

Quaternary adsorption of cadmium(II)/chromium(III)/copper(II)/lead(II) ions from simulated and real wastewater by residual fennel seeds (*Foeniculum vulgare*) as a removal tool

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ABSTRACT

Proper management of wastewater contaminated with heavy metals through biosorption supports climate change mitigation, green growth, and the circular bioeconomy by generating innovative, biodegradable biosorbents. In this study, lignocellulosic materials derived from residual fennel seeds (*Foeniculum vulgare*), in both virgin (FS) and modified (MFS) forms, were employed for the simultaneous adsorption of Cd, Cr, Cu, and Pb ions from simulated and real wastewaters, for the first time. Physicochemical and instrumental characterisations confirmed the presence of diverse functional groups, high cation exchange capacity, and favourable morphology essential for efficient adsorption. The influence of pH, biosorbent mass, initial concentration, and contact time on the adsorption kinetics and capacity was evaluated. Under optimal conditions (solution pH: 5 (FS)/4 (MFS), initial individual analyte concentration: 50 mg/L, contact time: 20 min with 300 mg of biosorbent), maximum adsorption capacities reached 5.1/7.5 (Cr), 6.1/10.2 (Cu), 3.6/6.7 (Cd), and 7.9/14.7 mg/g (Pb) for FS/MFS, with corresponding removal efficiencies of 50–87.5% (FS) and 50–97.5% (MFS). The metal binding affinity followed the order: Cd < Cr < Cu < Pb. Kinetic analysis revealed a strong correlation with the pseudo-second-order and intraparticle diffusion models (average fit of the removal efficiency values: 99.60% (FS) and 99.85% (MFS), with determination coefficients (R^2) close to 1). Overall, the developed biosorption process is cost-effective, environmentally benign, and technically applicable, fully aligning with the principles of green chemistry.

Keywords: fennel seeds, wastewater, heavy metals, environmental sustainability and protection.

INTRODUCTION

Heavy metal toxicity, along with harmful health impacts even at trace-level concentrations, classifies them as a highly severe global environmental problem (Mitra et al., 2022; Balali-Mood et al., 2021). This has triggered many studies aimed at solving the problems of

quantification, distribution, mobility, and removal of these pollutants from wastewater. The most efficient heavy metal removal treatment for the aquatic phase should ensure the high-percentage removal of significant amounts of these contaminants from wastewater in a short period, thereby avoiding the generation of secondary pollutants or waste (Paluch et al., 2023). Most conventional

methods used for this purpose (i.e., ion exchange, filtration, flotation, membrane separation, and electrochemical methods) are highly effective for heavy metal removal; however, many of them are associated with limitations such as high capital and operational costs, membrane fouling, the generation of secondary sludge requiring further treatment, and challenges related to long-term environmental and economic sustainability (Barakat, 2011). However, in the meaning of the aforementioned, adsorption has been recognised as the most appropriate and effective method (Jiang et al., 2019). The effectiveness of adsorption in removing inorganic contaminants from aqueous solutions has been demonstrated for a variety of adsorbent materials, with reported performance depending strongly on the physico-chemical properties of the adsorbent and the operating conditions (Fiket et al., 2018). Previous studies have confirmed efficient pollutant uptake by both inorganic materials, such as geopolymers, and carbonaceous adsorbents, highlighting the potential of adsorption as a simple, efficient, and cost-effective approach for wastewater treatment (Fiket et al., 2018; Radjenovic and Medunic, 2015). According to recent studies, after coal, oil, and natural gas, biomass is the fourth energy source worldwide (Kalak, 2023). The use of non-edible agricultural parts that have no nutritional value as green, toxic-free, and biodegradable bioadsorbents makes this process even more suitable and a favoured alternative to traditional treatment methods.

In this regard, natural adsorbents, particularly agricultural wastes, are utilised to mitigate or resolve heavy metal contamination issues (Mahmudiono et al., 2022). *Foeniculum vulgare* production is mainly carried out in India, Egypt, China, Romania, Russia, Germany, France, Italy, Japan, Argentina, the USA, Indonesia, and Pakistan, Morocco, Spain, and Southern Europe (Ali et al., 2024). Characteristic structure and high availability of fennel seeds in combination with other factors make them an attractive candidate for biosorbent production (Taqui et al., 2023). Despite numerous research papers on how to produce plant residue-based adsorbents being annually published, the fennel seeds have not gained quite attention. The literature review has shown that fennel seeds have been insufficiently investigated through only a few biosorption reported studies (Rao et al., 2010; Sulthana et al., 2013; Mabungela et al., 2022; Abbas et al., 2023).

This novelty of the research lies in the preparation of novel fennel seeds (*Foeniculum vulgare*) residues biomaterial as a virgin (FS) and modified (MFS) form through the chemical activation via the sodium hydroxide treatment method. In addition, this is the first study focusing on the simultaneous bioremediation of wastewater with respect to four heavy metals by fennel seeds. Finally, the justification for its use as a biosorbent lies in the possibility of valorising spent fennel seed biomass remaining after the extraction of fatty acids, essential oils, aromatic compounds, and other valuable constituents. Such an approach promotes the beneficial reuse of agricultural by-products in accordance with circular economy principles by converting an otherwise discarded biomass into a low-cost biosorbent for wastewater treatment. Nevertheless, the environmental sustainability of this approach also depends on the appropriate post-treatment management of the metal-loaded biosorbent, including regeneration, metal recovery, or safe disposal. Both obtained products (FS/MFS) were characterised by the determination of physical and chemical composition as well as morphology and structure analysis. Sorption performance and capacities of the obtained biomass products for the simultaneous removal of inorganic contaminants (Cd^{2+} , Cr^{3+} , Cu^{2+} , and Pb^{2+}) from the liquid phase were determined. This quaternary heavy metal adsorption using the batch method (stationary conditions) was additionally optimised for key process factors such as pH, sorbent mass, contact time, and initial metal concentration studies. The data gained were further used to estimate the kinetics of the biosorption process on *Foeniculum vulgare*.

MATERIALS AND METHODS

Chemicals and instruments

A multi-element stock standard solution (containing 5 g/L of each heavy metal ion) was prepared by weighing (Metler Tolleo balance, ± 0.1 mg) and dissolving an accurate mass of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, and $\text{Pb}(\text{NO}_3)_2$ p.a. salts supplied by Merck. A mixed working solution was daily prepared by diluting the multi-element stock standard solution while the pH of the solution was adjusted with 1 mol/L HCl (p.a. 36%, Semikem) or NaOH (p.a.,

Semikem). Sodium hydroxide, 65% nitric acid (Carlo Erba) and 96% sulphuric acid (Merck) were utilised in various modification procedures of fennel seeds. Fat extraction from seeds was carried out using n-Hexane (Merck).

Experimental part of this study also required the usage of: shaker (BOECO PSU-10i), magnetic stirrer (MR Hei-Standard, Heidolph), dryer (SE-10 Bodalec&Havoic); rotavapor (Buchi); spectrophotometer (Cary 50 Varian), centrifuge (Mikro 22R Hettich); muffle furnace (VIMS elektrik), and a pH meter (CG 841 Schott GmbH).

