RESEARCH LETTER

Remediation of lead by pretreated red algae: adsorption isotherm, kinetic, column modeling and simulation studies

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Batch and column biosorption experiments were carried on for lead uptake using ecofriendly biosorbents (raw and calcium chloride [CaCl2] or formaldehyde pretreated form of red marine algae Jania rubens [Linnaeus]). The best-fit (linear and nonlinear) isotherms, kinetics, and column adsorption models were identified using statistical analysis. Freundlich, Langmuir, Temkin, Redlich–Peterson, and Elovich adsorption isotherm models were tested. Highest adsorption capacity (774 mg/g) has been observed with Jania algae pretreated with formaldehyde. Pseudo-first- and second-order adsorption kinetics were applicable. The column capacity for lead removal with Jania pretreated with CaCl2 was found to be 1089.6 (mg/g) from the breakthrough curve area method. Thomas, Yoon-Nelson, Yan, and Clark column models were tested with regression analysis. Thomas model is the best column model with capacity $q_{1B} = 1092.4$ mg/g. Overall, 98.5% regeneration of column was achieved, indicating the suitability of using algae materials in multioperational cycles. Adsorbed lead present in algae material was confirmed by thermal analysis.

Keywords: biosorption; Jania algae; column; lead

Introduction

Lead is one of the major environmental risk factors, with a number of associated deaths that doubled from 1990 to 2010 (1). Among these, cases of lead poisoning were reported in Zamfara State, Nigeria, which led to the death of several people and animals as a result of lead contamination of water bodies (streams and rivers) (2, 3). The imposition of strict regulations increased the demand for innovative treatment technologies to remove metals from wastewater and to attain today’s toxicity-driven concentration limits (4).

Adsorption is considered a simple and economical technique for wastewater treatment (5, 6). Adsorption onto activated carbon has been found competitive with other physical and chemical techniques, such as flocculation, coagulation, and precipitation, as they possess inherent limitations such as high cost, formation of hazardous by-products, and intensive energy requirements (7). Even though activated carbon showed advantages, its main drawback is its high cost and difficult regeneration (8). For this reason, there is a need for developing ecofriendly and economically alternative materials and methods for wastewater treatment (9).

The dead algae biomass have many features that make them ideal candidates for selective removal of heavy metals: cell wall containing sulfated ester polysaccharides and polyuronides (rich with sulfate and carboxylic acid functional groups capable of metal uptake), and large surface area/volume ratios (10). Biological materials, which have better performance and low cost for better remediation, are hindered by small particle size with low density, poor mechanical strength, and rigidity (11). In general, the algae materials are very soft with a tendency to disintegrate which prevents the follow-up experiments even in laboratory column. Immobilization of biomass within a suitable matrix through chemical pretreatment can overcome these problems by offering ideal size, improved mechanical strength, rigidity and porosity (12), and higher biomass concentration, which may be well suited for nondestructive recovery and industrial application (13). One method of immobilizing biomass is the addition of a cross-linker which leads to the formation of stable cellular aggregates. This technique was found useful for immobilization of algae (14).

Many researchers reported on a batch system, but batch operations are not available in practice, and the
Experimental

Chemicals
All materials and reagents used were of commercial grades and were stored under dry conditions. All reagents were purchased from Fluka and Aldrich: lead nitrate (98%), formaldehyde (37%), calcium chloride (CaCl₂), hydrochloric acid (37%), sodium hydroxide (98%) and sodium carbonate, acetic acid (100%), and sodium acetate. Stock solutions were prepared in deionized water, and standard solutions for biosorption experiments were prepared by dilution.

Equipment and instruments
Desiccators, pH meter (Mettler Toledo Model MP 220), centrifuge (Centuriol Scientific LTD), Water-bath (p-Selecta Precisterm), balance (Ohaus Adventurer), oven, Fourier transform infrared spectroscopy (FTIR; Shimadzu 83000), Atomic Absorption Spectrophotometer (Buck Scientific 500), Thermal analyzer (SETARAM LABSYS).

Preparation of biosorbent
Algae collection
The red algae Jania ruben (Linnaeus) was collected from the Lebanese coast (Mediterranean Sea) at Tripoli Bay, near Al Mina shore. The living seaweed Jania was picked up from 0.3 m depth by hand. The wet algae samples were taken into plastic bags which were filled with seawater and then taken to the laboratory immediately. In the laboratory, the wet algae were first washed twice with tap water to remove salt, epiphytes, and other contaminants, and then they were washed with deionized water again. The material was dried at 70°C for 16 h. The algae was then ground with mortar and pestle and stored in desiccators. Finally, the dried powder of Jania (J) was preserved in a glass bottle in a dark place for future use.

Pretreatment with CaCl₂
A quantity of 5 g of dried biomass was treated with 200 mL of 0.2 M CaCl₂ solution at pH 5. The mixture was shaken for 24 h on a rotary shaker at 175 rpm at 25°C, to ensure completeness of cross-linking and ion exchange of alginate materials. The biomass was filtered and washed with deionized water to remove excess calcium. The Jania algae pretreated with CaCl₂ (JC) was then dried in an oven at 60°C for 24 h (19).

Pretreatment with H₂CO
A quantity of 17 mL of 36% formaldehyde and 33 mL of 0.1 M HCl solutions were added onto 2.5 g of dried biomass. The mixture was stirred for 1 h, where polymerization and cross-linkage of alginate materials were achieved. The biomass was then filtered, washed with distilled water, 0.2 M Na₂CO₃ solution, and finally with deionized water. Jania pretreated with formaldehyde (JF) was dried overnight at 60°C and at 110°C for 2 h (20).

Adsorbate preparation
A stock of Pb(II) solution (2000 ppm) was prepared from lead nitrate in 1L volumetric flask using deionized water.

Adsorption kinetics and activation thermodynamic parameters
The experiment was done by soaking a mixture of 0.25 g of algae sorbent (raw or treated) in 250 mL lead solution (600 ppm) at neutral pH and at different temperatures. The concentration of lead solution remaining at time t is determined by atomic absorption.

