

Biosorption of lead ions from aqueous environment using Henna biomass

Fakhrosadat Mirnezami^a, Mehryar Jafari^b, Ali Jalali^c, Marzieh Lotfi^{d,*}, Mojtaba Shafiee^d, Amir H Mohammadi^{e,*}

^aDepartment of Chemistry, Razi University, Kermanshah, Iran, email: Mirnezami.f@gmail.com

^bDepartment of Environmental, Land and Infrastructure Engineering, Politecnico di Torino, Italy, email: Mehryar.jf@gmail.com

^cDepartment of Chemical Engineering, Amirkabir University of Technology, Tehran, Iran, email: ali.jaalali.aut@gmail.com

^dDepartment of Chemical Engineering, Jundi-Shapur University of Technology, Dezful, Iran, emails: marzyeh.lotfi@gmail.com (M. Lotfi), Shafiee_160@yahoo.com (M. Shafiee)

^eDiscipline of Chemical Engineering, School of Engineering, University of KwaZulu-Natal, Howard College Campus, King George V Avenue, Durban 4041, South Africa, email: amir_h_mohammadi@yahoo.com

Received 6 April 2021; Accepted 27 July 2021

ABSTRACT

The purpose of this study was to use Henna as a biosorbent to remove lead ions (Pb^{2+}) from an aqueous environment as an effective method for wastewater treatment. Dried leaves of Henna were ground and then passed through the standard screens to be used for the treatment process. The effects of main operating conditions, that is, time (20–200 min), biosorbent amount (0.1–1.2 g/L), and pH (2–9) on the percentage of removal of Pb^{2+} ions from aqueous solution using Henna were investigated. Maximum Pb^{2+} biosorption reached 90% at pH 5.5, 55 ppm initial concentration of Pb^{2+} ions, 1 g/L biosorbent amount, and 110 min time. Properties of biosorbent (before and after biosorption process) were characterized by Fourier-transform infrared spectroscopy and scanning electron microscopy. The Freundlich and Langmuir isotherm models were used to represent biosorption mechanisms so that the results of the Langmuir model with $R^2 = 0.9473$, are in better agreement with experimental data. Thermodynamic study indicates the biosorption process is exothermic in nature and thermodynamic parameters, $\Delta H = -25.16$ (kJ/mol) and $\Delta S = +55.146$ (J/mol K) were obtained. Kinetic studies were undertaken to determine the biosorption mechanism. The R^2 value of the pseudo-second-order kinetic model was found close to unity ($R^2 = 0.994$) indicating that the outcomes can adapt to this model better than a first-order kinetic model with $R^2 = 0.923$. The most important impact of using Henna is the high performance for the removal of the Pb^{2+} ions (90% removal efficiency) as the possible reason is due to its irregular surface structures and its availability and low price.

Keywords: Biosorption; Henna; Lead ions removal; Thermodynamic study; Kinetics; Isotherm

1. Introduction

Heavy metal (e.g., Pb, Hg, Cr, Cd, etc) ions in industrial wastewaters can pollute groundwater resources [1]. Lead is a shiny, toxic, soft metal with atomic number of 82, atomic mass equal to 207.2 g mol^{-1} , and Van der Waals radius of $202 \times 10^{-12} \text{ m}$ which is produced through industrial activities

such as mining, pigments, and printing processes, car batteries, petroleum and plating industries [2]. Heavy metals ions are considered as the top environmental pollutants and can cause serious environmental problems. Due to the high solubilities of heavy metals ions in aqueous environments, living organisms can adsorb them. By entering the food chain, they can cause harmful effects on human and

* Corresponding authors.

animal's health [3]. Thus, it is essential to remove heavy metals ions from wastewaters using conventional treatment processes to protect the environment [4].

There are various approaches for the development of technologies for wastewater treatment such as chemical precipitation [5], osmosis [6,7], ion exchange [8], filtration [9], electrochemical treatment [10], photocatalytic degradation [11,12], oxidation/reduction [13] and adsorption [14]. On the other hand, there are many limitations and problems in the application of these technologies, such as high-energy requirements, high costs, imperfect removal, and fabrication of toxic sludge. Adsorption process is strongly recommended for heavy metals ions removal as an effective and reasonably priced process. Selecting the right adsorbent with maximum adsorption characteristics and adsorption capacity and minimum consumption has been the subject of many studies in the last decade. In this regard, several research studies have been conducted to evaluate natural materials, agricultural waste materials, and agricultural products as adsorbents to remove Cd, Cr, Pb, Cu ions from aqueous solutions. [15–23] This approach is called biosorption and these natural adsorbents are well known as biosorbents that can be used without functionalization with high proficiency. Sometimes in order to make the biosorption process more suitable for industrial applications, natural materials are functionalized with numerous chemical reagents [24]. Local accessibility, technical possibility, being economical and technical applicability are the important factors in selecting these adsorbents for wastewater treatment processes. These natural materials have several compounds for instance lignin, cellulose, and pectin with different functional groups such as amino, carbonyl, hydroxyl, alkoxy, and carboxylic on their cells walls that have high affinities for the metal ions [25]. Some reported biosorptions such as tomato waste and apple juice residue [26], pine nuts shell [27], banana peels [18], rice husk [28], etc have proven that these natural compounds can be considered appropriate choices to remove heavy metals ions from aqueous solutions in the adsorption process.

Henna is a plant 5–6 m long with green, gray, elliptical leaves that mainly grows in some areas of Iran and some tropical areas of Asia and Africa [29]. Numerous studies have given the idea to use Henna as a potential adsorbent for removing heavy metals ions [29–32]. It is decided to use Henna in the biosorption process because of its availability and its low price. The main objective was to use Henna leaves as biosorbent for removing Pb^{2+} ions from an aqueous solution. Also, effective parameters on the percentage of removal of Pb^{2+} such as time, biosorbent amount, and pH were investigated and analyzed carefully. Thermodynamic and kinetic studies were conducted to determine the biosorption mechanism and thermodynamic parameters such as ΔH , ΔG , and ΔS . In order to study the interaction of Pb^{2+} ions with Henna, Freundlich, and Langmuir isotherm models [33,34] were applied. Furthermore, scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR) studies were conducted before and after the biosorption process. This process is facile and cheap for the treatment of the aqueous environment from the hazardous effects of Pb^{2+} ions.

2. Experimental section

2.1. Equipment and materials

SEM was performed using a LEO1450 VP microscope with a scanning range from 0 to 30 keV. FTIR was recorded as KBr pellets using a PerkinElmer spectrophotometer (USA) in the 400–4,000 cm^{-1} range. Pb^{2+} ions sorption capacity was measured using a Shimadzu Model AA-680 (Japan) atomic absorption spectrophotometer (AA). The solution pH was measured using a Metrohm pH meter model 691. Henna leaves powder was dried using a laboratory oven model OF-11E (JeioTech Company, South Korea). The solutions were stirred and heated using LABINCO mixer-heater model L-81. $Pb(NO_3)_2$ (Merck, Germany) was used as purchased. High-grade NaOH and HCl 37% (Merck, Germany) were used for the tests without further purification. Distilled water (Merck, Germany) was used in all experiments. Henna leaves were collected from Golbadestan, Yazd, Iran.