Preparation of biosorbent

Fennel seeds purchased from a local healthy food pharmacy were primarily treated with n-hexane (4 hours) in order to carry out Soxhlet fat extraction (Hewavitharana et al., 2020). The schematic preparation protocol of biosorbents is given in Figure 1.

The fat-free residue was washed (distilled water), dried (105 °C), milled to a fine powder (household blender), passed through a sieve mesh (0.25 mm) and divided into two parts: one part labelled as virgin fennel seeds (FS) and other part was further modified using an excess of 1 mol/L NaOH (2 hrs stirring on a magnetic stirrer at a speed of 250 rpm) at room temperature according to the procedure given by Šehović et al. (2022), filtered through a Büchner funnel and washed to a neutral reaction. The resulting chemically modified fennel seeds (MFS) were finally dried for 8 hours at 105 °C, again milled and sieved (ϕ 0.25 mm).

Measurements

The physicochemical characterisation of powdered fennel seeds in this way included the implementation of (i) gravimetric method (moisture (at 105 °C) and ash content (at 700 °C) (Nocoń et al., 2019); (ii) Kürschner-Hoffer method (cellulose content (Ghavidel et al., 2020)); (iii) Klason method (lignin content (Lu et al., 2021)); (iv) Biuret reaction (total protein (Mæhre et al., 2018); (v) Folin-Ciocalteu method (total flavonoids and total phenols (Martins et al., 2021)). Surface characterisation of prepared biomaterials was performed by (i) Boehm titration (acidic and alkaline functional groups (Charmas et al., 2023)); (ii) cation exchange capacity (Sulejmanovic et al., 2023a); (iii) pH at the point zero charges (pH_{pzc}) value (Tang et al., 2019); (iv) pH of the suspension (pH_{sus}) (Sulejmanovic et al., 2023a)).

A Varian SpectrAA model 240 FS flame atomic absorption spectrometer (FAAS) was used for all metal ion content measurements using the calibration curve method prepared from 1000 mg/L stock solutions (CertiPUR) of each analyte. Virgin (FS) and modified fennel seeds (MFS) before and after Cd/Cr/Cu/Pb adsorption were multiple characterised by a PerkinElmer BX FT-IR spectrometer - infrared spectroscopy with Fourier transformation (identification of the functional groups), scanning electron microscope instrument coupled with electron dispersive spectroscopy (JEOEL JSM-6610 LV SEM model) for surface morphology analysis and to record qualitative and semi-quantitative information in relation to various elements attendance on the surface of the biosorbent. FTIR

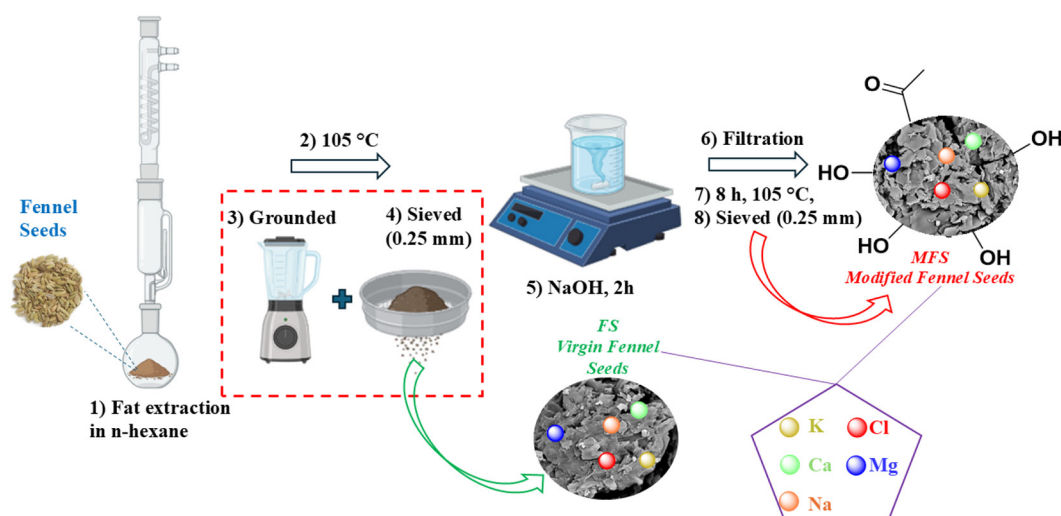


Figure 1. Schematic preparation protocol of fennel seeds: virgin (FS) and modified (MFS)

spectral data were collected (4000 to 400 cm^{-1}) using the KBr pellet technique in transmission mode and spectral resolution of 4 cm^{-1} . SEM-EDS were employed at 25 keV of the working acceleration voltage with records at magnification $\times 1000$.

Batch biosorption methodology

The general quaternary batch adsorption procedure involved six steps:

1. Preparing 50 mL of multi-metal solution (total concentration of 40, 80, 120, 160, or 200 mg/L, wherein individual concentration of each Cd/Cr/Cu/Pb ion was 10, 20, 30, 40, or 50 mg/L, respectively).
2. Adjusting pH (to 3, 4, or 5).
3. Suspending 50–600 mg of prepared biosorbent into simulated wastewater (SWW).
4. Mixing on orbital shaker at 200 rpm (per 5, 10, 20, 30, 40, 50, 60, 90 or 120 min).
5. Filtering the suspension and determining the concentration of non-adsorbed ions in the filtrate by flame atomic absorption technique (FAAS).
6. Calculating:
 - a) the removal efficiency, R_{eff} (%), of each metal ion according to Equation 1:

$$R_{\text{eff}} (\%) = \frac{(c_i - c_f)}{c_i} 100 \quad (1)$$

where: R_{eff} – removal efficiency (%); c_i and c_f – initial and final concentration of metal ions in the filtrate (mg/L);

- b) the capacity of the sorbent (amount of metal ion adsorbed per unit mass), q (mg/g), according to Equation 2:

$$q = \frac{(c_i - c_f) V}{m} \quad (2)$$

where: q – sorption capacity (mg/g); V – volume of metal ions solution (L); m – biosorbent mass (g).

Each of the tested parameters (steps 1–4) was changed successively, while other parameters were fixed at defined optimal values. Control probes (without biosorbent addition) were also analysed to ensure that analyte concentration does not decrease due to precipitation or similar irrelevant processes other than adsorption. All experiments were conducted in triplicate, and the results are given as mean values $\pm$ SD.

The individual influence of Co(II), Mn(II), Ni(II), and Zn(II) as co-existing ions (50 mg/L of each) on the simultaneous bioremoval of Cd/Cr/Cu/Pb analytes was carried out by a general procedure with previously determined optimal biosorption conditions.

Finally, a developed biosorption procedure has been applied to a real wastewater (RWW) sample from an electroplating plant. The wastewater generated from electroplating industries contains large quantities of various cationic species, detergents, dyes, complexing reagents, biological pollutants, etc. (Rahman et al., 2021). This highly complex sample matrix could seriously affect the sorption efficiency of target metal ions. The RWW was filtered, Fe ions were precipitated by $\text{NH}_4\text{OH}(\text{aq})$, and then filtered again. After biosorption, FAAS analysis of 8 ions content (Cd, Cr, Cu, Pb, Co, Mn, Ni, and Zn - analytes and interferents), before and after biosorption treatment, was carried out.

