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Removal of heavy metals from aqueous media by sunflower husk: A comparative study of biosorption efficiency by using ICP-OES and LIBS

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Abstract: Presented research aimed to develop an alternative approach for the estimation of biosorption capability of sunflower husk. The acid-pretreated sunflower biomass was characterized by scanning electron microscopy combined with energy dispersive X-Ray spectroscopy (SEM-EDX) analysis and Fourier transform infrared (FTIR) spectroscopy. Biosorption efficiency has been evaluated using inductively coupled plasma optical emission spectroscopy (ICP-OES) and laser-induced breakdown spectroscopy (LIBS). The adsorption capacity of the adsorbent was determined as the function of the pH of the solution, the initial concentration of heavy metal solutions, and contact time. The optimal conditions were achieved after 15 min of contact at pH 6, while the percentage of the removal was from 80.0–98.7 %, depending on the element. The results obtained from the kinetic and isotherm studies show that maximum adsorption of ions was quickly reached and followed the pseudo-second-order kinetic model. Real samples were tested and obtained Ni values by LIBS method were 3100±200 and 1240±100 mg kg⁻¹, while estimated values by the ICP-OES were 2995±20 and 1130±10 mg kg⁻¹, respectively. The obtained results prove that LIBS method can be used as a “green alternative” for the evaluation of biosorption efficiency.

Keywords: spectrochemistry; adsorption; wastewater treatment; laser; green analytical chemistry.

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INTRODUCTION

In the past decades, rapid world progress and the constant rise of anthropogenic activities caused serious contamination of the environment by a whole range of pollutants. As a result of growing industrial and technological applications wastewater can often contain a wide range of heavy metals. Heavy metals represent metallic elements that have at minimum 5 times larger atomic weight and a density than water.¹ These elements are known as non-degradable in the environment and due to their toxicity for living organisms, their presence in the water resources making those resources unavailable for ecosystem and human activities. Furthermore, these elements are usually persistent in the soil with a very long residence time because heavy metal ions do not reduce into harmless compounds.²

At the same time, there is a general recognition that future global prosperity is directly dependent on the availability of clean water and soil and consequently wastewater polluted by heavy metals should be treated prior to their release to the environment. However, removing metal ions from wastewater is a great challenge for their significant solubility in water solutions. There are various conventional treatment technologies developed for the removal of heavy metals from the wastewater such as chemical precipitation, ion exchange, membrane filtration and separation, solvent extraction, reverse osmosis, electrochemical treatment, *etc.*³ However, these techniques are commonly having some drawbacks associated with incomplete metal removal, generation of sludge with secondary pollution, and generally high cost due to high reagent and energy requirements.

As an alternative, the biosorption process was proposed approximately 70 years ago and since then it has been a target of numerous research in order to prepare more efficient, more effective, and more economic biomaterials.^{4,5} Due to the fascinating features primarily the availability of different low-cost adsorbents and easy operation, this eco-friendly method can be considered a sustainable and more efficient method for the removal of heavy metals from aqueous solutions.^{5,6} According to Robalds *et al.*, metals biosorption is a process of catching heavy metals by physical adsorption, chemisorption (complexation, coordination, and chelation), ionic exchange, and microprecipitation.⁷ Biomaterials have no significant costs and their sorption potentials are mainly due to the presence of carboxylic and phenolic functional groups in the cellulosic matrix or components associated with cellulose such as lignin and hemicellulose which are found to be responsible for metal sorption.⁶

Biosorbents are typically prepared from naturally waste biomass and therefore agricultural waste materials have been used as a rich source for low-cost biosorbents.^{5,8} Serbia is traditionally an agricultural country while sunflower is the most common oil plant. It is grown on around 180,000 ha and it is one of the most important export products.⁹ After industrial processing of sunflower,

between 325,000 and 360,000 t of the sunflower husk waste often ends up at landfills or being used as an energy source.¹⁰

Toxic and not biodegradable heavy metals, included in this study are Pb, Cu, Ni, Co, Cd, and their toxicity can be determined from the absorbed amount, the route of introduction and duration of exposure.¹¹ They tend to accumulate in the living organisms and induce numerous health problems including the weakening of the immune system, cardiac dysfunction, fetal malformation, impaired psychological and neurological behavior, and cancer when present in the range of ppb.¹² Sunflower residues such as stalk and husk can be used for the removal of heavy elements and there are several reports regarding this topic.^{2,10,13–15} Sunflower-derived adsorbents as raw material, such as in this manuscript, or as thermally treated materials (biochar and activated carbons) have shown great efficiency for the removal of various toxic elements and organic pollutants from synthetic wastewaters.¹⁵

