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Optimizing the Biosorption Behavior of *Ludwigia stolonifera* in the Removal of Lead and Chromium Metal Ions from Synthetic Wastewater

Yasser A. El-Amier ^{1,*}, Ashraf Elsayed ¹, Mohamed A. El-Esawi ^{2,*}, Ahmed Noureldeen ³, Hadeer Darwish ⁴ and Hala Fakhry ^{5,6}

- ¹ Botany Department, Faculty of Science, Mansoura University, Mansoura 35516, Egypt; ashraf-badawy@mans.edu.eg
- ² Botany Department, Faculty of Science, Tanta University, Tanta 31527, Egypt
- ³ Department of Biology, College of Sciences, Taif University, P.O. Box 11099, Taif 21944, Saudi Arabia; a.noureldeen@tu.edu.sa
- ⁴ Department of Biotechnology, College of Sciences, Taif University, P.O. Box 11099, Taif 21944, Saudi Arabia; hadeer@tu.edu.sa
- ⁵ City of Scientific Research and Technological Applications (SRTA-City), New Borg El-Arab City P.O. Box 21934, Egypt; halaelhossany@gmail.com
- ⁶ National Institute of Oceanography and Fisheries (NIOF), Baltium 33735, Egypt
- Correspondence: yasran@mans.edu.eg (Y.A.E.-A.); mohamed.elesawi@science.tanta.edu.eg (M.A.E.-E.); Tel.: +20-101-722-9120 (Y.A.E.-A.)

Abstract: In this study, a natural low-coast, efficient, and eco- bio-sorbent plant material (Ludwigia stolonifera), with both parts of the root and shoot, were studied for the removal of the cationic metal ions, lead Pb^{2+} and chromium Cr^{6+} , via batch mode experiments to evaluate their maximum adsorption capacity, and held a comparison between the used bio-sorbent roots and shoots, based on the highest bio-sorption potential. Optimization of the bio-sorption parameters, such as contact time, pH, bio-sorbent (root and shoot) dosage, and initial ion concentration was conducted. The results indicated that 1.6 g of the used bio-sorbent shoot material removed 81.4% of Pb²⁺, and 77% of Cr⁶⁺ metal ions from liquid media under the conditions of 100 ppm of initial metal ions concentration at room temperature for 60 min of contact time with the static condition. Different isotherms and kinetic models were fit to the experimental data to understand the nature of the bio-sorption process. The experimental data were best fit by the pseudo-second-order kinetic model with a high correlation coefficient ($R^2 = 0.999$), which reveals the chemisorption nature of the bio-sorption process. The chemical and structural analysis of the used bio-sorbent, before and after Cr⁶⁺ and Pb²⁺ bio-sorption, were performed using different techniques of characterization, such as Scanning Electron Microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR). The used bio-sorbent proved to be a low-cost, efficient, and eco-friendly material to remove heavy metal ions from aqueous solutions.

Keywords: wastewater treatment; heavy metals bio-sorption; Cr^{6+} ; Pb^{2+} ; equilibrium isotherms; kinetic studies

1. Introduction

Freshwater is essential to all living organisms' survival as it is the main source of health, food, and energy. The whole world is facing a water crisis nowadays, due to the rapid growth of population and the consumption of large quantities of water by many industries, household, and agriculture activities. The effluent wastewater from some industries such as paper and pulp production, ceramics, smelting, and battery production is considered to be the main source of toxic heavy metals to the environment [1,2] This issue is of increasing concern, due to the adverse health effects of these effluents contaminated with various types of heavy metals types, such as; Cr^{6+} , Pb^{2+} , Cd^{2+} , Zn^{2+} , Ni^{2+} , As^{3+} and



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Hg²⁺ which are not biodegradable and cause severe health risks such as skin damage, liver, and lung cancer [3,4].

Of these heavy metals Chromium is of significant interest, due to it being considered the 16th most toxic element causing severe adverse health effects, according to the Agency for Toxic Substances and Disease Registry (ATSDR). It has two oxidation states in nature: trivalent Cr^{3+} and hexavalent Cr^{6+} . Cr^{6+} is 500 times more toxic than Cr^{3+} , Cr^{6+} moves faster in ground and surface waters in a wide range of pH and causes adverse health effects such as asthma, eye irritation, and liver damage. It is involved in various industries such as mining, textile, and anti-corrosion materials [5,6].

