



Biosorption of lead ion from aqueous environment using wheat stem biomass

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

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

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

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

^dDiscipline 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

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ABSTRACT

In this study, lead ion biosorption from aqueous environment was investigated in a batch system using wheat stem and different lead ion concentrations (2.5–20 ppm), pH (2–8), mixing rates (280–360 rpm), biosorbent amounts (0.2–1 g), and contact times (10–180 min). The Freundlich, Langmuir, Temkin, and Dubinin–Radushkevich isotherm models were applied as adsorption isotherms. Kinetic studies (pseudo-first-order, pseudo-second-order, and intraparticle diffusion models) were undertaken to determine the biosorption mechanism. It is concluded that the wheat stem is a good choice for lead ion removal from aqueous solutions considering its high performance, abundance, and affordability.

Keywords: Adsorption; Biosorption; Lead ion; Water treatment; Wheat stem

1. Introduction

Enormous amounts of different forms of heavy metals ions are discharged into water resources by human activities and industries such as electro-plating, lead smelting, mining, and metal finishing industries, etc. The increase in concentration of these metals ions in wastewater can pose dangers to livestock [1]. The presence of heavy metals ions such as chromium, nickel, copper, zinc, cadmium, and lead ions in the drinking water considering their toxicity is a serious problem in line with the World Health Organization guidelines [2]. Among these metals ions, the lead ion due to its high level of toxicity is of great importance that can cause brain damage in children [3]. Therefore, lead ion removal from water is taken much attention due to its harmfulness and extensive being in the environment [4].

Various metals ions removal processes have been studied such as chemical precipitation, reverse osmosis, ion exchange, oxidation/reduction and filtration, electrochemical treatment to remove lead ion from aqueous solutions. But the metal ion removal processes are often costly and imperfect [5]. Many researchers have been trying to introduce new approaches on metal ion removal that are environmentally [6] and economically [7–9] desirable. The adsorption method using natural materials [10], which is called biosorption, could be helpful in this regard. The usage of biological and natural materials for the treatment of water-containing dyes and heavy metals ions has been proposed since 1980 [11,12]. The biological and natural materials could be agricultural waste materials, agricultural products, algae, plants, yeasts, bacteria, the skin of animals, fungi, etc. [5,13–15]. Home-grown accessibility, methodological possibility, being

* Corresponding author.

inexpensive, technical applicability, etc. are important factors in selecting these adsorbents for water treatment. The affinity of these biological and natural materials to metals ions arise from present functional groups containing donor atoms such as O and N, S in their structures [16].

The new trend is to use biomass to trap lead ion in line with “Green Chemistry” or “Sustainable Chemistry” standards. Reduction of toxic chemical reagents is one of them; also, the avoidance of non-recyclable waste; the reuse of reagents; the elimination of carbon emissions; the introduction of an environmentally sustainable analytical method for analyte detection; and the application of technology and microscale innovations [17]. Natural materials can be used to extract metals ions from aqueous solutions in both single and multi-metals ions, according to the findings. Natural materials have been used to treat contaminated wastewater containing high levels of heavy metals ions such as Co^{2+} , Cr^{2+} , Pb^{2+} , Zn^{2+} , Fe^{3+} , Mn^{2+} , Cu^{2+} , Cd^{2+} , and Ni^{2+} [18].

The wheat stem is one of the main agricultural wastes that is produced in large amounts all over the world. The stems are normally burnt directly which make atmospheric pollution problems. The main compositions of the wheat stem are cellulose (37%–39%), hemicellulose (30%–35%), lignin (14%), sugars, and the other compounds holding O and N, S-donor functional groups [19,20]. The porous surface of the wheat stem is suitable to adsorb metals ions. Some studies have reported using the straw stem as biosorbent [21,22].

There are several reports for removing metals ions like cadmium, copper, chromium, and mercury ions from aqueous environment using wheat-based biosorbents. The adsorption of cadmium ion from aqueous solution by wheat stems was studied to better understand the physicochemical process and to see whether wheat stems could be used in the wastewater treatment. According to the findings, wheat stems have a high potential for removing cadmium ion from aqueous solution in a cost-effective and environmentally friendly manner [21,23–25].