Conventional and well-established spectrochemistry methods (ICP-OES, AAS and XRF) are usually dedicated to the estimation of biosorption efficiency of heavy metals by providing information about heavy metals concentration before and after sorption.^{16,17} However, laser-induced breakdown spectroscopy (LIBS) that uses a pulsed laser as an excitation source attaches more and more interest and importance as a modern analytical method for fast, easy scale-up and *in situ* elemental analysis of the various types of samples.¹⁸ Furthermore, as a cost-effective alternative to commercial LIBS systems, a transversely excited atmosphere carbon dioxide (TEA CO₂) laser-based LIBS setup was proposed by Momcilovic *et al.*¹⁹ Some exclusive properties such as rapid, multi-element analysis of any kind of material, non-contact and almost nondestructive, independent of sample conductivity, geometry and size make this method superior to the other standard optical emission techniques.^{20,21} Moreover, TEA CO₂ LIBS method does not use any hazardous reagents and solvents and maximizes safety for operators and the environment which creates it in full accordance with the principles of green analytical chemistry.^{21,22}

The main aim of the present research was to study the adsorption properties of sunflower seeds husk in relation to heavy metal ions present in mono- and multi-cationic aqueous solutions in order to obtain a higher sorption capacity. The influence of various metal ion concentrations, pH levels, contact time, and the kinetics of adsorption were investigated. To the best of our knowledge, this is the first report on the application of transversely excited atmospheric (TEA) CO₂ based LIBS for fast and effective estimation of biosorption efficiency.

EXPERIMENTAL

Biosorbent preparation

Treatment of sunflower husk and stock solutions of heavy metals. Sunflower seeds were obtained from a local market, and husks were manually separated from the core. Then, in

order to remove the potential impurities, obtained husk was washed thoroughly with deionized water. Furthermore, obtained material was treated with a 0.5 % solution of hydrochloric acid. The mixture was stirred periodically, and the pretreatment was carried out for 1 h. The residue material was rinsed with deionized water. The sunflower husk was dried in an oven at 100 °C. In addition, dried sunflower husk was grounded and sieved to obtain sorbent with a size of grains less than 1 mm and stored in the desiccator.

Stock solutions of heavy metals were prepared by resolving the appropriate amount of water-soluble salts of these elements in deionized water (CuSO₄·5H₂O Centrohem; CdNO₃·4H₂O Superlab; NiCl₂·6H₂O Merck and Pb(NO₃)₂ Centrohem). The final concentrations in these solutions were determined by ICP-OES method, and were used for adsorption experiments.

The percent of metal ion removal ($R / \%$) was calculated using the following equation:

$$R = 100 \frac{c_i - c_e}{c_e} \quad (1)$$

where c_i and c_e are the initial and final concentrations of metal ions in the solution, respectively.^{2,12} The adsorption capacity of adsorbent for the metal ions at equilibrium is calculated using the following formula:

$$q_e = \frac{V(c_i - c_e)}{m} \quad (2)$$

where V is the volume of solution and m mass of the used biosorbent.¹²

Effect of pH. The effect of pH on biosorption was investigated by using batch mode in a pH range of 2.0–7.0. Other parameters that were held constant were as follows: concentrations of Cu, Ni, Pb and Cd ions (50.1, 51.7, 53.6 and 52.0 mg L⁻¹, respectively), time of contact between sorbent and solution (15 min) and mass of adsorbent (0.5 g). A 40 mL of stock solutions of Cu, Ni, Pb and Cd were measured and placed in polyethylene (PE) bottles. After that the pH was adjusted with 1% solutions of hydrochloric acid or sodium hydroxide to the desired value. Then, the sorbent material was weighed in the amount of 0.50 g, and the PE bottles with this content were agitated at 200 rpm on a platform shaker for 15 min. Finally, the supernatant was filtered and stored in the refrigerator for the ICP-OES analysis.

Effect of contact time. Effect of contact time was studied in a batch system, maintaining the constant initial conditions as the following: concentrations of Cu, Ni, Pb and Cd ions (obtained by ICP-OES analysis) were 50.1, 51.7, 53.6 and 52.0 mg L⁻¹, respectively, pH of ions solution was set at 6, and the mass of the adsorbent was 0.50 g. A 40 mL of Cu, Ni, Pb and Cd solutions were mixed with 0.50 g of sorbent material in PE bottles. The samples were shaken for 1, 3, 5, 15, 30 and 45 min, and thereafter the supernatant was filtered and stored in the fridge for the ICP-OES analysis. The residual sorbent was dried in an oven at 70 °C. The dried sorbent was placed in a plastic bag and stored in the desiccator for the LIBS analysis.