RESULTS AND DISCUSSIONS

Composition analysis of Fennel seeds

A summary, along with a comparative overview of the chemical analysis results for FS and MFS biosorbents, is given in Table 1.

The significant increase in the cellulose content of MFS was similar to the case of apricot shells reported by Šoštarić et al. (2018) due to a decrease in the content of many extractable substances. This is highly favourable for biosorption processes since this constituent contributes to the chemical and mechanical resistance of the material and also is rich in hydroxyl and carbonyl functional groups that attract metal ions (Basu et al., 2019). Although alkaline hydrolysis decreased the content of the lignin via saponification of intermolecular ester bonds, the remaining 37.6% is still a relatively high content. Similar lignin content (36%) was obtained in defatted grape seeds (Adamovicet al., 2021). This is highly important since the thermal stability and hydrophobicity of a biosorbent, which are important for the usage of the biomaterial in more than one biosorption cycle, are ensured by lignin (Dias et al., 2022). Similar to cellulose, this constituent is also rich in hydroxyl, methoxy, carbonyl, and carboxylic functional groups. The total protein content of 11.8% is relatively high for lignocellulosic

Table 1. Chemical composition of native and modified biomaterial

Parameter	Moisture	Mineral residue	Cellulose	Lignin	Total protein	Phenols	Flavonoids
FS	11.0%	11.1%	12.0%	45.6%	11.8%	4.46 (mg GAE/g _{sample})	2.02 (mg GAE/g _{sample})
MFS	-	6.3%	27.3%	37.6%	-	-	-

biosorbents; however, it is known that plant seeds contain a higher percentage of protein than other parts of the plant (Sá et al., 2020). Furthermore, according to this data, the fennel seed can be used as a source of protein and fibres, provided in a dry fibrous mix of defibrated lignocellulosic material and defibrated plant seed (Xavier and Pastori, 2025). The low moisture content of the air-dried pulverised biosorbent (11%) allows for storage without risks such as sticking of particles and granulation. This is further important for the handling of the biosorbent when applied in water treatment systems. The results of the content of total phenols and flavonoids indicate a higher presence of phenolic compounds compared to flavonoids. Given that the modification was done by strong alkali, it did not make sense to determine the content of moisture, phenols, flavonoids, and proteins in the modified sample of fennel seeds.

Biosorbent's surface characterisation outcomes

The basic and acidic functional groups of FS detected by Boehm's method (Table 2) revealed a lower presence of acidic (phenolic, lactone, and carboxylic) groups than basic functional groups.

This is in accordance with its structure, considering that it consists mainly of cellulose and lignin, and also a relatively high protein proportion (having nitrogenous basic groups). However, only a few studies reported a similar acidic-basic trend for different sorts of seeds, such as the outcome of the Rodrigues et al. (2011) characterisation results of the avocado kernel seed-activated carbons, where basic group (0.85 mmol/g) sites dominated compared to the acid sites (0.40 mmol/g). Overall, the number and dominance of acidic over basic functional group sites and their dominance at the adsorbent surface depend on the experimental conditions for the material preparation (Ahmad and Danish, 2022).

Although the dominance of basic functional groups was determined, FS suspended in distilled water (pH 6.2) slightly decreased its pH value to

5.8 (this value represents pH_{sus} of FS). Suspension of MFS increased the pH from 6.2 to 7.2. Interestingly, the same trend and very similar data occurred for pH_{pzc} values, where FS and MFS had a zero charge at pH 5.6 and 7.9, respectively. The general basic nature of the final product could probably be attributed to the alkali agent, which was used during the modification process, making MFS more negatively charged (or less positively charged), which should result in higher affinity to bind positively charged Cd/Cr/Cu/Pb ions. The cation exchange capacity (CEC) of the utilised seeds was 4.2 mmol/g (FS) and 5.3 mmol/g (MFS). Higher obtained CEC value due to alkali treatment implies better removal of cations such as Cd/Cr/Cu/Pb ions from the water, based on the replacement process of protons or cations from the inorganic biosorbent part. Nevertheless, both CEC values are higher compared to other similar materials reported in the literature. When mango seeds were applied by Wang et al. (2022) for the removal of Cd and Pb ions, they had a notably lower cation exchange potential compared with this study, of only 0.15 mmol/g. This parameter, in general, confirms that cationic species can be effectively removed from water by the proposed biosorbents through the exchange of their own proton species with heavy-metal cations from wastewater, as one of the possible biosorption mechanisms. Moreover, this means that it could be used for the uptake of both anionic/cationic species simultaneously from the specified matrix (Kyzioł-Komosińska, 2018). Infrared spectra (FTIR) of FS and MFS powder, before and after sorption of metal ions, are shown in Figure 2.

Infrared spectrum (1) reflects the expected chemical heterogeneity of the native fennel-seed residue, in accordance with its lignocellulosic composition and the presence of a measurable protein fraction established independently by compositional analysis (*vide supra*) (Chang et al., 2016). The intense and broad absorption extending through the 3500–3200 cm^{-1} region, with a maximum around 3400 cm^{-1} , is predominantly associated with hydrogen-bonded O–H stretching

Table 2. Total acid and basic groups determined by Boehm titrations in fennel seeds

Parameter	Total acidic groups (mmol/g)	Phenol groups (mmol/g)	Lactone groups (mmol/g)	Carboxylic groups (mmol/g)	Total basic groups (mmol/g)
FS	4.77	1.54	2.16	1.07	5.88

vibrations of alcoholic and phenolic groups present in cellulose, hemicellulose and lignin/polyphenolic constituents, although an overlapping N–H contribution from proteinaceous components cannot be excluded (Yang et al., 2007; Beć et al., 2020). The medium-intensity bands at approximately 2925 and 2855 cm^{-1} originate predominantly from asymmetric and symmetric C–H stretching vibrations of aliphatic CH_2/CH_3 groups occurring throughout the organic matrix (Gök et al., 2019).

The 1760–1600 cm^{-1} interval requires particular caution because, in a chemically

heterogeneous plant-derived material, such as FS, it represents a strongly overlapping spectral envelope, rather than a set of vibrations that can be assigned uniquely to individual functional groups. The higher-wavenumber part of this region, particularly approximately 1760–1700 cm^{-1} and including the experimentally observed envelope around 1740 cm^{-1} , is expected to be dominated by stretching vibrations of ester and other non-conjugated carbonyl groups (Tahir et al., 2019).

In lignocellulosic plant matrices, absorptions around 1745–1730 cm^{-1} are characteristic of esterified carbonyl functionalities occurring in hemicellulosic, pectic, and lignin-associated structures, with possible contributions from other residual ester-containing constituents (Beć et al., 2020). In contrast, the lower-wavenumber part of the envelope is intrinsically more complex. Contributions around 1650–1630 cm^{-1} may arise from the amide I vibration, dominated by peptide C=O stretching, as well as from water associated with cellulose/lignin structures, while phenolic or other unsaturated C=C contributions may occur at approximately 1630–1620 cm^{-1} . Lignin-associated aromatic/carbonyl vibrations may additionally contribute toward the lower-frequency edge of this region (Beć et al., 2020). The presence of an amide I contribution is chemically reasonable for FS in view of the independently determined protein content of 11.8% (vide supra), whereas an analogous protein-related assignment for MFS should remain tentative because the protein content was not independently quantified after alkaline modification.