Adsorption isotherm
The experiment was done by soaking a mixture of 0.1 g of algae sorbent and 100 mL of lead (100–1000 ppm) for 6 h (when biosorbent is J or JF) and for 1 h (when biosorbent is JC) at constant temperature, and pH 7. The solutions were then separated from the sorbent by centrifugation for 5 min at 3000 rpm. The concentration of remaining lead solution at time t is determined by atomic absorption spectrophotometer.

Column studies
Column adsorption studies
Column flow studies were carried out using a Pyrex glass column (20 cm length × 2.5 cm diameter) filled with 1 g of JC by tapping so that the column was filled without gaps. The influent aqueous solution containing a known concentration C₀ (500 ppm) of lead was passed through the column bed in a
downward manner at a constant flow rate of 2 ml/min at 25°C. The effluent solution was collected as a function of time, and the concentration of lead in the effluent solution was determined by atomic absorption after dilution. The results of column flow experiments were used to obtain the breakthrough curves by plotting $C_t/C_0$ versus the volume of effluent $V_{ef}$ or $C_{ads}$ versus time $t$ where $C_{ads}$ (mg/L) is the concentration of adsorbed pollutant.

**Column desorption studies**

Desorption of solute from the loaded adsorbent was carried out by adding HCl eluent solution (0.1 M) into the column at a fixed flow rate of 2 ml/min at room temperature. Effluent samples were collected at different time intervals and the concentration of adsorbates therein determined. When the concentration of the outlet solution was zero or close to zero, it was assumed that the column had been regenerated. The adsorbent column was then washed with distilled water till pH 7 is attained to remove any traces of the HCl solution before the influent adsorbate solution was reintroduced for subsequent adsorption/desorption cycles.

**Thermal analysis procedure**

Thermal Gravimetric Analysis – Differential Scanning Calorimetry (TGA-DSC) curves were recorded on SETARAM LABSYS Thermal analyzer in the flow of N$_2$ within the 20–850°C temperature range, with a heating rate of 3°C/min.

**Theory, models, and calculations**

**Computational method, error, and regression coefficient calculation**

The computational part of the obtained experimental measurements is introduced to obtain the curve which best fits the data in least-squares sense, and the following minimization problem is solved by calculating the error equations defined in (1–6) and the regression coefficients defined in (7–8) and listed in Table 1.

**Adsorption kinetics**

**Pseudo-first-order kinetic model (Lagergren model)**

This model assumes that the rate of change of solute uptake with time is directly proportional to the difference in saturation concentration and the amount of solid uptake with time. The rate constant of adsorption is expressed as a first-order rate expression given in Equation (1) (21):

$$\frac{dq}{dt} = k_1 (q_e - q_t)$$

(1)

The nonlinear form of pseudo-first-order kinetic equation of Lagergren is expressed as Equation (2):

$$q_t = q_e (1 - \exp(-k_1t))$$

(2)

where $k_1$ is the rate constant of pseudo-first-order adsorption (1/h), and $q_e$ and $q_t$ are the amounts of lead adsorbed per gram of biosorbent (mg/g) at equilibrium and at time $t$ (h).

**Pseudo-second-order kinetic model (Ho model)**

The kinetics of adsorption process may also be described by pseudo-second-order rate equation (21),

| Error and regression coefficient functions for best-fitting model estimation. |
|---------------------------------------------|
| $SSE$ = \sum (y_{exp} - y_{cal})^2$          |
| $MPSED$ = $\sqrt{\frac{\sum(y_{exp} - y_{cal})^2}{N-p}} \times 100$ |
| $\rho^2$ = $\frac{S^2}{S(XX)S(YY)}$          |
| ARED = $\frac{1}{N} \sum \frac{|y_{exp} - y_{cal}|}{y_{exp}} \times 100$ |
| RMSE = $\sqrt{\frac{\sum(y_{exp} - y_{cal})^2}{N}}$ |
| Hybrid = $\frac{1}{N-p} \sum \frac{|y_{exp} - y_{cal}|}{y_{exp}} \times 100$ |
| Chi-square = $\sum \frac{(y_{exp} - y_{cal})^2}{y_{cal}}$ |
| $r$ = $\frac{N(\sum XY) - (\sum X)(\sum Y)}{\sqrt{[N\sum X^2 - (\sum X)^2][N\sum Y^2 - (\sum Y)^2]}}$ |
Equation (3):
\[
\frac{dq}{dt} = k_H (q_e - q)^2
\]  
(3)

The nonlinear form of pseudo-first- and second-order kinetic equation is expressed as Equation (4):
\[
q_t = \frac{q_e^2 k_H t}{1 + q_e k_H t}
\]  
(4)

where \( k_H \) is the equilibrium rate constant for pseudo-second-order sorption (g/mg·h). Pseudo-second-order kinetic model is used as a presentation of chemisorptions behavior of the reaction (22–24).

**Intraparticle diffusion model**

Weber-Morris found that in many biosorption cases, solute uptake varies almost proportionally with \( t^{1/2} \) rather than with the contact time \( t \) (23):

The intraparticle diffusion model (26) is expressed as Equation (5):
\[
q_t = K_i t^{1/2} + I
\]  
(5)

where \( q_t \) is the fraction dye uptake (mg/g) at time \( t \), \( K_i \) is the intraparticle diffusion rate constant (mg/g min\(^{1/2}\)), and \( I \) is the intercept (mg/g). The plot of \( qt \) versus \( t^{1/2} \) gives \( K_i \) as slope and \( I \) as intercept.

**Activation parameters**

The activation energy (\( Ea \)) for biosorption of Pb(II) onto algae was calculated from the slope of the plot \( \ln(k_H) \) versus \( 1/T \) using the Arrhenius equation (27), \( k_H \) being the second-order rate constant. The activation enthalpy \( \Delta H^a \) at each temperature can be calculated from \( E_a - RT \). The \( \Delta H^a \) value can also be calculated from the slope of the plot of \( \ln(k_H/T) \) versus \( 1/T \) by the use of Eyring equation. The intercept gives the value of activation entropy \( \Delta S^a \) (27). The free activation Gibbs energy \( \Delta G^a \) at each temperature can be calculated from \( \Delta H^a - T \Delta S^a \).

