

Bio-adsorbent chemically modified with TEMPO for enhanced Pb(II) adsorption from aqueous solutions

Bio-adsorbente modificado químicamente con TEMPO para mejorar la adsorción de Pb(II) en soluciones acuosas

Research article

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Abstract

Biomaterials are being investigated for their potential to remove Pb ions from water. *Luffa cylindrica*, in particular, is a biomaterial of interest due to its three-dimensional structure. Nevertheless, its low removal efficiency requires strategies to enhance the interaction between the contaminant and the biomaterial. This study explores methods to improve removal efficiency through organosolv pre-treatment and functionalization via TEMPO-mediated oxidation, resulting in three materials: R Luffa (raw), Org Luffa (organosolv pre-treated), and F Luffa (functionalized treated). Subsequently, both raw and treated Luffa were subjected to adsorption processes, tested in Pb solutions under varying conditions. The F Luffa showed a notable adsorption capacity of 3.13 mg/g and a removal efficiency of 92.79 %. All materials developed in this study were characterized using ATR-FTIR, pH_{pzc}, TGA and chemical composition analysis.

Keywords: *Luffa cylindrica*, TEMPO, adsorption, heavy metals.

Resumen

Se está investigando el potencial de los biomateriales para eliminar los iones de Pb del agua. La *Luffa cylindrica*, en particular, es un biomaterial de interés debido a su estructura tridimensional. Sin embargo, su baja eficiencia de remoción requiere estrategias para mejorar la interacción entre el contaminante y el biomaterial. Este estudio explora métodos para mejorar la eficiencia de eliminación mediante un pre-tratamiento organosolv y funcionalización por medio de oxidación por TEMPO, dando como resultado tres materiales; R Luffa (crudo), Org Luffa (pretratado con organosolv) y F Luffa (tratado funcionalizado). Posteriormente, tanto la Luffa cruda como las tratadas fueron sometidas a proceso de adsorción, ensayados en soluciones de Pb bajo condiciones variables. La F Luffa demostró una notable capacidad de adsorción de 3.13 mg/g y una eficiencia de remoción de 92.79 %. Todos los materiales desarrollados en este estudio se caracterizaron mediante FTIR- ATR, pH_{pzc}, ATG y análisis de composición química.

Palabras clave: *Luffa cylindrica*, TEMPO, adsorción, metales pesados.

1. Introduction

The proliferation of industrial activities has led to substantial environmental contamination, particularly through the release of emerging contaminants into aquatic systems, thereby posing risks to the environment and human health (Masindi & Muedi, 2018). Lead (Pb(II)), a heavy metal used in the manufacture of paints, pipes, ammunition, and batteries, is of significant concern due to its persistence, non-biodegradability, and its detrimental effects on physiological functions in living organisms. It is associated with cardiovascular diseases, nervous system disorders, and premature births (Kaur et al., 2017; malik & kaur sandhu, 2023). Consequently, to regulate Pb levels in water, the EPA and WHO have established maximum permissible limits for drinking water at 0.015 mg/L and 0.01 mg/L, respectively (Briffa et al., 2020). Despite these regulations, Pb tends to persist in water bodies, which has driven the development of various methods to control its presence including chemical precipitation, flocculation, photocatalysis, membrane separation, and adsorption (Chowdhury et al., 2022). Among these, adsorption is advantageous due to its low cost, ease of handling, and high efficiency. This process relies on adsorbent materials that capture water pollutants, such as activated carbon, zeolite, chitosan, and bio-based materials. Biomaterials are particularly advantageous due to their affordability and biodegradability, and their use as adsorbent materials is increasing (Bilal et al., 2022).

The *Luffa cylindrica* or natural sponge offers a significant advantage over other biomaterials due to its fibers, which are intertwined to form a three-dimensional structure (Khadir et al., 2021). These fibers consist of cellulose, hemicellulose, lignin, and non-structural compounds (pectin, waxes, composite inorganics, proteins) (Caicedo et al., 2018). However, the presence of non-structural compounds in these biomaterials can hinder their removal efficiency by affecting the interaction between the *Luffa* surface and contaminants. Therefore, integrating both physical and chemical treatments can enhance the removal adsorption performance of biomaterials, including ultraviolet radiation, acids, alkalis, and organosolv treatments, which remove extractives and inorganic components from biomaterials (Cai et al., 2017). Among pre-treatments, organosolv is notable for its operational simplicity and the use of environmentally benign solvents. Additionally, functionalization through modification of functional groups on the surface of biomaterials can improve pollutant adsorption, for example, through acetylation, esterification, silylation, carbamation, and oxidation by TEMPO methods (Rana et al., 2021). Oxidation by TEMPO is particularly efficient, as it does not require prior mechanical processing and results in minimal loss of crystallinity and depolymerization. Furthermore, this method achieves high yield and conversion of functional groups on the fiber surface.

This research aims to enhance the surface properties of *Luffa* through treatments and modifications. The study evaluates the adsorption capacity of both the raw

and treated biomaterials for Pb removal in water and employs characterization techniques for a comprehensive analysis of the biomaterials to identify and evaluate changes post-pre-treatment and functionalization, and how these modifications could improve the interaction between Pb ions and the biomaterial. A successful outcome would position this biomaterial as a viable alternative for contaminant removal in water.