Deconvolution of the strongly overlapping 1760–1600 cm^{-1} envelope (Figure 3) resolved eight underlying spectral components. These components should not be interpreted as eight chemically independent carbonyl functionalities. Rather, their number reflects the resolution of several partially overlapping vibrational contributions originating from the heterogeneous organic matrix. Components above approximately 1700 cm^{-1} are attributable predominantly to ester/non-conjugated carbonyl stretching, whereas those between approximately 1700 and 1600 cm^{-1} may contain different proportions of

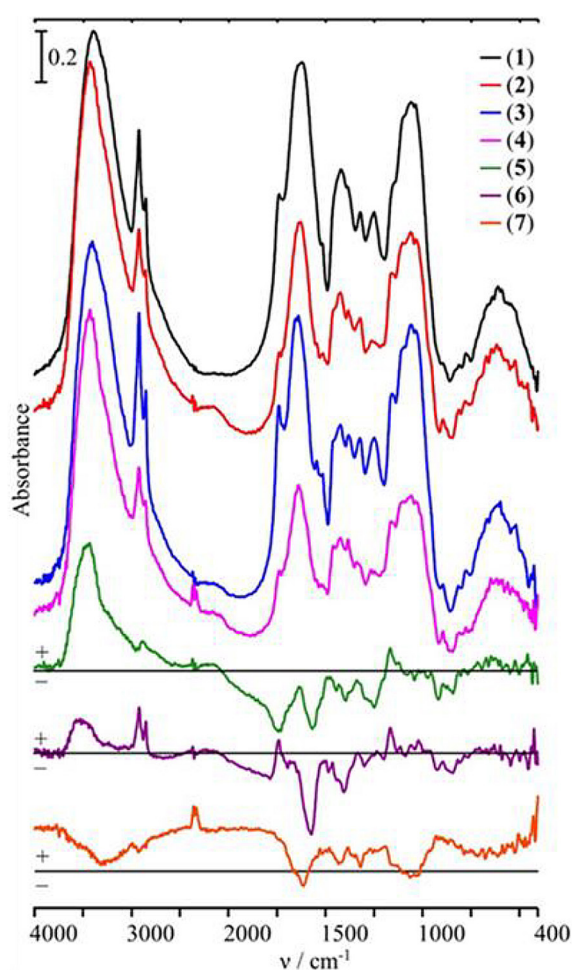


Figure 2. Infrared spectra of FS powder before (1) and after (3) sorption of metals and MFS powder before (2) and after (4) sorption of metals.

The difference spectra are (5) = (2) – (1),
(6) = (3) – (1), (7) = (4) – (2)

conjugated carbonyl, amide I, aromatic/phenolic C=C, and water-associated contributions (Tahir et al., 2019). Accordingly, the chemical interpretation is based on characteristic spectral ranges and the known composition of the material rather than on an artificial one-band/one-functional-group correspondence. This distinction is particularly important for a multicomponent biosorbent because the position and relative intensity of individual components are affected by hydrogen bonding, conjugation, and the local chemical environment of the respective functional groups (Beć et al., 2020).

Outside this highly overlapped region, the band near 1545 cm^{-1} should not be assigned exclusively to aromatic C=C vibrations. Considering the measurable protein fraction in FS (*vide supra*), an amide II contribution, involving primarily N–H deformation coupled with C–N stretching, is chemically plausible in this region, whereas the feature near 1515 cm^{-1} is considerably more characteristic of aromatic skeletal C=C vibrations of lignin and related polyphenolic structures (Beć et al., 2020). The feature in the $1320\text{--}1340\text{ cm}^{-1}$ region is likewise unlikely to originate from a single vibration and may contain contributions from C–N/amide-related and lignocellulosic skeletal modes (Sulthana et al., 2022). Therefore, no unique assignment is imposed. Similarly, the band around 1385 cm^{-1} occurs in a region in which C–H deformation vibrations of cellulose/hemicellulose and other oxygen-containing structural contributions may overlap.

Of particular relevance to metal binding is the approximately $1260\text{--}1230\text{ cm}^{-1}$ region (Taqi et al., 2023). In plant-derived lignocellulosic matrices, this interval may comprise C–O stretching contributions from lignin/xylan together with overlapping vibrations of esterified and other oxygen-containing structures (Kacurkova et al., 2000; Beć et al., 2020). Following simultaneous Cd(II)/Cr(III)/Cu(II)/Pb(II) adsorption, the band occurring in this region exhibited a reproducible shift toward higher wavenumbers by approximately $13\text{--}16\text{ cm}^{-1}$. Rather than being interpreted as direct evidence for the formation of a “weaker metal–oxygen bond”, as the observed vibration belongs predominantly to the organic C–O-containing framework, rather than to an isolated M–O stretching mode, this shift is more appropriately attributed to perturbation of the electronic and bonding environment of

oxygen-containing surface functionalities upon metal uptake. The observation is therefore consistent with participation of O-donor sites in specific metal–surface interactions, including surface coordination/complexation, potentially accompanied by changes in the protonation state of ionisable oxygen-containing groups (Nakamoto, 2006; Amar et al., 2020). Importantly, FTIR establishes involvement of these functional groups but does not, by itself, quantify their individual contributions or establish a unique coordination geometry for the four simultaneously adsorbed metal ions.

The intense group of absorptions between approximately 1100 and 1000 cm^{-1} constitutes the characteristic polysaccharide fingerprint region, dominated by C–O and C–O–C stretching vibrations of the carbohydrate framework (Kacurkova et al., 2000; Beć et al., 2020; Krysa et al., 2022). The band around 895 cm^{-1} is consistent with the vibrations associated with β -glycosidic linkages in the polysaccharide fraction and therefore further supports the pronounced contribution of cellulose-related structural units to the spectra.

Overall, comparison of spectra (1–4) indicates preservation of the principal lignocellulosic spectral pattern after both alkaline modification and metal adsorption, whereas chemically relevant differences are manifested mainly through changes in relative band intensities and local band positions, rather than through the appearance of an entirely new set of absorptions. In the FS-to-MFS difference spectrum (5), alkaline treatment produced a pronounced decrease in the relative contribution of the carbonyl/ester-rich region together with an increased contribution of the broad O–H envelope. These changes are chemically consistent with alkaline cleavage and saponification of ester-containing moieties and with increased exposure and/or relative contribution of hydroxyl-containing sites in MFS, in agreement with the compositional changes described above (*vide supra*). The post-adsorption spectral perturbation in the C–O-rich region, in turn, provides independent spectroscopic evidence that oxygen-containing surface functionalities participate directly in metal retention. This FTIR evidence should specifically be interpreted in terms of surface coordination/complexation and should be distinguished from ion exchange, for which complementary evidence is provided by the CEC and post-adsorption EDS results discussed subsequently (*vide infra*). Thus, the FTIR

data support involvement of oxygen-donor functionalities in metal binding without requiring the assumption that a single functional group type or a single adsorption pathway controls the overall quaternary biosorption process.

