

The Journal of Phytopharmacology

(Pharmacognosy and phytomedicine Research)

Research Article

ISSN 2230-480X
JPHYTO 2016; 5(2): 71-78
March- April
© 2016, All rights reserved

Keno David Kowanga

Unit of Science, Jordan University
College, Morogoro, Tanzania

Erastus Gatebe

Chief Research Scientist, Kenya
Industrial Research and
Development Institute, Nairobi,
Kenya

Godfrey Omare Mauti

Health Sciences Department,
Kampala International University
College, Dar es Salaam, Tanzania

Eliakim Mbaka Mauti

School of Pure and Applied
sciences, Biochemistry and
Biotechnology Department,
Kenyatta University, Nairobi,
Kenya

Correspondence:

Keno David Kowanga

Unit of Science, Jordan University
College, Morogoro, Tanzania
Email: kenokowanga[at]gmail.com

Kinetic, sorption isotherms, pseudo-first-order model and pseudo-second-order model studies of Cu(II) and Pb(II) using defatted *Moringa oleifera* seed powder

Keno David Kowanga*, Erastus Gatebe, Godfrey Omare Mauti, Eliakim Mbaka Mauti

ABSTRACT

In the recent decades, there has been a concern on heavy metals in waste water and high cost of conventional methods of removing heavy metals, for this reason search on adsorbents of biological origin which is low cost and efficient is necessary. In this work defatted *Moringa oleifera* seed powder was studied as a potential alternative adsorbent for removal of Cu(II) and Pb(II) from aqueous solution. Physicochemical parameters such as pH, contact time, adsorption kinetics and initial ions concentration adsorption capacity using sorption models were evaluated. The results showed that the optimum pH for biosorption of Cu(II) was 6.5 while that of Pb(II) was 5.5. Contact time for Cu(II) was observed to occur after 30 min while that of Pb(II) occurred after 40 min. FTIR analysis revealed that defatted *Moringa oleifera* seed biomass had presence of amino, carboxyl, hydroxyl and carbonyl groups, these groups were responsible for biosorption of Cu(II) and Pb(II) from aqueous solution. Biosorption kinetic data fitted well with pseudo-second-order kinetic model ($r^2 \leq 0.9997$) giving equilibrium rate constant (k_2) of $0.0350 \pm 0.0275 \text{ g mg}^{-1} \text{ min}^{-1}$ for Cu (II) loaded biomass and $0.0206 \pm 0.0114 \text{ g mg}^{-1} \text{ min}^{-1}$ for Pb (II) loaded biomass; the biosorption isotherms for the biosorbent fitted well with Freundlich isotherm model than with Langmuir isotherm model. However, the separation factor R_L of Langmuir model was between 0 and 1 indicating favourable sorption process and the low value of mean sorption energy of $9.19 \times 10^{-2} \text{ kJ}$ from D-R model showed that the forces of attraction involved were Van der Waal forces indicating the process of adsorption was physical adsorption. In conclusion, the study revealed that defatted *Moringa oleifera* seed is an efficient biosorbent for removal of Cu(II) and Pb(II) from aqueous solution.

Keywords: Biosorption, Freundlich, Langmuir, Van der Waal, Physical adsorption.

INTRODUCTION

Industrialization in developing countries like Kenya and Tanzania is related to serious environmental pollution. Waste waters from these industries are polluted with toxic heavy metals like lead, copper, mercury among others^[1]. The effects of these heavy metals can be avoided by treatment of contaminated waste water to meet set guidelines on waste water treatment prior to discharge into water bodies^[2]. Conventional methods like reverse osmosis, nanofiltration, electro dialysis among others used to remove these heavy metals from waste water require high energy consumption and generate large amount of waste products that need more treatment^[3]. Recent research tries to find alternative low cost and effective method for removal of these toxic metals^[4]. Biosorption has emerged as the best alternative as it is based on the ability biological materials to remove heavy metals based on their metal binding capacities by means of ion exchange, electrostatic forces and precipitation^[4]. This study evaluates effectiveness of defatted *Moringa oleifera* seed powder as an adsorbent.

MATERIALS AND METHODS

Sampling and Preparation of defatted *Moringa oleifera* seed powder

Samples of *Moringa oleifera* seeds were collected from a single tree grown by a farmer in Meru; the seeds were de-shelled to remove the kernels. Seed kernels, were further dried at ambient temperatures for a period of five days; they were then milled into a fine powder using a mill (Model; SK-M10R Grinding Mill) at 8000 rpm. Extraction of oil from *Moringa oleifera* seed powder was carried out by adding hexane to the seed powder. Electro Thermal Soxhlet apparatus was used as follows: Weighing of 10 gm of *Moringa oleifera* seed powder and setting it in the thimbles of the electro thermal soxhlet extraction chamber. Adding 170 ml of hexane in the heating chamber; evaporating of hexane within three cycles each for 30 min to ensure the extraction of oil from the seeds (until the hexane became colourless); drying of defatted *Moringa oleifera* seed cake residue from the soxhlet thimbles and weighing the dry sample^[6]. The oil content from the defatted *Moringa oleifera* seed powder was found

to be 33.35±0.08%. The defatted *Moringa oleifera* seed cake residue stock after oil extraction was sieved with a sieve with an aperture of 0.5mm before used for biosorption.

FTIR Analysis for *Maerua subcordata* root tubers

Samples of defatted *Moringa oleifera* seed powder were dried in the sun for two days, then in oven at 60°C for eight hours. Each sample was divided into two portions. One portion was batch-equilibrated with 200 mg/L solution of Cu(II) and Pb(II) for two hours. They were then filtered and dried in the sun for a day followed by oven for eight hours at 100°C. Fourier-Transform Infrared spectra of the free and metal loaded of defatted *Moringa oleifera* seed powder was obtained using shimadzu FTIR (Model, FTIR-8400) in the range 500 – 4000 cm⁻¹ to identify the active functional groups.

pH Optimization

Batch biosorption was conducted on aqueous solutions of Cu(II) and Pb(II) to determine the optimum pH for metal uptake by defatted *Moringa oleifera* seed powder. The stock solution was diluted to 200 mg/L using 0.1 M acetate buffer solution and divided into two 50 ml batches. Both batches were adjusted to pH values of 2.0, 3.0, 4.0, 5.0, 5.5, 6.0, 6.5 and 7.0 using 0.1M sodium hydroxide and 0.1M nitric acid. One batch was equilibrated with 0.2 g of defatted *Moringa oleifera* seed powder for two hours. The solution was filtered through a 0.45 µm filter membrane and the filtrate analyzed for residual metal ion using flame atomic absorption spectrophotometer (FAAS). The second batch (control) was treated like the first one but no defatted *Moringa oleifera* seed powder was added. This was used to determine the amount of metal lost due to precipitation.