Besides Cr^{6+} , one of the most toxic heavy metal ions is lead (Pb²⁺, The reported levels of lead in waterways across Egypt are between 20–30 µg/L [7,8], which is up to double or triple the amount considered safe to drink, set by US Environmental Protection Agency (EPA) at 15 µg/L. These high levels of Pb²⁺ lead to retardation in children and reduced breast milk in young mothers in addition to anemia, kidney damage, and mental retardation [9–11]. Any exposure to Pb causes a wide range of physiological, biochemical, and behavioral effects. Most serious effects occur in the central and peripheral nervous systems, the cardiovascular system, the hematopoietic system, and in some organs such as the liver and kidneys [12].

This makes us choose the removal of Cr^{6+} and Pb^{2+} metal ions from aqueous solutions to protect human beings and the environment [13]. Different chemical and physical methods are used to remove heavy metals, including advanced oxidation, membrane separation, and solvent extraction, but these techniques are expensive and produce unwanted by-products. Therefore, we must search for alternative methods, especially bio-based technologies such as bioremediation and phytoremediation, as they are safer, cheaper, environmentally friendly, and without adverse effects.

Bio-sorption has been shown to be an effective method for the removal of various toxic metal ions, due to the bio-sorption systems ease of use and simple, inexpensive design [14–16]. The bio-sorption process includes a reversible adsorption reaction between adsorbent and adsorbate, which allows for the constant reuse of the bio-sorption material in a sustainable fashion. The bio-material also boasts efficient removal of Cr^{6+} and Pb^{2+} metal ions due to many bio-sorption sites that contain functional groups such as OH and C=O which have a high binding affinity to the metal ions [16–19]. In Egypt, *Ludwigia stolonifera* (family Onagraceae) is one of the most common invasive macrophyte plant of high growth and spread rates in waterways [20], causing the blocking of waterways.

However, these perennial weeds have white spongy floats, and can float on water, or crawl on the surface of wetlands, and have an incredible ability to collect and adsorb metal ions in waterways [21]. The used bio-sorbent (*L. stolonifera*) possess many functional groups as carbonyl, amino, hydroxyl, and phenolic groups, which are very important to the bio-sorption process of Cr^{6+} and Pb^{2+} metal ions, as they can form chelates and complexes with them [4,22].

In this study, we aim to evaluate the efficacy of *L. stolonifera* with both parts of the root and shoot as an eco-bio-sorbent material for the removal of Cr^{6+} and Pb^{2+} metal ions from aqueous solutions. The powdery mass of roots and shoots of the used bio-sorbent were characterized before and after the bio-sorption process using SEM and FTIR techniques. Different bio-sorption parameters were optimized for the maximum bio-sorption capacity of Cr^{6+} and Pb^{2+} metal ions onto the used bio-sorbent material. The bio-sorption equilibrium and kinetics were also employed.

2. Materials and Methods

2.1. Sample Collection and Preparation of the Used Bio-Sorbent (L. stolonifera)

During the spring of 2020, composite samples of a common perennial floating macrophyte plant (*Ludwigia stolonifera*) were prepared. This plant was selected according to the field observations, where they are naturally growing in all sampled sites. The plant was collected from River Nile Damietta branch, Dakahlia Governorate, Egypt (31°90′53.46″ N 31°29′50.97″ E) in plastic bags. The plant samples were washed by tap water and distilled water to remove dust and then separated into shoots and roots. The samples were dried completely at 65 °C in an oven and ground into a powder with an electric grinder. Nomenclature and identification of the plant species were carried out according to Tackholm [23] and Boulos [24].

2.2. Preparation of Pb (II) and Cr (VI) Metal Ions Standard Solutions

Stock solutions of Pb^{2+} and Cr^{6+} metal ions were prepared by dissolving a known weight of K₂Cr₂O₇, and Pb (C₂H₃O₂). 3H₂O in Double-Distilled Water (DDW), standards of 1000 mg/L. A series of working solutions were prepared with different concentrations varying between 100 and 1000 ppm. Solution pH 2–10 was adjusted by using diluted solutions of 0.1 N HCl and 0.1 N NaOH. All chemicals are pure and analytical reagent grade acquired from Sigma Aldrich, Cairo, Egypt.

2.3. The Used Bio-Sorbent (L. stolonifera) Characterization

The surface morphology and topography of the used bio-sorbent (*L. stolonifera*) root and shoot before and after their bio-sorption of Pb²⁺ and Cr⁶⁺ metal ions were observed using scanning electron microscopy (SEM) (JSM-6510, JEOL/EO, Tokyo, Japan) at an accelerated voltage of 30 kV. Additionally, their chemical structure and functional group were analyzed using Fourier transform Infrared (FTIR) spectroscopic analysis. Pellets were formed through mixing samples with KBr, and then they were compressed into disks to be able to enter the FTIR instrument. The spectra were recorded in the wavenumber range from 400–4000 cm⁻¹ and 32 scans per sample with a resolution of 8.000 from 400.1737 to 3999.8091. FTIR spectra were estimated with an FTIR spectrometer (FTIR-8400 S, Shimadzu, Kyoto, Japan).