Morphology analysis of the used biosorbents, shown in Figure 4, revealed that the somewhat flaky horizontal and relatively porous surface of pure fennel seeds (A) had changed upon both metal loading (B) and sodium hydroxide treatment (C) into a more disorganised bulged surface of the irregularly shaped particles with the appearance of cavities of different shapes and sizes.

Moreover, alkali treatment resulted in the smoother particle surface forming a layered structure, facilitating metal ions diffusion through the material's structure toward groups onto the surface of this lignocellulosic material, resulting in a more accessible adsorption process, with facilitated adhesion. The main possible reason for the morphological changes and refinements is the occurrence of cellulose, lignins, and hemicellulose hydrolysis in the biomaterial during chemical treatment (Mabungela et al., 2022).

When MFS was loaded with Cd/Cr/Cu/Pb (D), significant surface disruption and transformation of origin particles were obtained. The quaternary adsorption of metals caused the formation of rotini-like spiral particles, which indicates that the biosorption process takes place not only superficially on the MFS material but also deeper

into the particles themselves. The elements registered by EDS analysis are compared in Table 3.

The EDS data indicated that the dominant constituents/elements present in the used biomaterials are carbon and oxygen (C and O). Since fennel seeds are considered lignocellulosic materials, these elements typically represent the main ingredients of agricultural materials (Chen et al., 2021). This is further in correspondence to the characterisation analysis with FTIR and Boehm's titrations. Mabungela et al. (2022) also recorded the phosphorus (P) and chloride (Cl) in their study. In addition, present alkali (Na, K) and alkaline earth (Ca and Mg) metals naturally occur in plant-based materials (Figueira et al., 2022). The presence of these elements could be highly beneficial in the case of ion exchange with cationic species (Bashir et al., 2019), which favours the quaternary removal of Cd/Cr/Cu/Pb.

Although it was expected that EDS would also give the nitrogen content (w, %), considering the protein content (Table 1), this was not the case. A reasonable explanation could be the possible inhomogeneity of the sample in addition to the fact that a significantly larger sample weight (0.5 g) was used for the Biuret reaction, which is more representative, compared to the quite small sample amount for the EDS analysis (Sulejmanović et al., 2023b). The most relevant EDS evidence regarding the possible contribution of ion exchange was the marked decrease, or complete disappearance, of naturally occurring alkali and alkaline-earth cations after metal loading. The simultaneous detection of Cd, Cr, Cu, and Pb on the loaded biosorbents, together with the decrease in Na, K, Mg, and Ca contents, is consistent with the displacement of native cations by the target metal ions, indicating that ion exchange may contribute as one of the mechanisms involved in binding the targeted cationic species onto fennel seed biomass (Šabanović et al., 2020). Finally, the tabular data further confirmed successful biosorption of Cd/Cr/Cu/Pb according to the detected weight percentages of all four elements (Unugul and Nigiz, 2020).

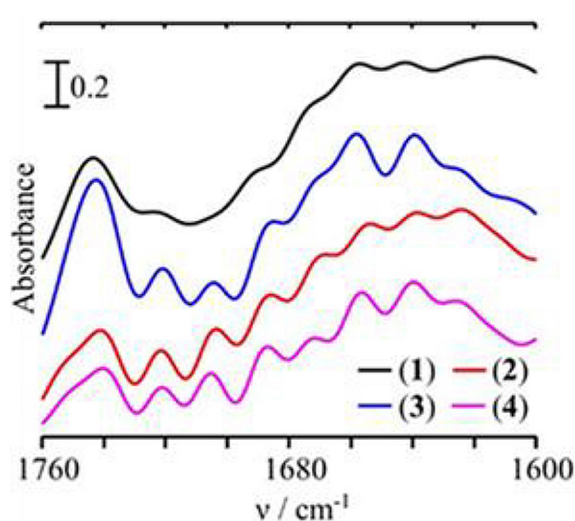


Figure 3. Deconvoluted carbonyl and carbon-carbon double bond region of infrared spectra of FS powder before (1) and after (3) sorption of metals, as well as MFS powder before (2) and after (4) sorption of metals

Optimal solution pH, sorbent mass, and initial metal concentration of the sorption process

According to Figure 5, pH value variations in the interval 3 to 5 caused a similar tendency for

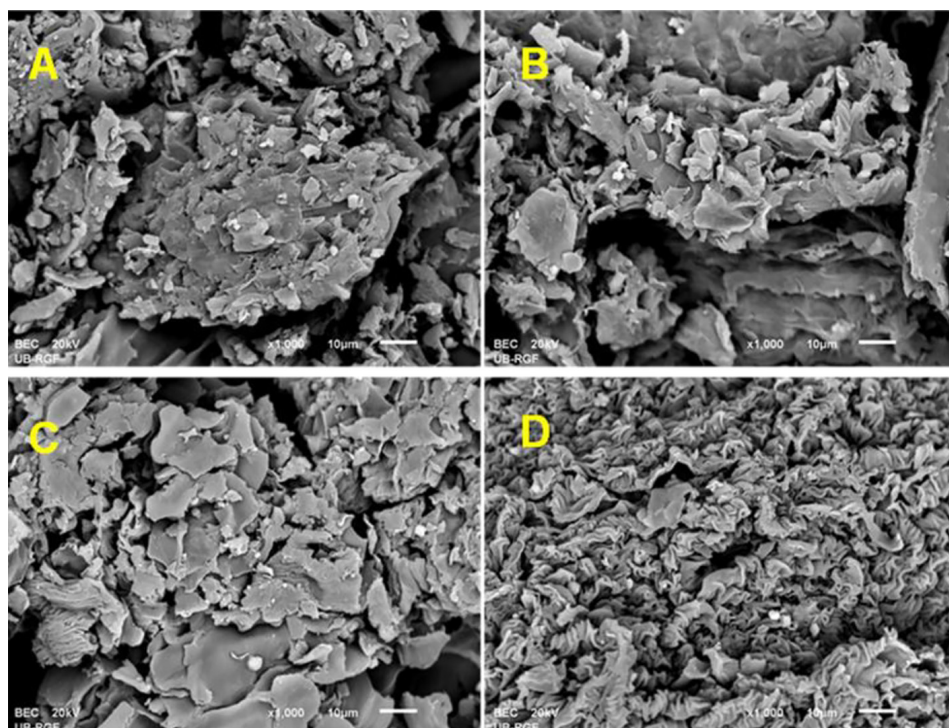


Figure 4. SEM images of FS (A), FS loaded with Cd/Cr/Cu/Pb (B); MFS (C), and MFS loaded with Cd/Cr/Cu/Pb (D) at 1000x

Table 3. EDS chemical composition comparison study of FS and MFS biosorbents

Element/Material	Fennel seeds (FS)	FS with Cd/Cr/Cu/Pb	Modified fennel seeds (MFS)	MFS with Cd/Cr/Cu/Pb
	Weights percentage (%)			
C	41.26	47.82	43.01	50.44
O	50.33	46.74	53.47	42.30
Na	0.63	-	0.88	0.24
Mg	0.44	0.24	0.23	-
P	0.53	0.65	0.45	0.40
S	0.46	0.53	-	-
Cl	0.97	-	0.19	-
K	3.33	0.19	0.20	-
Ca	2.05	1.74	1.57	0.49
Cr	-	0.23	-	0.85
Cu	-	0.78	-	2.17
Cd	-	0.40	-	0.47
Pb	-	0.67	-	2.64
Total	100.00	100.00	100.00	100.00

Cd/Cr/Cu ions (as pH-independent) and, on the other hand, Pb ions (as pH-dependent) behaviour when biosorption was performed by FS (A1).