Optimization of Contact Time

The 1000 mg/L stock solution of copper and lead was each diluted with acetate buffer solution to obtain 500 mL of 200 mg/L, 100 mg/L and 50 mg/L of Cu(II) and Pb(II). The pH of solutions was adjusted to the optimum values then 2.00 g of defatted *Moringa oleifera* seed powder was added to the 500 mL of each solution and stirred continuously with a shaker (KS 250 basic: Model, IKALABORTECHNIK) at 300 rpm. 10 ml portions of this solution were withdrawn at measured time intervals, first 10 mL was withdrawn before addition of defatted *Moringa oleifera* seed powder (t = 0). Subsequent withdrawals were done between 2 and 140 minutes. Each portion was immediately filtered through 0.45 µm membrane filter and the residual metal ion concentration determined by FAAS in triplicates. A plot of percentage metal ion removal against time was used to determine the contact time for the adsorption process.

Initial Metal ion Concentration and Adsorption Capacity

50 mL of standard metal ion solutions of concentrations between 50 – 1000 mg/L at their respective optimum pH were equilibrated with 0.2 g of defatted *Moringa oleifera* seed powder for 30 min. for Cu(II) and for 40 min. for Pb(II) stirring at 300 rpm. The solution was filtered through a 0.45 µm membrane filter and the residual metal ion concentration determined by FAAS; the data obtained was fitted to adsorption isotherms models.

Analytical techniques

The concentration of metals was analyzed with an AAS (Model, 210 VGP Buck Scientific), equipped with an air-acetylene flame. As a quality assurance procedure, a 5-point calibration through zero was applied with blank as well as standard solutions. The resulting linear calibration line (r² ≥ 0.996) was the requirement for all sample measurement. After every 10 measurements, the 1.0 mg L⁻¹ standard solution was checked for accuracy; the calibration was repeated in cases where incorrect values were obtained. Finally, the standard

solution for the required absorbance was checked as part of the quality assurance process.

CALCULATIONS

The metal uptake per gram of sorbent and the percentage removal was calculated according to the following equations:

$$q_e = \frac{(C_0 - C_e)}{m} \times V \dots\dots\dots(1)$$

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

Where: q_e was the equilibrium adsorption capacity (mg g⁻¹), C_0 was the initial concentration (mg L⁻¹) of metal ions in solution, C_e was the equilibrium concentration (mg L⁻¹) of metal ions in solution, V was the volume of aqueous solution (L) and m was the dry weight of the adsorbent (g).

The Langmuir Isotherm Model

It is represented by the following equation [7]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \dots\dots\dots(3)$$

Where: q_e is the amount of metal adsorbed per specific amount of adsorbent (mg g⁻¹), C_e is the equilibrium concentration of the solution (mg L⁻¹) and q_m is the maximum amount of metal ions required to form a monolayer (mg g⁻¹). The Langmuir equation can be rearranged to a linear form for the convenience of plotting and determination of the Langmuir constant (K_L) as below. The values of q_m and K_L can be determined from the linear plot of C_e/q_e versus C_e :

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e \dots\dots\dots(4)$$

The essential characteristics of the Langmuir isotherm parameters can be used to predict the affinity between the sorbate and the sorbent using the separation factor or dimensionless equilibrium parameter ‘ R_L ’, expressed as in the following equation [8]:

$$R_L = \frac{1}{1 + K_L C_0} \dots\dots\dots(5)$$

Where: K_L is the Langmuir constant and C_0 is the initial concentration of the metal ion. The value of the separation factor R_L provides important information about the nature of adsorption. The value of R_L is between 0 and 1 for favourable adsorption, while $R_L > 1$ represents unfavourable adsorption and $R_L = 1$ represents linear adsorption. The adsorption process is irreversible if $R_L = 0$.

The Freundlich Isotherm Model

It is described by the following equation:

$$q_e = K_F C_e^{1/n} \dots\dots\dots(6)$$

In its linear form, this equation assumes the following form: [8].

$$\log q_e = \log K_F + (1/n) \log C_e \dots\dots\dots(7)$$

Where: q_e is the metal uptake (mg g⁻¹) at equilibrium, K_F is the measure of the sorption capacity, $1/n$ is the sorption intensity, and C_e is the final ion concentration in solution, or equilibrium concentration (mg L⁻¹). The Freundlich isotherm constants K_F and $1/n$ are evaluated from the intercept and the slope respectively, of the linear plot of $\log q_e$ versus $\log C_e$.

Dubinin–Radushkevich Isotherm (D-R) Model

It is represented in the linear form by the equation [9]:

$$\ln q_e = \ln Q_D - 2B_D RT \ln(1 + 1/C_e) \dots\dots\dots(8)$$

Where: Q_D is the theoretical maximum capacity (mol g^{-1}), B_D is the D-R model constant ($\text{kJ mol}^{-1} \text{K}^{-1}$), T is the absolute temperature (K) and R is the gas constant (kJ mol^{-1}). The value of Q_D and B_D can be obtained from the intercept and slope of the plot of $\ln(q_e)$ versus $\ln(1 + 1/C_e)$. The mean energy of sorption, E (kJ mol^{-1}) is calculated from the relation [10]:

$$E = 1\sqrt{2B_D} \dots\dots\dots(9)$$

Flory–Huggins Isotherm Model

The generalized and linearized forms of the model are given by Equations (10) and (11), respectively [11]:

$$C_0 = \frac{\theta}{K_{FH}(1-\theta)^n} \dots\dots\dots(10)$$

$$\log \frac{\theta}{C_0} = \log K_{FH} + n \log(1-\theta) \dots\dots\dots(11)$$

Where: $\theta = (1 - C_e/C_0)$ is the degree of coverage, n is the number of metal ions occupying sorption sites and K_{FH} is the equilibrium constant of adsorption. From Equation (11), a plot of $\log(\theta/C_0)$ versus $\log(1 - \theta)$ gives a straight line from which n and K_{FH} can be calculated from the slope and intercept. The Gibbs free energy of adsorption is computed from the equation below [11]:

$$\Delta G = -RT \ln K_{FH} \dots\dots\dots(12)$$

Temkin Isotherm Model

The linearized form is expressed by the following equation [11]:

$$q_e = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln C_e \dots\dots\dots(13)$$

Where: K_T (L g^{-1}) is the Temkin isotherm constant, b_T (J mol^{-1}) is a constant related to the heat of sorption and R ($8.314 \text{ J mol}^{-1} \text{K}^{-1}$) is the gas constant. A plot of q_e versus $\ln(C_e)$ gives a straight line from which K_T and b_T can be evaluated from the slope and the intercept.