Simultaneous adsorption of Cd, Cu, Pb and Ni by treated sunflower husk. In order to test a tendency of Cd, Cu, Pb and Ni to be adsorbed from multielement solutions, seven samples containing similar concentrations of elements were prepared: Cu–Pb; Cu–Cd; Cu–Ni; Pb–Cd; Pb–Ni; Ni–Cd; Cu–Pb–Cd–Ni. A 40 mL of each sample was mixed with 0.50 g of sorbent material and the PE bottles with this content were agitated at 200 rpm on a platform shaker for 15 min. Finally, the supernatant was filtered and stored in the refrigerator for the ICP-OES analysis.

Adsorption isotherm. Adsorption isotherm experiments were carried out using seven single element solutions per element in a concentration range from 10 to 200 mg L⁻¹. A 20 mL of each solution was mixed with 0.50 g of sorbent material in PE bottles, and this content was

agitated at 200 rpm on a platform shaker for 15 min. The supernatant was filtered and metal concentrations in the filtrates were determined by ICP-OES. The experiment data have been analyzed by the use of linear forms of Langmuir and Freundlich isotherms. The Langmuir isotherm model is represented by the following equation, in linear expression:

$$\frac{c_e}{q_e} = \frac{1}{q_m K_L} + \frac{c_e}{q_m} \quad (3)$$

where q_e is the sorption uptake; c_e is the equilibrium concentration of the sorbate; q_m is the maximum amount of the sorbate per unit of the weight of the sorbent, and K_L is the Langmuir constant and it is related to the free energy of sorption.¹⁴

The linear expression of the Freundlich isotherm is represented by the following equation:

$$\log q_e = \log K_F + \frac{1}{n} \log c_e \quad (4)$$

where q_e is the metal uptake at equilibrium, K_F is the measure of the sorption capacity, $1/n$ is the sorption intensity, and c_e is the final ion concentration in the solution.²³

Calibration set preparation for LIBS analysis. In order to prepare a calibration, set for the LIBS analysis, a previously developed method for the matrix-matched standards was applied.²⁴ A 2 g of biosorbent were mixed with appropriate amounts of multielement standard. Mixtures were diluted with deionized water, homogenized, and dried at 70 °C overnight. The resulting dry mixture was homogenized. To check the concentration of the analytes in the LIBS calibration set, a small amount of samples were acid digested in the microwave and analyzed by ICP-OES.

Use of sorbent in wastewater. Two real samples were used in this study: a sample of technical water was spiked with a solution of the spectroscopically pure standard of Ni and one sample of industrial wastewater with elevated concentrations of Ni. A 40 mL of sample was treated with ~0.50 g of sorbent in a polypropylene bottle. The sample was shaken for 30 minutes at pH 6. The supernatant was filtered and stored in a fridge for ICP-OES analysis. The residual sorbent was dried in an oven at 70°C after that were placed in a plastic bag and stored in the desiccator for LIBS analysis.

ICP-OES analysis

All aqueous solutions, stock solutions of heavy metals, synthetic wastewater (spiked sample of technical water), and the real sample of wastewater, used for this research, were analyzed by Thermo Scientific iCap 7400 duo ICP-OES instrument before and after contact with the biosorbent. For calibration, 1000 mg L⁻¹ Multi-element ICP Standard solution (Chem-Lab, Belgium) was used. All measurements were performed in triplicate. The Thermo Scientific Qtegra Intelligent Scientific Data Solution (ISDS) software was used for data acquisition and processing.

LIBS analysis

The experimental setup used for the determination of heavy metals in the biosorbent is shown in Fig. 1. A 10.6 μm TEA CO₂ laser with a repetition rate of 1 Hz and output energy of 160 mJ was used to induce a plasma on the biosorbent surface. Optical emission from plasma was recorded using a Carl Zeiss PGS2 spectrometer equipped with an Apogee CCD camera. The entrance slit of the spectrometer was set at 30 μm, while the time of spectra acquisition was 5 s. Biosorbent sample was applied with adhesive tape on the metal sub-target (>99.9 % pure aluminum) and it was put on a continual motor to achieve that with every single pulse a fresh area of the sample was analyzed.