Since pH did not influence the adsorption process of Cd/Cr/Cu ions, while the efficiency of Pb removal increased until pH 5, pH 5 was set as optimal for the simultaneous removal of the given

analytes. However, when MFS was used (B1), Cd/Pb ions behaved pH-independently, while for Cr/Cu biosorption, pH 5 was highly inappropriate. To minimise the competition among different cationic species, preference is given to a solution with a pH value of 4 (lower concentration of H^+ ions). At these selected pHs, the surface of

both FS and MFS biosorbent is positively charged (solution pH is lower than each of the pH_{pzc} values); therefore, the electrostatic attraction forces would be weakly involved in the removal process of metal cations. This indicates that another binding/removal mechanism should dominate through the biosorption process.

According to Figure 5 B2, even three times smaller weights of used MFS (200 mg) resulted in 10, 20, or even 50% higher removal efficiencies for Pb, Cr/Cu, and Cd, respectively, than with FS (A2). This observation justifies the applied chemical treatment of the origin FS, which implies that the modification resulted in an increased number of new or more accessible already existing functional groups. Since experimental results showed that the modified sorbent has higher metal ion removal ability, it becomes obvious that oxygen sites from hydroxyl groups are more significant for the sorption process than oxygen sites from carbonyl groups, which is in accordance with FTIR data. The initial metal concentration effect on sorption was carried out in a suspension where each metal ion concentration was 10, 20, 30, 40, or 50 mg/L (Figure 5). Similar to mass optimisation, in the case of this parameter, MFS (B3) has also proved to be more effective for quaternary biosorption compared to FS (A3). However, with both FS and MFS, the variations of lead's R_{eff} at the tested concentration interval were negligible, with an average efficiency of about 95% and 98%, respectively, which further indicates the strong affinity of Pb ions to the active functional groups of fennel seeds. In addition, the biosorption trend for Cd was similar for both biosorbents, in the sense that increasing the initial concentration negatively correlated with Cd ion R_{eff} , with the efficiency decreasing by about 15% (FS) and 46% (MFS) for concentration from 10 to 50 mg/L.

This is also consistent with the EDS data, according to the ion-preference order: $\text{Pb} > \text{Cu} > \text{Cr} > \text{Cd}$. Namely, with virgin fennel seeds, the removal of lower concentrations of analytes was less effective. This may be a consequence of the presence of impurities and increased content of “inactive” parts of biomass that disrupt biosorption by masking or blocking active spots on the surface of the biomaterial (Thakur et al., 2020). Also, at lower concentrations, the diffusion force is weaker, so analyte ions are not able to penetrate the binding site (this also can explain the biosorption trends for

Cu and Cr by FS) (Sen, 2023). Using modified fennel seed, the removal of lower concentrations was quite more efficient ($R_{\text{eff}} > 90\%$), which means that the modification reduced “inactive” biomass parts and similar impurities, which made the biosorbent's surface “active” – abundant with a significant quantity of functional groups and available for the binding of analytes.

As the experimental results showed that the modified sorbent has a greater ability to remove metal ions, it is obvious that the active centres of hydroxyl groups are more important for the sorption process than carbonyl groups. These results indicate significant potential for modified fennel seed for simultaneous quaternary removal of tested metals in wastewater treatment.

Optimal contact time and kinetics of the sorption process

The experimental results provided an insight into the time-independent nature of the simultaneous removal process of Cd/Cr/Cu/Pb ions with completion after only 20 min by both FS/MFS (Figure 5 A4/B4). The high initial heavy metal ion rate of adsorption by lignocellulosic agricultural waste powders has, in general, been reported (Thakur et al., 2020). Finally, 20 minutes was chosen for the optimal adsorption contact time, required to establish the equilibrium of the process. In addition to R_{eff} (%), the obtained adsorption capacities were: 5.1/7.5 mg/g (Cr), 6.1/10.2 mg/g (Cu), 3.6/6.7 mg/g (Cd) and 7.9/14.7 mg/g (Pb) for FS/MFS for the multi-element quaternary model solution with an initial concentration of 50 mg/L of each analyte within 20 minutes. Moreover, given that energy, economic, and technological factors directly influence the design and performance of wastewater treatment in a batch system at the industrial level, such a short time interval in which the conditions for efficient biosorption are provided makes this procedure far more favourable than commercial techniques.

The prediction of the heavy metal ions removal rate from solution was researched in accordance with kinetic models, to better understand the biosorption dynamics, estimate the degree of analyte removal over time, and define the nature of the sorption process (Rai et al., 2023). Significant parameters of the process expressed by the use of kinetic models, as well as intraparticle diffusion models, are shown in Tables 4 (FS) and 5 (MFS).

