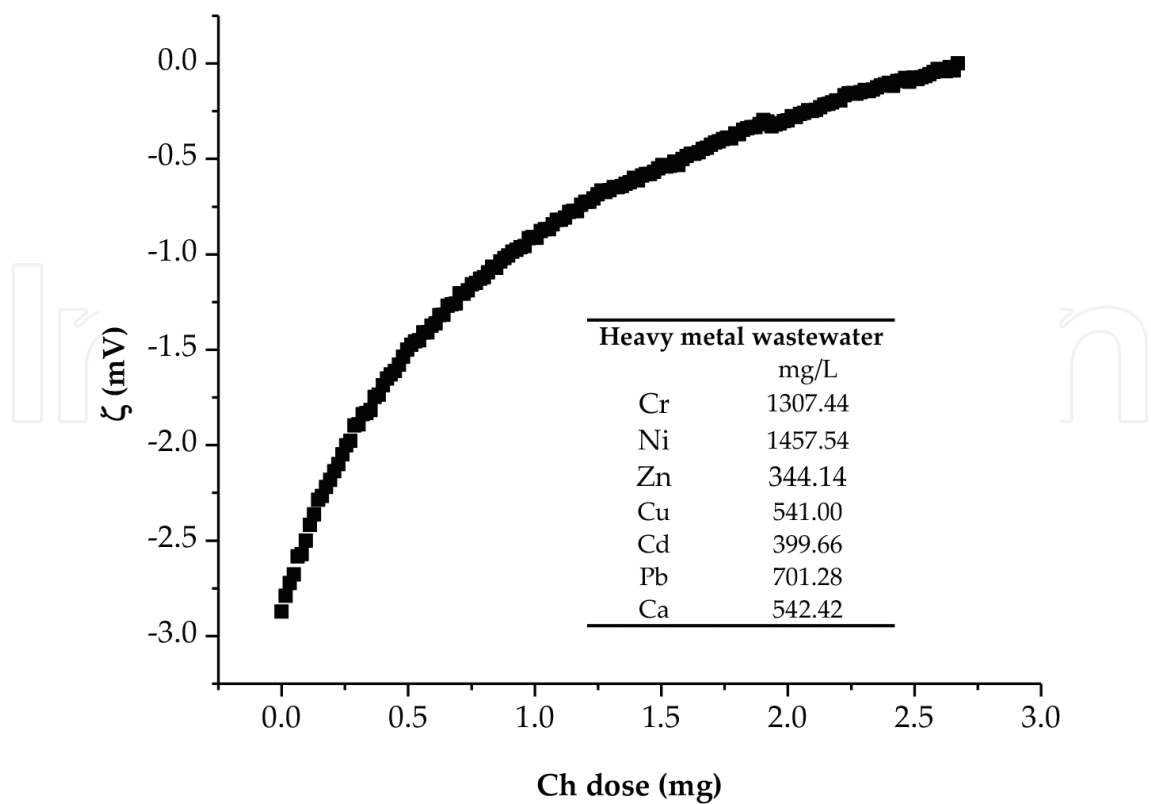


Figure 6. $\zeta = f(\text{Ch dose})$ profile with heavy metals wastewater model.