This study aims to illustrate the feasibility of lead ion removal from aqueous environment using the wheat stem as a low-cost biosorbent by a set of experiments at various conditions such as different lead ion concentrations (2.5–20 ppm), pH (2–8), mixing rates (280–360 rpm), biosorbent amounts (0.2–1 g), and contact times (10–180 min). According to the current environmental, economic, and technological considerations, the use of wheat stem due to the abundance of this agricultural waste resource, its low cost, and its high potential for heavy metals ions sorption assure us of this choice. Another important aspect is that, as far as we know, there has been no report on the use of wheat stem for removing lead ion from aqueous environment. This water treatment method can introduce facile and reasonably priced approach to protect the environment from dangerous properties of heavy metals ions.

2. Experimental section

1.6 g of $\text{Pb}(\text{NO}_3)_2$ (from Sigma-Aldrich company (St. Louis, MO, USA), $\geq 99.5\%$) was dissolved in 1-L of distilled water to obtain a 1,000 mg/L stock solution. The needed concentrations of the lead ions solution were 2.5, 5, 10, 15

and 20 ppm. Hence, the stock solution was diluted to obtain the lower concentrations using Eq. (1) [14].

$$C_1 \times V_1 = C_2 \times V_2 \quad (1)$$

where C_1 and C_2 are the lead ions concentrations in the stock solution and after dilution, respectively. V_1 is the sample volume removed from the stock solution and V_2 is the diluted sample volume.

In order to remove the dust or mud and layers, the wheat stem was washed with water, then it was rinsed twice with distilled water to eliminate possible fungi and mildew. The wheat stem was placed in a watch glass in an oven to remove any traces of water. The oven was set at 100°C for 5 h, then they were ground in a laboratory mortar. Then, 100 mL of the solution with particular lead ion concentration and pH was poured into a 250 mL Erlenmeyer flask. The biosorbent was then weighed and shed in the Erlenmeyer flask. The mixture was intermixed using a shaker. After a particular time, the shaker was paused and after 30 min to settle, the solution was filtered with a Whatman filter paper (Grade 40), and finally the lead ion concentration of the solution was determined by the atomic absorption spectrophotometer. Every test was carried out with 100 mL of solution. To examine the effect of pH, HCl or NaOH 0.1 M solutions were used. Biosorption tests at different contact times of 10, 20, 30, 45, 60, 90, 120 and 180 min and different lead ion concentrations of 2.5, 5, 10, 15, and 20 ppm were carried out.

The percent removal of metal ion was calculated using the following equation [14]:

$$\text{Removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

where C_0 is the initial concentration, and C_e represents the equilibrium concentration (mg/L). Q_e that is biosorption capacity at equilibrium can be calculated by Eq. (3) [14]:

$$Q_e = \frac{(C_0 - C_e)}{m} \times V \quad (3)$$

where V represents the volume of the solution (L), and m stands for the mass of the biosorbent (g).

3. Results and discussion

3.1. Investigating the effect of pH of the solution on lead ion removal

The pH of the solution is the most key parameter makes a difference to the efficiency of lead ion removal process using wheat stems [26]. Lead ion removal as a function of pH is shown in Fig. 1. According to the results, the optimum pH of the biosorption process is about 5 and by decreasing the pH, the amount of lead ion adsorbed diminishes due to the releasing of hydrogen ion in the solution. The hydrogen ion is smaller than lead ion, hence it gets adsorbed faster [27]. Also, in pH higher than 5 biosorption efficiency decreases because of the presence of hydrogen oxide ion and the fact that lead ion precipitates as hydroxide form in the solution [28,29].

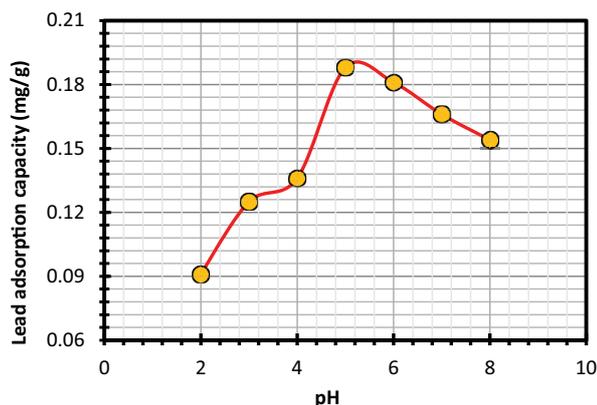


Fig. 1. The lead ion-adsorbing capacity in terms of pH using the wheat stem.