2.2. Preparation of biosorbent

Henna leaves powder was washed carefully with distilled water in order to remove dust and the soluble particles or the other contaminants present in it and it was then dried in an air oven at about 100°C for 24 h. Then, the powder was separated using an ASTM filter (70–100 mesh) and it was stored in a sample for subsequent experiments.

2.3. Batch biosorption studies

First, an aqueous solution of $Pb(NO_3)_2$ 55 ppm was prepared. Then, 100 mL of solution with pH (2–9) was poured into a 250 mL beaker [29]. The desired amount of biosorbent (0.1–1.2 g/L) was then weighed and shed in a beaker [29]. The mixture was intermixed using a mixer-heater (600 rpm) according to the desired temperature. After each test, the biosorbent was removed by filtration from the solution using the Whatman filter paper (no. 42). A few drops of HCl were added to the filtrated sample to prevent metal deposits. The samples were stored in a refrigerator at 4°C to be analyzed by the AA. Moreover, FTIR analysis was conducted to investigate the bonds position and changes of functional groups of biosorbent during the Pb^{2+} ions removal process. The surface morphology of Henna was investigated using SEM. All experiments were performed in a beaker with a volume of 250 mL at room temperature (24°C). Every test was carried out with 100 mL of solution. In order to investigate the effect of pH, solution of HCl or NaOH of 0.1 M was used.

2.4. Thermodynamic study, isotherm, and kinetic models

Different isotherm models have been developed for describing sorption equilibrium. In this study, Freundlich and Langmuir adsorption models [33,34] were used [17] to study the interaction of Pb^{2+} with biosorbent (Henna).

The Langmuir sorption isotherm [33] assumes that the adsorption takes place on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules [21] that is given by Eq. (1) [33]:

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

where C_e (mg/L) and q_e (mg/g) are the equilibrium concentration of adsorbate and the amount of adsorbate per unit mass of adsorbent, respectively, q_m (mg/g) is the maximum adsorption capacity, and K_L (L/mg) is the adsorption equilibrium constant. The constants K_L and q_m can be determined from the slope and intercept of the plot between C_e/q_e and C_e .

The Freundlich isotherm [34] assumes that the adsorption occurs with multilayer adsorption on the heterogeneous surface and the adsorption increases with an increase in concentration [21].

The Freundlich model is given by Eq. (2) [34]:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (2)$$

where n and K_F (L/mg) are the constants of Freundlich equation [34]. K_F represents the adsorption capacity for the absorbed material and n is the heterogeneity factor. By plotting the linear regression of $\log q_e$ vs. $\log C_e$ from the intercept and slope, K_F and n can be obtained.

It is required to determine the thermodynamic parameters to evaluate the nature of the biosorption between the Henna and Pb^{2+} ions using Eqs. (3) and (4) [35,36]:

$$\Delta G = -RT \ln K_c; \Delta G = \Delta H - T\Delta S \quad (3)$$

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT}, K_c = \frac{C_e}{C_0 - C_e} \quad (4)$$

where K_c is the equilibrium constant, ΔS represents the entropy (J/mol K), ΔH stands for the enthalpy (J/mol) and ΔG is the Gibbs free energy (J/mol), and C_0 and C_e are the initial and equilibrium concentrations of the adsorbate, respectively. T is the absolute temperature (K), and R represents the gas constant (8.314 J/mol K). In general, adsorption is accompanied by a thermal process that can either be exothermic $\Delta H < 0$ or endothermic $\Delta H > 0$. The measurement of the heat of ΔH is the main criterion that differentiates chemisorption from physisorption.

To investigate the adsorption mechanism, the adsorption constants of adsorbate can be measured using the Lagergren equation, pseudo-first-order kinetic model [37], and Ho equation, pseudo-second-order kinetic model [38]:

The pseudo-first-order kinetic model can be described by Eq. (5) [37]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (5)$$

In this equation, q_e and q_t (mg/g) are the amounts of adsorbate adsorbed at equilibrium and at any contact time t , respectively, and k_1 (1/min) represents the rate constant of adsorption reaction. In this equation, if $\log(q_e - q_t)$ is plotted vs. t , a straight line is obtained, which can be used to obtain the constant k_1 and R^2 .

The adsorption kinetics can also be explained by the pseudo-second-order kinetic model that can be described by Eq. (6) [38]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

where k_2 (g/mg min) is the pseudo-second-order rate constant, q_t (mg/g) represents the amount of adsorbate adsorbed at any time t , and q_e (mg/g) stands for the amount of adsorbate adsorbed in equilibrium.

3. Results and discussion

3.1. Thermodynamic study

The thermodynamic parameters at different temperatures are listed in Table 1 and are shown in Fig. 1. The negative values of ΔG and ΔH confirm the spontaneous and exothermic nature of the biosorption process of Pb^{2+} ions from an aqueous solution onto Henna. In addition, considering the data of Table 1, decreased solution temperature would result in increased values of ΔG that is desirable from thermodynamics point of view. There is a physical biosorption between Pb^{2+} and Henna because of the low value of ΔH (<40 kJ/mol). The positive value of entropy suggests spontaneity of the Pb^{2+} ions biosorption process [35,39].

3.2. SEM study

SEM was used to investigate the morphology of the biosorbent before and after the metal ions removal process. Fig. 2 illustrates that the Henna is made up of irregular surface structures with some pores, which are very suitable for metal ions biosorption. It can be observed that the structure of treated Henna is aggregated after the metal ions removal process and indicates Pb^{2+} biosorption and binding on its surface porosity [32].