2. Methodology

2.1 Materials

Deionized water and HPLC-grade water were used throughout the experiments. The following reagents were employed: absolute ethanol (96 wt%, PanReac), sodium bromide (99 %), sodium hypochlorite (5 wt%), (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO), potassium nitrate (Sigma-Aldrich), hydrochloric acid (37 % MerckMillipore), sulfuric acid (97 % MerckMillipore), nitric acid (69 % PanReac), sodium hydroxide granules (MerckMillipore), and lead (II) nitrate. Raw *Luffa cylindrica* fruits, previously peeled, de-seeded, and cut into segments of equal size, were purchased from a local market.

2.2 Organosolv pretreatment on *Luffa* surface

A cleaning and homogenization process was performed to extract non-structural compounds from Raw *Luffa* using an organosolv pre-treatment to improve the accessibility of the lignocellulosic matrix

for subsequent chemical modification. This procedure employed a solid-liquid extraction method via the Soxhlet technique using deionized water and ethanol (96 %wt.) as solvents. Each solvent was evaluated individually over extraction periods of 12 and 24 hours. For each run, 2 to 4 g of Raw *Luffa* were placed in the Soxhlet tube, ensuring that the biomaterial did not exceed the height of the siphon tube. Subsequently, 150 ± 5 mL of the first solvent (water) was added to the Soxhlet flask, and the extraction was carried out. Afterward, $150 \text{ mL} \pm 5 \text{ mL}$ of the second solvent (ethanol) was added to the same flask for the additional extraction stage under identical conditions. Upon completion, the treated samples were removed dried in a desiccator for 1 hour, and labelled as Organosolv-treated (Org) (Sluiter, Ruiz, et al., 2008).

2.3 Oxidation on *Luffa* surface by TEMPO

A negative surface chemical modification was performed by selective oxidation using NaBr/TEMPO/NaOCl (Tang et al., 2017). A quantity of 0.016 g of TEMPO and 0.1 g of NaBr were dissolved in 250 mL of deionized water, the experiment being conducted under continuous stirring. Thereafter, 1 g of Org *Luffa* was immersed in the above solution. Subsequently, the pH of the solution was adjusted to 10 – 11 with 0.1 M HCl, after which a solution of 5 wt.% NaOCl was added, corresponding to an equivalent amount of 1 – 8 moles per anhydroglucose unit (AGU) of *Luffa* fibers. During the oxidation process, the pH of the solution was carefully main-

tained at 10 – 11 using 0.5 M NaOH. The reaction was then halted with 10 mL of ethanol (96 wt.%) for 2 hours. Therefore, the Org Luffa was meticulously washed on multiple occasions with deionized water, subsequently dried at room temperature, and designated as Functionalized (F). This process was also repeated on Raw Luffa. The oxidation degree and content of carboxylates were measured by conductimetric titration using equations 1 and 2, respectively.

$$\% GD = \left(\frac{162.15 C (V_1 - V_2)}{w - (35.97 C (V_2 - V_1))} \right) 100 \quad (1)$$

$$COONa \left(\frac{mmol}{g} \right) = \left(\frac{\left(\frac{80}{30} \right) C (V_2 - V_1) 1000}{w} \right) \quad (2)$$

Wherein, C represents the concentration of NaOH (M), V_1 denotes the volume initial of NaOH (L) y V_2 denotes the volume of NaOH consumed (L), w is the dry mass of Luffa (g), 162.15 is the molecular weight of AGU and 35.97 is the difference between the molecular weight of AGU and the molecular weight of the sodium salt of the glucuronic acid group.

2.4 Characterization

The chemical composition of the Raw, Org, and F Luffa was determined based on the methodologies established by the National Renewable Energy Laboratory (NREL) (Sluiter, Hames, et al., 2008). The analysis included the quantification of moisture, cellulose, hemicellulose, lignin extractives and ash content.

Fourier Transform Infrared Spectroscopy (FTIR) coupled with an Attenuated Total

Reflectance (ATR) diamond crystal accessory was used to identify functional groups present in the Raw, Org, and F Luffa samples. Spectra were recorded using an IRPrestige-21 FTIR spectrometer (Shimadzu), averaging 32 scans per sample over a spectral range of 4000 to 700 cm^{-1} , with a resolution of 16 cm^{-1} .

The point of zero charge (pH_{pzc}) of Raw, Org, and F Luffa was determined using the solid addition method described by Lataye et al., (2006). A Series of 45 mL aliquots of 1% KNO_3 solution were prepared in separate Erlenmeyer flasks, and their initial pH values were adjusted between 2 and 10 using 0.1 M NaOH or 0.1 M HCl solution. Each solution was then brought to a final volume of 50 mL with 0.01 M KNO_3 solution. Subsequently, 0.1 g of Luffa fibers was added to each flask. The suspensions were stirred continuously for 24 hours at 30 °C, after which the final pH values were measured.