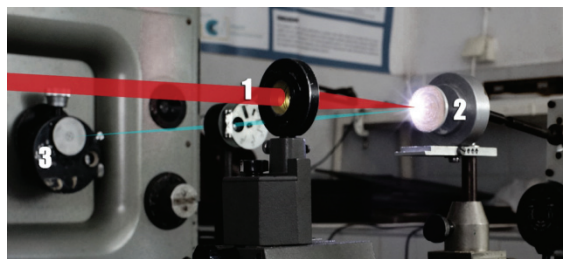


Fig. 1. LIBS experimental setup: 1) TEA CO₂ laser beam focus by ZnSe lens in front of the 2) metal sub-target covered with the biosorbent; 3) spectrometer for the acquisition of optical emission from laser-induced plasma.

Fourier transform infrared spectroscopy and scanning electron microscopy

Before and after being used, biosorbents were analyzed by Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM). FTIR spectra of the samples were recorded at ambient conditions in the mid-IR region (400–4000 cm⁻¹) with a Nicolet IS 50 FT-IR spectrometer (Thermo Fisher Scientific) operating in the ATR mode and measuring resolution of 4 cm⁻¹ with 32 scans. The peaks existing in the 2300–1800 cm⁻¹ spectral range represent artifacts from diamond crystal. ATR-FTIR spectra analyses served as a probe for the identification of surface functional groups before and after copper sorption. SEM was used to characterize the morphological changes of the surface of the sunflower husk before and after the biosorption process. SEM analysis of samples was performed using a JEOL JSM-6610LV scanning electron microscope (JEOL GmbH, Germany). The SEM instrument was operated at 20 kV. Before analysis, all samples were gold coated for electrical conduction.

RESULTS AND DISCUSSION

Biosorbent characterization

Fourier transform infrared spectroscopy. The ATR-FTIR spectra of biosorbent before and after copper ions sorption are presented in Fig. 2. Several absorption bands were detected which is in accordance with the complex nature of adsorption material. The spectra of non-treated biosorbent (Fig. 2a) contain bands that stem from vibrations of functional groups characteristic for lignocellulosic material. Strong and wide band originating from O–H stretching vibrations caused by the presence of alcoholic (cellulose, lignin) and phenolic hydroxyl groups (lignin) is appearing at 3337 cm⁻¹ in the spectrum of non-treated biosorbent (Fig. 2a). This band is shifted towards 3342 cm⁻¹ after Cu(II) solution adsorption, indicating the involvement of the OH group in the Cu²⁺ adsorption process. A very weak band observed at 3008 cm⁻¹ is due to =C–H stretching vibrations of phenyl propane lignin structure or unsaturated fatty acid,¹⁰ which disappeared after treatment of the sunflower seed hull sample with Cu(II) solution (Fig. 2b). The presence of –CH₂– (acyclic) in the sample was confirmed by the existence of two bands at 2923 and 2854 cm⁻¹ that are assigned to asymmetric and symmetric C–H stretching vibrations, respectively.²⁵ The structure of these two bands has been disrupted after treatment with a copper ions solution. A sharp

band of medium intensity appearing at 1741 cm^{-1} originates from characteristic vibration of the carbonyl group ($\text{C}=\text{O}$)²⁶ and is shifted towards 1734 cm^{-1} after $\text{Cu}(\text{II})$ sorption. The bands appearing at 1637 , 1508 and 1420 cm^{-1} are related to the aromatic skeletal vibrations of benzene ring in lignin and are assigned as follows:²⁷ $\text{C}=\text{O}$ stretching conjugated to the aromatic ring, aromatic skeletal vibrations of the benzene ring in lignin and $\text{C}-\text{H}$ deformation vibrations, respectively. The shift of a band originating from the $\text{C}=\text{O}$ stretching conjugated to the aromatic ring to a higher wavenumber value (1653 cm^{-1}) has been observed. Strong absorption observed at 1031 cm^{-1} is attributed to $\text{C}-\text{O}-\text{C}$ pyranose ring skeletal vibration (cellulose).²⁸

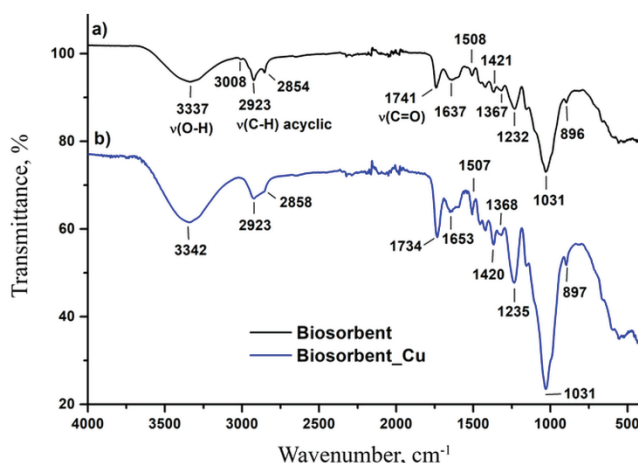


Fig. 2. Comparison of ATR FT-IR spectra of sunflower seed husk before (a) and after (b) sorption of $\text{Cu}(\text{II})$.