3.3. FTIR analysis

The FTIR spectra is useful to study the characteristics of the biosorbent functional groups involved in Pb^{2+} ions during biosorption processes. FTIR spectrum of Henna is illustrated in Fig. 3, comparing with that of the after Pb^{2+} ions removal processes. The broadband around 3409 cm^{-1} is related to O–H functional group and its shift of band position to 3400 cm^{-1} indicates Pb^{2+} ions binding to the O–H group. The strong band at 1,632 cm^{-1} is assigned to the C=O

Table 1
Thermodynamic parameters values for Pb^{2+} biosorption from aqueous solution using Henna

T (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol K)
298	–8.66		
308	–8.31		
318	–7.65	–25.166	+55.146
328	–7.03		

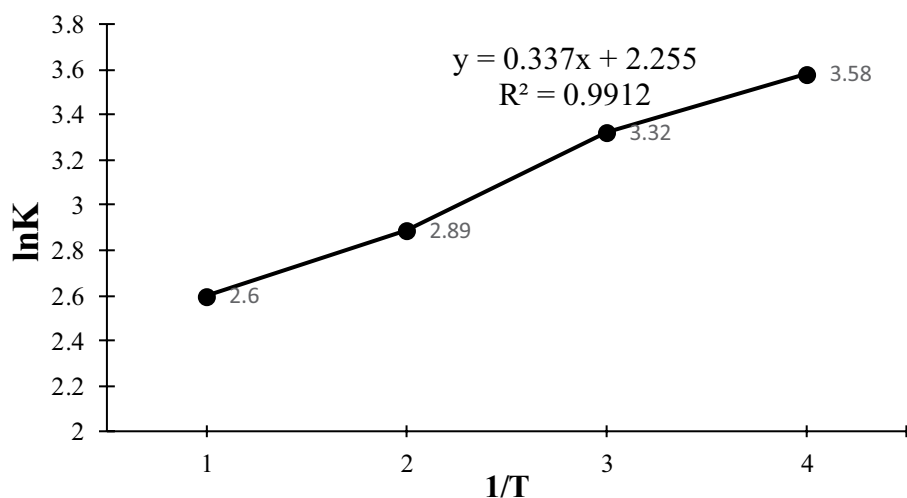


Fig. 1. Determination of thermodynamic parameters of Pb^{2+} ions biosorption from aqueous solution using Henna.

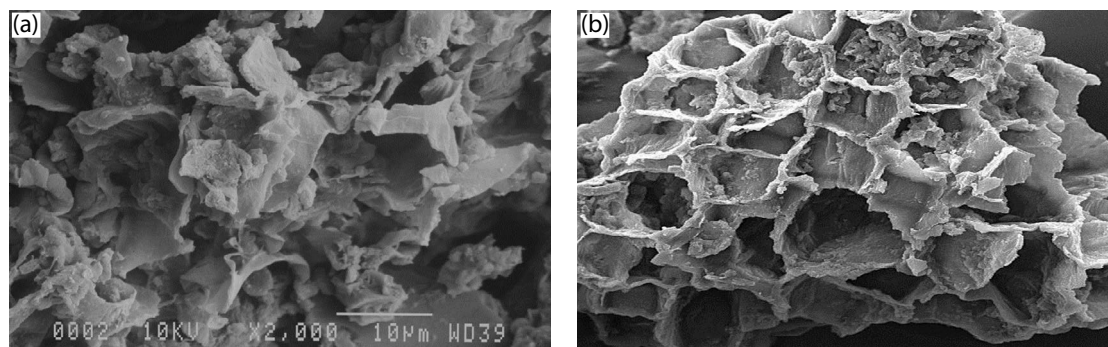


Fig. 2. SEM image of Henna: before (a) and after (b) Pb^{2+} ions removal process.

functional group while shows a slight shift to $1,641\text{ cm}^{-1}$ indicating Pb^{2+} ions biosorption onto $\text{C}=\text{O}$ functional group. Additionally, the band at $1,055\text{ cm}^{-1}$ can be attributed to the presence of $\text{C}-\text{O}$ stretching vibration along with a shift to $1,035\text{ cm}^{-1}$ due to Pb^{2+} ions binding to $\text{C}-\text{O}$ [32]. The new bands at $500\text{--}700\text{ cm}^{-1}$ are probably due to the presence of the $(\text{Pb}-\text{O})$ band [19]. These observations once more confirm that the functional groups existing in Henna provide an electron, which increases Pb^{2+} biosorption tendency [29–31].

3.4. Effect of pH

pH is a significant factor in the biosorption process that can affect the surface charge of the biosorbent, the amount of ionization, and speciation of the adsorbate. On the other hand, the sorption process is pH-dependent. Hence, biosorption efficiency was assayed in the pH range of 2–9 and adjusted using NaOH or HCl solution. The tests were carried out at a mixing rate of 600 rpm, 55 ppm initial concentration of Pb^{2+} ions, 0.55 g/L biosorbent, and 110 min time. Pb^{2+} ions removal as a function of pH is shown in Fig. 4a. Initially, at pH = 2, Pb^{2+} ions removal was 19.77%. By increasing the pH to 5.5, the efficiency of Pb^{2+} ions removal was improved and reached 72%. This trend is due to competition between Pb^{2+} ions and the protons on the

active sites of biosorbent surface in high concentration of H^+ ions. There are many protons at lower pH, which surround the binding sites of Henna and easily adsorb functional groups on its surface [19,21,40,41]. Increasing the pH to a higher value, 9, showed 45.2% Pb^{2+} ions removal, which was decreased since at higher pH, most of the functional groups are protonated and Pb^{2+} ions precipitate as they form hydroxides like $\text{Pb}(\text{OH})_2$ and $\text{Pb}(\text{OH})^+$ in the solution [19,21,40,41]. Considering the aforementioned results, pH = 5.5 was chosen as the optimum value and this state was used in the further steps of this study. This trend is in good agreement with the experimental results, which report a pH between 5–6 as the optimum value for the biosorption of Pb^{2+} ions onto several biosorbents [42].

3.5. Effect of biosorbent–adsorbate contact time

Fig. 4b demonstrates the effect of biosorbent–adsorbate contact time during the removal of the Pb^{2+} ions. These tests were carried out at a mixing rate of 600 rpm, pH of 5.5, 55 ppm initial concentration of Pb^{2+} ions, 0.55 g/L biosorbent, and time period of 20–200 min. The biosorption process involves two fast and slow steps.

With a biosorption time period of 0–110 min, the efficiency of Pb^{2+} ions removal was reached 80%. The initial