3.2. Investigating the effect of contact time on lead ion removal

Fig. 2 illustrates the lead ion-adsorbing capacity in terms of contact time using the wheat stem as biosorbent. This test was carried at the mixing rate of 320 rpm, the pH of 5, 2.5 ppm initial concentration of lead ion and 1 g biosorbent. As it can be seen, at an early stages of the process, the gradient of the graph is very high owing to the great surface area of the wheat stem and the high activity of active groups to build lead ion complexes. It is observed that the process becomes stable after about 90 min and the lead ion-adsorbing capacity is almost constant. The reason of this stability is the saturation of biosorption sites by lead ion. Therefore, the optimum biosorption time period is determined to be about 90 min [30,31].

3.3. Investigation of the effect of mixing rate on lead ion removal

The effect of mixing rate was investigated by the calculation of lead ion biosorption at mixing rates of 280, 320 and 360 rpm, the pH of 5, contact time of 90 min, 2.5 ppm initial concentration of lead ion and 1 g biosorbent. Fig. 3 exhibits the effect of mixing rate. It is observed that the highest biosorption rate is achieved at 320 rpm.

3.4. Investigating the effect of biosorbent amount on lead ion removal

The other controlling parameter of lead ion removal is biosorbent amount. Fig. 4 shows the lead ion removal percentage based on biosorbent amount (pH of 5, contact time of 90 min, 2.5 ppm initial concentration of lead) that demonstrates that with the increase in the biosorbent amount more lead ion is adsorbed. It is because of more surface area available for the biosorption.

3.5. Effect of initial concentration on lead ion removal

The effect of the initial concentration of lead ion solution on the biosorption was investigated by conducting tests with different lead ion concentrations of 2.5, 5, 10, 15 and 20 ppm. Fig. 5 illustrates the percentage of lead ion adsorbed in terms of the initial concentration of lead ion. Also, it can be concluded that for a certain amount of wheat stem, the

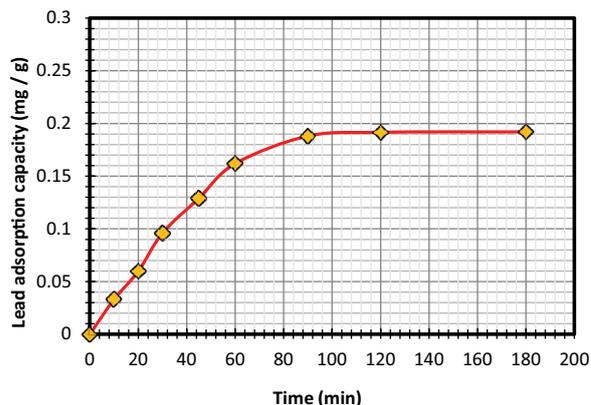


Fig. 2. The lead ion-adsorbing capacity in terms of contact time for the wheat stem.

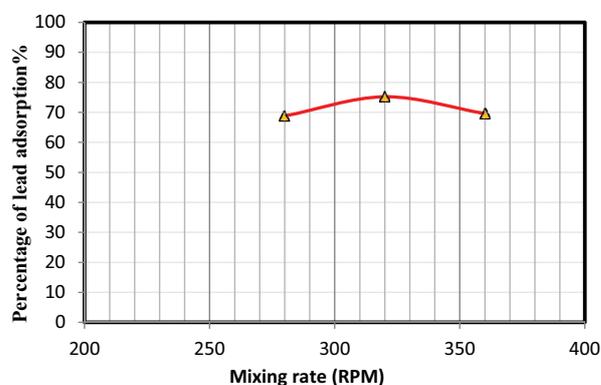


Fig. 3. The lead ion-adsorbing capacity in terms of mixing rate.