2.4. Batch Bio-Sorption Studies

Bio-sorption of Pb²⁺ and Cr⁶⁺ metal ions onto the used bio-sorbents were performed through batch-mode experiments at room temperature. 50 mL of the prepared working metal solutions (100 ppm) was added to a defined weight of roots and shoots of the used bio-sorbent (*L. stolonifera*) in 250 mL Erlenmeyer flasks, then they were shaken on a mechanical shaker at 200 rpm for a specified bio-sorption contact time of 60–180 min, then, the adsorbate- adsorbent solutions were centrifuged (at 15.000 rpm for 15 min followed by filtration. The filtrates were collected, and their Pb²⁺ and Cr⁶⁺ metal ion concentration differences were measured using atomic absorption spectroscopy (Buck Scientific Accusys 211 Atomic Absorption Spectrophotometer, East Norwalk, CT, USA) with air-acetylene flame at the wavelength of 357.87 and 283.31. The conducted batch experiments include: contact time (10–300 min), pH (2–10), bio sorbent (root and shoot) dosage (0.2–1.6 g), and initial metal ion concentration (50–700 ppm) were studied and optimized to find out the maximum bio sorption capacity of the selected metal ions onto the used bio-sorbent (*L. stolonifera*) root and shoot. The heavy metal removal percentage and bio-sorption capacity (represent the amount of metal ion uptake) were calculated using Equations (1) and (2).

Removal efficiency (%) =
$$\frac{(C_{i-} C_e)}{C_i} \times 100$$
 (1)

$$q_{e=} \frac{(C_{i-}C_{e})}{m} \times V \tag{2}$$

where C_i and C_e are the initial and final (equilibrium) metal ions concentration (ppm); m is the mass of the used bio-sorbent (*L. stolonifera*) (g), and *V* is the volume of used metal ion solution. All tests were performed in triplicate. The equilibrium studies of Pb²⁺ and Cr⁶⁺ metal ions bio-sorption onto the used bio-sorbent (*L. stolonifera*) root and shoot were conducted, and the obtained data were fit to three isotherms models. However, the kinetic studies were carried as a function of contact time.

3. Results and Discussion

3.1. Bio-Sorbent Characterization

3.1.1. Scanning Electron Microscopy (SEM)

We observed the surface morphology, topography, and dimensions of the used biosorbent (root and shoot), before and after their bio-sorption of Cr^{6+} and Pb^{2+} metal ions, using SEM instrument. As can be seen in Figure 1, the used bio-sorbent root (A) and shoot (D) cells, before the bio-sorption process, almost have the same outfit and morphological structure, as the cellular structure of both cells might be the same or relatively similar from the morphological point of view. The root and shoot of the used bio-sorbent have smooth surfaces with a lack of pores. Moreover, from the figure (B,C) which represent the bio-sorption process of Cr^{6+} and Pb^{2+} , respectively, onto the used bio-sorbent root and (E,F), which point out the used bio-sorbent shoot after the bio-sorption process of Cr^{6+} and Pb^{2+} , respectively, that the surface topography of the used bio-sorbent (*L. stolonifera*) was different from the native cells through increasing the surface roughness. The bio-sorbed Cr^{6+} and Pb^{2+} ions were clearly aggregated on the used bio-sorbent surface, which approve the bio-sorption process.



Figure 1. SEM images of the used bio-sorbent *L. stolonifera* root (**A**) and shoot (**D**), before the biosorption process, (**B**,**C**) represent root and shoot cells after bio-sorption of Cr^{6+} and (**E**,**F**) of root and shoot cells after bio-sorption of Pb^{2+} .

3.1.2. FTIR Analysis

The used bio-sorbent, *L. stolonifera* (root and shoot), adsorption capacity relay on porosity and chemical reactivity of their surface functional groups [25]. The chemical structure of the used bio-sorbent material (root and shoot), before and after the bio-sorption of Pb^{2+} and Cr^{6+} metal ions, were analyzed using the FTIR technique to figure out the difference in the spectra due to the reaction of the used bio-sorbent functional groups with the chosen metal ions and to understand their possible bio-sorptive interactions.

The spectra of root and shoot of the used bio-sorbent in this study are quite similar which shows that they have similar functional groups on their surfaces. It was pretty clear from Figure 2 that there were clear shifts in the wavenumber, between the used bio-sorbent (root and shoot) sample, before and after the bio-sorption of Cr^{6+} and Pb^{2+} metal ions, which approved the binding process of the metals onto the used bio-sorbent surfaces [25]. As in the Figure, there was a clear shift from wavenumber at 1043 cm⁻¹ in the root sample to 1057 cm⁻¹ in Cr bio-sorbed root, which attributed to lignin's -OCH₃ group stretching vibration appearing in cellulose [26].