Acidic and basic surface functional groups were quantified using the Boehm titration method. Two sets of 0.25 g of each Luffa sample (Raw, Org, and F) were added to 50 mL of 0.1 M NaOH solution and 0.1 M HCl, respectively. The suspensions were stirred for five days at 30 °C. Afterward, a 10 mL aliquot was withdrawn from the flask and titrated with standard acidic or basic solutions to determine the concentration of surface functional groups.

The thermal stability was evaluated by thermogravimetric analysis using a Mettler Toledo TGA 1 STAR system. Samples of Raw, Org, and F Luffa were subjected

to a heating ramp from 30 °C to 900 °C at a rate of 10 °C/min under two different atmospheres: air and nitrogen, both with a flow rate of 50 cm³/min.

2.5 Adsorption studies – operating conditions

The removal of Pb by Raw, Org, and F Luffa was evaluated in a 500 mL glass-jacketed batch reactor equipped with a propeller stirrer driven by an IKA RW 20 motor. The experiments were initially conducted using a one-factor-at-a-time approach, assessing the effects of contact time (up to 24 h), agitation speed (60, 100 and 150 rpm), and adsorbent mass (0.2, 0.4 and 0.8 g), while maintaining constant conditions of pH 3 and a temperature of 20 °C. Subsequently, an experiment was performed to simultaneously evaluate the effect of the aqueous solution of initial Pb(II) concentration (5.5 and 10.5 mg/L) and pH (3 and 6) of Pb(II) solution, using citrate and phosphate buffer solutions to maintain stable pH conditions. For each run, 250 ± 5 mL of Pb(II) were used. The residual Pb(II) concentration in solution was

quantified by atomic absorption spectroscopy (AAS) using a Thermo Scientific Solaar S Series instrument equipped with a nebulizer and an air-acetylene burner. Measurements were performed at a wavelength of 217 nm. A calibration curve was previously established using a 1000 mg/L PbNO₃ standard solution prepared in HNO₃, ensuring accurate quantification of Pb(II) in all analyzed aliquots. Moreover, the adsorption capacity and percentage removal were determined through equations 3 and 4.

$$q_{e,t} = \frac{(C_i - C_{e,t})V}{w} \quad (3)$$

$$\text{Removal (\%)} = \frac{C_o - C}{C_o} \times 100 \quad (4)$$

3. Results and discussion

3.1 Organosolv pretreatment on the Luffa surface

Organosolv pretreatment was conducted using deionized water and ethanol (96 wt%) as solvents, with extraction durations of 12 and 24 hours being assessed as shown in Figure 1.

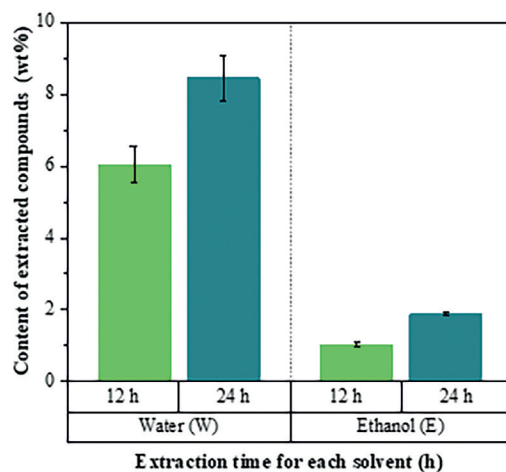


Figure 1. Content of extracted compounds by organosolv pre-treatment at 12 and 24 h using deionized water and ethanol as solvents.

The total yield of extracted compounds was 7.08 ± 0.59 wt% for 12-hour duration and 10.32 ± 0.68 wt% for 24-hour duration, suggesting that prolonged extraction time enhances the quantity of extracted compounds due to increased interaction between the biomaterial and the solvent (NagarajaGanesh & Muralikannan, 2016). Therefore, it is crucial to assess the extraction time to ensure the thorough cleaning of the fiber's surface. Furthermore, a fivefold increase in the amount of extracted compounds was observed with deionized water compared to ethanol for both extraction durations (12 and 24 hours), attributable to water's affinity for inorganic compounds (such as sodium salts, calcium, and aluminum) and non-structural com-

pounds (such as succinic acid and acetic acid). Conversely, the quantities of compounds extracted with ethanol for 12 and 24 hours were 1.04 ± 0.08 wt% and 1.87 ± 0.04 wt%, respectively, which are associated with polar compounds such as waxes, oils, proteins, and lipids (Nanda et al., 2013).

3.2 Oxidation on Luffa surface by TEMPO

The oxidation process utilizing the NaBr/TEMPO/NaOCl system in both Raw and Org Luffa is illustrated in Figure 2. The molar ratios considered were 1:1, 2:1, 4:1, and 8:1 for Org Luffa, while a molar ratio of 0 was used for Raw Luffa.