**Adsorption isotherm**

Adsorption is usually modeled by isotherms which relate the relative concentrations of the solute adsorbed to the solid \( (Q_s) \) and in the solution \( (C_e) \). The equilibrium data were analyzed using most commonly used isotherm equations: Langmuir, Freundlich, Redlich–Peterson, Temkin, and Elovich models. The nonlinear isotherm model expressions are given by the following equations:

**Langmuir model (28).** The Langmuir isotherm considers sorption as a chemical phenomenon. Langmuir’s isotherm is known as monolayer adsorption onto a surface with a finite number of similar active sites. The well-known nonlinear expression of Langmuir model is given by Equation (6):
\[
Q_e = \frac{Q^0 K_L C_e}{1 + K_L C_e}
\]  
(6)

where \( Q^0 \) (mg/g) is the maximum sorbate uptake and \( K_L \) is a coefficient related to the affinity between the sorbent and the sorbate.

**Freundlich model** is based on sorption onto a heterogenous surface (29). The Freundlich relationship is exponential, and the nonlinear expression of the Freundlich model is given by Equation (7):
\[
Q_e = K_F (C_e)^{1/n}
\]  
(7)

where \( K_F \) and \( n \) are Freundlich constants.

**Redlich–Peterson** model is a general equation (Equation 8) that includes both Freundlich and Langmuir features (30).
\[
Q_e = \frac{A_{RP} C_e}{1 + K_{RP} C_e^n}
\]  
(8)

where \( A_{RP} \), \( K_{RP} \), and \( n \) are parameters to be estimated. \( n \) lies between 0 and 1, it has two limiting behaviors: Langmuir form for \( n = 1 \) and Henry’s law form for \( n = 0 \).

**Temkin model** explains the sorbent/sorbate interactions in relation to the heat of adsorption (31). The nonlinear Temkin Equation (9) is:
\[
Q_e = (RT/b) \ln(K_T C_e)
\]  
(9)

where \( B_T = (RT/b) \) is a factor related to the heat of adsorption and \( K_T \) is Temkin equilibrium constant (L/mg).

**Elovich model** deals with multilayer adsorption, based on a kinetic principle that adsorption site increase exponentially with adsorption. \( K_E \) is Elovich equilibrium constant, and \( Q_E \) is Elovich maximum adsorption capacity (32). The nonlinear Elovich form is described in Equation (10):
\[
\frac{Q_e}{Q_E} = K_E C_e e^{-\frac{Q_e}{Q_E}}
\]  
(10)
Table 2. Column adsorption capacity calculation.

\[
A = \int_{t=0}^{t_{total}} C_{ad} dt
\]

\[
\frac{QA}{1000} = \frac{C_{o}Q_{t_{total}}}{1000}
\]

\[
\frac{q_{total}}{m_{total}} = \frac{q_{t_{total}} \times 100}{m}
\]

\[
C_{e} = \frac{A}{t_{total}}
\]

Column models

Theory

The effectiveness of a biomass and the dynamic behavior of a fixed-bed column can be evaluated from the breakthrough curve of the effluent concentration (33). The breakthrough curves explain the loading behavior of heavy metal to be eliminated from wastewater in a fixed-bed operation. It is the plot of adsorbed metal concentration \(C_{ad}\) or normalized concentration \(C/Co\) as a function of volume of effluent or time for a given bed height (34). The volume of the effluent, \(V\) (ml), is equal to \(Q\cdot t\), where \(t\) and \(Q\) are the total flow rate (min) and volumetric flow rate (ml/min), respectively. Integrating the adsorbed concentration \(C_{ad}\), mg/l versus \(t\) (min) gives the area under the breakthrough curve \(A\). The total adsorbed metal quantity or the maximum of column capacity \(q_{total}\), mg, for a given feed concentration and flow rate, can be calculated from the area \(A\) using the equation in Table 2. The total amount of heavy metal ion pollutant sent to column \(m_{total}\), mg, can be evaluated from the equation in Table 2. Total\% removal of heavy metal ion (column performance) can be evaluated from the ratio 100 \((q_{total}/m_{total})\). The column adsorption capacity \(q_{e}\) mg/g is the ratio of \(q_{total}\) (mg) per \(m\) the mass of sorbent in (g). The equilibrium Pb(II) concentration, \(C_{e}\) (mg/L), can be calculated as 1000 \((m_{total}-q_{total})/V_{eff}\) or rearranged to the equation given in Table 2.

Modeling

The different linear and nonlinear column models used to study adsorption of lead into various algae materials are listed in Table 3.

Thomas model solution is one of the most general and widely used methods in column performance theory. The model equation is described in Table 3, where \(K_{Th}\) is the Thomas rate constant (ml/min/mg) and \(q_{T}\) is the maximum solid-phase concentration of the solute (mg/g) (35, 36).

Yan et al. (37) proposed an empirical equation (Table 3) which could overcome the drawback in Thomas model especially its serious deficiency in predicting the effluent concentration with respect to time zero. \(K_{Y}\) is the kinetic rate constant for Yan model (L/min/mg); \(q_{y}\) is the maximum adsorption capacity (mg/g) of adsorbent estimated by Yan model (37).