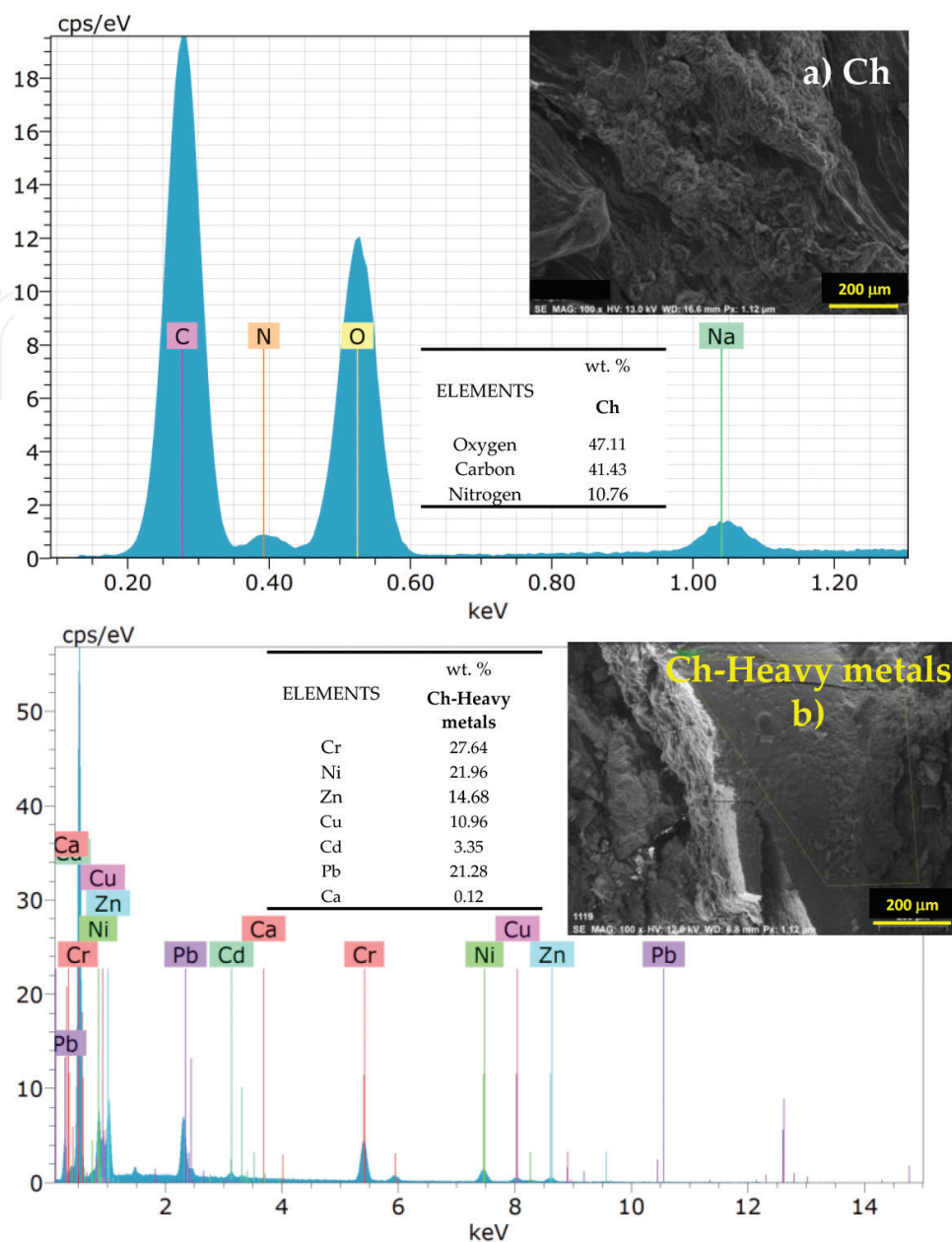


Figure 7. SEM micrograph and EDS spectrum of (a) Ch and (b) flocs of Ch-heavy metals.

The coffee lignin showed an average negative zeta potential value ($\zeta = -40$ mV) at a pH of 6–12, decreasing linearly according to the low pH ($\zeta = -40$ mV to $\zeta = -10$ mV). The lignin chains of coffee present their IEP at pH = 2.0.

Similarly, tule lignin showed this tendency, but with a lower negative charge density ($\zeta = -30$ mV) at pH 2–12, and its IEP at pH = 4.0. This behavior is attributed to the difference in the composition of the three main monomers that contain the lignin and which is a function of its source of origin.

The profiles of $\zeta = f(\text{pH})$ of the BPE allow to determine and predict the physicochemical behavior of the macromolecules in the coagulation processes of flocculation of residual water with heavy metals. Through these profiles, it is possible to determine the pH at which the

BPE have their highest surface charge density (negative or positive), define a strategy to make additions of BPE mixtures sequentially, and orient the dose needed to carry out the separation of heavy metals from waste water.

3.3. Evaluation of the chelating performance of the BPE

The BPE have a great potential to get to replace the synthetic coagulant-flocculant-chelating agents, considering their chemical structure and their surface charge density in aqueous solution. The BPE contain in their structure different functional groups that give rise to the surface charge of the macromolecules and that can interact with the heavy metals frequently found in industrial wastewater. As shown in **Figure 5**, the evaluation of the performance of each BPE can be performed for the separation of metals in a natural way as well as to carry out strategies for modifying the macromolecules to make them more efficient in terms of coagulation-flocculation kinetics and removal of heavy metals. In this chapter, the evaluation of chitosan for the separation of heavy metals in wastewater model is presented.

In **Figure 6**, the profile of $\zeta = f(\text{Ch dose})$ is shown with the residual water model with heavy metals. The model wastewater has a zeta potential value ($\zeta = -2.8 \text{ mV}$) at $\text{pH} = 5.0$, as the Ch dose increases, the zeta potential of the wastewater rises linearly ($\zeta = -2.8 \text{ mV}$ to $\zeta = -0.5 \text{ mV}$), in a dose range of Ch 0–1.5 mg. The isoelectric point of the wastewater model was reached with a dose of 2.5 mg of Ch.