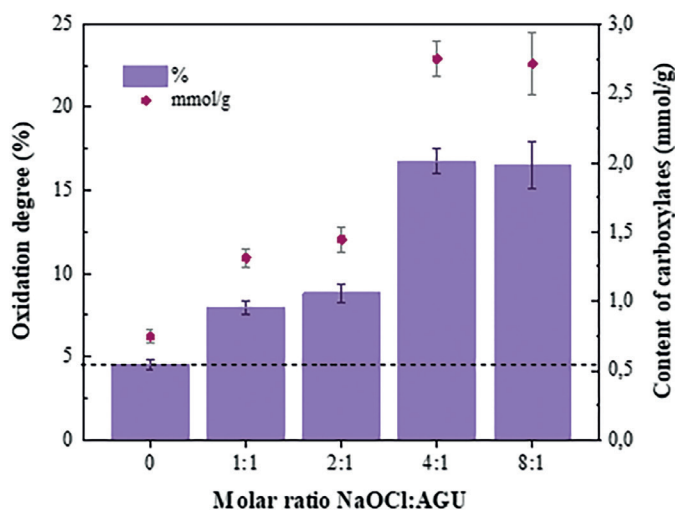


Figure 2. Oxidation degree (%) and content of carboxylates (mg/g) in molar ratio (0) on Raw and (1:1, 2:1, 4:1, 8:1) on Org Luffa by oxidation with TEMPO.

Notably, the 4:1 molar ratio exhibited a threefold increase in the oxidation degree compared to Raw Luffa (molar ratio: 0). The presence of carboxyl groups in Raw Luffa (molar ratio: 0) was confirmed, with a measured value of 0.75 ± 0.05

mmol/g. Consequently, the quantity of oxidized carboxyl groups from the baseline (dashed line in Figure 2) was determined to be 0.57 ± 0.07 mmol/g, 0.70 ± 0.09 mmol/g, 2.00 ± 0.12 mmol/g, and 1.97 ± 0.23 mmol/g, for molar ratios of

1:1, 2:1, 4:1, and 8:1, respectively. Moreover, molar ratios exceeding 4:1 between NaOCl and AGU demonstrated stabilization in both the oxidation degree and content of carboxylate. This stabilization can be attributed to the limited availability of conversion sites, primarily located on the fiber surface, which restricts the penetration of reactants into the interior due to inter- and intramolecular hydrogen bonds. This indicates a limitation in available sites for the oxidation of C6 hydroxyl to carboxylate groups (Tang et al., 2017). Additionally, it has been shown

that the amount of NaOCl influences surface conversion, as an increase in the molar ratio, ie., the quantity of oxidants during the reaction, results in an elevated oxidation degree, as noted by Hao et al. (2017); Khadraoui et al. (2022).

3.3 Characterization

The chemical composition of Raw, Org, and F Luffa is summarized in Table 1, as quantified using the NREL methodology.

Table 1. Chemical composition (wt%) of Raw, Org, and F Luffa.

Compound	Raw	Org	F
Content (wt%)			
Moisture	6.08 ± 0.54	5.63 ± 0.46	3.86 ± 0.25
Cellulose	50.39 ± 0.97	56.03 ± 0.72	42.56 ± 0.78
Hemicellulose	8.06 ± 0.02	8.72 ± 0.83	8.13 ± 0.14
Lignin	21.14 ± 0.64	23.64 ± 0.19	21.97 ± 0.87
Extractives	10.32 ± 0.68	3.29 ± 0.30	18.49 ± 0.33
Ashes	2.52 ± 0.16	0.27 ± 0.14	5.16 ± 0.24

This composition reflects the typical structure of lignocellulosic materials, which are characterized by a high content of hydroxyl groups that participate in intra- and intermolecular hydrogen bonds. Consequently, the formation of these bonds and their interaction with water molecules determine the moisture content (Mohanty et al., 2001). The moisture in Org Luffa decreased by approximately 0.45 % compared to Raw Luffa. Conversely, F Luffa exhibited a re-

duction of about 2.22 % relative to Org Luffa, indicating the oxidation by TEMPO results in a material with reduced hydrophilic characteristics. This is attributed to the replacement of hydroxyl groups, thereby diminishing its hygroscopic nature (Hasan et al., 2022).

In the context of cellulose analysis, the Org Luffa demonstrated a 5.6 % increase compared to Raw Luffa, indicating that the pre-treatment effectively exposed

the cellulose without altering its structure during a 24-hour extraction process using deionized water and ethanol. On the other hand, F Luffa exhibited a reduction of approximately 13.5 % relative to the Org Luffa, attributed to a chemical modification wherein some -OH groups were oxidized to -COO⁻ groups (Tang et al., 2017). The reagents employed in this reaction can induce depolymerization and solubilization, leading to a decrease in molecular weight by breaking some linear crystalline chains, thereby resulting in a lower quantification of cellulose (Duceac et al., 2022).

Regarding hemicellulose content, the Org Luffa showed an increase of approximately 0.6 % compared to Raw Luffa. In contrast, the F Luffa exhibited a decrease of about 0.7 % relative to the Org Luffa. Similarly, lignin content increased by around 2.5 % in the Org Luffa while the F Luffa experienced a reduction of approximately 1.7 % compared to the Org Luffa. These results indicate that pre-treatment and functionalization processes induced only minor alterations in the overall composition of the Luffa. This phenomenon can be explained by the removal of extractives by solvents, which in turn enhances the accessibility of the underlying macromolecules (Tang et al., 2017). Furthermore, the TEMPO-mediated oxidation process facilitates the removal of non-structural compounds from the macromolecules, resulting in minimal changes to the quantified percentages of the major components on the surface of the material (Pierre et al., 2017).