Yoon and Nelson have developed a relatively simple model (38). This model not only is less complicated than other models but also requires no detailed data concerning the characteristics of adsorbate, the type of adsorbent, and the physical properties of the adsorption bed. The Yoon and Nelson equation for a single component system is expressed in Table 3, where \(K_{YN}\) is the rate constant (1/min); \(\tau\), the time required for 50% adsorbate breakthrough (min); and \(t\) is the breakthrough (sampling) time (min). The calculation of theoretical breakthrough curves for a single-component system requires the determination of the parameters \(K_{YN}\) and \(\tau\) for the adsorbate of

Table 3. Nonlinear and linear equations of different kinetic column models.

| Kinetic models       | Nonlinear equations | Linear equations |
|---------------------|---------------------|------------------|
| Thomas model        | \(\frac{C_{e}}{C_{o}} = \frac{1}{1+exp\left(\frac{Q_{y}X-C_{o}}{Q_{o}}\right)}\) | \(\ln\left(\frac{C_{e}}{C_{o}}\right) + 1 = \left(\frac{K_{YN}Q_{y}}{Q_{o}}\right) - (K_{Th}C_{o}t)\) |
| Yoon-Nelson model   | \(\frac{C_{e}}{C_{o}} = 1 - \frac{1}{1+\left(\frac{Q_{y}}{Q_{o}}\right)^{\frac{1}{n}}}\) | \(\ln\left(\frac{C_{e}}{C_{o}}\right) = \frac{K_{YN}}{Q_{o}}t \ln\left(\frac{Q_{y}}{Q_{o}}\right) + \left(\frac{Q_{y}}{Q_{o}}\right)\) |
| Yan et al. model    | \(\frac{C_{e}}{C_{o}} = 1 - \frac{1}{1+\left(\frac{Q_{y}}{Q_{o}}\right)^{\frac{1}{n}}}\) | \(\ln\left(\frac{C_{e}}{C_{o}}\right) - 1 = \lnA - \tau t\) |
| Clark model         | \(\frac{C_{e}}{C_{o}} = \left(\frac{1}{1+\tau t}\right)^{n}\) | \(n = \text{Freundlich exponent}\) |
interest. These values may be determined from available experimental data (38, 39).

Model developed by Clark is based on the use of mass transfer concept in combination with the Freundlich isotherm, (40), where $A$ and $r$ are parameters of the kinetic equation and $n$ corresponds to the exponent of the Freundlich isotherm, Table 3.

Results and discussion

The experimental data are fitted to various kinetics, isotherm, and column adsorption models. In each case, the best fitted model chosen is the one with highest $R^2$ and $r$ and the lowest ARED, MPSED, HYBRID, SSE, RMSE, and $\chi^2$ values.

Ad sorption kinetics

The experimental data-sets were fitted to the nonlinear form of each model. Figures 1–3 illustrate the kinetic models fitted to experimental data obtained at 30°C. The determined kinetic parameters are summarized in Tables 4–7.

Kinetic studies show that a contact time of 6 h is needed for the system to reach the equilibrium when the biosorbents are raw Jania algae (J) or JF, while a contact time of 1 h was enough for the system to reach the equilibrium when the biosorbent is JC.

The correlation coefficient ($R^2$) for pseudo-first-order kinetic adsorption model with $J$ and $JF$ is higher than for pseudo-second-order model, while for $JC$ algae, the regression coefficient ($R^2$) for pseudo-second-order model is higher than pseudo-first-order kinetic adsorption model (Figures 1 and 2 and Tables 4 and 5). Thus for Jania and $JF$, pseudo-first-order kinetic model is applicable, while for $JC$, pseudo-second order kinetic model is more applicable.

The nonlinear regression has been performed to fit the intraparticle diffusion kinetic model by using the curve-fitting technique with Microcal Origin. The values of $k_i$ and $I$ are summarized in Table 6 along with the values of error functions for initial lead concentrations (600 ppm).

It may be found from the intraparticle diffusion representation of data that all plots are double linear (Figure 3 and Table 7). In the first straight line, the
sudden increase in slope (within a short time period) signifies that the Pb(II) ions diffuse onto macropores of the algae particles and its rate is fast. After that the Pb(II) ions diffuse through the mesopores of the algae particles, which is represented in a second straight line and its rate is slower. Both the lines do not pass through the origin which suggests that both film diffusion and intraparticle diffusion are simultaneously occurring during the adsorption of Pb(II) onto different algae materials.

Table 4. Parameter values, error, and regressions coefficient for pseudo-first-order model obtained by nonlinear approach for adsorption of lead at 30°C onto algae materials: J, JF, and JC.

| Sorbent | ppm | $Q_e$ exp (mg/g) | $k_1$ (1/h) (RMSE) | $Q_e$ calc (mg/g) (MPSED) | $R^2$ (HYBRID) | $\chi^2$ (ARED) | SSE ($r^2$) |
|---------|-----|-----------------|-------------------|------------------|--------------|---------------|-------------|
| J       | 600 | 341.8           | 0.343             | 425.7            | 0.937        | 577           | 7824        |
| JF      | 600 | 381.6           | 0.424             | 427.0            | 0.998        | 4.90          | 413         |
| JC      | 600 | 335.8           | 14.20             | 321.9            | 0.959        | 18.85         | 1735        |

Table 5. Parameter values, error, and regression coefficient for pseudo-second-order model obtained by nonlinear approach for adsorption of lead onto algae materials J, JF, and JC at 30°C.

| Sorbent | ppm | $Q_e$ exp (mg/g) | $k_{II}$ (g/mgh) (RMSE) | $Q_e$ calc (mg/g) (MPSED) | $R^2$ (HYBRID) | $\chi^2$ (ARED) | SSE ($r^2$) |
|---------|-----|-----------------|--------------------------|------------------|--------------|---------------|-------------|
| J       | 600 | 341.8           | 0.00115 (38.79)          | 443.1            | 0.892        | 373           | 13514       |
| JF      | 600 | 381.6           | 4.9 × 10^{-4} (7.18) (11.41) | 628.6            | 0.997        | 5.62          | 515         |
| JC      | 600 | 335.8           | 0.0406 (8.09)            | 390.7            | 0.988        | 5.34          | 524         |

Table 6. Parameter values, error, and regression coefficients for intraparticle diffusion model for adsorption of lead (600 ppm) onto J, JF, and JC adsorbents using nonlinear approach at 30°C.

| Sorbent | $k_i$ (mg/g/h^{1/2}) (RMSE) | $I_1$ (mg/g) (MPSED) | $R^2$ (HYBRID) | $\chi^2$ (ARED) | SSE ($r^2$) |
|---------|-----------------------------|---------------------|---------------|----------------|-------------|
| J       | 149 (39.71)                 | 3.72                | 0.886         | 93.57          | 14190       |
| JF      | 201 (11.84)                 | −55.48              | 0.990         | 12.44          | 1402        |
| JC      | 520 (14.37)                 | 56.11               | 0.961         | 8.19           | 1651        |

Table 7. Parameter values, error, and regression coefficient for intraparticle diffusion model for adsorption of lead (600 ppm) onto J, JF, and JC adsorbents using linear approach at 30°C.