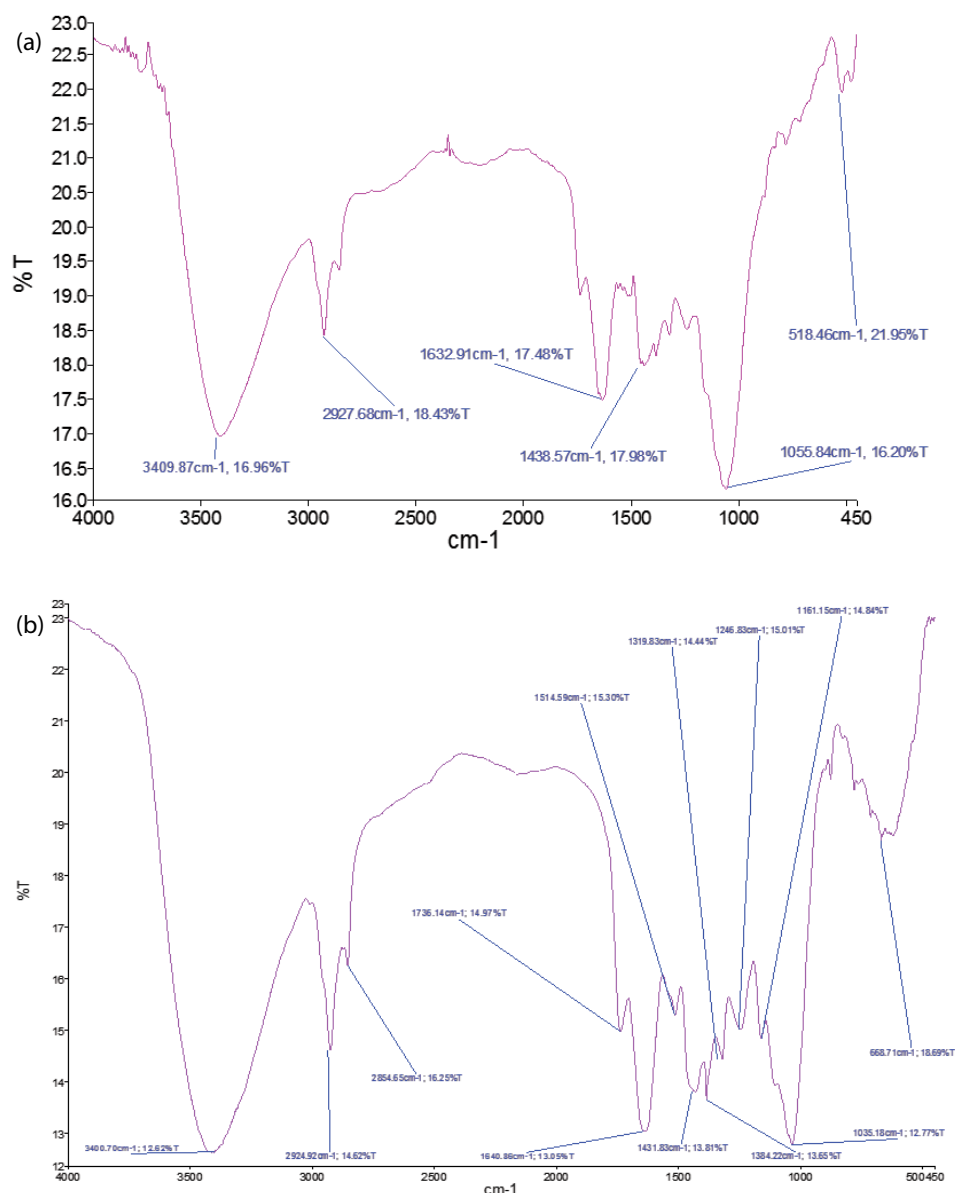


Fig. 3. FTIR spectra of Henna: before (a) and after (b) the Pb^{2+} ions removal process.

biosorption rate increased due to mass transfer driving force between the active sites of the biosorbent and the Pb^{2+} ions, and it remained constant until 200 min. Since Pb^{2+} ions occupied a portion of the active sites, the biosorption process remained constant (equilibrium) after 110 min. The parameters that affect the equilibrium adsorption time are the biosorbent's physical properties. Notably, equilibrium states were reached following the saturation of active sites [26]. Consequently, the optimum biosorption time for Pb^{2+} ions binding onto the Henna surface was estimated to be 110 min.

3.6. Effect of biosorbent amount

Biosorbent amount is an important factor that affects the metal removal process. Fig. 4c reveals the effect of

biosorbent mass on the Pb^{2+} biosorption at pH of 5.5, contact time of 110 min, 55 ppm initial concentration of Pb^{2+} ions, and 0.1–1.2 g/L biosorbent amount. With the increase in biosorbent amount, Pb^{2+} removal increased, maximizing at 90.5%. This might be due to an increase of sorptive surface area and the more availability of biosorption active sites [43,44]. Further increase in biosorbent does not enhance metal removal because the available metal ions are already adsorbed by the biosorbent [45]. Considering the abovementioned results, 1 g/L biosorbent was chosen as the optimum amount.

3.7. Biosorption isotherms study

Two isotherm models namely Langmuir [33] and Freundlich [34] were used in this study. The calculated

isotherm parameters are presented in Table 2 and Fig. 5. The R^2 coefficient is considered as a measure of agreement of experimental data with the isotherm models results [40]. In two cases, the R^2 values reveal the good applicability of both models for describing the biosorption of Pb^{2+} ions onto the biosorbent. However, as can be seen, the Freundlich isotherm model [34] is not suitable ($R^2 = 0.8185$). The R^2 value for the Langmuir [33] model ($R^2 = 0.9473$) is higher than the other so that it displays a better fit compared to the Freundlich model [34]. This indicates that there is likely a homogeneous distribution of active sites on the biosorbent surface and monolayer biosorption (considering the initial assumptions of the Langmuir model [33]). A dimensionless constant separation factor or the equilibrium parameter R_L

specified by Eq. (7) can be used to represent the feasibility of the Langmuir isotherm model [33]:

$$R_L = \frac{1}{(1 + K_L C_0)} \quad (7)$$

where the Langmuir constant is represented by K_L , and the initial metal concentration is C_0 (mg/L). The R_L value indicates whether the isotherm is unfavourable ($R_L > 1$), linear ($R_L = 1$), irreversible ($R_L = 0$), or favourable ($0 > R_L > 1$). The R_L value obtained in this work during the biosorption of Pb^{2+} by Henna was 0.17 indicating Pb^{2+} ions biosorption onto the Henna surface is favorable.