Figure 2. FTIR spectra of the used bio-sorbent *L. stolonifera* (root and shoot) before and after biosorption of Cr^{6+} and Pb^{2+} metal ions.

From 1368 cm⁻¹ in the root sample, to 1376 cm⁻¹ in Cr the bio-sorbed root, and 1442 cm⁻¹ in (root sample) to 1403 in Cr bio-sorbed root, shifting in the wavenumber might be due to the adsorption of Cr ions onto C-O and C-O-H respectively.

There were some peaks in the root sample that disappeared after the binding mechanism with Cr metal ions such as at 3805 and 3906 cm⁻¹ due to the adsorption of Cr onto the (N-H) group of the used bio-sorbent. While, for root samples bio-sorbed with Pb²⁺ metal ions, there was also shifting from wavenumber of 1056 cm⁻¹ in the root sample to 1043 cm⁻¹ in Pb bio-sorbed root, 1654 cm⁻¹ in root sample to 1634 cm⁻¹ in (Pb bio-sorbed root), and 3425 cm⁻¹ to 3448 cm⁻¹, this might be because of Pb binding with C-O, C=O, and O-H groups of the root adsorbent material. Moreover, some peaks were absent from the root sample, including 1232, 1325, and 1722 cm⁻¹ due to the adsorption mechanism of Pb onto C-C, C-N, and C=O groups of the adsorbent. The presence of peak at 1378 cm⁻¹ attributed to C-H vibrations in cellulose and at 2925 cm⁻¹ attributed to C-H bond of CH₃ and CH₂ in hemicellulose, cellulose, and lignin [27]. Additionally, the presence of (-COOH), and (-OH) functional groups, at the used bio-sorbents surfaces, can provide metal ions complexation sites. Moreover, the functional groups of nitrogen and oxygen atoms form a coordinate bond with metal cations, and that's the reason behind the high affinity to bio-sorb Pb²⁺ metal ions more than Cr⁶⁺ [28].

As for the shoot IR spectra, there was shifting from wavenumber 1440, in the shoot sample, to 1423 cm⁻¹ in the Cr bio-sorbed shoot, due to the adsorption of Cr on C-O-H of the shoot surface. As for the adsorption of Pb ions on the shoot surface, there was a clear shift from 1379 cm⁻¹ to 1440 cm⁻¹, and from 3426 cm⁻¹ to 3448 cm⁻¹ because of the binding of Pb metal ions with C-O-H and O-H groups of the adsorbent surface. In all samples, there is a broad absorption peak at 3448 cm⁻¹, which indicates the presence of intermolecular, free O-H groups and bands of carboxylic acids [19].

There is no remarkable shifting of this peak because we didn't make any chemical treatment to the used bio-sorbent. The presence of an intensive peak at 1645 cm⁻¹ might be attributed to the absorption of water molecules linked with cellulose fibers [29]. The peak at 1524 cm⁻¹ in root and shoot samples is due to stretching vibrations of C=C in the aromatic ring of lignin.

3.2. Batch-mode Experiments

3.2.1. Effect of Bio-Sorption Contact Time

The contact time between the bio-sorbent and bio-sorbate is a critical parameter affecting the bio-sorption process kinetics [30]. The equilibrium time for the bio-sorption of

 Pb^{2+} , and Cr^{6+} metal ions onto the used bio-sorbent root and shoot was obtained through studying their time-dependent behavior in a time range of 10–300 min with keeping other parameters constant as in Figure 3a, which prevail that the bio-sorption rate was fast in the first period of contacting between the bio-sorbent and bio-sorbate, then it slowed down till near stability. Equilibria of Pb^{2+} metal ions onto the used bio-sorbent root and shoot were 120, and 60 min, respectively, while they were 120 and 180 for Cr^{6+} ions bio-sorbed onto root and shoot.



Figure 3. Effect of Contact Time (**a**), pH (**b**), Pb^{2+} and Cr^{6+} metal ions concentration (**c**,**d**), and biomass dosage root and shoot (**e**,**f**) respectively.