Scanning electron microscopy. The micrographs were recorded at two magnification scales using secondary electron image (SEI). Topography images are shown in Fig. 3. As can be observed from Fig. 3a, the surface of the sunflower husk is asymmetrical, heterogeneous, and has a microporous structure. There are no significant differences between these two samples regarding the morphology, but it seems that the surface of the sunflower husk becomes more heterogeneous after the sorption of copper from the aqueous solution. Additionally, EDX analysis is performed and approximately 0.68 % of Cu was detected in the biosorbent after the contact of the biosorbent with the aqueous solution of copper.

Effect of contact time and pH on biosorption. The effect of the contact time on the batch adsorption of Cu , Ni , Pb and Cd in an aqueous solution with pH 6 is shown in Fig. 4A. According to the results, it can be concluded that the uptake of these elements occurred almost instantly within the first 5 min. This fact implies that, on the surface of the sunflowers husk, there was a large number of functional

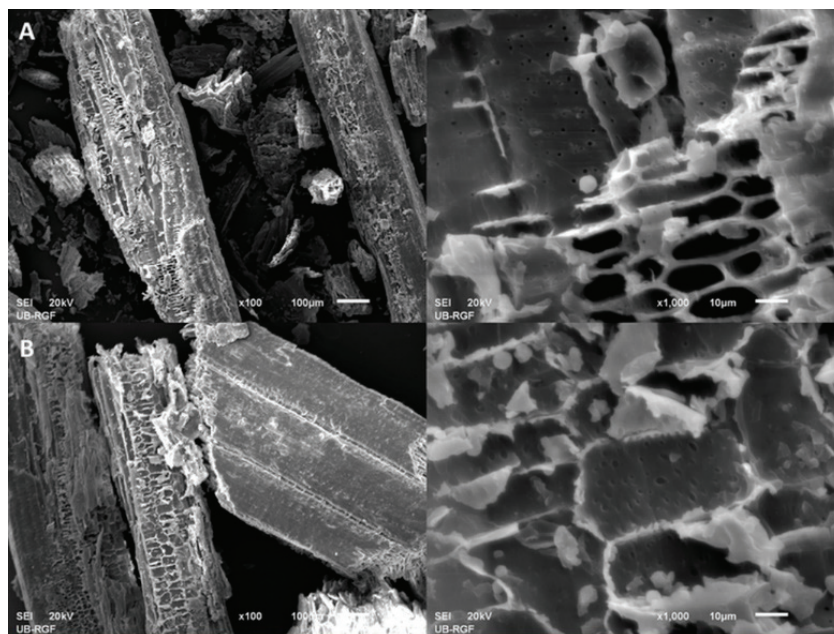


Fig. 3. Scanning electron micrographs of sunflower husk: A) before contact and B) after sorption of Cu from the aqueous solution (enlargement 100 and 1000×).

groups available to interact with the metal cations in the water solution. Two distinguished stages of adsorption can be observed. The first one is rapid and quantitatively predominant while the second one is slow and quantitative, Fig. 4A. This observation can be connected to the fact that initially the adsorption sites are available for interaction with these elements, and they can easily interact with them. After 5 min, these elements are accumulated in the large available

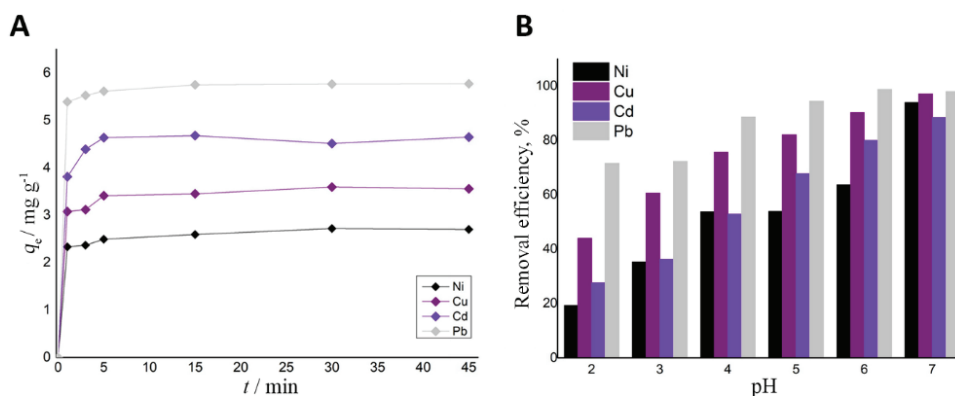


Fig. 4. Biosorbent efficiency evaluation using ICP-OES: A) effect of the time of contact and B) pH of aqueous solutions.