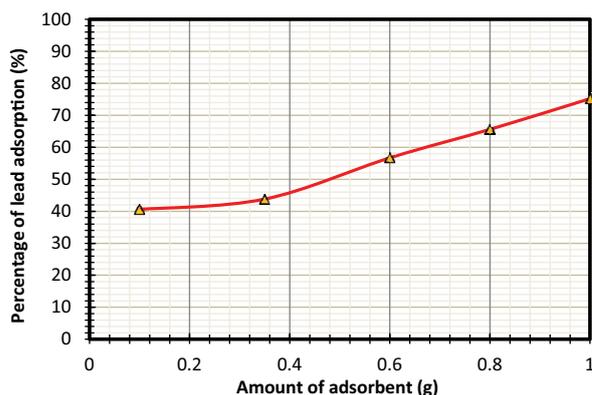


Fig. 4. Percentage of lead ion biosorption in terms of amount biosorbent.

percentage of lead ion adsorption decreases with the rise in the initial lead ion concentration. This phenomenon can be explained as in the low lead ion concentrations, lead ion is less than the available sites on biosorbent particles, but the increase in the lead ion concentration results in an excess amount of lead ion that cannot be adsorbed [32].

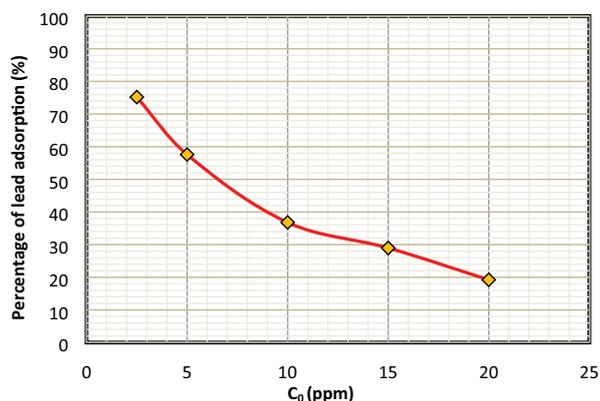


Fig. 5. Percentage of lead ion biosorption in terms of initial concentration.

3.6. Adsorption kinetics

The prediction of biosorption rate is one of the most key factors for a biosorption set [33]. The adsorption kinetics depends on the physical and chemical properties of the adsorbent, which affects the adsorption mechanism [34]. To investigate the adsorption mechanism, the adsorption constants of lead ion can be measured using the Lagergren equation, pseudo-first-order kinetic model, Ho equation, pseudo-second-order kinetic model, and intraparticle diffusion model [35,36].

The pseudo-first-order kinetic model could be described by Eq. (4) [14]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (4)$$

In this equation, q_e and q_t (mg/g) are the amounts of lead ion adsorbed at equilibrium and at any contact time t , respectively, and k_1 (1/min) is the rate constant of biosorption 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. (5) [37]:

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

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

To verify the diffusion process, the experimental data of lead ion biosorption by wheat stem were studied using the intraparticle diffusion model represented by Eq (6) [31]:

$$q_t = k_p t^{1/2} + X_i \quad (6)$$

where q_t is the concentration of lead ion adsorbed at a given time t (min), X_i stands for the intercept, and k_p

(mg/g min^{1/2}) represents the intraparticle diffusion rate constant. The k_p values were determined and presented using the straight line and the slope of the plot of q_t vs. $t^{1/2}$ (Fig. 6).

The curves of these models were plotted in Fig. 6. The plots are linear, which show the applicability of all three models. However, the value of R^2 for the pseudo-first-order kinetic model is higher. Therefore, the pseudo-first-order kinetic model provides a better fit for the adsorption of lead ion onto wheat stem than the other models.