Intraparticle diffusion model (linear)

| Sorbent | $k_{i,1}$ (mg/g/h^{1/2}) | $I_1$ (mg/g) | $R^2$ | $k_{i,2}$ (mg/g/h^{1/2}) | $I_2$ (mg/g) | $R^2$ |
|---------|---------------------------|--------------|-------|--------------------------|--------------|-------|
| J       | 109                       | 3.36         | 0.803 | 563                      | −710.3       | 0.998 |
| JF      | 205                       | −60.55       | 0.952 | 155                      | 32.66        | 0.997 |
| JC      | 692                       | 13.98        | 0.997 | 320                      | 151.3        | 0.999 |

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Kinetics activation parameters

The activation energy and other kinetics parameters were studied in the range of temperature (298–318 K), and the results are listed in Table 8 and in Figures 4 and 5.

In general, the $\Delta G^\#$ values are positive at all temperatures, suggesting that biosorption phenomenon requires some energy from an external source. A positive value of $\Delta H^\#$ suggests that the biosorption phenomenon is endothermic. The negative value of $\Delta S^\#$ suggests that the adsorption process involves an associative mechanism. The adsorption leads to an increase in order through the formation of an activated thermodynamics complex between the adsorbate and the adsorbent. Also a negative value of $\Delta S^\#$ reflects that more ordered adsorbent–sorbent structure is obtained during the adsorption process.

Adsorption isotherm

Data gave best fitting by both Temkin and Redlich–Peterson models for the biosorption of Pb(II) onto $J$, $JF$, and $JC$ based on the values of calculated error function (highest $R^2$ values and lowest for most of the rest ARED, MPSED, HYBRID, SSE, RMSE, and $\chi^2$ values); Table 9 and Figure 6. The suitability of Temkin model indicates that sorbent/sorbate interactions are governed by heat of adsorption. Redlich–Peterson model is also suitable which includes both Freundlich and Langmuir features. The obtained values with Redlich–Peterson model of 0.84–1.30 for $\beta$ (which is close to 1.0) are expected for Langmuir form indicating that adsorption can be explained more by monolayer adsorption onto a surface with a finite number of similar active sites rather than by adsorption onto a heterogenous surface (Freundlich model); Table 9.

The high Langmuir adsorption capacity of 696 mg/g, 774 mg/g and 716 mg/g for $J$, $JF$, and $JC$.
Table 9. The results of nonlinear approach of Langmuir, Freundlich, Temkin, Elovich, and Redlich–Peterson isotherm constants for the adsorption of lead at 30°C onto (A) J, (B) JF, and (C) JC:

|                | Langmuir | Freundlich | Temkin |
|----------------|----------|------------|--------|
| **A** Sorbent: J |          |            |        |
| \( Q_0^{\exp} \) (mg/g) | \( Q_0^{\calc} \) (mg/g) | \( b \) (L/mg) | \( R^2 \) | \( K_T \) (mg/g) \( \chi_{bT} \) (J/mol) | \( R^2 \) | \( \chi^2 \) |
| 632.5          | 696.4    | 0.0158     | 0.968  | 61.50 | 2.52 | 0.954 | 61.54 | 148.24 | 0.166 | 0.979 | 34.61 |
| \( \chi^2 \)  | SSE      | ARED       | HYBRID | MSE   | SSE  | ARED | HYBRID | MSE   | SSE  | ARED | HYBRID | MSE   |
| 1147           | 9182     | 11.88      | 14.85  | 22.80 | 13103 | 15.33 | 19.16  | 40.05 | 6106 | 10.51 | 13.14  | 22.61 |
|                |          |            |        |        | Elovich | Redlich–Peterson |
| \( Q_e \) (mg/g) | \( K_e \) (L/mg) | \( R^2 \) | \( \chi^2 \) | \( A_{kp} \) (L/mg) | \( \beta_{kp} \) | \( K_{kp} \) (L/g) | \( R^2 \) |
| 502.4          | 0.0126   | 0.737      | 606    | 15.52 | 0.84 | 0.0577 | 0.975 |
| SSE            | ARED     | HYBRID     | MSE    | SSE   | ARED | HYBRID | MSE   | SSE  | ARED | HYBRID | MSE   |
| 94406          | 25.55    | 31.94      | 36.62  | 40.15 | 7238 | 11.76 | 16.81  | 29.58 |
| **B** Sorbent: JF |          |            |        |
| \( Q_0^{\exp} \) (mg/g) | \( Q_0^{\calc} \) (mg/g) | \( b \) (L/mg) | \( R^2 \) | \( K_T \) (mg/g) \( \chi_{bT} \) (J/mol) | \( R^2 \) | \( \chi^2 \) |
| 645.6          | 774.0    | 0.00369    | 0.984  | 70.86 | 2.62 | 0.967 | 46.7 | 146.69 | 0.209 | 0.996 | 2.58 |
| \( \chi^2 \)  | SSE      | ARED       | HYBRID | MSE   | SSE  | ARED | HYBRID | MSE   | SSE  | ARED | HYBRID | MSE   |
| 384            | 3077     | 5.52       | 6.90   | 7.32  | 10372 | 13.2 | 16.5   | 29.5  | 1261 | 2.08  | 2.60   | 2.83  |
|                |          |            |        |        | Elovich | Redlich–Peterson |
| \( Q_e \) (mg/g) | \( K_e \) (L/mg) | \( R^2 \) | \( \chi^2 \) | \( A_{kp} \) (L/mg) | \( \beta_{kp} \) | \( K_{kp} \) (L/g) | \( R^2 \) |
| 531.1          | 0.0127   | 0.796      | 3263   | 18.17 | 0.86 | 0.0589 | 0.992 |
| SSE            | ARED     | HYBRID     | MSE    | SSE   | ARED | HYBRID | MSE   | SSE  | ARED | HYBRID | MSE   |
| 1622753        | 70.1     | 87.6       | 83.7   | 10.1  | 2392 | 5.30  | 7.60   | 12.0  |
| **C** Sorbent: JC |          |            |        |
| \( Q_0^{\exp} \) (mg/g) | \( Q_0^{\calc} \) (mg/g) | \( b \) (L/mg) | \( R^2 \) | \( K_T \) (mg/g) \( \chi_{bT} \) (J/mol) | \( R^2 \) | \( \chi^2 \) |
| 564.4          | 716.1    | 0.00974    | 0.964  | 44.95 | 2.32 | 0.894 | 108  | 169.79 | 0.078 | 0.966 | 41.3  |
| \( \chi^2 \)  | SSE      | ARED       | HYBRID | MSE   | SSE  | ARED | HYBRID | MSE   | SSE  | ARED | HYBRID | MSE   |
| 1154           | 9236     | 14.4       | 18.0   | 41.3  | 27232 | 24.4 | 30.5   | 59.5  | 8545 | 13.4  | 16.8   | 31.7  |
|                |          |            |        |        | Elovich | Redlich–Peterson |
| \( Q_e \) (mg/g) | \( K_e \) (L/mg) | \( R^2 \) | \( \chi^2 \) | \( A_{kp} \) (L/mg) | \( \beta_{kp} \) | \( K_{kp} \) (L/g) | \( R^2 \) |
| 425.9          | 0.0141   | 0.714      | 3369   | 5.35  | 1.30 | 0.00117 | 0.975 |
| SSE            | ARED     | HYBRID     | MSE    | SSE   | ARED | HYBRID | MSE   | SSE  | ARED | HYBRID | MSE   |
| 21837          | 94.9     | 119        | 115    | 38.8  | 6372 | 12.6  | 18.0   | 35.9  |
respectively, indicates the strong electrostatic force of attraction between lead ions and binding sites on the surface of the algae. These values are also high compared to other adsorbent materials described in the literature (algae and nonalgae materials).