surface binding sites slowing down adsorption.²³ Competition of these elements has also been investigated. Several multi-element models were evaluated using their removal efficiency: Cu–Ni (94.4, 77.7 %), Pb–Ni (98.8, 83.65 %), Cu–Pb (94.5, 99.0 %), Ni–Cd (73.7, 86.4 %), Pb–Cd (92.82, 87.9 %) and Cu–Cd–Pb–Ni (76.4, 66.7, 77.4, 63.2 %). As it can be seen the highest removal efficiency is obtained for Pb in all combinations, and it can be acknowledged that the biosorbent shows an affinity for these elements in the following order Pb > Cu > Cd > Ni at pH 6.

Biosorbent efficiency evaluation using ICP-OES technique

The initial pH of the aqueous solution can affect the sorption process due to complexation reactions, electrostatic interactions, and precipitation between the heavy metal ions and biosorbent.²⁹ Fig. 4B illustrates a variation of the removal efficiency of Ni, Cu, Cd and Pb by sunflower husk-based biosorbent. At pH > 8 precipitations of all hydroxides started, and hence, higher pH was not investigated for the present study. At pH 2 sorption is negligible compared to the higher pH values. This can be associated with the competition of H⁺ with heavy metals ions for the adsorption sites. The highest removal efficiency was achieved at pH 7 for Ni and pH 6 for Pb. In Fig. 4B it can be seen that the highest removal efficiency for Cu and Cd is at pH 7. Considering that at this pH concentration of both elements available for the sorption decrease due to the formation and precipitation in form of hydroxides, it cannot be considered as a maximum efficiency of removal with the proposed method.

Biosorbent isotherms and kinetics. The adsorption isotherms describe the relationship between amount of adsorbate per unit mass of biosorbent and the concentration of the adsorbate when the equilibrium is reached. The experimental results obtained, for this purpose, were fitted to Eqs. (3) and (4) according to Langmuir and Freundlich model. Results are summarized in Table I. The biosorption process was well described by the linear form of the Freundlich model, and the adsorption intensity $1/n$ was less than 1 for all investigated elements, showing that this is favorable sorption. Furthermore, the values of regression coefficients (R^2) higher than 0.97 for Cu, Ni and Cd suggest that Langmuir isotherm well described the sorbent process for these elements.

TABLE I. Parameters of Langmuir and Freundlich isotherms models used to describe the adsorption of heavy metals on sunflower husk

Ion	Langmuir model			Freundlich model		
	$q_m / \text{mg g}^{-1}$	$K_L / \text{L mg}^{-1}$	R^2	$1/n$	$K_F / \text{mg g}^{-1} (\text{L mg}^{-1})^{1/n}$	R^2
Cu (II)	4.1697	0.8628	0.998	0.6335	0.7191	0.981
Ni (II)	2.4297	0.3276	0.9727	0.5509	0.3368	0.9626
Cd (II)	5.3302	0.6517	0.9831	0.5214	0.7145	0.9803
Pb (II)	9.9124	1.2538	0.2878	0.7404	1.6911	0.8399

The pseudo-second-order Eq. (5) where q_t is metal uptake capacity at any time t and k_2 is the rate constant,²³ fitted the experimental data fit very well with the correlation coefficient $R^2 > 0.999$:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

The equilibrium rate constant of the pseudo-second-order k_2 was in the range from 0.31–2.60 g mg⁻¹ min⁻¹ while the q_e were 2.69, 3.54, 4.85 and 5.82 for Ni ($y = 0.1616 + 0.3714x$), Cu ($y = 0.1616 + 0.3714x$), Cd ($y = 0.1616 + 0.3714x$) and Pb ($y = 0.1616 + 0.3714x$) respectively which is in accordance with the experimentally obtained values. These observations indicate that the biosorption of the tested metal cations follows a pseudo-second-order kinetic model and suggest that the cation adsorption process is controlled by a chemical reaction that has already been successfully applied to describe heavy metal biosorption on similar biosorbents.^{30,31}