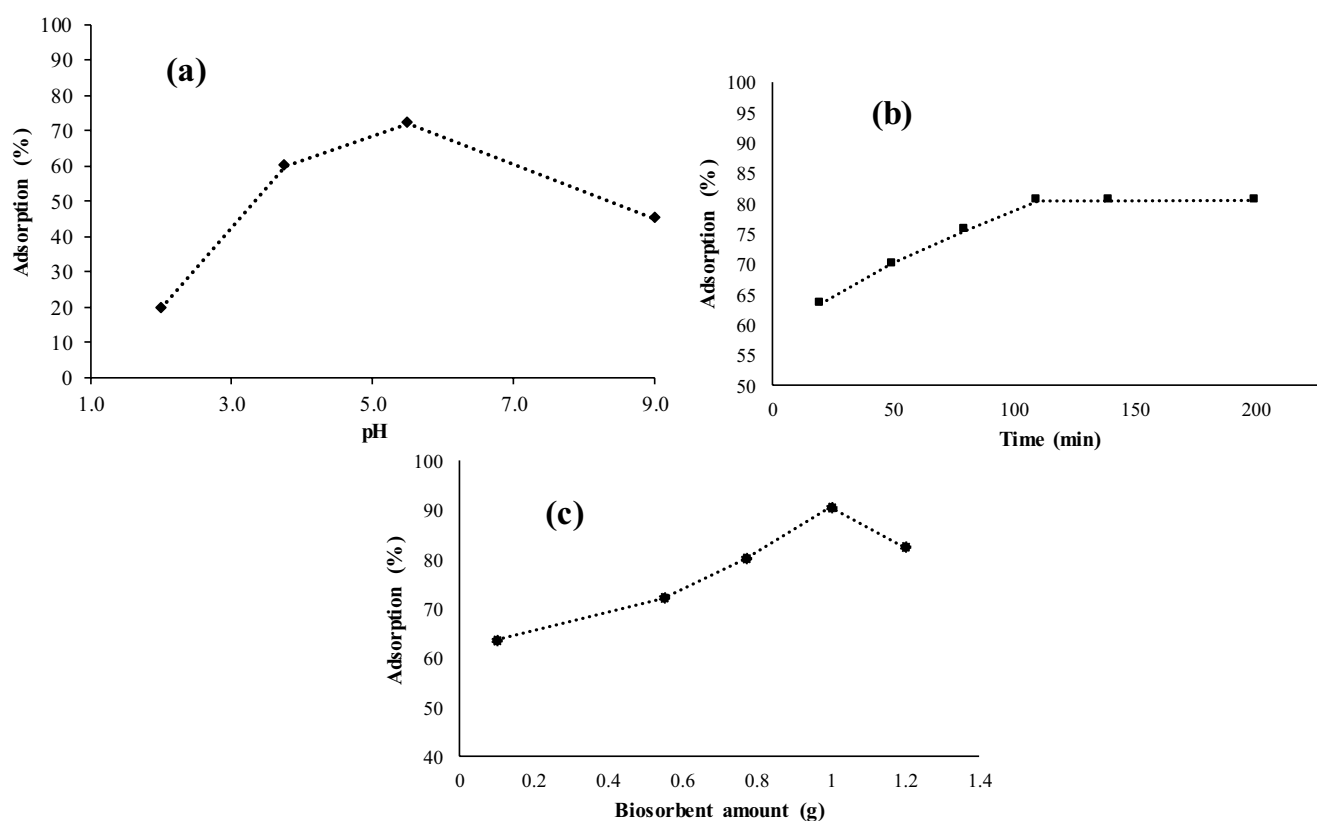


Fig. 4. Effect of pH on biosorption of Pb^{2+} ions from aqueous solution using Henna at mixing rate of 600 rpm, 55 ppm initial concentration of Pb^{2+} ions, 0.55 g/L biosorbent, 110 min time and 2–9 pH range (a), Effect of time on biosorption of Pb^{2+} ions from aqueous solution using Henna at mixing rate of 600 rpm, pH of 5.5, 55 ppm initial concentration of Pb^{2+} ions, 0.55 g/L biosorbent and 20–200 min time period (b), Effect of biosorbent on amount of biosorption of Pb^{2+} ions from aqueous solution using Henna at mixing rate of 600 rpm, pH of 5.5, contact time of 110 min, 55 ppm initial concentration of Pb^{2+} ions and 0.1–1.2 g/L biosorbent amount (c).

Table 2
Calculated isotherm parameters

Freundlich [34]	Langmuir [33]	Isotherm
$\ln q_e$ vs. $\ln C_e$	C_e/q_e vs. C_e	Plot
$\ln q_e = 0.5524 \ln C_e + 1.5374$	$C_e/q_e = 0.026 C_e + 0.3058$	Model
0.8185	0.9473	R^2
$K_F = 4.65$ (L/mg)	$K_L = 0.085$ (L/mg)	Adsorption isotherm parameters
$n = 1.81$	$q_{\max} = 38.46$ (mg/g)	

3.8. Biosorption kinetics

The adsorption rate is one of the most important factors in an adsorption process [46]. The biosorption kinetics depends on the physical and chemical properties of the adsorbent, which affects the biosorption mechanism [36]. In this section, the kinetic study of the biosorption process

was undertaken and the results of the pseudo-first-order kinetic model [37] were compared with the results of the pseudo-second-order kinetic model [38] to have an idea about the rate of adsorption and its nature such as chemical adsorption or physical adsorption. Curves for these models are shown in Fig. 6. Also, the results of the comparison

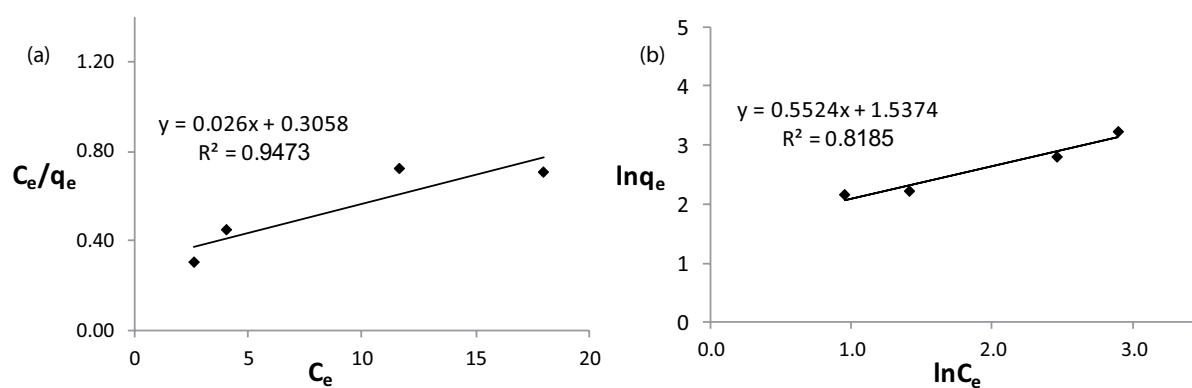


Fig. 5. Langmuir (a) and Freundlich (b) biosorption isotherms [33,34] for Pb²⁺ ions removal from aqueous solution using Henna.