3.2.2. Effect of Solution pH

Solution pH plays a vital role in changing the availability of metal ions in this solution besides, the functional groups and chemical status of the bio-sorbent, which are responsible for the bio-sorption process [31]. Variation of solution pH was studied in the range of 2.0 up to 10.0 for Pb^{2+} and Cr^{6+} metal ions bio-sorption onto the used bio-sorbent. The removal efficiencies and bio-sorption capacity increase with increasing the pH in the acidic medium until it reached neutral and without a significant increase in the bio-sorption capacity, in the case of Pb^{2+} ions, while they both decreased in neutral and basic solutions in case of

 Cr^{6+} metal ions, as in Figure 3b, which illustrates that the percentage of removal increased from 21.4 up to 38.19%, from 18.93 to 28.71% for the bio-sorption of Cr^{6+} onto the used bio-sorbent shoot and root, respectively, when the solution pH increased from 2 up to 7, and from 20.5 up to 35.35%, 30.98 to 41.77% for the bio-sorption of Pb²⁺ ions onto the used bio-sorbent shoot and root, respectively when the solution pH increase from 2 up to 7, while they decreased with the increase in pH in case of Cr^{6+} .

The bio-sorption capacity increase with increasing solution pH, as the increase in pH value, increases the negative charge on the used bio-sorbent surface which leads to a decrease in the competition between protons and metal ions. Moreover, at higher pH values (4–7), the used bio-sorbent surface possesses a negative charge which attracts the positively charged Pb²⁺ ions by electrostatic attraction. Furthermore, the maximum bio-sorption capacity of Cr^{6+} was in acidic medium and decreased in the neutral and basic medium due to the presence of excessive -OH groups in the alkaline medium hindered Cr^{6+} bio-sorption [15,32].

According to the figure, the % of removal of Pb²⁺ and Cr⁶⁺ metal ions, by using the bio-sorbent material shoot, was higher than roots due to the affinity of the shoot cells to certain heavy metal ions.

3.2.3. Effect of Initial Metal Ion Concentration

Figure 3c,d illustrates the effect of metal ions concentration variation on the biosorption process. The increase in Pb²⁺ and Cr⁶⁺ metal ions concentrations lead to a decrease in their removal efficiencies and increment in the bio-sorption capacities. As the percent of removal of Pb²⁺ decreased from 89.32 to 41.84%, and from 81.840 to 34.46% when the initial concentration of Pb²⁺ increased from 50 up to 700 ppm, while, the bio-sorption capacities increased from 3.722 to 24.407 mg/g, and from 3.410 to 20.103 mg/g when the Pb²⁺ concentrations raised from 50 to 700 ppm.

The same trend was also observed with the removal percentage efficiencies and biosorption capacities of Cr^{6+} metal ions, onto the used bio-sorbent root and shoot, as the removal percentage decreased from 82.70 to 24.16% and from 91.820 to 13.069% and from 91.820 to 13.069% and from 91.820 to 13.069% (for root and shoot respectively) with the increment of Cr^{6+} initial concentration from 50 up to 700 ppm, while the bio-sorption capacities were increased from 10.338 to 70 and from 11.478 up to 45 mg/g. This behavior might be attributed to that, above a certain metal ion concentration, all available active sites became saturated, which leads to a decrease in the removal efficiency, and the number of Pb^{2+} , and Cr^{6+} metal ions in the liquid phase is larger than the active bio-sorption sites numbers located on the used bio-sorbents surfaces, moreover, the higher absorption rate causes increment in the bio-sorption capacities of the both used metal ions [33,34]. Samra [35], reported similar results, as the bio-sorption capacities of the used bio-sorbent increased with increasing metal ions concentrations because of the increasing metals diffusions rate in the boundary layer.

3.2.4. Effect of Bio-Sorbent Dosage

The effect of biomass amount on the bio-sorption of Cr^{6+} and Pb^{2+} metal ions was studied by varying the dosage of the used bio-sorbent root and shoot, from 0.2 up to 1.6 g, as illustrated in Figure 3e,f. The removal efficiencies of the selected metal ions increase with the increase in the used bio-sorbent material dosage, while their bio-sorption capacities decrease with the increment doses, as percent of removal increased from 29.062 up to 67.644%, and from 38.622 to 77.645% for the bio-sorption of Cr^{6+} onto the used bio-sorbent root and shoot, respectively.

The biomass dosage increased from 0.2 to 1.6 g, from 32.767 to 71.342%, from 42.32 up to 81.343% for the bio-sorption of Pb^{2+} ions onto the used bio-sorbent root and shoot respectively with the same dosage used with Cr^{6+} ions. This is can be due to the availability of more active sites on the used bio-sorbent surface, which are responsible for the bio-sorption process, which increases the adhesion forces between metal ions and the bio-

sorbent material. However, the bio-sorption capacity decreases with the increase in the used bio-sorbent dose [36].