Biosorbent efficiency evaluation using LIBS technique

Plasma was induced by irradiation of the biosorbent by TEA CO₂ laser at atmospheric pressure. Optical plasma emissions were observed at 1 mm from the surface of the target and each spectrum (Fig. 1) was recorded three times. Each time-integrated LIBS spectrum was recorded by accumulation measurements of 5 consecutive spectra (from 5 different positions on the sample), and the obtained emission lines of the elements of interest are given in Fig. 5A. By using synthetic standards, calibration curves have been constructed and used for the evaluation of the adsorbed concentration of heavy metals by biosorbent, Fig. 6. These calibration curves showed a low sensibility. This is caused by the strong matrix effect due to the large size of biosorbent particles and the complex nature of laser-sample interaction processes.²¹ It can be concluded that using finely ground materials can provide lower limits of detection. Furthermore, the effect of the contact

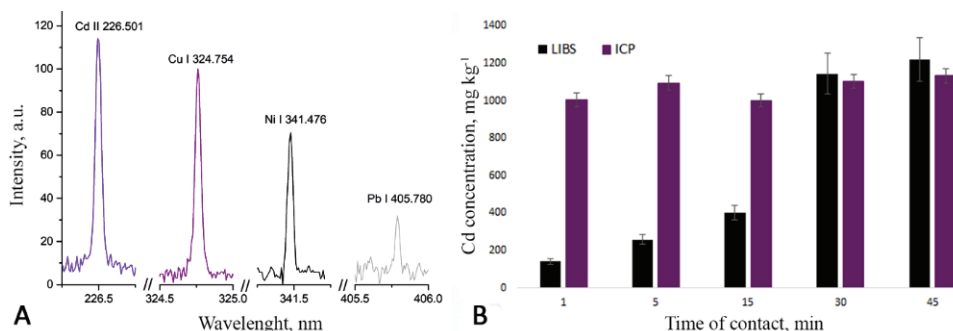


Fig. 5. LIBS analysis: A) segments of the LIBS spectra with the focus on the emission lines of analytes used in this study; B) comparison of measured concentration by LIBS and by ICP-OES technique.

time was investigated using this technique, and results were compared to the results estimated using the results of ICP-OES analysis of the supernatant. From Fig. 5B it can be observed that concentrations obtained by these two methods are in agreement when the contact time is about 30 min. Each LIBS spectrum represents an average spectrum from 5 different locations of the sample. Obtained results may indicate that sorption sites of biosorbent might be locally filled and need more time to achieve the equilibrium concentration. Even though the time for the batch testing is longer for the LIBS analysis than for the ICP-OES analysis, it cannot be considered time-consuming.

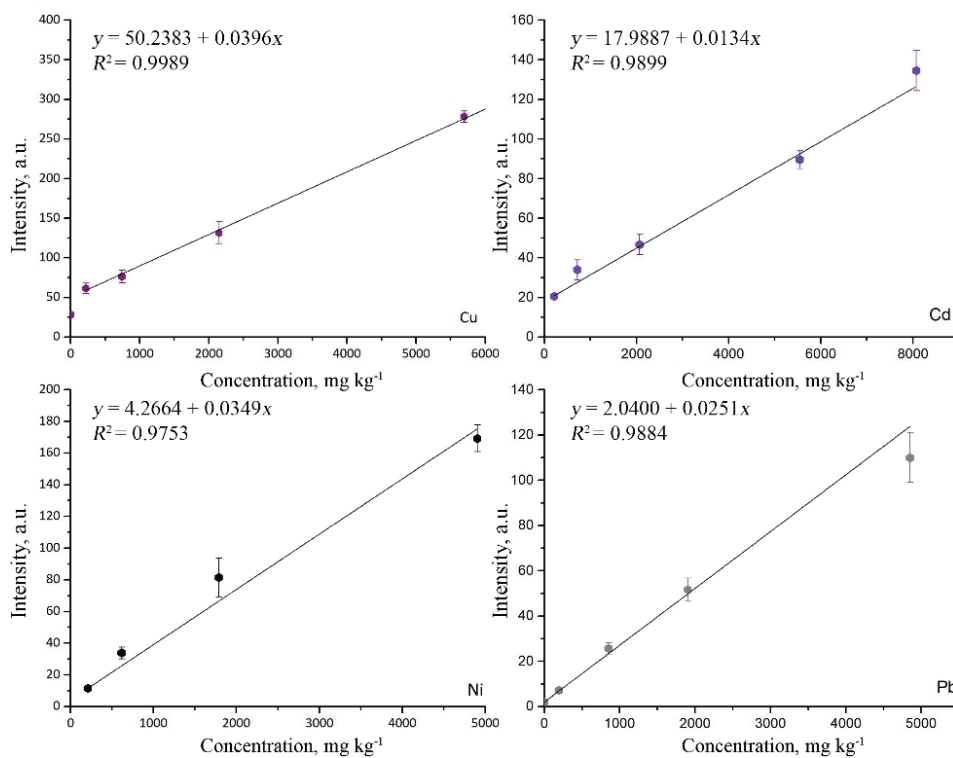


Fig. 6. LIBS calibration curves for 4 investigated elements.