Sorption Kinetics

Pseudo-First-Order Kinetic Model

It is given by equation is below:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \dots\dots\dots(14)$$

Where: q_t and q_e are the amount of solute sorbed per mass of sorbent (mg g^{-1}) at any time and equilibrium, respectively, and k_1 is the rate constant of first-order sorption (min^{-1}). The straight-line plot of $\log(q_e - q_t)$ against t gives $\log(q_e)$ as slope and intercept equal to $k_1/2.303$. Hence the amount of solute sorbed per gram of sorbent at equilibrium (q_e) and the first-order sorption rate constant (k_1) can be evaluated from the slope and the intercept.

Pseudo-Second-Order Kinetic Model

The model is represented by [12]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t \dots\dots\dots(15)$$

The initial sorption rate is defined by the following equation [13]:

$$h = k_2 q_e^2 \dots\dots\dots(16)$$

Where: k_2 is the rate constant, q_t is the metal uptake capacity at any time t .

RESULTS AND DISCUSSIONS

Figures 1, 2 and 3 represents FTIR spectra for the biomass of defatted *Moringa oleifera* powder before sorption (metal free biomass) and after sorption (metal ion loaded) with Cu(II) and Pb(II) respectively.

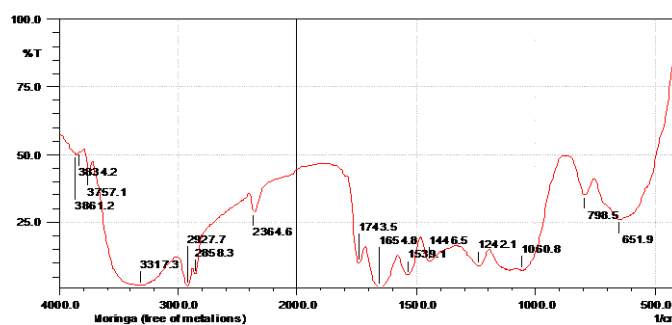


Figure 2: FTIR spectrum of defatted *Moringa oleifera* seed powder after Cu(II) sorption. (Experimental conditions: $C_0 = 500 \text{ mg L}^{-1}$, dosage = 0.2 g per 50 mL; particle size $\leq 0.5 \text{ mm}$; mixing rate = 300 rpm; $T = 25 \pm 1 \text{ }^\circ\text{C}$; contact time = 30 min.; $\text{pH} = 6.5 \pm 0.2$)

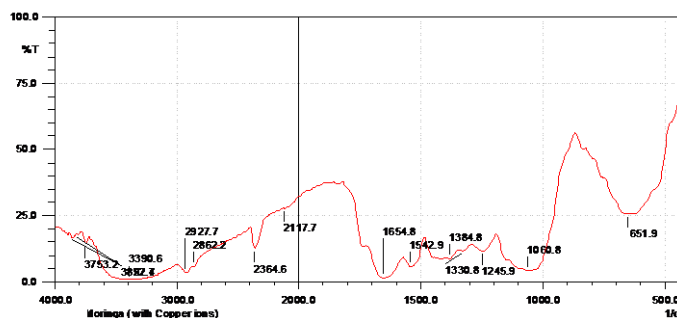


Figure 3: FTIR spectrum of defatted *Moringa oleifera* seed powder after Pb(II) sorption. (Experimental conditions: $C_0 = 500 \text{ mg L}^{-1}$, dosage = 0.2 g per 50 mL; particle size $\leq 0.5 \text{ mm}$; mixing rate = 300 rpm; $T = 25 \pm 1 \text{ }^\circ\text{C}$; contact time = 40 min.; $\text{pH} = 5.5$)

Bands characterizing hydroxyl and amine groups were assigned at $3861.2\text{--}3317.3 \text{ cm}^{-1}$, alkyl chains and CHO had band within the range $2927.7\text{--}2858.5 \text{ cm}^{-1}$ and C=O of amide groups appeared at 1654.8 cm^{-1} . The bands, 1743.5 cm^{-1} were an indication of the presence of COO^- anions those that are located at 1242.1 cm^{-1} was assigned to SO_3^- groups. Bands of organic phosphate groups were located at 1060.8 cm^{-1} . From the FTIR spectra of the loaded biomasses with Cu(II) and Pb(II) the following observation were observed: Broadening of the band 1654.8 cm^{-1} for Cu(II) loaded and for Pb(II) loaded indicated the interaction of the metal with C=O groups on the surface of defatted *Moringa oleifera* seed powder biomass. Shifting and broadening of the band located at 1539.1 cm^{-1} and that at 1242.1 cm^{-1} to 1542.9 cm^{-1} and 1245.9 cm^{-1} for Cu(II) loaded and to 1539.1 cm^{-1} and 1253.6 cm^{-1} were due to the loading effect of metal of COO^- anions. The broadening and shifting of the band that appeared at 1060.8 cm^{-1} to 1060.8 cm^{-1} for Cu(II) loaded and to 1056.9 cm^{-1} for Pb(II) loaded were attributed to the loading of metal as a result of the interaction of metal with phosphate groups. Broadening of the bands located at $3861.2\text{--}3317.3 \text{ cm}^{-1}$ on defatted *Moringa oleifera* seed powder verified the interaction takes place on both the hydroxyl and amine groups with Cu (II) and Pb (II) in aqueous solution. Change in the transmittance in the FTIR spectra for metal loaded biomass of defatted *Moringa oleifera* seed powder indicates that the above functional groups were involved in Cu(II) and Pb(II) biosorption. The results above are in agreement with Ahmady-Asbchin *et al.*, 2008 who stated that the biosorption of metals to the biosolids causes a decrease in the absorbance compared to the raw sample [14].

Effect of pH on Biosorption of defatted *Moringa oleifera* seed powder

Figure 4 represents effect of pH on the biosorption of Cu(II) and Pb(II); it was observed that both Cu(II) and Pb(II) removal sharply increased from pH 2.0 to optimum pH 6.5 for Cu(II) and to optimum pH 5.5 for Pb(II) thereafter biosorption of these metals decreases sharply. At low pH the surface of adsorbent (defatted *Moringa oleifera* seed powder) was surrounded by hydronium (H_3O^+) ions, this

decreases the interaction of Cu(II) and Pb(II) with the sites of defatted *Moringa oleifera* seed powder by repulsive forces hence low adsorption.

As pH was increased, the competing effect of hydronium ions was decreased and more ligands were available for Cu(II) and Pb(II) adsorption, this means at slightly high pH values, the overall surface of defatted *Moringa oleifera* seed powder became more negative and adsorption was increased. At high pH values greater than pH 7.0 biosorption recovery was reduced due to precipitation of insoluble $\text{Cu}(\text{OH})_2$ and $\text{Pb}(\text{OH})_2$ [15].