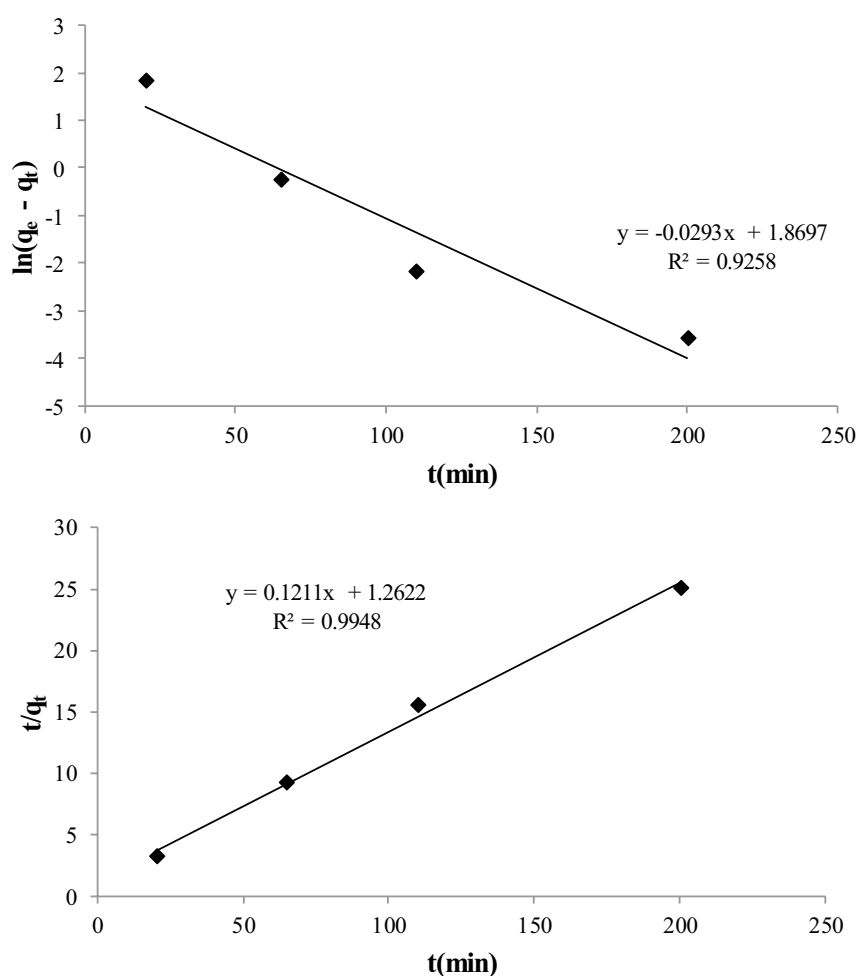


Fig. 6. Pseudo-first-order [37] and pseudo-second-order [38] kinetic plots for biosorption of Pb²⁺ ions from aqueous solution using Henna.

Table 3
Data of pseudo-first-order and pseudo-second-order kinetic models [37,38]

Pseudo-first-order kinetics [37]			Pseudo-second-order kinetics [38]		
q_e -Calculated (mg/g)	k_1 (1/min)	R^2	q_e -Calculated (mg/g)	k_2 (g/mg min)	R^2
6.423	0.029	0.923	8.25	0.01	0.994

Table 4
Comparison of the results of this work with other results for biosorption of Pb^{2+} ions from an aqueous environment reported in the literature

Biosorbent	Time	pH	Removal percentage	Initial concentration	References
Straw from <i>Triticum aestivum</i>	15 min	6	80%	10 ppm	[47]
Peanut husk powder	3 h	6	>90%	20 ppm	[48]
Coconut husk	30 min	5	72.4%	500 ppm	[49]
<i>Absidia cylindrospora</i>	3 d	5.4	59%	50 ppm	[50]
<i>Lactobacillus acidophilus</i>	–	4.0	>69%	35 ppb	[51]
Henna leaves	110 min	5.5	90%	55 ppm	This work

between pseudo-first-order and pseudo-second-order kinetic models [37,38] are displayed in Table 3.

According to the obtained results, the R^2 value of the first-order kinetic model [37] is 0.923, indicating that the results are not fully consistent with the first-order kinetic model [37]. On the other hand, the R^2 value of the pseudo-second-order kinetic model [38] is close to unity ($R^2 = 0.994$) indicating that the outcomes are more able to adapt to this model. Table 3 shows that the experimental value of q_e ($q_e = 8$) is closer to the value of q_e obtained from the pseudo-second-order model [38] ($q_e = 8.25$) rather than the value of q_e obtained from the pseudo-first-order model [37] ($q_e = 6.42$). This indicates that the chemical sorption incorporating valence forces through the exchange or sharing of electrons between Henna and Pb^{2+} ions is likely the rate-limiting stage in the biosorption process [23,26].

3.9. Proposed removal mechanism

There are many functional groups on the cell wall of the biosorbents, such as amine (NH_2), carboxyl ($C=O$), hydroxyl ($R-OH$), and sulfhydryl that carry out the removal of metal ions from the aqueous environment. These functional groups can serve as coordination and electrostatic interaction sites to adsorb metal ions. As mentioned in the FTIR section, OH and $C=O$ functional groups get involved in Pb^{2+} ions removal during biosorption process. A solid phase (Henna) and an aqueous phase containing lead ions are involved in the process. The following is a brief description of the proposed adsorption mechanism [17]:

- Ion exchange: $2(R'OH) + Pb^{2+} \leftrightarrow (R'O)_2-Pb + 2H^+$
- Hydrogen bonding: $(R'OH) + Pb^{2+} \leftrightarrow (R'OH)-Pb^{2+}$

where R' represents the matrix of Henna.

3.10. Other studies

In recent years, various studies have been carried out using biosorbents to remove toxic metals from an aqueous

environment, especially Pb^{2+} ions. A few examples of them with their experimental conditions are given in Table 4 [47–51]. Farooq et al. [47] reported the usage of powdered straw from *Triticum aestivum* for 80% removal of Pb^{2+} ions from aqueous solution. Abdelfattah et al. [48] worked on peanut husk powder for the removal of some metal ions like Pb^{2+} with over 90% removal efficiency from their aqueous solutions. Biosorption of Pb^{2+} , Cu^{2+} , Ni^{2+} and Zn^{2+} ions using agricultural waste, unmodified coconut husk from industrial wastewater with 72.4% removal of Pb^{2+} ions was reported by Lata's group [49]. There is a study on the use of fungus *Absidia cylindrospora* against three trace metals: Cd^{2+} , Cu^{2+} , and Pb^{2+} having 59% removal efficiency for Pb^{2+} ions [50]. Investigation of removal efficiency of Pb^{2+} (over 69% removal efficiency) and Cd^{2+} from their aqueous solutions using *Lactobacillus acidophilus* was carried out by Afraz et al. [51] to optimize the operational parameters. Their results are very promising indicating the good capabilities of these natural materials as adsorbents to replace other types of adsorbents. Comparing the results of this work with other results yields two points: First, the high performance of biosorbent for the removal of the Pb^{2+} ions (90% removal efficiency) using Henna after 110 min, which the possible reason is irregular surface structures with some pores of adsorbent, and second important point is the availability and low price of Henna.

4. Conclusion

This work confirms the application of Henna as an efficient biosorbent for removing Pb^{2+} ions from an aqueous solution. Different tests were conducted to assess the effect of process variables including biosorbent amount (0.1–1.2 g/L), pH of the solution (2–9), and time (20–200 min). Maximum Pb^{2+} biosorption reached 90% at pH 5.5, 55 ppm initial concentration of Pb^{2+} ions, 1 g/L biosorbent amount, and 110 min time. Thermodynamic results reveal the endothermic nature of the biosorption of Pb^{2+} ions from an aqueous solution using Henna. Freundlich and Langmuir

isotherm models [33,34] were used to fit the experimental data. The data are in better agreement with the results of the Langmuir isotherm model [33] considering a better R^2 value. FTIR and SEM techniques clearly show that Pb^{2+} ions are stabilized and coated on the surface of Henna. The pseudo-second-order kinetic model [38] is a suitable model for representing the kinetics of the studied system. From the obtained results, it is concluded that this water treatment method can offer several benefits such as facile and low-cost route that makes it an interesting method for applying and extending this biosorbent for removing heavy metals from an aqueous environment.

