Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.989268

57 (2016) 3964–3974
February

Taylor & Francis
Taylor & Francis Group

Biosorption of nickel (II) and copper (II) ions from aqueous solution using novel biomass derived from *Nannorrhops ritchiana* (Mazri Palm)

Sefath Ullah Khan[a], Farman Ullah Khan[a,*], Ihsan Ullah Khan[b],
Nawshad Muhammad[c,*], Syed Badshah[d], Adnan Khan[e], Asim Ullah[a],
Amir Sada Khan[a,f], Hazrat Bilal[a], Asma Nasrullah[a]

[a]*Department of Chemistry, University of Science and Technology, Bannu 28100, Pakistan, Tel. +923339730250; email: safe5754@gmail.com (S.U. Khan), Tel. +923348480892; email: farmandphil@yahoo.com (F.U. Khan), Tel. +923009392396; email: dawarasim@yahoo.com (A. Ullah), Tel. +00601116473142; email: aamirsada_khan@yahoo.com (A.S. Khan), Tel. +923339731300; email: bilalmphil2013@gmail.com (H. Bilal), Tel. +923349720250; email: Nasrullahadvent_chemis@yahoo.com (A. Nasrullah)*

[b]*Department of Fundamental and Applied Sciences, Universiti Teknologi PETRONAS (UTP), 31750 Tronoh, Perak, Malaysia, Tel. +0060163091782; email: ihsan_sagar@yahoo.com*

[c]*Interdisciplinary Research Center in Biomedical Materials COMSATS, Institute of Information Technology, Lahore, Pakistan, Tel. +923339223834; email: nawshadchemist@yahoo.com*

[d]*Department of Chemistry, Gomal University D.I. Khan, D.I. Khan, Pakistan*

[e]*Institute of Chemical Sciences, University of Peshawar, Peshawar, Pakistan, Tel. +923009890269; email: adnanics@yahoo.com*

[f]*PETRONAS Ionic Liquid Centre, Department of Chemical Engineering, Universiti Teknologi PETRONAS (UTP), 31750 Tronoh, Perak, Malaysia*

Received 6 February 2014; Accepted 11 November 2014

ABSTRACT

In the present research work, *Nannorrhops ritchiana* (Mazri Palm) was used as an effective biosorbent for removal of Cu^{2+} and Ni^{2+} ions from aqueous solution. *Nannorrhops ritchiana* (Mazri Palm), a dead biomass powder, was used as a low-cost adsorbent without any chemical treatment. In order to estimate the equilibrium parameters, the equilibrium adsorption data were analyzed using Freundlich, Langmuir, and Temkin isotherms. Freundlich isotherms indicated that the sorption capacities on the biomass surfaces increased with increasing initial concentrations of both metals. The adsorption isotherms were correlated with a comparison of linear and non-linear regression analysis. The squares of the errors (SSE) and chi-square test (χ^2) along with the coefficient of determination (R^2) were used to determine the best fit isotherm. Langmuir type I was found the best fitting isotherm for adsorption of both Cu^{2+} and Ni^{2+} ions as compared to the other three Langmuir linear isotherms on the basis of the values for R^2 and other error functions like SSE and χ^2 obtained from Langmuir-type I linear equation. The present study revealed that *Nannorrhops ritchiana* proved to be an effective, inexpensive, alternative, and environmentally friendly biosorbent for the removal of Cu^{2+} and Ni^{2+} ions from aqueous solution.

---

*Corresponding authors.

Keywords: Nannorrhops ritchiana; Biosorption; Cu and Ni; Adsorption isotherm

1. Introduction

Environmental pollution is a key challenging problem for the globe and it is increasing day by day due to the fast growth in population, science, technology, and industries [1,2]. It has been estimated that the surface of earth consists of approximately 70% water. That is the mainly precious source for life present on earth globe. Devoid of this important resource, the possibility of life on planet earth would not survive. Even if this reality is generally accepted, however, the origin of water from where contaminations occur is a common problem which we are facing day today. The effluents coming out from various industries containing both inorganic and organic toxic substances which are being discharged into the surface water severely affect biodiversity and aquatic life. Contamination of drinking water occurs by direct or indirect method. In direct method, sewage elution is from refineries, factories, and from devastatingly handling vegetation; and in indirect method, the pollutants pierce the water supply from two sources i.e. soil and ground water systems and also from the environment through rain [3,4]. Modern engineering and technology is also to a huge extent accountable for contamination of our clean environment [5]. Among these pollutants, metals ions are considered to be the most common and toxic water pollutants. Metals are released into the environment as a result of activities such as industrial, mining pigment and paint industries, and agricultural activities [6,7]. The heavy metals such as lead, copper, cadmium, zinc, and nickel are among the most common pollutants found in industrial effluents. Even at low concentrations, these metals can be toxic to organisms, including humans [8].