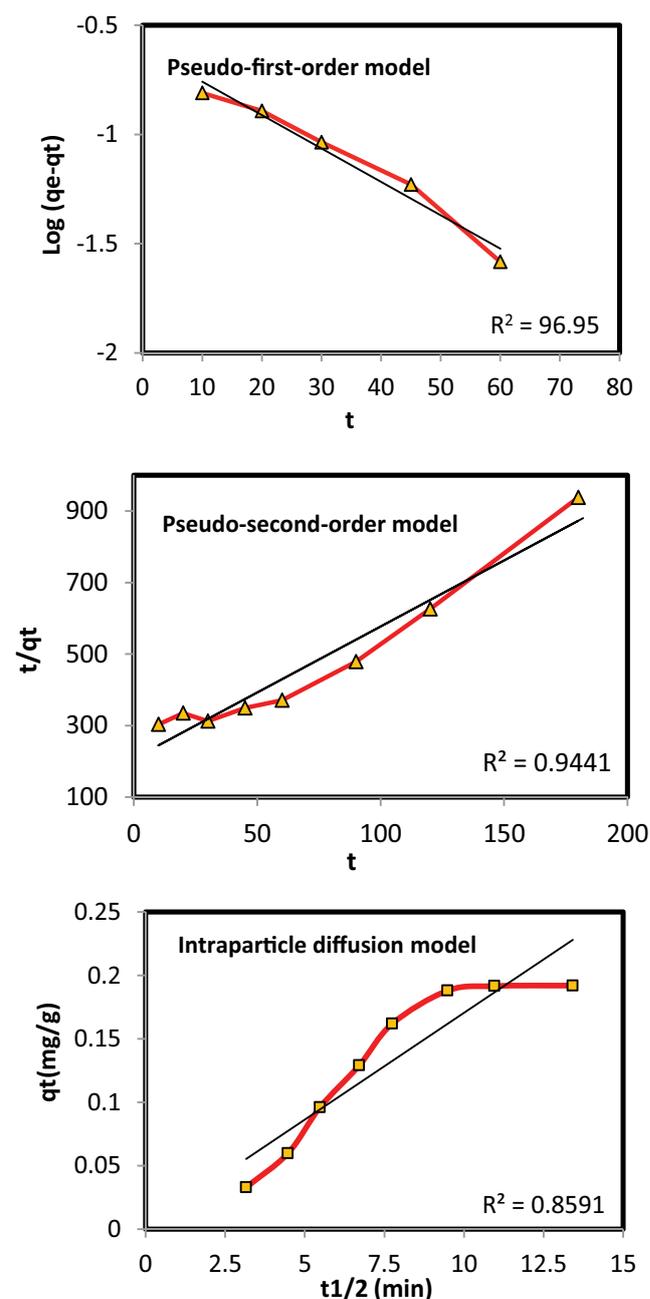


Fig. 6. Pseudo-first-order [14], pseudo-second-order [37], and intraparticle diffusion [31] kinetic plots for adsorption of lead ion onto wheat stem as biosorbent.

3.7. Adsorption isotherm study

The Freundlich, Langmuir, Temkin, and Dubinin–Radushkevich isotherm models were applied to study the interaction of lead ion with biosorbent [38,39]. The simplest theoretical model for adsorption was proposed by Langmuir in 1918. This model is actually used to describe the chemical adsorption on the surface of a homogeneous adsorbent. The Langmuir model contains assumptions for instance monolayer adsorption, surface uniformity and elimination of the interactions of the adsorbed molecules. The Langmuir equation for monolayer adsorption is expressed by Eq. (7) [40].

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (7)$$

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) represents the adsorption equilibrium constant. The constants K and q_m can be determined from the slope and intercept of the plot between C_e/q_e and C_e .

The Freundlich model is an exponential equation that as the adsorbent concentration in the solution increases, the adsorbent concentration in the adsorbent surface increases. This model is often better suited to the surface adsorption of liquid phases and is represented by Eq. (8) [41]:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (8)$$

where n and K_F (mg/g) (L/g)^{1/n} are the constants of Freundlich equation. K_F represents the adsorption capacity for the adsorbed 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.

The Temkin isotherm model offers insight and information about the relationship between adsorbate and adsorbent [42]:

$$q_e = B \ln A_T + B \ln C_e \quad (9)$$

Eq. (9)'s B constant could be written as Eq. (10) [42]:

$$B = \frac{RT}{b_T} \quad (10)$$

where A_T is the Temkin equilibrium binding constant (L/g), b_T represents the Temkin constant, B stands for the heat of sorption constant (J/mol), R is the gas constant (8.31 J/mol K), C_e represents the concentration of ion at equilibrium (mmol/L), and T is the absolute temperature (K).

The Dubinin–Radushkevich isotherm is similar to Langmuir type isotherm, but it is more common since it does not require a homogeneous surface or a constant sorption potential. The equation for the linearized Dubinin–Radushkevich isotherm is Eq. (11) [43]:

$$\ln q_e = \ln q_{\max} - \beta \varepsilon^2 \quad (11)$$

where q_e denotes the number of metal ions adsorbed per unit weight of adsorbent (mol/g), q_{\max} denotes the maximum sorption capacity (mol/g), β stands for the biosorption coefficient (mol/J)² related to mean sorption energy and ε denotes the polar potential which is given by Eq. (12) [43]:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (12)$$

The gas constant is 8.314 J/mol K and the temperature is T (K). The sorption power q_{\max} is determined by the intercept of the plot of $\ln q_e$ vs. ε^2 and the slope gives β .