**Adsorption thermodynamic study**

The thermodynamic adsorption experiment was done by soaking 0.1 g *Jania* algae material in 100 mL of 600 ppm lead solution at pH = 7 for 6 h at different temperatures.

The adsorption equilibrium constant $K_d$ which is equal to $C_e/C_s$ has been calculated. $C_e$ is the equilibrium concentration of dye (mg/L) remaining in aqueous solution, and $C_s$ is the amount of lead at equilibrium (mg/L) adsorbed onto the solid algae materials. Using the Van’t Hoff equation $\ln(K_d)$ versus $1/T$ was plotted. The enthalpy $\Delta H^\circ$ and entropy $\Delta S^\circ$ values were calculated from the slope and the intercept, respectively. The values of $\Delta G^\circ$ were also calculated from $\Delta H^\circ - T\Delta S^\circ$. The results are shown in Table 10.

$\Delta H^\circ$ was found to be positive, indicating that the interaction between lead and different algae materials is endothermic. The positive value of $\Delta S^\circ$ suggested an increase in randomness at the solid-solution interface during the adsorption. At all temperatures, the negative values of $\Delta G$ show that the adsorption was spontaneous.

**Biosorption mechanism**

The mechanisms involved in biosorption are usually complicated, dependent on the type and nature of biomass employed and the type of metals. The
applicability of the pseudo-second-order model by JC and JF algae materials suggested that the biosorption of lead metals was via chemisorptions (Figure 2 and Table 5). The obtained adsorption activation energy \( E_a \) for JF and JC (41 and 62 KJ/mol, respectively) are higher than 40 KJ/mol (Figure 4, and Table 8). This also suggests the occurrence of chemisorptions mechanism. Hence, the mechanism of metal uptake by biosorption process can involve an ion exchange and a surface complexation (16, 41–43).

The properties of algae biomass are analogous to conventional ion exchange resins. The ion exchange mechanism can be described by Equation (11):

\[
\text{AlgR}^-n \text{Ex}^+ + \text{M}^{n+} \rightarrow \text{AlgR}^-n \text{M}^{n+} + \text{Ex}^+, \tag{11}
\]

where \( \text{AlgR}^-n \) is algae surface material containing \( R^- \) (functional group: carboxylate or hydroxylate anion) and \( \text{Ex}^+ \) (leaving exchangeable cation: \( \text{Na}^+ \) or \( \text{Ca}^{2+} \)…). \( \text{M}^{n+} \) is the entering exchangeable cation \( \text{Pb}^{2+} \).

The algae cell wall contains sulfated ester polysaccharides and polyuronides (rich with sulfate and carboxylic acid functional groups capable of metal uptake). The surface complexation mechanism can be described by Equation (12):

\[
\text{Alg} (\text{RH})_n^n + \text{M}^{n+} \rightarrow \text{AlgR}^-n \text{M} + n\text{H}^+ , \tag{12}
\]

where \( \text{M}^{n+} \) is the entering complexing cation and \( \text{Alg} (\text{RH})_n \) is the algae surface material containing the functional group \( \text{RH} \) (carboxylic or hydroxyl functional group). When \( \text{RH} \) is an ammine group, the surface metal complex alginate becomes \( \text{AlgR}^-n \text{M}^{n+} \).