Effect Contact Time on Biosorption of defatted *Moringa oleifera* seed powder

Figure 5 represents effect of contact time of the biosorption of defatted *Moringa oleifera* seed powder it was observed that the rate of metal uptake increased rapidly in the first 6 minutes of contact time. After about 6 minutes, the rate decreased until a constant metal concentration was reached, this occurred after about 30 minutes for Cu(II) and 40 minutes for Pb(II). It was presumed that this time represented the equilibrium time at which equilibrium metal concentration occurred.

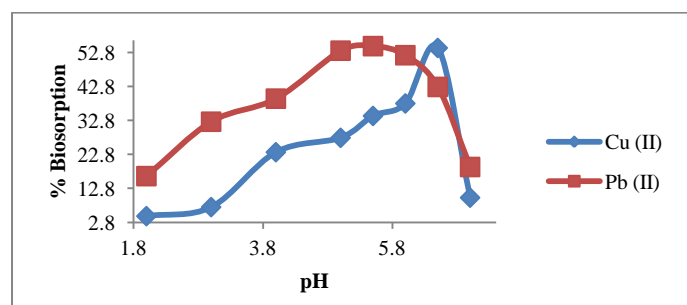


Figure 4: Effect of pH on the biosorption of Cu(II) and Pb(II) by dried biomass of defatted *Moringa oleifera* seed powder (Experimental conditions: $C_o = 200 \text{ mg L}^{-1}$, dosage = 0.2 g per 50 mL; particle size $\leq 0.5 \text{ mm}$; mixing rate = 300 rpm; $T = 25 \pm 1 \text{ }^\circ\text{C}$)

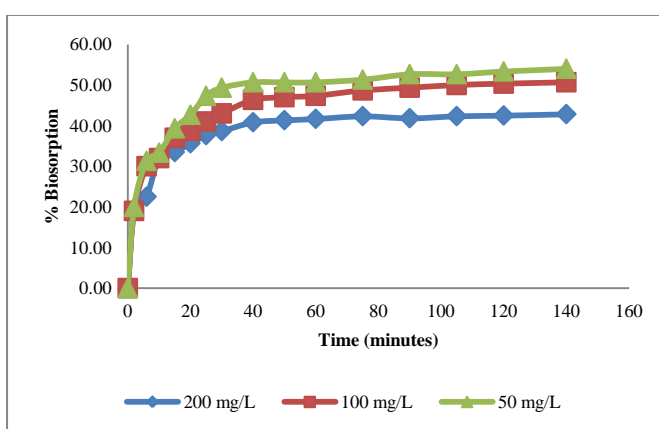
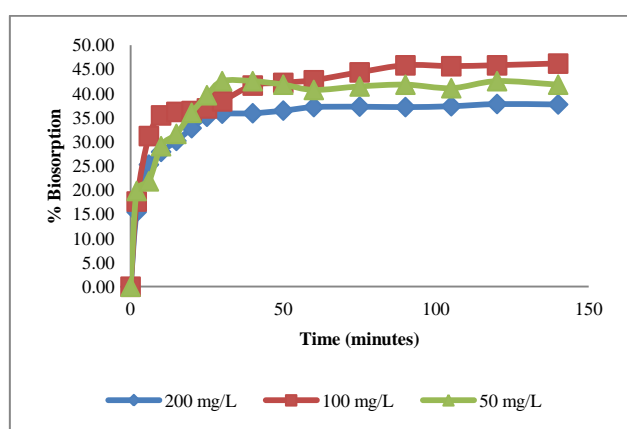


Figure 5: Cu(II) and Pb(II) percentage biosorption onto defatted *Moringa oleifera* seed powder biomass against time. (Experimental conditions: $C_o = 200 \text{ mg L}^{-1}$, 100 mg L^{-1} and 50 mg L^{-1} ; dosage = 2.0 g per 500 mL, particle size $\leq 0.5 \text{ mm}$, mixing rate = 300 rpm, $T = 25 \pm 1 \text{ }^\circ\text{C}$, pH = 6.5 ± 0.2 for Cu(II) and pH = 5.5 ± 0.2 for Pb(II))

The observation can be explained as follows, initially the sites for adsorption were open and the Cu(II) and Pb(II) interacted easily with the site and the concentration difference between the bulk solution and the solid liquid interface was initially higher this lead to higher rate of adsorption observed after 6 minutes. Afterwards, Cu(II) and Pb(II) were accumulated in the large available surface of defatted *Moringa oleifera* seed powder biomass which lead to occupation of surface binding sites making biosorption to be slowed down [16].

Figures 6 and 7 show the linear plot of $\log(q_e - qt)$ versus t for the Lagergren pseudo-first-order model and t/qt versus t for the Lagergren pseudo-second-order model for the biosorption of Cu(II) and Pb(II) for defatted *Moringa oleifera* seed powder. The equilibrium rate constant of the pseudo-first-order sorption (k_1) was observed to be $0.0091 \pm 0.0032 \text{ min}^{-1}$ for Cu(II) and $0.0127 \pm 0.0018 \text{ min}^{-1}$ for Pb(II). The equilibrium rate constant of the pseudo-second-order model (k_2) was $0.0350 \pm 0.0275 \text{ g mg}^{-1} \text{ min}^{-1}$ for Cu(II) and $0.0206 \pm 0.0114 \text{ g mg}^{-1} \text{ min}^{-1}$ for Pb(II), table 1.

Adsorption Kinetics

Table 1: Coefficients of sorption kinetics for Cu(II) and Lead (II) removal defatted *Moringa oleifera* seed powder and their correlation coefficient (R^2).

(Experimental conditions: $C_o = 200 \text{ mg L}^{-1}$, 100 mg L^{-1} and 50 mg L^{-1} ; dosage = 2.0 g per 500 mL; particle size $\leq 0.5 \text{ mm}$; mixing rate = 300 rpm; $T = 25 \pm 1 \text{ }^\circ\text{C}$; pH = 6.5 ± 0.2 for Cu(II) and pH = 5.5 ± 0.2 for Pb(II))

Coagulants	Metals	Initial conc. (mg/L)	First Order			Second Order			
			Calculated equil. uptake q_e (mg g ⁻¹)	k_1 (min ⁻¹)	R^2	Calculated equil. uptake q_e (mg g ⁻¹)	k_2 (g mg ⁻¹ min ⁻¹)	h (mg g ⁻¹ min ⁻¹)	R^2
<i>Moringa oleifera</i>	Cu(II)	200	7.55	0.0122	0.6195	19.23	0.0192	7.1000	0.9996
		100	6.70	0.0094	0.7119	11.82	0.0190	2.6545	0.9983
		50	4.00	0.0058	0.4698	5.37	0.0668	1.9263	0.9983
		Average k_1 and k_2		0.0091 ± 0.0032			0.0350 ± 0.0275		
	Pb(II)	200	10.44	0.0108	0.6451	22.22	0.0129	6.3691	0.9992
		100	6.46	0.0145	0.8061	13.08	0.0151	2.5834	0.9986
		50	3.30	0.0129	0.7120	6.89	0.0337	1.5998	0.9988
		Average k_1 and k_2		0.0127 ± 0.0018			0.0206 ± 0.0114		