Finally, the content of extractives and ashes obtained post-pretreatment ex-

hibited a decrease of 7.03 % and 2.25 %, respectively, compared to Raw Luffa, due to the elimination of non-structural compounds such as waxes, proteins, lipids, and inorganic material, which are components of the biomaterial (Gandolfi et al., 2013). For the F Luffa, there was an increase of 15.2 % and 4.89 % for extractives and ashes, respectively, compared to the Org Luffa, possibly related to the presence of Na⁺ introduced by the NaOH used during the TEMPO oxidation reaction to neutralize the carboxylate groups converted in the biomaterial (Pierre et al., 2017).

Figure 3 shows the ATR-FTIR results for the Raw, Org, and F Luffa samples. The Org Luffa illustrated a modest decline in intensity at the 3356 cm⁻¹ and the 894 cm⁻¹ bands associated with the presence -OH groups and β-(1,4) glycosidic bonds. This observation is indicative of disruptions in the cellulose structure, a phenomenon that is accompanied by the presence of waxes and oils extracted from Luffa. By contrast, the spectrum of F Luffa displayed an increment in the 3356 cm⁻¹ band concerning the -OH stretching of the Org Luffa, thereby confirming that not all the hydroxyl groups of the AGU underwent oxidation, as indicated in the selective reaction at C6 by TEMPO. Furthermore, an increase in the intensity and displacement of the bands 1735 cm⁻¹ to 1728 cm⁻¹ and 1635 cm⁻¹ to 1629 cm⁻¹ (wavelength approach from 1900 cm⁻¹ to 1500 cm⁻¹ in Figure 3), indicate the increment of carboxylate groups (-COO⁻) in the cellulose stabilized by the sodium salt (-COONa), confirmed by the quantification in the conductimetric titration (Xiao et al., 2022).

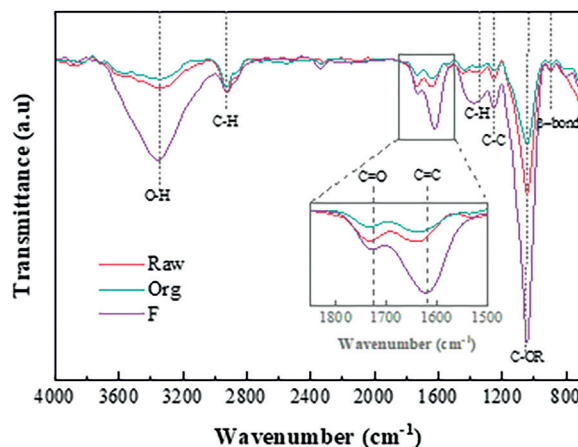


Figure 3. ATR-FTIR of Raw, Org, and F Luffa from 4000 to 700 cm^{-1} (zoom from 2400 to 1300 cm^{-1}).

The point of zero charge (pH_{pzc}) of the Raw, Org, and F Luffa were determined using the solid addition method. The pH_{pzc} of the Raw Luffa was 6.0 ± 0.1 , with a slight increase to 6.3 ± 0.1 for the Org Luffa, indicating a minor change in pH_{pzc} following the extraction process, while maintaining a slightly acidic surface. In contrast, the F Luffa revealed a pH_{pzc} 5.5 ± 0.2 , likely due to an increase

in acidic functional groups (carboxylic) post-functionalization, as confirmed by the FTIR technique (Tang et al., 2017).

The acidic and basic sites of the Raw, Org, and F Luffa (Table 2) were determined using the Boehm method, which provides complementary information regarding surface behavior.

Table 2. Acidic and basic sites (meq/g) of the Raw, Org and F Luffa.

Material	Acidic sites (meq/g)	Basic sites (meq/g)
Raw	1.001 ± 0.015	0.950 ± 0.035
Org	1.072 ± 0.026	1.072 ± 0.003
F	1.363 ± 0.061	1.021 ± 0.021

As shown in Table 2, Raw Luffa shows a slightly acidic surface character, corroborating the value obtained for the point zero charge pH ($\text{pH}_{\text{pzc}} = 6$) mentioned earlier. Similarly, the Org Luffa has nearly equal values of both acidic (carboxylic, phenolic and lactones) (Goertzen et al., 2010) and basic (hydroxyl and amino)

functional groups, indicating the exposure of -OH groups in cellulose following the extraction process, which is related to the increase in surface pH ($\text{pH}_{\text{pzc}} = 6.3 \pm 0.1$). In contrast, the F Luffa indicates an increase in the number of acidic sites due to the presence of carboxylate groups added through TEMPO-media-

ted selective oxidation at C6 of AGU in cellulose, resulting in a decrease in surface pH ($\text{pH}_{\text{pzc}} = 5.5 \pm 0.2$) (Saha & Reza, 2021).