3.2.5. Equilibrium Modeling

Models of bio-sorption isotherms give up information about bio-sorbates distributions between the solid and liquid phases at the equilibrium state. We fit the obtained experimental equilibrium data of Pb^{2+} , and Cr^{6+} metal ions onto the used bio-sorbent root and shoot to Langmuir, Freundlich, and Temkin isotherm models [37] to find out the best-fit model, which described the bio-sorption process well. The used bio-sorption isotherms model linear forms are showed in Table 1, their bio-sorption parameters, and their constants, are illustrated in Table 2 and Figure 4.

Table 1. Adsorption equilibrium models applied in the present study.

Bio-Sorption Models	Equation	Parameters		
Langmuir	$C_{e}/q_{e} = 1/q_{m}K + C_{e}/q_{m}$ $\frac{C_{e}}{q_{e}} = \frac{1}{q_{m}Kl} + \frac{C_{e}}{q_{m}}$	q_e is the bio-sorbate amount in the bio-sorbent at equilibrium (mg/g), q_m is the maximum monolayer coverage capacities (mg/g), K_l is the Langmuir constant (L/mg), and C_e is the equilibrium concentration (mg/L).		
Freundlich	$ln q_e = ln K_F + 1/n_f ln c_e$ $lnq_e = lnK_F + \frac{1}{n_f} lnC_e$	q_e is the of bio-sorbed ions amount at equilibrium (mg/g); Ce is the bio-sorbate equilibrium ions concentration (mg/L); K_F and n_f are Freundlich constants related to the bio-sorption capacity and bio-sorption intensity, respectively		
Temkin	$q_e = B \ln KT + B \ln C_e$	<i>KT</i> is the Temkin constant refer to equilibrium maximum binding energy and <i>B</i> is the Temkin constant related to bio-sorption heat.		

Table 2. Parameters of bio-sorption isotherm models.

Isotherm Parameters	Cr ⁶⁺		Pb ²⁺	
isotherin i utumeters	Root	Shoot	Root	Shoot
Langmuir				
$q_m (mg g^{-1})$ calculated	43.478	25.641	80.796	65.519
K_L (L mg ⁻¹)	0.056	0.045	0.018	0.017
\mathbb{R}^2	0.975	0.944	0.988	0.992
Freundlich				
$K_{\rm F} ({ m mg}1^{-1}/{ m n}{ m L}1/{ m n}{ m g}^{-1})$	6.619	11.658	6.056	4.926
nf	3.074	5.913	2.352	2.369
R ²	0.852	0.979	0.990	0.952
Temkin				
BT (L mg $^{-1}$)	8.210	3.483	14.590	12.507
$KT (KJ mol^{-1})$	0.566	23.169	0.298	0.239
R ²	0.831	0.531	0.976	0.989

The Langmuir model assumes monolayer coverage with a homogeneous surface bio-sorption without transmigration of the bio-sorbate molecules to the inner layers of the used bio-sorbent, and subsequently uniform, energies of bio-sorption on its surfaces. The Freundlich model means a heterogeneous and multi-layer of the bio-sorption process [38].



Figure 4. Adsorption isotherm models of Pb²⁺ and Cr⁶⁺ metal ions onto of the used bio-sorbent (*L. stolonifera*) (**a**) Langmuir, (**b**) Freundlich, and (**c**) Temkin.

High R² (0.975 and 0.944 for the bio-sorption of Cr⁶⁺ onto the used bio-sorbent root and shoot, respectively, and it was equal to 0.988 and 0.992 for the bio-sorption of Pb²⁺ onto the used material root and shoot, respectively) values illustrate a good curve fitting to the Langmuir model. Almost in all the fit bio-sorption isotherms models, the bio-sorption capacities of Cr⁶⁺ were lower than Pb²⁺, which might be because of the heavy metals' complexation abilities, related to their functional groups, and solution pH. Nickel and copper can form such complexes, meanwhile, cadmium and lead possess higher biosorption capacities via ion exchange [39]. The obtained q_m (mg g^{-1}), which represent the maximum monolayer coverage capacities and calculated from the slope of (Figure 4a), were 43.478 and 25.641 mg/g for the bio-sorption of Cr^{6+} onto the used bio-sorbent root and shoot, respectively, while they were 80.796 and 65.519 for Pb²⁺ bio-sorption onto the used root and shoot bio-sorbent material. Furthermore, Kl represent the bio-sorption energy (L/mg), and their values were obtained from the intercept of (Figure 4a), as they were (0.056 and 0.045 for bio-sorption of Cr^{6+} and 0.018, and 0.017 (L/mg) for Pb²⁺ bio-sorption onto the used bio-sorbent root and shoot, respectively, which means that the used bio-sorbent material possesses high bio-sorption ability with low bio-sorption energy.