*The coefficients were calculated from linearized forms of pseudo-first/second-order kinetic model equations; standard deviations were calculated from k_1 and k_2 from initial concentrations of 200 mg L^{-1} , 100 mg L^{-1} and 50 mg L^{-1}

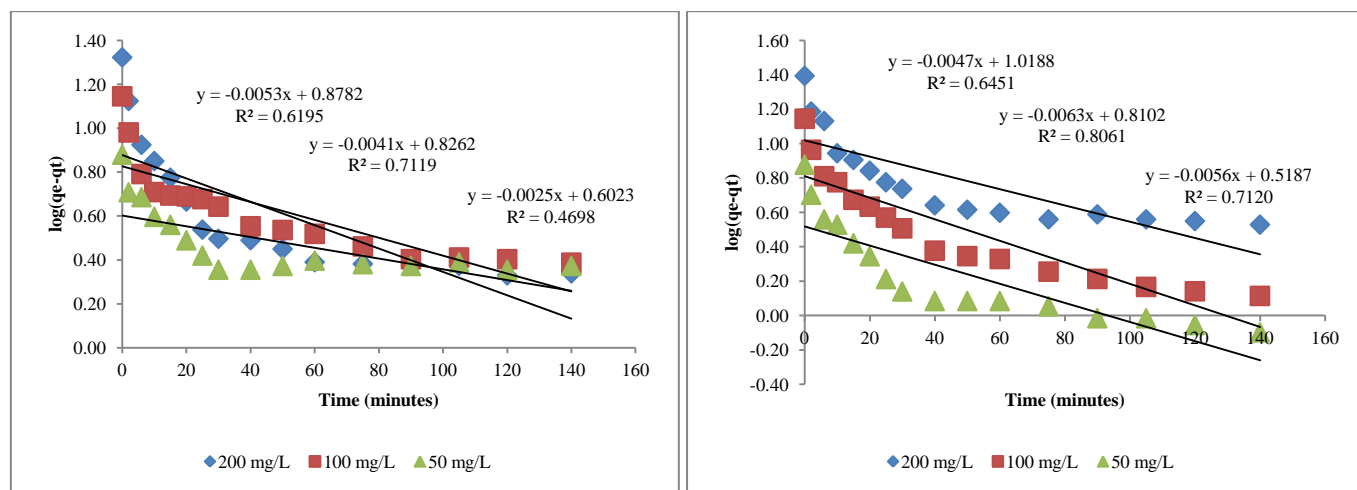


Figure 1: Lagergren pseudo-first-order kinetics biosorption for Cu(II) and Pb(II) onto defatted *Moringa oleifera* seed powder biomass (Experimental conditions: $C_o = 200 \text{ mg L}^{-1}$, 100 mg L^{-1} and 50 mg L^{-1} ; dosage = 2.0 g per 500 mL, particle size $\leq 0.5 \text{ mm}$, mixing rate = 300 rpm, $T = 25 \pm 1 \text{ }^\circ\text{C}$, pH = 6.5 ± 0.2 for Cu(II) and pH = 5.5 ± 0.2 for Pb(II))

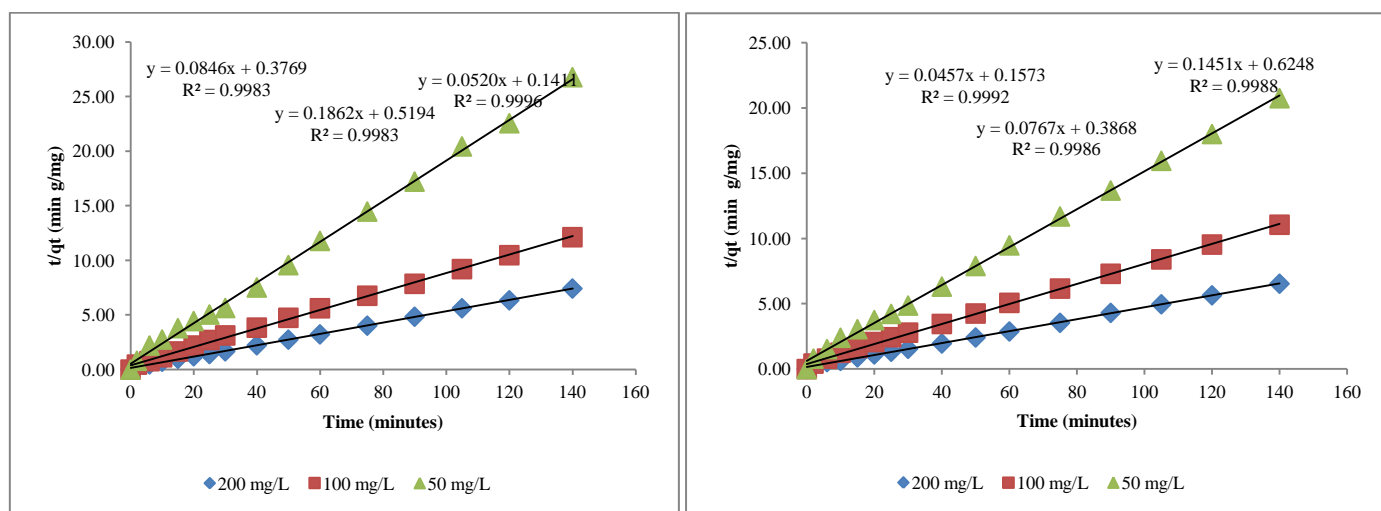


Figure 2: Lagergren pseudo-second-order kinetics biosorption for Cu(II) and Pb(II) onto defatted *Moringa oleifera* seed powder biomass. (Experimental conditions: $C_o = 200 \text{ mg L}^{-1}$, 100 mg L^{-1} and 50 mg L^{-1} ; dosage = 2.0 g per 500 mL, particle size $\leq 0.5 \text{ mm}$, mixing rate = 300 rpm, $T = 25 \pm 1 \text{ }^\circ\text{C}$, pH = 6.5 ± 0.2 for Cu(II) and pH = 5.5 ± 0.2 for Pb(II))

The pseudo-second-order equation fitted the experimental data well with a correlation coefficient (R^2) close to unity - table 1 and figures 6, compared with the first-order model, table 1 and figures 7. The deviation from the straight line in the first 30 min of sorption - figure 6, observed for the pseudo-first-order model, was attributed to the fast initial uptake of Cu(II) and Pb(II) onto the defatted *Moringa oleifera* seed powder biomass before slow adsorption. On the basis of the correlation coefficients, the biosorption of Cu(II) and Pb(II) by defatted *Moringa oleifera* seed powder biomass follows a second-order reaction pathway^[13].