The thermogravimetric analysis was conducted on Raw, Org, and F Luffa under both oxidizing and inert atmospheres. Figure 4a illustrates the thermogram of the Raw, Org and F Luffa in an oxidizing atmosphere. In both Raw and Org Luffa, the initial mass loss occurred at 105 °C, associated with the evaporation of water molecules (Heidari et al., 2022). Subsequently, the Raw Luffa exhibited a mass loss of approximately 60 wt% between 255 and 355 °C, whereas the Org Luffa showed a mass loss of about 69 wt% between 236 to 384 °C with an inflection point at 334 °C, corresponding to the degradation of hemicellulose, cellulose degradation, low molecular weight lignin compounds, and volatile

materials (Khadir et al., 2021). This variation in thermal stability is due to the low content of extractives, indicating the degradation of these non-structural compounds at lower temperatures compared to the macromolecules, thereby confirming the reduced number of extractives in the Org Luffa (3.29 ± 0.30 wt%) as also reported by Alvarado Flores & Rutiaga Quiñones (2018). In addition, the decomposition of residual lignin and other compounds was observed up to 500 °C in both Raw and Org Luffa. However, the residual mass was 2.79 wt% and 0.29 wt% in Raw and Org Luffa, respectively, corroborating the ash content identified by the NREL methodology. The differences between the two materials are attributed to the number of inorganic compounds, which were removed following the organosolv pretreatment.

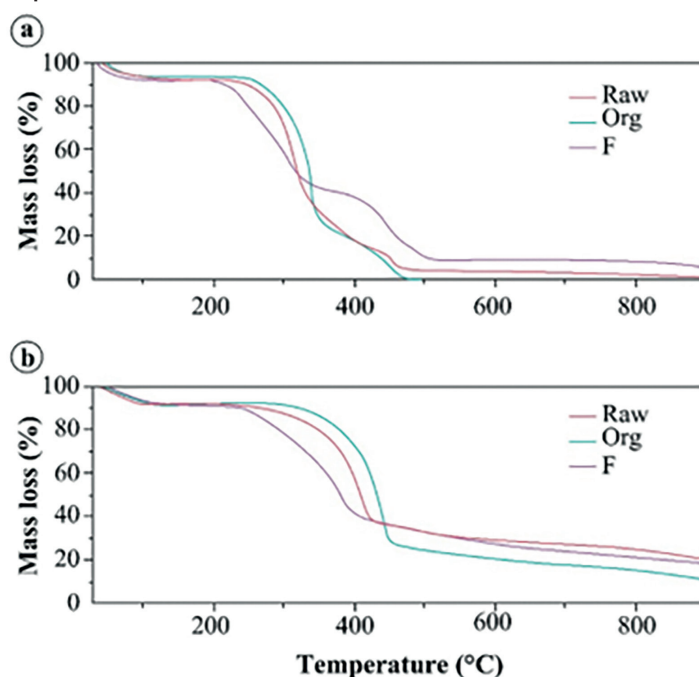


Figure 4. The thermograms of the Raw, Org, and F Luffa in two atmospheres: a) oxidant, and b) inert.

In reference to the F Luffa, Figure 4a illustrates a mass loss of approximately 52 % between 207 °C and 384 °C, attributable to the degradation of hemicellulose and cellulose, as well as the presence of low molecular weight and volatile material (Khadir et al., 2021). The initial thermal reduction can be ascribed to the formation of low molecular weight, resulting from the depolymerization of macromolecules due to the application of strong reagents in TEMPO-mediated oxidation (Alvarado-Flores & Rutiaga-Quíñones, 2018; Sbiai et al., 2011). This observation aligns with the quantification of cellulose (42.56 ± 0.78 wt%) and hemicellulose (8.13 ± 0.14 wt%) obtained via the NREL methodology. Furthermore, a mass loss of 29 % at 502 °C is noted, which is attributed to lignin and residual cellulose compounds. Nonetheless, in this instance, the residual material amounted to 6.74 %, likely due to the presence of Na^+ from NaOH used in the neutralization of the carboxylate oxidized during functionalization. This is corroborated by a similar value (5.16 ± 0.24 wt%) in the ash content determined through NREL methodology. Consequently, the selective oxidation by TEMPO slightly reduces thermal stability, owing to the alteration of functional groups in certain AGU of cellulose, as reported by Cao et al. (2012).

Conversely, Figure 4b illustrates the thermogram of Raw, Org, and F Luffa in an inert atmosphere, which displays a similar behavior to that observed in an oxidizing atmosphere. However, the initial degradation points differ for each material, with Raw at 270 °C, Org at

310 °C, and F at 250 °C. The mass loss is approximately 70 % for Raw and Org and 65 % for F Luffa, corroborating the previous description regarding the removal of extractives and the modification of AGU in cellulose. Moreover, the residual material for Raw, Org and F Luffa was 18, 11 % and 19 %, respectively. This outcome is attributed to the extraction of non-structural compounds during the organosolv process and the presence of Na^+ following TEMPO oxidation in the functionalization (Alvarado-Flores & Rutiaga-Quíñones, 2018; Sbiai et al., 2011).