Column studies

Column adsorption studies of lead were done using a pyrex column loaded with 1 g of \( J. \ rubens \) (Linnaeus) algae pretreated with \( \text{CaCl}_2 \) (JC) and eluting lead aqueous solution of (500 ppm) at a flow rate of 2.0 ml/min. A breakthrough graph was plotted for \( C_{ads} \) of lead (mg/L) versus time \( t \) (min). The maximum volume of eluted lead solution that causes exhaustion of column was found to be around 4500 mL (Figure 7).

The values of column parameters: area \( A \), total% removed, \( q_{\text{total}} \), and \( m_{\text{total}} \) were listed in Table 11. The total JC column adsorption capacity \( q_e \) for Pb(II) was calculated from the area \( A \) under the breakthrough curve for the adsorption of Pb(II) onto JC (adsorbent dose = 1 g, sorbent dose = 500 ppm, \( T = 25^\circ C \)).

Table 11. Data parameters of a column loaded with 1 g of JC eluted with lead 500 ppm at a flow rate of 2 ml/min.
Curve using the integration method (equations in Table 2 and Figure 7). $q_e$ was found to be equal to 1089.6 mg/g (5.264 mmol/g). The equilibrium Pb(II) concentration, $C_e$, was equal to 290.5 (mg/L) (Table 11).

Column desorption
The JC column after exhaustion with Pb(II) ions (500 mg/L) was regenerated with 0.1 M HCl (flow rate, $Q = 2$ mL/min). It was found that column regeneration requires washing with 2200 mL of HCl (0.1 M) indicating that column packed with JC can be reused for several biosorption cycles (Figure 8 and Table 11).

The total desorbed lead quantity $q_{total(desorbed)}$ (mg), for a given flow rate, was found equal to 1073.04 mg calculated as $Q \times A_{des}/1000$, where $A$ is the area under the regeneration curve ($C_{des}$ vs. $t$) (Figure 8). The total% regeneration calculated from $100 \times (q_{total(desorbed)}/q_{total(adsorbed)})$ is equal to 98.5% (Table 11).

Figure 8. Regeneration curve for column loaded with 1 g JC and exhausted with Pb (500 ppm) solution ($T = 25^\circ$C).

Figure 9. Linear plot of the Thomas, Yoon-Nelson, Yan, and Clark models for the removal of Pb(II) by JC (adsorbent dose = 1 g, [Pb$^{2+}$] = 500 ppm, $T = 25^\circ$C).
column models

Thomas, Yoon-Nelson, Yan, and Clark models were applied using linear and nonlinear regression statistical techniques according to the equations listed in Table 3 and Figures 9 and 10. The values of the maximum capacity $q$, the rate constant $K$, and error functions for each model are presented in Table 12. The nonlinear regression technique was found more suitable than linear equation, with higher $R^2$ and $r$ and smaller error function ($\chi^2$, SSE, ARE, HYBRID, MPSED, and RMSE; Table 12). The results confirmed the applicability of several kinetic models, namely, Thomas, Yoon-Nelson, and Clark kinetic models. Application of Yoon-Nelson model indicated that $\tau$, the half-life of adsorbate breakthrough, is equal to 1092 min (nonlinear approach). A comparison of values of error functions indicates that Thomas model fits best the experimental breakthrough curves (Figures 9 and 10), with $q_{TH} = 1092.4$ mg/g (5.277 mmol/g) (Table 12).

Thermal analysis

The TGA-dTG-DTA curves of algae materials were drawn versus temperature for a temperature range from 25°C to 850°C. The temperature range and the percentage mass loss of the decomposition reaction are given with the associated heat as in Figure 11 and Table 13 (44–47). The weight loss occurring between 150°C and 450°C is due to decomposition and volatilization of organic materials. It is also evident that a sharp decrease in mass start at temperature above 700°C with an endothermic process of very high heat values of 1297.9 J/g for $J$, 1165.8 J/g for $JF$, and 1288.2 J/g for $JC$. This major weight loss is due to the conversion of CaCO$_3$(s) to CaO(s) and CO$_2$ (g). The theoretical% weight loss of CO$_2$ gas in this step is 44%. The experimental% loss for $J$ is 41.4%, $JF$ is 39.5%, and $JC$ is 41.9%.

The percentage weight of gray residue obtained at the end of thermal analysis residue is 47.5, 50.0, and 50.2 for $J$, $JF$, and $JC$. These values are lower compared to the corresponding algae materials with adsorbed lead of 56.2, 63.6, and 60.1 for $J$, $JF$, and $JC$, respectively, indicating that some lead is present in the residue in addition to the usual content of residue of calcium oxide and carbonaceous materials. In addition, the major mass loss at about 300°C and 750°C observed for free algae materials gave additional mass loss peaks at 360°C and 660°C in the case of lead-algae materials ($J$-$Pb$, $JF$-$Pb$, $JC$-$Pb$) as shown in dTG peaks (Figure 11 and Table 13).

Conclusion

(1) Temkin and Redlich–Peterson isotherms were found to be best for fitting the experimental adsorption data. The values of lead adsorption capacity by different $J$. ruben (Linnaeus) material are high compared to other adsorbent materials described in the literature (algae and nonalgae materials), with the maximum ($Q = 774$ mg/g) obtained with $JF$. The pretreatment of Jania algae with formaldehyde and CaCl$_2$ enhanced its adsorption capacity for lead uptake.

(2) Jania algae is a promising material that can be used for removal of lead from water. The pretreatment of biomass with formaldehyde and CaCl$_2$ resulted in a significant improvement in the algae stability and offers wide range of applications.

(3) The calculation of various error functions proved to be valuable for predicting the best adsorption isotherms, kinetics, and column models.

(4) The nonlinear methods would be more appropriate techniques in predicting the adsorption isotherms, kinetics, and column models.

(5) The sorption of Pb(II) by $JC$ was found to be rapid whereby the pseudo-second-order rate constant is highest compared to other algae materials.

(6) Thomas model was found to be the best model to explain column adsorption with a high capacity for lead uptake onto $JC$ being equal to 1092.4 mg/g and close to the value obtained by breakthrough curve area method (1089.6 mg/g).