Sorption Isotherms

Table 1: Coefficients of five different sorption isotherm models for Cu(II) and Pb(II) removal by defatted *Moringa oleifera* seed powder and their correlation coefficient (R^2)

(Experimental conditions: Dosage = 0.2 g per 50 mL; particle size $\leq 0.5 \text{ mm}$; mixing rate = 300 rpm; $T = 25 \pm 1 \text{ }^\circ\text{C}$; contact time = 30 min. for Cu(II) and 40 min. for Pb(II); pH = 6.5 ± 0.2 for Cu(II) and pH = 5.5 ± 0.2 for Pb(II))

Isotherm Parameters	<i>Moringa oleifera</i>	
	Copper (II)	Lead (II)
Freundlich		
$1/n$	0.3987	0.6516
K_F	3.8230	1.4921
R^2	0.9977	0.9959
Langmuir		
q_{max} (mg/g)	3.36	22.22
K_L	1.16×10^{-1}	2.30×10^{-2}
R_L	0.0142	0.0675
R^2	0.9681	0.9253
Dubinin-Radushkevich (D-R)		
Q_D	41.23	66.45
B_D	3.42×10^{-3}	6.69×10^{-3}
E (kJ)	8.27×10^{-2}	1.16×10^{-1}
R^2	0.7852	0.7805
Flory-Huggins		
N	2.1480	5.0007
K_{FH}	2.2136	99.257
ΔG^0_{ads} (kJ mol ⁻¹)	-1.9489	-11.2765
R^2	0.9896	0.9970
Temkin		
b_T (J)	93.13	65.60
K_T	0.1211	0.0964
R^2	0.9402	0.8903

*The coefficients were calculated from linearized forms of sorption isotherms models equations.

The biosorption process was well described by the linear form of the Freundlich equilibrium isotherm model, which yielded R^2 values of 0.9977 for Cu(II) and 0.9959 for Pb(II) onto defatted *Moringa oleifera* seed powder, table 2; the adsorption intensity $1/n$ was less than 1 for both Cu(II) and Pb(II) sorption this indicated favourable sorption. Even though the Langmuir isotherm model described the sorption process poorly, the separation factor (R_L) was found to be between 0 and 1; table 2, this indicated a favourable biosorption process^[8]. The Langmuir model contains assumptions such as all binding sites should possess an equal affinity for the adsorbate and adsorption should be limited to the formation of a monolayer. The other assumption is that the number of adsorbed species should not exceed the total number of surface sites and it also assumes that the number of uniform adsorption sites should be finite and that there should be absence of lateral interactions between adsorbed species; it is likely that none of these assumptions apply in biological systems^[9]. For this reason, the Langmuir model could not fit the data well compared with the Freundlich model, which takes surface roughness into account. The low value of the mean sorption energy (E) of 8.27×10^{-2} kJ for Cu(II) and 1.16×10^{-1} kJ for Pb(II) in D-R model showed that the forces of attraction were Van der Waal and not chemical bonding; hence, the sorption processes involved in *Moringa oleifera* seed powder was physical adsorption (physisorption), $\Delta G_{ads}^0 \leq -20$ kJ mol⁻¹ shows physisorption and the negative value of ΔG_{ads}^0 confirmed the feasibility of the process and the spontaneous nature of the sorption (Horsfall et. al., 2004). Low value of the Temkin isotherm constant b_T of 93.13 J for Cu (II) and 65.60 J for Pb (II) obtained in table 2 indicated a weak interaction between the *Moringa oleifera* seed powder, Cu(II) and Pb(II) supporting an ion exchange mechanism^[12].

ACKNOWLEDGEMENT

The principal author would like to acknowledge National Council of Science and Technology for providing funds to carry out this study. This manuscript was extracted from the author's M.Sc. Thesis "Clarification of Turbid River Water and Biosorption of Cu(II) and Pb(II) using Natural Coagulants: *Maerua subcordata*, *Prosopis juliflora* and *Moringa oleifera*".