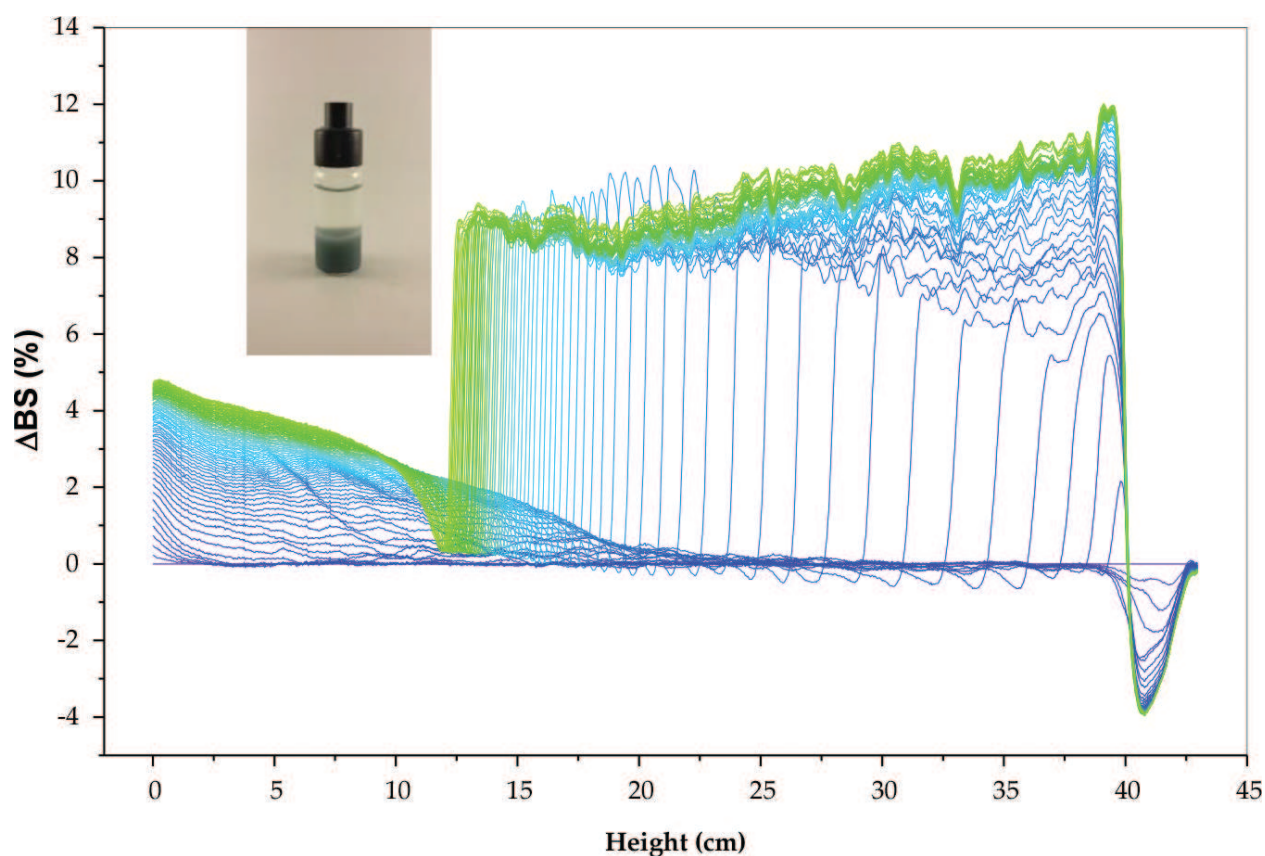


Figure 8. Backscattering profile of NP at optimum dose; data are reported as a function of time (0–120 min).

The superficial chemical analysis of the flocs formed in the coagulation-flocculation process using the best dose of Ch (2.5 mg), at pH = 5.0, **Figure 7a** shows the morphology of the chitosan without interacting with the heavy metals. The EDS spectrum of chitosan shows that it does not contain heavy metals in its natural form. In **Figure 7b**, the morphology of flocs formed with heavy metals and chitosan is shown.

The determination of heavy metals in the treated wastewater demonstrates the effectiveness of chitosan to perform the separation by 85% removal of heavy metals. In **Figure 8**, the back-scattering profile (% BS) vs. the height of the vial is shown, with the best dose of chitosan a clarification kinetics = 187.49%T/h and sediment kinetics = 93.96 mm/h.

4. Conclusions

One of the alternatives for the treatment of wastewater with a high content of heavy metals consists of the use of BPE extracted from waste from the food industry and gives it an added value. The zeta potential allows the coagulant-flocculant-chelating agents to be strategically applied for the separation of heavy metals, defining the best physicochemical conditions to make the coagulation-flocculation processes more efficient. At a dose of 2.5 mg chitosan, was reached 85% efficiency of separation of heavy metals and clarification kinetics = 187.49% T/h and sediment kinetics = 93.96 mm/h in wastewater treatment.

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Conflict of interest

The authors state that there is no conflict of interest.

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