References

- [1] N.S. Satarkar, J.Z. Hilt, Hydrogel nanocomposites as remote-controlled biomaterials, *Acta Biomater.*, 4 (2008) 11–16.
- [2] L. Joseph, B.-M. Jun, J.R.V. Flora, C.M. Park, Y. Yoon, Removal of heavy metals from water sources in the developing world using low-cost materials: a review, *Chemosphere*, 229 (2019) 142–159.
- [3] S. Babel, T.A. Kurniawan, Cr(VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan, *Chemosphere*, 54 (2004) 951–967.
- [4] P. Dhiman, S. Sharma, A. Kumar, M. Shekh, G. Sharma, Mu. Naushad, Rapid visible and solar photocatalytic Cr(VI) reduction and electrochemical sensing of dopamine using solution combustion synthesized $ZnO-Fe_2O_3$ nano heterojunctions: mechanism elucidation, *Ceram. Int.*, 46 (2020) 12255–12268.
- [5] Q. Chen, Y. Yao, X. Li, J. Lu, J. Zhou, Z. Huang, Comparison of heavy metal removals from aqueous solutions by chemical precipitation and characteristics of precipitates, *J. Water Process Eng.*, 26 (2018) 289–300.
- [6] J. Wang, X. Liu, Forward osmosis technology for water treatment: recent advances and future perspectives, *J. Cleaner Prod.*, 280 (2020) 124354, doi: 10.1016/j.jclepro.2020.124354.
- [7] N. Abdullah, M.H. Tajuddin, N. Yusof, Chapter 10 – Forward Osmosis (FO) for Removal of Heavy Metals, A. Ahsan, A.F. Ismail, Eds., *Nanotechnology in Water and Wastewater Treatment: Theory and Applications Micro and Nano Technologies*, Elsevier, Amsterdam, The Netherlands, 2019, pp. 177–204.
- [8] J.P. Bezzina, L.R. Ruder, R. Dawson, M.D. Ogden, Ion exchange removal of Cu(II), Fe(II), Pb(II) and Zn(II) from acid extracted sewage sludge – resin screening in weak acid media, *Water Res.*, 158 (2019) 257–267.
- [9] S. Haas, V. Boschi, A. Grannas, Metal sorption studies biased by filtration of insoluble metal oxides and hydroxides, *Sci. Total Environ.*, 646 (2019) 1433–1439.
- [10] T.-K. Tran, K.-F. Chiu, C.-Y. Lin, H.-J. Leu, Electrochemical treatment of wastewater: selectivity of the heavy metals removal process, *Int. J. Hydrogen Energy*, 42 (2017) 27741–27748.
- [11] G. Sharma, A. Kumar, S. Sharma, A.H. Al-Muhtaseb, Mu. Naushad, A.A. Ghfar, T. Ahamad, F.J. Stadler, Fabrication and characterization of novel Fe^0 @Guar gum-crosslinked-soya lecithin nanocomposite hydrogel for photocatalytic degradation of methyl violet dye, *Sep. Purif. Technol.*, 211 (2019) 895–908.
- [12] A. Kumar, G. Sharma, Mu. Naushad, A.H. Al-Muhtaseb, A. García-Peñas, G.T. Mola, C. Si, F.J. Stadler, Bio-inspired and biomaterials-based hybrid photocatalysts for environmental detoxification: a review, *Chem. Eng. J.*, 382 (2020) 122937, doi: 10.1016/j.cej.2019.122937.
- [13] E.J. Kim, K. Baek, Selective recovery of ferrous oxalate and removal of arsenic and other metals from soil-washing wastewater using a reduction reaction, *J. Cleaner Prod.*, 221 (2019) 635–643.
- [14] R. Shahrokhi-Shahraki, C. Benally, M.G. El-Din, J. Park, High efficiency removal of heavy metals using tire-derived activated carbon vs commercial activated carbon: insights into the adsorption mechanisms, *Chemosphere*, 264 (2021) 128455, doi: 10.1016/j.chemosphere.2020.128455.
- [15] A.F. El-Kafrawy, S.M. El-Saeed, R.K. Farag, H.A. Al-Aidy El-Saied, M. El-Sayed Abdel-Raouf, Adsorbents based on natural polymers for removal of some heavy metals from aqueous solution, *Egypt. J. Pet.*, 26 (2017) 23–32.
- [16] S. Chowdhury, P. Saha, Sea shell powder as a new adsorbent to remove Basic Green 4 (Malachite Green) from aqueous solutions: equilibrium, kinetic and thermodynamic studies, *Chem. Eng. J.*, 164 (2010) 168–177.
- [17] M.R. Lasheen, N.S. Ammar, H.S. Ibrahim, Adsorption/desorption of Cd(II), Cu(II) and Pb(II) using chemically modified orange peel: equilibrium and kinetic studies, *Solid State Sci.*, 14 (2012) 202–210.
- [18] A. Ali, K. Saeed, F. Mabood, Removal of chromium(VI) from aqueous medium using chemically modified banana peels as efficient low-cost adsorbent, *Alexandria Eng. J.*, 55 (2016) 2933–2942.
- [19] H. Khoshshang, A. Ghaffarinejad, Rapid removal of lead(II) ions from aqueous solutions by saffron flower waste as a green biosorbent, *J. Environ. Chem. Eng.*, 6 (2018) 6021–6027.
- [20] M.J. Rwiza, S.-Y. Oh, K.-W. Kim, S.D. Kim, Comparative sorption isotherms and removal studies for Pb(II) by physical and thermochemical modification of low-cost agro-wastes from Tanzania, *Chemosphere*, 195 (2018) 135–145.
- [21] Ş. Taşar, F. Kaya, A. Özer, Biosorption of lead(II) ions from aqueous solution by peanut shells: equilibrium, thermodynamic and kinetic studies, *J. Environ. Chem. Eng.*, 2 (2014) 1018–1026.
- [22] Y. Wang, B. Yi, X. Sun, L. Yu, L. Wu, W. Liu, D. Wang, Y. Li, R. Jia, H. Yu, Removal and tolerance mechanism of Pb by a filamentous fungus: a case study, *Chemosphere*, 225 (2019) 200–208.
- [23] G. Wang, S. Zhang, P. Yao, Y. Chen, X. Xu, T. Li, G. Gong, Removal of Pb(II) from aqueous solutions by *Phytolacca americana* L. biomass as a low cost biosorbent, *Arabian J. Chem.*, 11 (2018) 99–110.
- [24] L. Bulgariu, D. Bulgariu, Functionalized soy waste biomass – a novel environmental-friendly biosorbent for the removal of heavy metals from aqueous solution, *J. Cleaner Prod.*, 197 (2018) 875–885.
- [25] S. Kamel, H. Abou-Yousef, M. Yousef, M. El-Sakhawy, Potential use of bagasse and modified bagasse for removing of iron and phenol from water, *Carbohydr. Polym.*, 88 (2012) 250–256.
- [26] E. Herald, W.W. Lestari, D. Permatasari, D.D. Arimurti, Biosorbent from tomato waste and apple juice residue for lead removal, *J. Environ. Chem. Eng.*, 6 (2018) 1201–1208.
- [27] G. Blazquez, M. Calero, C. Trujillo, A. Martin-Lara, A. Ronda, Binary biosorption of Cu(II)-Pb(II) mixtures onto pine nuts shell in batch and packed bed systems, *Environ. Eng. Manage. J.*, 17 (2018) 1349–1361.
- [28] B. Singha, S.K. Das, Adsorptive removal of Cu(II) from aqueous solution and industrial effluent using natural/agricultural wastes, *Colloids Surf., B*, 107 (2013) 97–106.
- [29] R. Davarnejad, P. Panahi, Cu(II) and Ni(II) removal from aqueous solutions by adsorption on Henna and optimization of effective parameters by using the response surface methodology, *J. Ind. Eng. Chem.*, 33 (2016) 270–275.
- [30] R. Davarnejad, P. Panahi, Cu(II) removal from aqueous wastewaters by adsorption on the modified Henna with Fe_3O_4 nanoparticles using response surface methodology, *Sep. Purif. Technol.*, 158 (2016) 286–292.
- [31] R. Davarnejad, Z.K. Dastnaji, J. Kennedy, Cr(VI) adsorption on the blends of Henna with chitosan microparticles: experimental and statistical analysis, *Int. J. Biol. Macromol.*, 116 (2018) 281–288.
- [32] M. Shafiee, A. Akbari, B. Ghiassimehr, Removal of Pb(II) from wastewater using Henna; optimization of operational conditions, *Iran. J. Chem. Eng.*, 15 (2018) 17–26.
- [33] I. Langmuir, The constitution and fundamental properties of solids and liquids. Part I. Solids, *J. Am. Chem. Soc.*, 38 (1916) 2221–2295.
- [34] H. Freundlich, Over the adsorption in solution, *J. Phys. Chem.*, 57 (1906) 1100–1107.