The Temkin isotherm deals with the indirect effects between bio-sorbent and biosorbate interactions on the bio-sorption process. The bio-sorption heat of all layer molecules decreases linearly with coverage due to bio-sorbent, and bio-sorbate reactions [40].

Finally, higher R^2 values for Langmuir than Freundlich for the bio-sorption of Cr^{6+} onto the used bio-sorbent material root and shoot, suggesting a monolayer coverage of the bio-sorption process. While, their values were smaller for Langmuir than Freundlich, for the bio-sorption of Pb²⁺ onto the used bio-sorbent material root and shoot, suggesting that the chemisorption is not the only the bio-sorption mechanism in this process, both chemisorption and physisorption must be taken into consideration under studied condi-

tions [41]. A comparison of the calculated maximum monolayer adsorption capacity for different adsorbent materials and the used material illustrated in Table 3.

3.2.6. Bio-Sorption Kinetic Models

It very important for the bio-sorption process to study the kinetic models, as it points out the uptake rate of the used bio-sorbent material. The bio-sorption kinetics of Pb^{2+} and Cr^{6+} metal ions onto the used bio-sorbent root and shoot were evaluated using four kinetic models (pseudo-first-order [42], pseudo-second-order, Elovich, and intra-particle Diffusion). The non-linearized equations of these models are tabulated in Table 4, and their bio-sorption Parameters were illustrated in Figure 5 and Table 5.

Table 3. Comparison of calculated maximum monolayer adsorption capacity for different adsorbent materials.

Metal Ion	Adsorbent Material	Adsorption Capacity (mg/g)	Reference
	Current study	80.796	
P1 2+	bael tree (BT) leaf powder	4.065	[43]
Pb ²⁺	Polyethyleneimine and carbon disulfide co-modified alkaline lignin	79.9	[44]
	Moringa Oleifera	15.38	[45]
	Current study	43.478	
Cr ⁶⁺	Soy Sauce Residue Biochar cr	25.80	[46]
	Low-Cost Adsorbent Prepared from Neem Leaves	10	[47]
	Durian Peel	10.67	[48]
-			

Table 4. Bio-sorption kinetic models equations.

Bio-Sorption Kinetic Models	Equation	Parameters
Pseudo-First-Order	$Ln (q_e - q_t) = ln q_e - K_1 t$	q_t is the bio-sorbed metal ions amount at time t , q_e , is the bio-sorbed metal ions amount at equilibrium (mg/g). k_1 (min ⁻¹) is the first-order reaction rate constant
Pseudo-Second-Order	$t/q_t = (1/K_2 q_e^2)$	q_t is the bio-sorbed metal ions amount at time $t q_e$, the bio-sorbed metal ions amount at equilibrium (mg/g), k_2 is the second-order reaction rate equilibrium constant (g/mg min).
Elovich	$q_t = \dot{a} + \beta \ln t$	\hat{a} is the initial sorption rate (mg/g min) and β is the extent of surface coverage and activation energy for chemisorption (g/mg)
Intra-particle Diffusion	$q_t = k_{id}t^{1/2} + I$	<i>kid</i> is the intra-particle diffusion rate constant, and <i>I</i> give prediction about the boundary layer thickness



Figure 5. First-order plots (**a**), Second-order plots (**b**), Elovich plots (**c**), and Intra-particle diffusion plots (**d**) for bio-sorption of Cr^{6+} , and Pb^{2+} onto the used bio-sorbent (*L. stolonifera*) roots and shoots.

Table 5. Parameters obtained from different kinetic models for bio-sorption of Cr ⁶⁺ , and Pb ²⁺ o	nto
the used bio-sorbent (<i>L. stolonifera</i>) roots and shoots.	

Kinetic Model		Cr ⁶⁺		Pb ²⁺	
Killette Wibuei	_	Root	Shoot	Root	Shoot
Pseudo-First- Order	q_e (mg/g) Calculated	12.541	7.478	3.712	2.335
	<i>q_e</i> (mg/g) Experimental	14.748	14.523	15.838	16.625
	$\bar{k_1}$ (min ⁻¹)	0.013	0.009	0.006	0.005
	R ²	0.938	0.830	0.693	0.193
	q_e (mg/g) Calculated	16.944	16.313	16.807	15.625
Pseudo-Second- Order	<i>q_e</i> (mg/g) Experimental	14.748	14.523	15.838	16.625
	k_2 (g/mg min)	0.038	0.044	0.081	0.247
	R^2	0.990	0.999	0.991	0.998
Elovich	ß (g/mg)	3.347	3.266	1.980	1.248
	\hat{a} (mg/g min)	3.899	3.202	5.655	9.360
	R^2	0.977	0.971	0.928	0.657
Intra-particle Diffusion	ki _d ,	0.779	0.726	0.440	0.249
	Ι	2.707	3.574	9.794	12.227
	\mathbb{R}^2	0.971	0.938	0.825	0.477