3.4 Adsorption studies

Contact time

The initial variable assessed was the contact time under the following experimental conditions: initial concentration of Pb(II): 5.5 mg/L, adsorbent mass: 0.4 g, agitation speed: 100 rpm, pH: 3, temperature ~ 25 °C. Figure 5a depicts an adsorption capacity of 1.50 ± 0.06 mg/g at 30 min, indicative of rapid adsorption due to the availability of sites on the Luffa. Nevertheless, an adsorption capacity of 2.06 ± 0.01 mg/g and removal percentage of 62.40 ± 0.17 % were achieved at equilibrium after 24 hours (Figure 5b), demonstrating a reduction in rapid adsorption in comparison to the initial minutes of contact, attributed to saturation of available sites on the Raw Luffa surface. Consequently, a contact time of 24 hours was established for subsequent experiments. Similarly, the effect of contact time was evaluated in the Org and F Luffa, with adsorption

capacities of 1.99 ± 0.01 mg/g and 3.14 ± 0.08 mg/g, respectively, and removal percentages of 62.63 ± 0.80 % and 92.80 ± 0.95 %, respectively, as observed in Figure 5b. It is inferred that the adsorption capacity of Org Luffa was comparable to that of Raw Luffa, as the removal of non-structural compounds and fiber cleaning did not alter the surface. Meanwhile, F Luffa achieved a higher adsorption capacity compared to Raw and Org Luffa

under the previously established conditions, because of the oxidation of -OH groups to $-\text{COONa}^+$ groups, enhancing the acidic character of the surface through the presence of carboxylates ($-\text{COO}^-$). This is attributed to electrostatic interactions between the functional group (anionic) and the heavy metal (cationic), thereby improving the material's efficacy in contaminant removal (Adewuyi & Pereira, 2017).

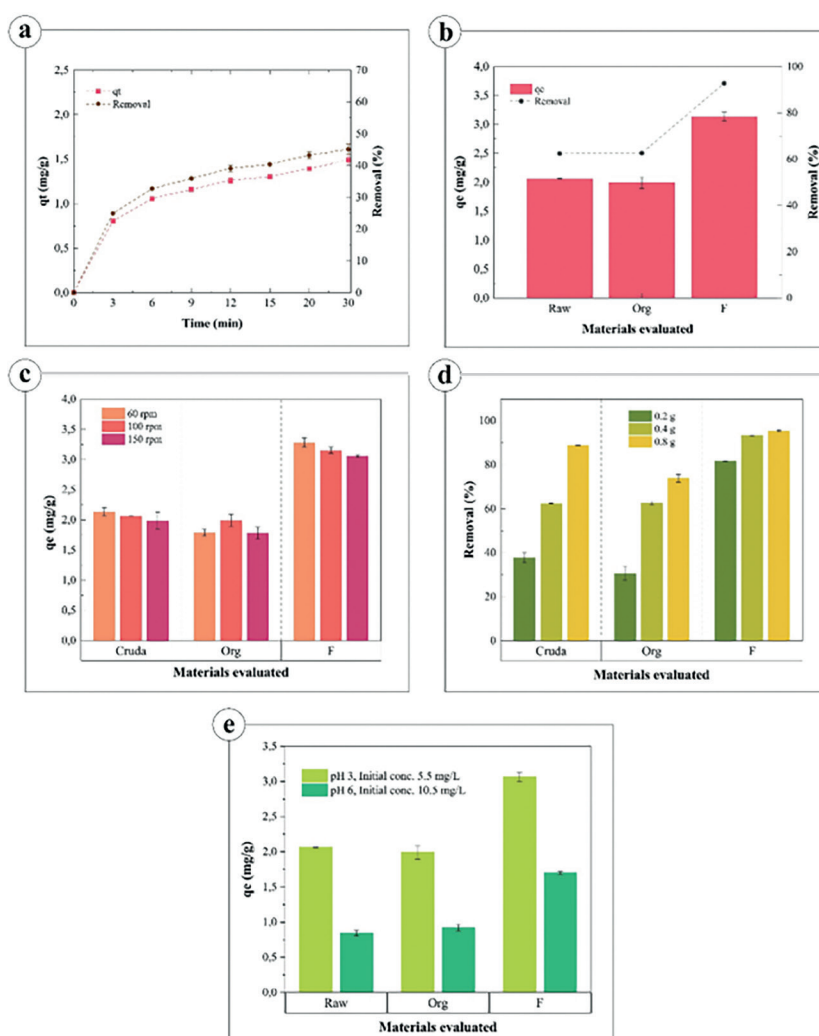


Figure 5. Operating conditions evaluating adsorption capacity (mg/g) and removal percentage (%) on Raw, Org, and F Luffa: a) contact time up to 30 min (only on Raw Luffa) b) contact time, (24 h) c) agitation speed (60, 100 and, 150 rpm), d) adsorbent mass (0.2, 0.4 and, 0.8 g), and e) pH (3, and 6) and initial concentration solution Pb (5.5 and, 10.5 mg/L).