- [35] B. Houari, S. Louhibi, K. Tizaoui, L. Boukli-Hacene, B. Benguella, T. Roisnel, V. Dorcet, New synthetic material removing heavy metals from aqueous solutions and wastewater, *Arabian J. Chem.*, 12 (2019) 5040–5048.
- [36] M. Sharma, J. Singh, S. Hazra, S. Basu, Adsorption of heavy metal ions by mesoporous ZnO and TiO₂@ZnO monoliths: adsorption and kinetic studies, *Microchem. J.*, 145 (2019) 105–112.
- [37] I. Vishan, B. Saha, S. Sivaprakasam, A. Kalamdhad, Evaluation of Cd(II) biosorption in aqueous solution by using lyophilized biomass of novel bacterial strain *Bacillus badius* AK: biosorption kinetics, thermodynamics and mechanism, *Environ. Technol. Innovation*, 14 (2019) 100323, doi: 10.1016/j.eti.2019.100323.
- [38] Y.-S. Ho, G. McKay, Pseudo-second-order model for sorption processes, *Process Biochem.*, 34 (1999) 451–465.
- [39] C. Xiong, S. Wang, W. Sun, Y. Li, Selective adsorption of Pb(II) from aqueous solution using nanosilica functionalized with diethanolamine: equilibrium, kinetic and thermodynamic, *Microchem. J.*, 146 (2019) 270–278.
- [40] E.-S. El-Ashtouky, N.K. Amin, O. Abdelwahab, Removal of lead(II) and copper(II) from aqueous solution using pomegranate peel as a new adsorbent, *Desalination*, 223 (2008) 162–173.
- [41] D. Mohan, K.P. Singh, Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse—an agricultural waste, *Water Res.*, 36 (2002) 2304–2318.
- [42] L.N. Nemeş, L. Bulgariu, Optimization of process parameters for heavy metals biosorption onto mustard waste biomass, *Open Chem.*, 14 (2016) 175–187.
- [43] N. Nasuha, B. Hameed, A.T.M. Din, Rejected tea as a potential low-cost adsorbent for the removal of methylene blue, *J. Hazard. Mater.*, 175 (2010) 126–132.
- [44] J. Goel, K. Kadirvelu, C. Rajagopal, V. Garg, Removal of lead(II) from aqueous solution by adsorption on carbon aerogel using a response surface methodological approach, *Ind. Eng. Chem. Res.*, 44 (2005) 1987–1994.
- [45] K. Cronje, K. Chetty, M. Carsky, J. Sahu, B. Meikap, Optimization of chromium(VI) sorption potential using developed activated carbon from sugarcane bagasse with chemical activation by zinc chloride, *Desalination*, 275 (2011) 276–284.
- [46] R.K. Mohapatra, P.K. Parhi, S. Pandey, B.K. Bindhani, H. Thatoi, C.R. Panda, Active and passive biosorption of Pb(II) using live and dead biomass of marine bacterium *Bacillus xiamenensis* PbRPSD202: kinetics and isotherm studies, *J. Environ. Manage.*, 247 (2019) 121–134.
- [47] U. Farooq, M. Khan, M. Athar, *Triticum aestivum*: a novel biosorbent for lead(II) ions, *Agrochimica*, 51 (2007) 309–318.
- [48] I. Abdelfattah, A.A. Ismail, F. Al Sayed, A. Almedolab, K. Abouelghait, Biosorption of heavy metals ions in real industrial wastewater using peanut husk as efficient and cost effective adsorbent, *Environ. Nanotechnol. Monit. Manage.*, 6 (2016) 176–183.
- [49] R. Malik, S. Dahiya, An experimental and quantum chemical study of removal of utmostly quantified heavy metals in wastewater using coconut husk: a novel approach to mechanism, *Int. J. Biol. Macromol.*, 98 (2017) 139–149.
- [50] Q. Albert, L. Leleyter, M. Lemoine, N. Heutte, J.-P. Rioult, L. Sage, F. Baraud, D. Garon, Comparison of tolerance and biosorption of three trace metals (Cd, Cu, Pb) by the soil fungus *Absidia cylindrospora*, *Chemosphere*, 196 (2018) 386–392.
- [51] V. Afraz, H. Younesi, M. Bolandi, M.R. Hadiani, Optimization of lead and cadmium biosorption by *Lactobacillus acidophilus* using response surface methodology, *Biocatal. Agric. Biotechnol.*, 29 (2020) 101828, doi: 10.1016/j.bcab.2020.101828.