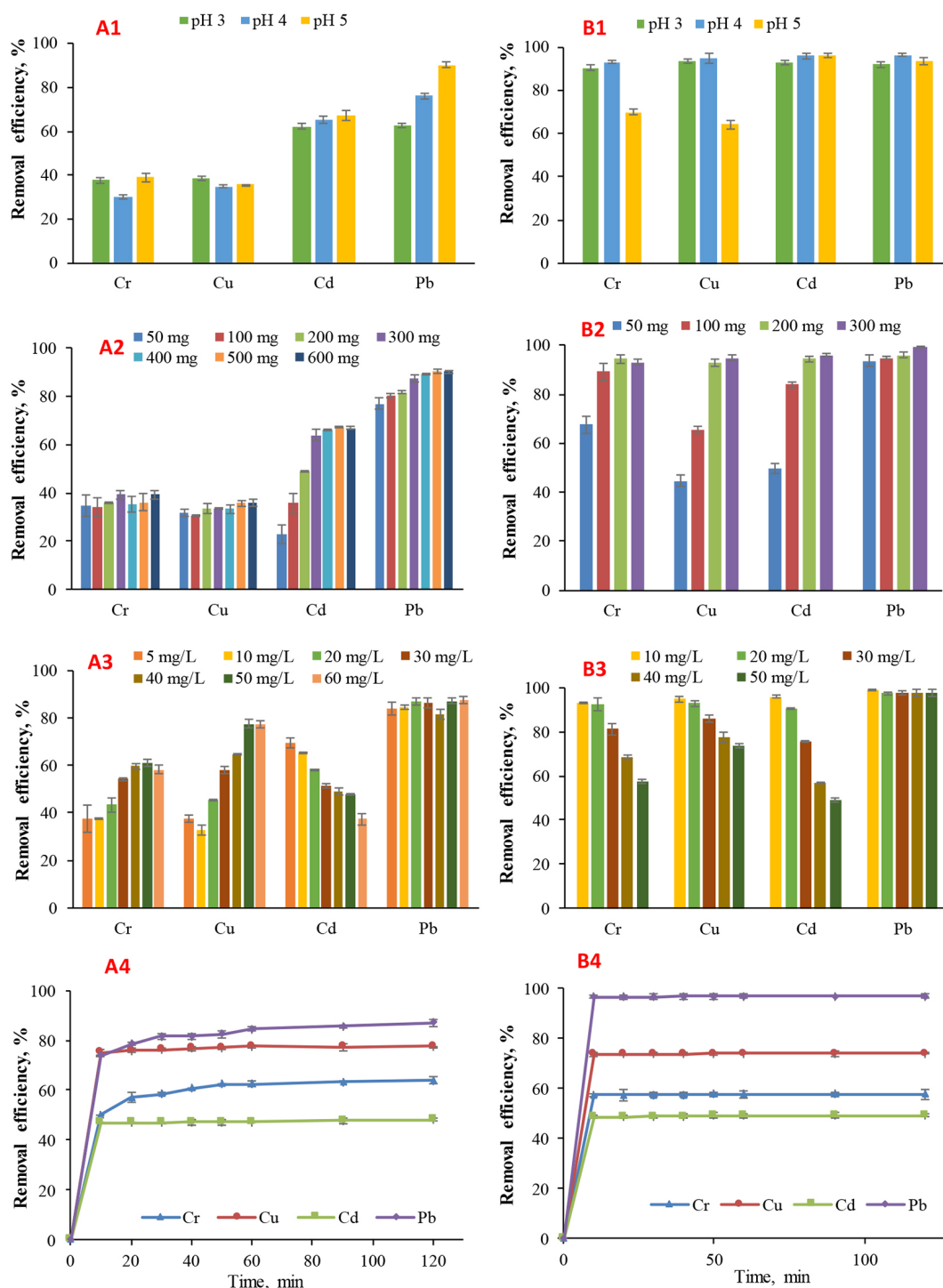


Figure 5. Comprehensive overview of the optimisation of key process parameters for quaternary biosorption by FS (A) and MFS (B): (1) effect of solution pH; (2) effect of adsorbent mass (mg); (3) effect of initial analyte concentration (mg/L); and (4) effect of contact time (min)

Considering the kinetic models and the equilibrium sorption capacity q , for each of the metal ions using both types of biosorbents, it was clear that the results for the pseudo-first-order reaction significantly varied from the experimental ones. On the contrary, the capacity values gained by the pseudo-second-order

model are very close to the experimental data (average fit 99.60% (FS) and 99.85% (MFS)), with determination coefficient values (R^2) close to 1, indicating that the biosorption of the tested metals follows this kinetic model.

This further means that the biosorption uptake of metals takes place by ion exchange and

Table 4. Kinetic parameters for the removal of Cr³⁺, Cu²⁺, Cd²⁺, and Pb²⁺ under optimal conditions using the native phase of fennel seeds ($q_{\text{exp}} = 5.1; 6.1; 3.6; 7.9$ mg/g, respectively)

Metal ion	Pseudo first-order			Pseudo second-order			Intraparticle diffusion					
	q_{max} (mg/g)	k_1 (min ⁻¹)	R^2	q_{max} (mg/g)	k_2 (g/mg·min)	R^2	k_{11}	R_1^2	k_{12}	R_2^2	k_{13}	R_3^2
Cr	0.3	0.02	0.9511	5.1	0.18	0.9999	0.04	0.9999	0.01	0.2223	0.03	0.9729
Cu	0.6	0.04	0.8189	6.1	0.20	0.9999	0.05	0.9999	0.02	0.3964	0.03	0.9729
Cd	0.7	0.03	0.7979	3.6	0.15	0.9996	0.05	0.9999	0.04	0.9048	0.04	0.9166
Pb	0.3	0.04	0.9220	7.9	0.21	0.9999	0.04	0.9999	0.01	0.2788	0.01	0.8203

Table 5. Kinetic parameters for the removal of Cr³⁺, Cu²⁺, Cd²⁺, and Pb²⁺ under optimal conditions using the modified phase of fennel seeds ($q_{\text{exp}} = 7.5; 10.2; 6.7; 14.6$ mg/g, respectively)

Metal ion	Pseudo first-order			Pseudo second-order			Intraparticle diffusion					
	q_{max} (mg/g)	k_1 (min ⁻¹)	R^2	q_{max} (mg/g)	k_2 (g/mg·min)	R^2	k_{11}	R_1^2	k_{12}	R_2^2	k_{13}	R_3^2
Cr	0.1	0.01	0.0825	7.5	0.58	0.9999	0.02	0.9999	0.01	0.0011	0.02	0.8597
Cu	0.4	0.03	0.9211	10.2	0.19	0.9999	0.04	0.9999	0.01	0.2223	0.02	0.9490
Cd	1.0	0.03	0.7306	6.8	0.09	0.9996	0.08	0.9999	0.06	0.9989	0.07	0.9432
Pb	0.4	0.03	0.8974	14.7	0.16	0.9999	0.07	0.9999	0.06	0.7777	0.02	0.7051

chemisorption, which involves chemical bondings and sharing/exchange of electrons of metal ions and functional groups of the biosorbent (Sahoo and Prelot, 2020), as shown in Figure 6.

Furthermore, the cooperative mechanism of this kinetic model and intraparticle diffusion model -first phase ($R_1^2 = 0.9999$) was established. This is in correspondence with EDS data, which has indicated ion exchange as one of the possible removal pathways at the fennel seeds' surface (Tanasă et al., 2020)

Comparison of the theoretical equilibrium capacity of fennel biosorbents with the results of similar research

The adsorption of heavy metal ions on different biosorbents is the subject of extensive research. Table 6 shows the theoretical equilibrium capacities of similar solid phases used to remove the tested heavy metals.

In general, the adsorption capacities of MFS are very comparable with the other given materials, except for modified sunflower seed husk (for Cd). Even the FS prepared in this study was better compared to fennel seeds prepared by Mabungela et al. (2022). The possible reasons for this are multiple: in their study, the seeds were boiled in hot water for 30 minutes, which could cause degenerative changes and destruction of

lignocellulosic components. Meanwhile, the conducted research used the fat-free residue seeds in which fat, as an inactive component, was extracted, which increased the reactivity of the functional groups present in FS. Also, a fraction of 0.8–1 mm was used by Mabungela et al. (2022), while 0.25 mm were used by the authors of this paper, indicating that particle size is a factor that needs further investigation.

Co-existing ions study and application to a real wastewater (RWW) sample

Before testing the prepared biosorbents on a real sample – industrial wastewater, the possible influence of other metal ions that are usually present in the specified type of wastewater was checked. For this purpose, 50 mg/L of a single competitive ion (Mn, Ni, Co or Zn) was added into a quaternary model solution (concentration of 50 mg/L of each of Cd/Cr/Cu/Pb ions), and biosorption was carried out by a general procedure with previously determined optimal conditions.