REFERENCES

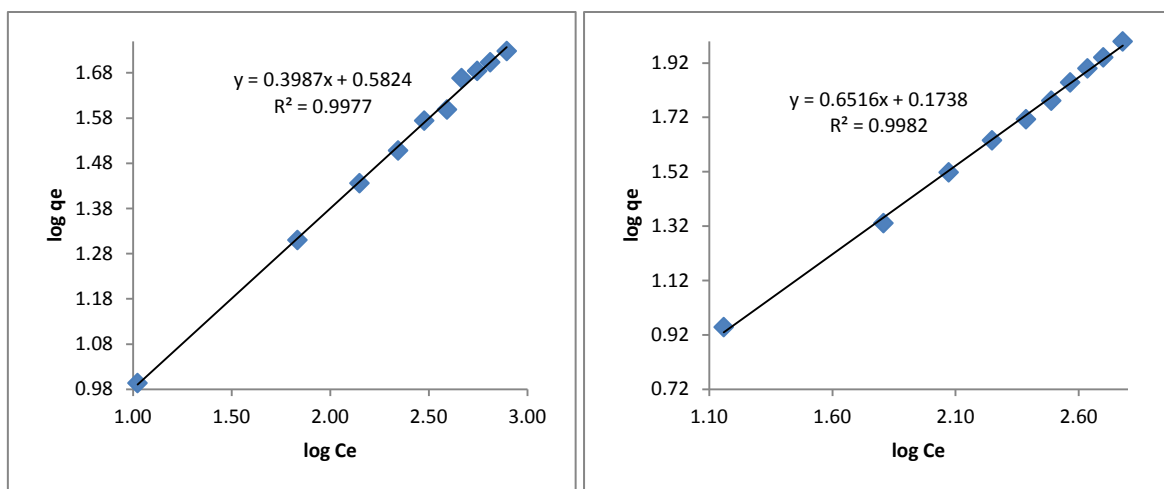
- Dundar M., Nuhoglu C. and Nuhoglu Y. Biosorption of Cu(II) ions onto the litter of natural trembling poplar forest. Journal of Hazardous Materials 2008;151: 86–95.
- Gulnaz O., Saygideger S. and Kusvuran E. Study of Cu (II) biosorption by dried activated sludge: effect of physico-chemical environment and kinetics study. J Hazard Mater 2005;120: 193–200
- Ayoub G.M., Semerjian L., Acra A., E.I. Fadel M. and Koopman B. Heavy Metal Removal by Coagulation with Seawater Liquid Bittern. Journal of Environmental Engineering 2001;127: 196–202.
- Gadd G.M. Biosorption: critical review of scientific rationale, environmental importance and significance for pollution treatment. Journal of Chemical Technology 2009;84: 13–28
- Amuda O.S., Giwa A.A. and Bello I.A. Removal of heavy metal from industrial wastewater using modified activated coconut shell carbon. Journal of Biochemical Engineering 2007;36: 174–181.
- Muyubi S.A. and Evison L.M. Flocc Settling Characteristics of Turbid Water Coagulated with *Moringa oleifera* Seeds. International of Environmental Studies 1999;6: 483-495.
- Langmuir I. The adsorption of gases on plain surface of glass, mica and platinum. Journal of American Chemists Society 1916;40: 1361–1368.
- Rahman M.S and Islam M.R. Effects of pH on isotherms modeling for Cu (II) ions adsorption using maple wood sawdust. Journal of Chemical Engineering, 2009;149: 273–280
- Igwe J.C. and Abia A.A. Equilibrium sorption isotherm studies of Cd(II), Pb(II) and Zn(II) ions detoxification from waste water using unmodified and EDTA-modified maize husk. Electron Journal of Biotechnology 2007; 10: 536–548.
- Horsfall Jr M., Spiff A.I. and Abia A.A. Studies on the influence of mercaptoacetic acid (MAA) modification of cassava (*Manihot sculenta* Cranz) waste biomass on the adsorption of Cu²⁺ and Cd²⁺ from aqueous solution. Bulletin Korean Chemical Society 2004;25: 969–976.
- Mahamadi C and Nharingo T. Utilization of water hyacinth weed (*Eichhornia crassipes*) for the removal of Pb (II), Cd (II) and Zn (II) from aquatic environments: an adsorption isotherm study. Journal of Environmental Technology 2010;31: 1221–1228.
- Ho Y.S. and McKay G. Pseudo-second-order model for sorption processes. Journal of Process Biochemistry 1999; 34: 451–465.
- Kalavathy M.H., Karthikeyan T., Rajgopal S. and Miranda L.R. Kinetic and isotherm studies of Cu (II) adsorption onto H₃PO₄-activated rubber wood sawdust. Journal of Colloidal Interface Science 2005; 292: 354–362.
- Ahmady-Asbchin S., Andres Y., Gerente C. and Cloirec P.L. Biosorption of Cu(II) from Aqueous Solution by *Fucus serratus*: Surface Characterization and Sorption Mechanism. Journal of Bioresource Technology 2008;99: 6150–6155.
- Deng S. B and Ting Y. P. Polyethylenimine-Modified Fungal Biomass as a High-Capacity Biosorbent for Cr(VI) anions: Sorption Capacity and Uptake Mechanisms. Journal of Environmental of Science and Technology 2005;39: 8490-8496.
- Kurniawan T.A., Chan G.Y.S., Lo W. H. and Babel S. Physico-Chemical Treatment Techniques for Wastewater Laden with Heavy Metals. Journal of Chemical Engineering 2006; 118: 83–98.

HOW TO CITE THIS ARTICLE

Kowanga KD, Gatebe E, Mauti GO, Mauti EM. Kinetic, sorption isotherms, pseudo-first-order model and pseudo-second-order model studies of Cu(II) and Pb(II) using defatted *Moringa oleifera* seed powder. The Journal of Phytopharmacology 2016;5(2):71-78.

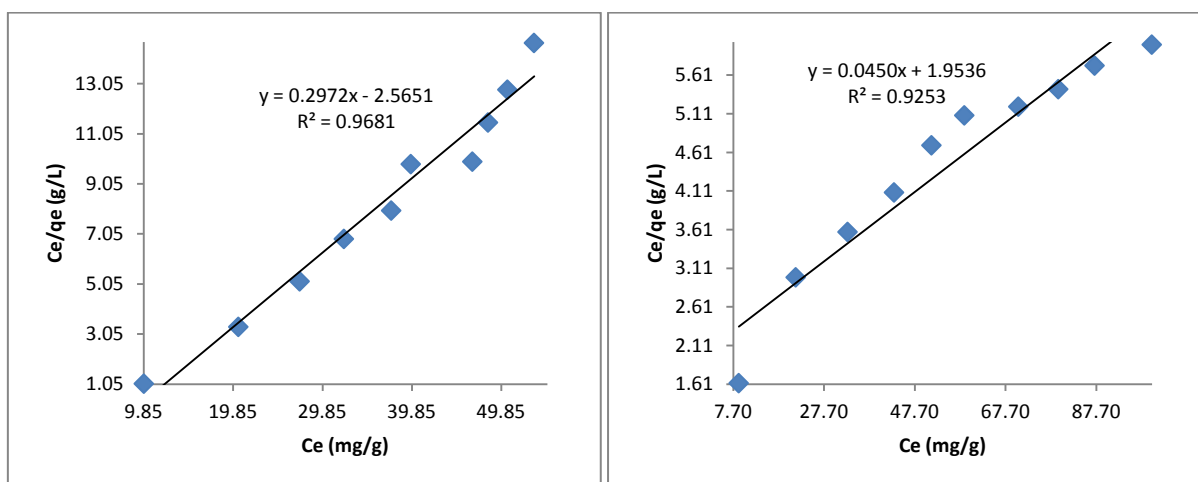
Sorption Isotherms (Linear form)

The Freundlich Isotherm Model



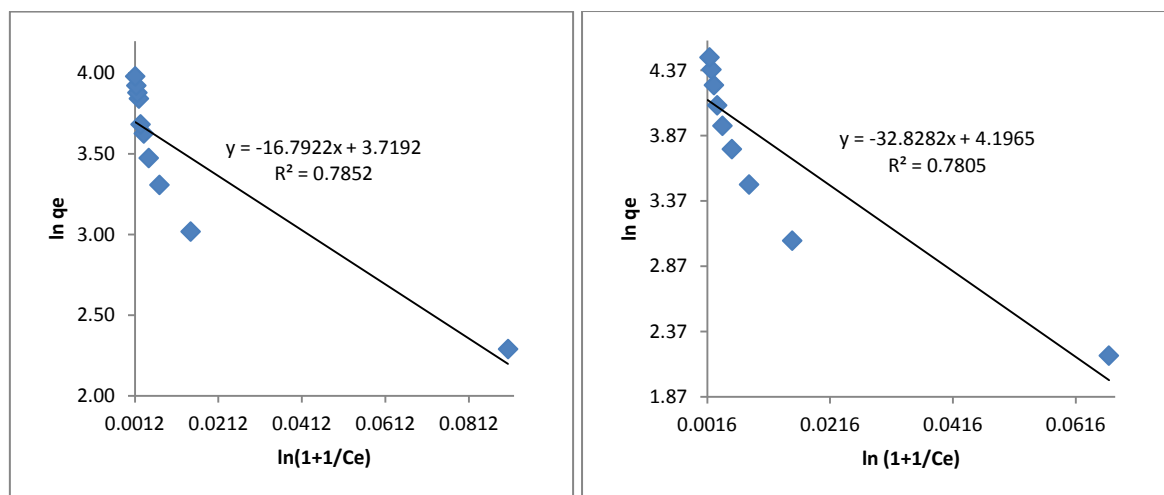
The Freundlich Isotherm Model biosorption for Cu(II) and Pb(II) onto defatted *Moringa oleifera* seed powder biomass. (Experimental conditions: Dosage = 0.2 g per 50 mL; particle size ≤ 0.5 mm; mixing rate = 300 rpm; T = 25 ± 1 °C; contact time = 30 min. for Cu(II) and 40 min. for Pb(II); pH = 6.5 ± 0.2 for Cu(II) and pH = 5.5 ± 0.2 for Pb(II))