Furthermore, the proposed method has been tested on the real sample of the industrial wastewater and one spiked sample of technical water. After the treatment, the biosorbent was analyzed by LIBS method while the supernatant was tested by ICP-OES technique. Using the results obtained by the ICP-OES analysis, the concentration of Ni in the sorbent after sorption was estimated. The obtained Ni values by LIBS method were 3100 ± 200 mg kg⁻¹ for the wastewater sample and 1240 ± 100 mg kg⁻¹ for the spiked technical water, while estimated values by the reference method (ICP-OES) were 2995 ± 20 and 1130 ± 10 mg kg⁻¹,

respectively. The difference between values obtained by these two methods is within the uncertainty of the LIBS method, proving that LIBS can be used as a “green alternative” for the evaluation of biosorption efficiency. Furthermore, LIBS instrumentation can be modified to be mobile, and it can be used for on-site measurements, which is not the case with the ICP-OES method. Moreover, zero waste is generated during the LIBS analysis while the sustainable character of the proposed method is additionally reinforced by the possibility of recovery and reuse of biosorbent.

CONCLUSION

The obtained results in the presented study revealed that acid pretreated biomass of sunflower husk can be used for the removal of heavy metals from aqueous solutions. Prepared biosorbent material was characterized by FTIR and SEM-EDS which showed shifting the bands of –OH and carbonyl (C=O) groups while the surface of the biosorbent became more heterogeneous affected by the adsorptions of copper ions. The removal percentage of heavy metals by biosorbent was investigated and results showed that for the Pb, Cu, Cd at pH 6 removal efficiency were 98.7, 90.3 and 80.0 %, respectively, and for Ni at pH 7 was 94.0 %. Langmuir and Freundlich isotherm models provide a good fit with the experimental data. The pseudo-second-order kinetic model fit excellent the experimental data while the calculated q_e these elements were in accordance with the experimentally obtained values. Furthermore, the efficiency to remove toxic metal ions from the real wastewater sample by the usage of the sunflower husk as a biosorbent was evaluated by LIBS, and these results were validated by the standard ICP-OES method. Even though TEA CO₂ LIBS method cannot be used for kinetic studies, from a green analytical chemistry point of view, it is a promising tool for on-site measurements.

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ИЗВОД

УКЛАЊАЊЕ ТЕШКИХ МЕТАЛА ИЗ ВОДЕНИХ РАСТВОРА ПОМОЋУ ЉУСКЕ СУНЦОКРЕТА: УПОРЕДНА СТУДИЈА ЕФИКАСНОСТИ БИОСОРПЦИЈЕ КОРИШЋЕЊЕМ ICP-OES И LIBS МЕТОДЕ

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Представљено истраживање имало је за циљ развој алтернативног поступка за процену биосорпционе ефикасности љуске сунцокрета. Биомаса сунцокрета, модификована

киселином, окарактерисана је скенирајућом електронском микроскопијом у комбинацији са енергетски дисперзивном спектроскопијом рендгенског зрачења (SEM-EDX) и инфрацрвеном спектроскопијом са Фуријеовом трансформацијом (FT-IR). Ефикасност биосорпције је процењена коришћењем оптичке емисионе спектроскопије индуктивно спрегнуте плазме (ICP-OES) и спектроскопије ласерски индуковане плазме (LIBS). Капацитет адсорпције адсорбента одређен је као функција рН раствора, почетне концентрације раствора тешких метала и времена контакта. Оптимални услови су постигнути након 15 min контакта на рН 6, док је проценат уклањања био од 80,0-98,7 %, у зависности од елемента. Резултати добијени кинетичким и изотермним студијама показују да је максимална адсорпција јона брзо постигнута и да прати кинетички модел псеудо-другог реда. Реални узорци су тестирани и добијене концентрације никла LIBS методом су биле 3100 ± 200 и 1240 ± 100 mg kg⁻¹, док су процењене вредности ICP-OES методом биле 2995 ± 20 и 1130 ± 10 mg kg⁻¹, респективно. Добијени резултати потврђују да се LIBS метода може користити као „зелена алтернатива“ за процену ефикасности биосорпције.

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