The Freundlich [41], Langmuir [40], Temkin [42], and Dubinin–Radushkevich [43] isotherm models for the wheat stem are shown in Fig. 7. The calculated parameters values are presented in Table 1. The R^2 is considered as a measure of agreement of experimental data on the isotherm models [44]. The R^2 values of the Freundlich [41] and Langmuir [40] isotherm models are higher than the R^2 values of the Temkin [42] and Dubinin–Radushkevich [43] isotherm models, according to Table 1 [34]. The Dubinin–Radushkevich [43] isotherm was found to be unsuitable ($R^2 = 0.8477$). The applicability of the four isotherm models for the present data approximately follows the order: Freundlich > Langmuir > Temkin > Dubinin–Radushkevich.

3.8. Proposed removal mechanism

The removal of lead ion from aqueous environment by the wheat stem is done due to the presence of functional groups on the cell wall of the wheat stem, such as amine (NH₂), carboxyl (C=O), hydroxyl (R–OH), and sulfhydryl. A solid phase (wheat stem) and an aqueous phase containing lead ion are involved in the process. Due to the concentration causing diffusion through the cell wall and membrane, lead ion is attracted and bound to the wheat stem through a complex process that includes physisorption, chemisorption, ion exchange, surface precipitation, complexation, and chelation [43]. The following is a description of the adsorption mechanism [43]:

- 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 wheat stem.

3.9. Comparative study

In recent years, various studies have been undertaken using different biosorbents to remove toxic metals ions, especially lead ion. A few examples of them with their experimental conditions are given in Table 2 [27,45–48]. Studies show the capabilities of natural biosorbents in the lead ion removal. Comparing the results of this work with other results gives two points: the first point is the high performance of biosorbent for the lead ion removal using wheat stem in 90 min. Another important point is the availability and low price of the wheat stem.