Taking into account the adsorption capacity, the ratio of the maximum adsorption capacity for single heavy metal ion in the quaternary solution (q_4) and the adsorption capacity for that heavy metal ion within the solution with added Mn, Ni, Co or Zn (q_5) determines the ionic

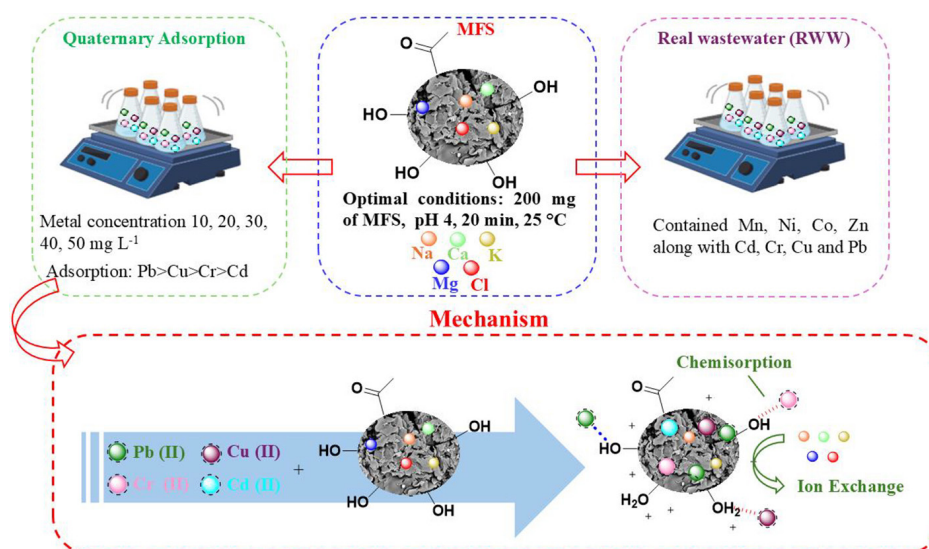


Figure 6. Proposed adsorption mechanism process of Cd/Co/Cr/Pb ions on MFS

Table 6. Comparison of adsorption equilibrium capacities (q , mg/g) for the removal of heavy metal ions by different biosorbents

Biosorbent	$q(\text{Cr})$	$q(\text{Cu})$	$q(\text{Cd})$	$q(\text{Pb})$	Reference
Bottle gourd	-	-	5.8	6.7	(Mitić-Stojanović, 2012)
Banana peel	6.9	-	3.7	20.9	(Mahmood-ul-Hassan et al., 2015)
Modified sunflower seed husks	-	-	19.6	19.9	(Srisorrachatr, 2017)
Tangerine peel	1.5	1.6	0.7	1.6	(Memić et al., 2018)
Modified lemon peel	7.5	7.1	7.3	8.1	(Šabanović et al., 2020)
Pure fennel seeds	-	3.2	-	5.5	(Mabungela et al., 2022)
Coriander seeds	-	-	-	8.8	(Shamkhi and Hussein, 2022).
Virgin fennel seeds	5.1	6.1	3.6	7.9	This research
Modified fennel seed	7.5	10.2	6.7	14.7	

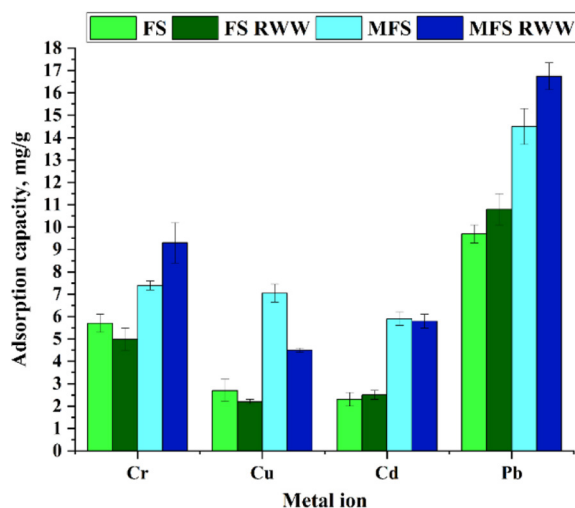
interactions effect on the process biosorption (Bayuo et al., 2023) by the following model: $q_5/q_4 > 1$ the sorption process is promoted by the coexistence of added ion – suggesting synergism (Touihri et al., 2021); $q_5/q_4 = 1$ the added ion does not influence the sorption process - indicating non-interaction (Du et al., 2021); $q_5/q_4 < 1$ the biosorption process is significantly inhibited by added ion - points to antagonism (Bayuo et al., 2023). The calculated q_5/q_4 values (Table 7) indicated the synergistic impact of all added ions on Pb removal. One (Zn), two (Mn and Zn), and three (Mn, Co and Zn) of four added ions showed antagonistic impact on the removal of Cd, Cr, and Cu, respectively.

According to FAAS analysis (after Fe ions precipitation), RWW contained significantly high concentrations of nickel (788.3 mg/L), zinc (648.4 mg/L), and chromium (174.8 mg/L)

with twice or multiple lower levels of other heavy metals (Pb: 81.0; Cu: 29.8; Cd: 27.1; Co: 17.6 and Mn: 9.9 mg/L). Adsorption capacities obtained by both FS and MFS biosorbents for the RWW treatment (Figure 7) had the same trend and were in accordance with the co-existing ions study findings. Synergistic influence on Pb removal was confirmed once again, as well as antagonistic effects on Cu and Cr biosorption. In the case of Cd removal, despite the antagonistic effect of Zn being expected, a very high nickel concentration prevented this, considering that nickel enhances copper removal (Table 7), so for RWW, Cd removal can be described as a non-interacting model type. Since other possible matrix components did not have a major influence on the adsorption capacity values, this is a positive feature of these fennel seed-based biosorbents.

Table 7. Added ionic species impact (q_s/q_4 values) on the Cr/Cu/Cd/Pb biosorption process

Added ion	Cr	Cu	Cd	Pb
Mn	0.67	0.66	0.92	1.12
Co	0.92	0.83	0.93	1.13
Ni	0.97	0.97	1.06	1.31
Zn	0.83	0.85	0.74	1.24

**Figure 7.** Comparison of adsorption capacity (q , mg/g) of FS and MFS biosorbents obtained for model solutions and real wastewater (RWW) under optimal conditions

CONCLUSIONS

To achieve optimal results for simultaneous quaternary biosorption of Cd/Cr/Cu/Pb ions by the hereby prepared fennel seeds-based materials, defined operational parameters (pH, mass, and contact time) should be employed. Under the determined optimum conditions the maximum adsorption capacities were 5.1/7.5 mg/g (Cr), 6.1/10.2 mg/g (Cu), 3.6/6.7 mg/g (Cd) and 7.9/14.7 mg/g (Pb) for FS/MFS, corresponding to removal efficiency values ranged from 50–87.5% (FS) and 50–97.5% (MFS). In this regard, FS and MFS, as low-cost and locally available and abundant agro-wastes, have stood out as promising candidates for simultaneous heavy metal removal on a higher than laboratory scale (i.e. industrial). Moreover, the physical preparation of these biosorbents is based on the principles of green chemistry. This biowaste is rich in multi-chemical functional groups and possesses high cation-exchange capacity, with appropriate morphology for accessibility and optimisation of

the adsorption process, which further enhances cost-effectiveness/profitability and sustainability. The maximum sorption capacity followed the order $Cd < Cr < Cu < Pb$ and was very comparable to other similar biomaterials, with the additional advancement of rarely studied simultaneous removal. Despite these advances, further research is needed to optimise the performance of FS and MFS targeting both the removal of other emerging substances (i.e., pharmaceuticals, pesticides, organic dyes, etc.) and other types of wastewater for the development of more sustainable and cost-effective methods for their treatment.

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