The Langmuir Isotherm Model



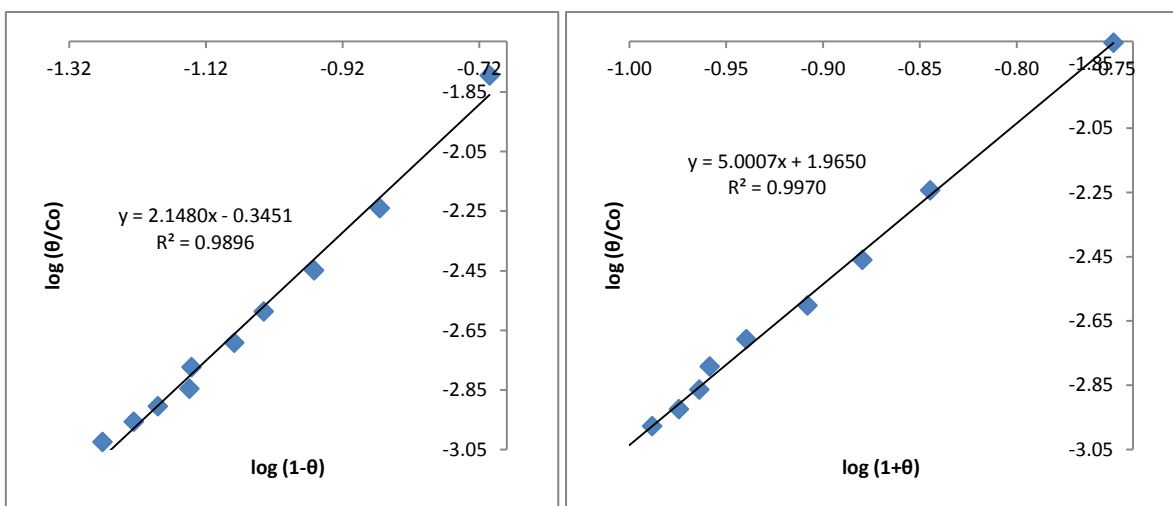
The Langmuir Isotherm Model biosorption for Cu(II) and Pb(II) onto defatted *Moringa oleifera* seed powder biomass (Experimental conditions: Dosage = 0.2 g per 50 mL; particle size ≤ 0.5 mm; mixing rate = 300 rpm; T = 25 ± 1 °C; contact time = 30 min. for Cu(II) and 40 min. for Pb(II); pH = 6.5 ± 0.2 for Cu(II) and pH = 5.5 ± 0.2 for Pb(II))

Dubinin–Radushkevich Isotherm (D-R) Model



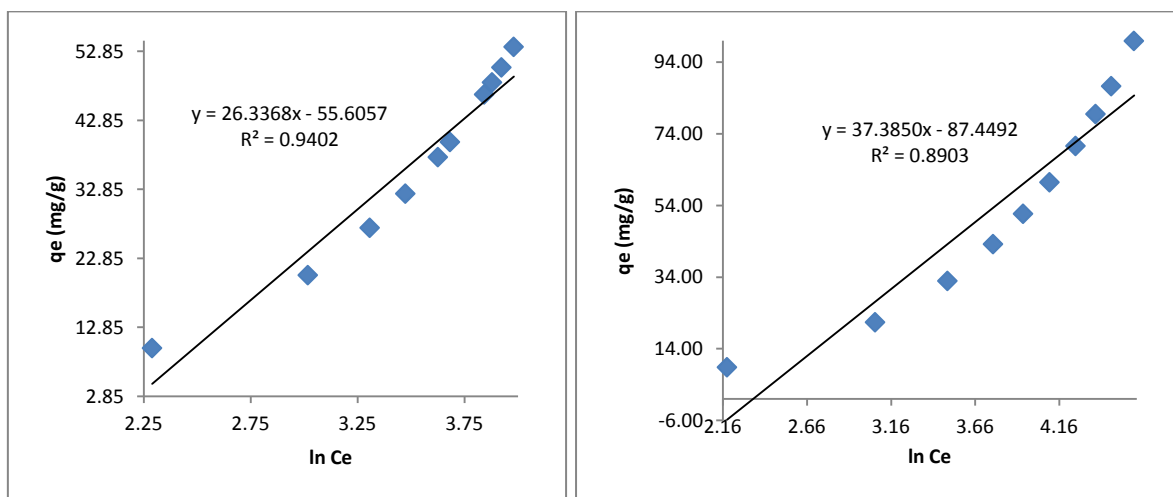
Dubinin–Radushkevich Isotherm (D-R) Model biosorption for Cu(II) and Pb(II) onto defatted *Moringa oleifera* seed powder biomass. (Experimental conditions: Dosage = 0.2 g per 50 mL; particle size ≤ 0.5 mm; mixing rate = 300 rpm; T = 25 ± 1 °C; contact time = 30 min. for Cu(II) and 40 min. for Pb(II); pH = 6.5 ± 0.2 for Cu(II) and pH = 5.5 ± 0.2 for Pb(II))

Flory–Huggins Isotherm Model



Flory–Huggins Isotherm Model biosorption for Cu(II) and Pb(II) onto defatted *Moringa oleifera* seed powder biomass. (Experimental conditions: Dosage = 0.2 g per 50 mL; particle size ≤ 0.5 mm; mixing rate = 300 rpm; $T = 25 \pm 1$ °C; contact time = 30 min. for Cu(II) and 40 min. for Pb(II); pH = 6.5 ± 0.2 for Cu(II) and pH = 5.5 ± 0.2 for Pb(II))

Temkin Isotherm Model



Temkin Isotherm Model biosorption for Cu(II) and Pb(II) onto defatted *Moringa oleifera* seed powder biomass (Experimental conditions: Dosage = 0.2 g per 50 mL; particle size ≤ 0.5 mm; mixing rate = 300 rpm; $T = 25 \pm 1$ °C; contact time = 30 min. for Cu(II) and 40 min. for Pb(II); pH = 6.5 ± 0.2 for Cu(II) and pH = 5.5 ± 0.2 for Pb(II))