Agitation speed

The subsequent variable assessed was the agitation speed, evaluated at three levels: 60, 100, and 150 rpm. Figure 5c illustrates the equilibrium adsorption capacity (q_e) of three materials (Raw, Org, and F Luffa) under the following conditions: initial concentration Pb(II) of 5.5 mg/L, adsorbent mass of 0.4 g, pH of 3, temperature $\sim 25^\circ\text{C}$, and a contact time of 24 hours. It is demonstrated that the highest adsorption capacity was observed for the F Luffa, associated with the increased presence of carboxylate groups on the Luffa surface following chemical treatment. In contrast, the data for agitation speeds of 60, 100, and 150 rpm give values ranging from approximately 0.1 to 0.3 mg/g, indicating that this variable does not significantly impact the adsorption process. However, this behavior can be linked to the diffusion of Pb(II) ions from the solution to the material's surface, as the mass transfer between the outer boundary layer of the material enhanced, facilitating the movement of the ions towards the material's pores and thus occupying the available sites of the biomaterial. Consequently, it can be inferred that as the agitation speed increases, the thickness of the boundary layer surrounding the biomaterial decreases, improving the diffusion of the Pb ions towards the material's surface. In contrast, excessively high agitation speeds may result in the detachment of the Pb ions interacting with the material's active sites of the material (Sasan Narkesabad et al., 2023). Therefore, an agitation speed of 100 rpm showed optimal adsorption behaviour

of Pb on the material's surface and was selected for replication in subsequent experiments.

Adsorbent mass

The adsorbent mass was evaluated at three levels (0.2, 0.4, and 0.8 g) under the following conditions: initial concentration Pb(II) of 5.5 mg/L, agitation speed of 100 rpm, pH of 3, temperature $\sim 25^\circ\text{C}$ and a contact time of 24 hours. Figure 5d depicts the removal percentage as a function of the adsorbent mass across the three materials (Raw, Org and F Luffa). Increasing the adsorbent mass increases the removal percentage. This enhancement is particularly pronounced for Raw Luffa, where the removal efficiency improves from 38 % to 88 % with the use of 0.2 g and 0.8 g of bio-material. A similar trend is observed for the Org Luffa, with removal efficiency increasing from 30 % to 73 %. Furthermore, the F Luffa exhibits the highest removal efficiency, ranging from 80 % to 95 %, depending on the mass utilized. This can be associated with a more homogeneous surface and a higher concentration of -COOH groups.

pH and the aqueous solution of initial Pb(II) concentration

Figure 5e displays the adsorption capacity of the Raw, Org, and F Luffa, with evaluations conducted at two pH levels and initial concentrations of Pb(II) solution: pH 3 with an initial concentration of 5.5 mg/L and pH 6 with an initial con-

centration of 10.5 mg/L. The selected pH range for the Pb(II) solution is informed by prior studies that analyzed Pb(II) in water using various adsorbent materials (Khadir et al., 2020; Mashkoo & Nasar, 2019; Sasan Narkesabad et al., 2023; Shahidi et al., 2015). In addition, the Pourbaix diagram of Pb was utilized to identify potential species as pH varies. It is noted that at pH levels exceeding 8, the Pb predominantly exists in the form of $\text{Pb}(\text{OH})_2$, which is why such conditions were excluded from this study. The results indicate that all three materials exhibit enhanced adsorption capacity under the conditions of pH 3 and an initial concentration of 5.5 mg/L, compared to other conditions. This is attributed to the influence of solution pH on the charge of the adsorbent material. Specifically, when the pH is close to the point of zero charge (pH_{pzc} , approximately 6), electrostatic interactions are limited due to surface neutrality relative to the Pb solution. Consequently, at pH 3, the interaction between the material and the Pb in the solution is intensified. Additionally, it is demonstrated that the F Luffa achieves an adsorption capacity of the order of 3 mg/g, emphasizing the importance of oxidation by TEMPO on the Luffa fibers.

4. Conclusions

This study demonstrated the potential of chemically modified *Luffa cylindrica* as an efficient bio-adsorbent for the removal of Pb(II) from aqueous solutions. The research focused on enhancing the adsorption capacity of Luffa through organosolv pretreatment and TEMPO-me-

diated oxidation, which significantly enhanced the material's surface properties. Organosolv pretreatment effectively removed non-structural compounds such as waxes, lipids, and proteins, leading to increased cellulose exposure without compromising the structural integrity of the material. The subsequent oxidation with TEMPO resulted in a fivefold increase in carboxylate groups on the Luffa surface, enhancing its adsorption efficiency due to improved electrostatic interactions with Pb(II) ions. Characterization techniques confirmed the chemical modifications and their effects on adsorption performance. ATR-FTIR analysis revealed the successful introduction of carboxyl functional groups, while pH_{pzc} and Boehm titration results confirmed an increase in the acidic character of the modified biomaterial. Thermogravimetric analysis indicated a slight reduction in thermal stability due to oxidation, yet the material remained structurally viable for adsorption applications. The modified Luffa exhibited a significantly higher adsorption capacity compared to the raw and pretreated materials, with a removal efficiency exceeding 90%. Overall, the chemical modification of *Luffa cylindrica* via TEMPO oxidation proved to be an effective strategy for enhancing heavy metal adsorption.

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Authors' contribution

Cindy Katherine Ardila-González: data curation, formal analysis, investigation,

resources, visualization, writing—original draft.

Karen Giovanna Bastidas-Gómez: conceptualization, validation, methodology, supervision, writing—review editing.

Hugo Ricardo Zea-Ramírez: conceptualization, validation, methodology, project administration, resources, supervision, writing—review editing.

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