(7) Comparative study of thermal analysis of algae materials clearly proves the presence of adsorbed lead in the algae materials.
Table 12. Statistical evaluation of parameters of a column loaded with 1 g JC and eluted with 500 ppm lead using linear and nonlinear fit of breakthrough data to Thomas, Yoon-Nelson, Yan, and Clark kinetic models.

|                      | Linear approach | Nonlinear approach |
|----------------------|-----------------|-------------------|
|                      | $K_{Th}$ mL (mg/min) | $q_T$ (mg/g) | $R^2$ | $r$ | $\chi^2$ | $K_{Th}$ mL (mg/min) | $q_T$ (mg/g) | $R^2$ | $r$ | $\chi^2$ |
| Thomas model         | 7.80 x 10^{-6} | 1112.4 | 0.995 | 0.997 | 0.72 | 8.50 x 10^{-6} | 1092.4 | 0.999 | 1.000 | 0.023 |
|                      | SSE             | ARED       | HYBRID  | MPSED | RMSE | SSE             | ARED       | HYBRID  | MPSED | RMSE |
|                      | 1.15            | 15.12      | 16.33   | 40.15  | 0.21 | 0.0032         | 5.21       | 5.57    | 8.11   | 0.010 |
|                      | $R^2$           | $r$        | $\chi^2$ | $R^2$ | $r$ | $\chi^2$ | $R^2$ | $r$ | $\chi^2$ | $R^2$ | $r$ | $\chi^2$ |
|                      | 0.995           | 0.997      | 0.72    | 0.999 | 1.000 | 0.023 |
| Yoon-Nelson model    | 0.00387         | 1126.2     | 0.995   | 0.997 | 0.91 | 0.00425        | 1092.4     | 0.999   | 1.000 | 0.023 |
|                      | SSE             | ARED       | HYBRID  | MPSED | RMSE | SSE             | ARED       | HYBRID  | MPSED | RMSE |
|                      | 1.05            | 20.02      | 21.62   | 60.61  | 0.20 | 0.0032         | 5.25       | 5.61    | 8.20   | 0.010 |
|                      | $R^2$           | $r$        | $\chi^2$ | $R^2$ | $r$ | $\chi^2$ | $R^2$ | $r$ | $\chi^2$ | $R^2$ | $r$ | $\chi^2$ |
|                      | 0.996           | 0.999      | 0.023   | 1.000 | 0.023 |
| Yan model            | $K_Y$ L/(mg·min) | $q_Y$ (mg/g) | $R^2$ | $r$ | $\chi^2$ | $K_Y$ L/(mg·min) | $q_Y$ (mg/g) | $R^2$ | $r$ | $\chi^2$ |
|                      | 9.97 x 10^{-6} | 326.4      | 0.857   | 0.925  | 63.38 | 1.91 x 10^{-5} | 222.9      | 0.996   | 0.999 | 410.6 |
|                      | SSE             | ARED       | HYBRID  | MPSED | RMSE | SSE             | ARED       | HYBRID  | MPSED | RMSE |
|                      | 28.90           | 95.06      | 102.67  | 276.9  | 1.03 | 0.018           | 29.81      | 31.86   | 52.44  | 0.024 |
|                      | $R^2$           | $r$        | $\chi^2$ | $R^2$ | $r$ | $\chi^2$ | $R^2$ | $r$ | $\chi^2$ | $R^2$ | $r$ | $\chi^2$ |
|                      | 0.996           | 0.999      | 410.6   | 0.999 | 0.024 |
| Clark model          | $A$ (1/min)     | $r$        | $R^2$   | $\chi^2$ | $A$ (1/min) | $r$ | $R^2$ | $\chi^2$ |
|                      | 242.1           | 0.0043     | 0.989   | 0.995  | 0.11 | 278.1           | 0.00475   | 0.999   | 1.000 | 0.027 |
|                      | SSE             | ARED       | HYBRID  | MPSED | RMSE | SSE             | ARED       | HYBRID  | MPSED | RMSE |
|                      | 2.85            | 29.40      | 31.76   | 72.04  | 0.32 | 0.0051          | 4.97       | 5.31    | 8.74   | 0.013 |
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Table 13. Thermal analysis data TGA and DTA for Jania adsorbents J, JF, and JC and lead-adsorbed Jania materials: J-Pb, JF-Pb, and JC-Pb.

| Sorbent | Experimental mass loss | Peak at (T°C) | ΔH (J/g) |
|---------|------------------------|---------------|----------|
| J       | 11.09                  | 297.41        | –        |
|         | 41.40                  | 771.75        | 1297.89  |
|         | –                      | 820.46        | 28.07    |
| JF      | 10.52                  | 312           | –        |
|         | –                      | 608.31        | 86.72    |
|         | 39.50                  | 779.58        | 1165.82  |
| JC      | 7.88                   | 309.00        | –        |
|         | –                      | 395.10        | 40.66    |
|         | 41.88                  | 777.21        | 1288.16  |
| J-Pb    | 1.44                   | 46.52         | 70.05    |
|         | 10.41                  | 292.76        | 65.84    |
|         | 8.94                   | 351.42        | 68.31    |
|         | 3.69                   | 656.57        | –9.12    |
|         | 19.37                  | 756.54        | 369.99   |
| JF-Pb   | 9.81                   | 292.89        | 103.04   |
|         | 6.44                   | 377.25        | 23.90    |
|         | 4.49                   | 595.29        | 22.89    |
|         | 15.94                  | 751.19        | 430.05   |
|         | –                      | 831.56        | 26.59    |
| JC-Pb   | 8.72                   | 298.08        | 6.90     |
|         | 5.54                   | 369.58        | 79.68    |
|         | 7.87                   | 680.27        | –        |
|         | 17.77                  | 765.80        | 548.59   |

Figure 11. Spectrum of thermal analysis of Jania algae modified with calcium chloride with adsorbed lead JC-Pb.
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