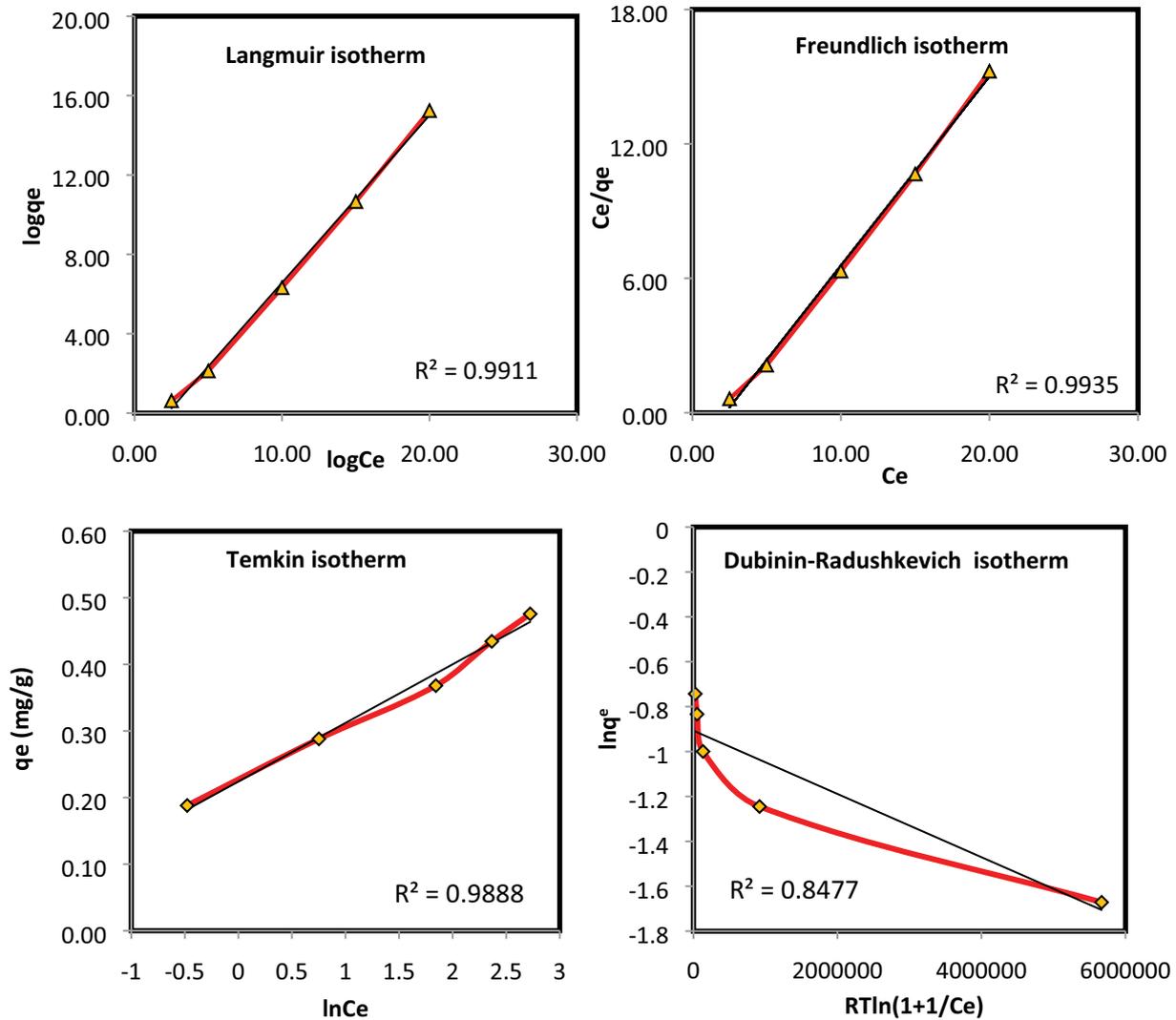


Fig. 7. Langmuir [40], Freundlich [41], Temkin [42], and Dubinin–Radushkevich [43] adsorption isotherms in the process of removing lead ion from aqueous environment by the wheat stem as biosorbent.

Table 1
The calculated isotherm parameters

Isotherm	Freundlich [41]	Temkin [42]	Dubinin–Radushkevich [43]	Langmuir [40]
Plot	$\ln q_e$ vs. $\ln C_e$	q_e vs. $\ln C_e$	$\ln q_e$ vs. ε^2	C_e/q_e vs. C_e
R^2	0.9935	0.9888	0.8477	0.9911
Adsorption isotherm parameters	$K_F = 0.2215$ $1/n = 0.2843$	$B = 0.0875$ $A_T = 13.1839$	$q_{max} = 0.4036$ $\beta = 0.0062$	$K_L = 0.607$ $q_{max} = 0.512$

4. Conclusion

This study indicates that the wheat stem is a suitable biosorbent for lead ion removal from water. Effect of different factors such as pH, mixing rate, contact time, initial concentration, and biosorbent amount on the lead ion removal from aqueous solution was considered. The finding results

show that the optimum pH is 5 and the optimum contact time period is about 90 min. The Freundlich [41], Langmuir [40], Temkin [42], and Dubinin–Radushkevich [43] isotherm models were used to fit the experimental data. Kinetic studies (pseudo-first-order [14], pseudo-second-order [37], and intraparticle diffusion [31] models) were undertaken to determine the biosorption mechanism. The consequences of

Table 2

Comparison of the results of this study with other results for biosorption of lead ion from aqueous environment reported in the literature

Biosorbent	Time	pH	References	Initial metal concentration	Removal percentage	Maximum adsorption capacity
Waste fungal biomass	30 min	–	[45]	1 ppm	80%	–
Native garlic peel	1–120 min	–	[46]	1–200 ppm	–	51.73 (mg/g)
Peanut husk	3 h	6	[47]	20 ppm	25%–99%	(19.7–49.4)
Banana peel	30 min	5	[48]	30–80 ppm	–	2.18 (mg/g)
Saffron flower waste	9 min	6	[27]	10–100 ppm	–	45.6
Wheat stem	90 min	5	This work	2.5 ppm	75.2%	–

data show that using wheat stem can be a promising process to remove lead ion from water considering the low cost and availability of the wheat stem and its proper biosorption capacity. Additionally, it is expected that wheat stem can be used not only in the laboratory scale but also in industrial processes in the future.

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