For the first-kinetic model, the q_e calculated values differed from their experimental ones, which means that this model was not good enough to describe this bio-sorption process. The pseudo-second order kinetic model R² values obtained from the linear relationship between t/qt versus t were 0.999, 0.991, and 0.998 for the bio-sorption of

 Pb^{2+} and Cr^{6+} metal ions onto the used bio-sorbent material root and shoot, respectively, meaning that this model describes the bio-sorption process well and, subsequently, the chemisorption rate-limiting step is dominant in this process with sharing electrons between bio-sorbent and bio-sorbate [40,49].

The calculated q_e (16.944 and 16.313 mg/g for the bio-sorption of Cr⁶⁺ onto the used bio-sorbent root and shoot, while they were 16.807 and 15.625 mg/g for Pb²⁺ bio-sorption onto the used material) values were compared with their experimental values (14.784 and 14.523 for Cr⁶⁺ sorption onto bio-sorbent root and shoot and 15.838 and 16.625 mg/g for Pb²⁺ sorption onto bio-sorbent root and shoot) and we found that they were so close, which shows that the gained data fit the second-order rate model.

K represents the reaction rate equilibrium constant (g/mg min) of the second-order and it can be calculated from (Figure 5b) intercept. The obtained K values were 0.038 and 0.044 for the bio-sorption of Cr^{6+} root and shoot, while they were 0.081 and 0.247 for Pb²⁺ bio-sorption onto the used bio-material root and shoot.

The obtained K values of the second-order kinetic model indicate a fast bio-sorption rate of Cr^{6+} , and Pb^{2+} metal ions onto the used bio-sorbent (*L. stolonifera*) root and shoot.

Moreover, according to the above-mentioned results, which cleared the chemisorption attitude of the bio-sorption process, the simple Elovich model is used, which describes the chemisorption kinetics [50]. According to Table 4, it was pretty clear that the experimental data fit well with the Elovich equation with high R² values, which confirms the above-mentioned conclusion about the chemisorption nature of the bio-sorption process utilizing the used bio-sorbent material.

Finally, we fit the obtained data with the intra-particle diffusion model. There is a multi-stage process that controls the bio-sorption of metal ions from liquid to solid phase: in the first step, metal ions transport from the liquid to the solid phase surface (bulk diffusion), followed by diffusion of the metal ions through the boundary layer of the used bio-sorbate surface (film diffusion), and finally, their transmigration from the solid bio-sorbate surface to its inner layers (intra-particle diffusion). From the intra-particle diffusion equation, the intercept represents the boundary layer thickness, so, the increment of the intercept value leads to increasing the boundary layer effect. If the linear relationship between q_t against t ^{1/2}, results in a line that passes through the origin, in this case, the intra-particle diffusion is the controlling step [51]. In this study, no line passed through the origin for both metal ions' bio-sorption, so this shifting of lines might be due to the mass transfer rates in the first and last diffusion stages not being stable [52].

4. Conclusions

Phytoremediation technologies are considered an effective, eco-friendly, and cheap way to clean up water contaminated with hazardous pollutants, such as the heavy metals $(Cr^{6+}, and Pb^{2+})$. Many factors affect the bio-sorption of metal ions onto the bio-sorbent L. stolonifera, such as metal ion content, medium pH-value, biomass dosage, and contact time between the bio-sorbent and bio-sorbate and were evaluated through a series of benchscale experiments which revealed that the maximum removal uptake percentage of Pb²⁺ (81.34%) was achieved with the used bio-sorbent shoot, while it was 77.64% for Cr⁶⁺ onto the used bio-sorbent shoot, with a maximum bio-sorption capacity of 80.79 mg/g at room temperature, according to the Langmuir isotherm. The Langmuir isotherm model was the best fit model among the three tested models, which suggested monolayer coverage of the bio-sorption of Cr⁶⁺ and Pb²⁺ metal ions onto the used bio-sorbent with a maximum biosorption capacity of 43.5 and 80.79 mg/g, respectively, at room temperature. The kinetics of the Cr⁶⁺ and P²⁺ bio-sorption rate were best explained by the pseudo-second-order kinetic equation and the simple Elovich and intraparticle diffusion models as the bio-sorption kinetics can be explained by many independent processes. According to the gained data, the % of removal of Pb²⁺ and Cr⁶⁺ metal ions by using the bio-sorbent material shoot was higher than roots, due to the affinity of the shoot cells to certain heavy metal ions, moreover, its affinity to adsorb Pb²⁺ is higher than Cr⁶⁺ due to the same reason.

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