Among these metals, copper (Cu^{2+}) and nickel (Ni^{2+}) ions are metals of major concern because of their widespread uses in developing countries and their toxic nature. Ni(II) concentrations varies from 0 to 40 and 0.25 to 67 with an average concentration of ~22 mg/L. The Ni(II) concentration of these levels are seriously dangerous for human beings and other livestock due to the intrinsic carcinogenic nature. Cu(II), in particular, are among the most widely used metal ions in industries, they are highly toxic and can cause a variety of negative effects on human health, for example, neurotoxicity, jaundice, liver toxicity, anemia, encephalopathy, hepatitis, and nephritic syndrome [9]. The permissible limit of copper in drinking water as set by the World Health Organization is $10\,\mu g\,L^{-1}$ is $1.5\,mg\,L^{-1}$ [10]. The EPA requires lead, copper, cadmium, zinc, and nickel in drinking water not to exceed 0.015, 1.3, 0.005, 5, and $0.04\,mg\,L^{-1}$, respectively [8]. Due to the aforementioned reasons, in recent years, there is great interest generated for removing these metal ions from aqueous solution due to their supreme toxicity to human health and ecological systems [4].

There are various methods used for removal of metals ions from aqueous media such as chemical redox reaction, chemical precipitation, evaporative recovery, filtration, electrochemical treatment, reverse osmosis (membrane technologies), solvent extraction, and ion-exchange. However, most of these methods have some major shortcoming, such as applicable where the concentration of metals is relatively high, costly, insufficient metals removal, production of toxic slush, and high energy required. Presently, the sorption technique is proved to be quite simple, affective, economic, attractive, and most easily available technique for the dyes removal from the metals-bearing wastewater [11]. Thus, there is a great demand for such type of adsorbents which are made from low cost material, environmentally benign, and have great potential for adsorption without any additional expensive pretreatment [12,13]. Thus, there is a great demand for such type of adsorbent which are cheaper and still have high adsorption capability toward pollutants and metals without any additional expensive pretreatment. Presently, cellulose and lignocellulosic biomass have got considerable attraction because of its abundance in nature, effectiveness, low cost, and environmentally friendly nature of biopolymers. Thus, biosorption has been proved to be the most effective technique for the removal of Cu and Ni from the aqueous solution [4, 13–17].

Adsorption isotherm is very useful to describe the adsorption phenomenon and mobility of adsorbate from aqueous media to the solid phase adsorbent. These equilibrium models are very important in terms of describing the adsorption mechanism and also the surface properties of adsorbent. Linear regression is an important technique used for the determination of the adsorption isotherm parameters. In this research work, *Nannorrhops ritchiana* (Mazri Palm) was collected from hilly areas of North Waziristan Agency, Khyber Pakhtunkhawa, Pakistan, and used as an effective biosorbent without any chemical treatment for removal of Cu^{2+} and Ni^{2+} ions from aqueous solution. The utilization of this alternative, abundantly available and environmentally benign biosorbent, will solve both waste discarding problems as well as give access to an inexpensive material for wastewater decontamination. The main aim of this study to investigate the potential of *Nannorrhops ritchiana* for Cu^{2+} and Ni^{2+} ions from aqueous solution. Langmuir, Freundlich, and Temkin isotherms models were used for adsorption of Cu^{2+} and Ni^{2+} ions from aqueous solution. In addition, linear and non-linear regression methods, in selecting the optimum adsorption isotherm, were applied on the experimental data.

2. Experimental

2.1. Collection of plant material (biosorbent)

The plant *Nannorrhops ritchiana* (Mazri Palm), used as a biosorbent, was collected from the hilly areas of North Waziristan Agency, KPK, Pakistan, in June 2012. The plant leaves were dried and grounded into powder form with the help of electrical grinder. The ground *Nannorrhops ritchiana* (Mazri Palm) leaves were sieved to smaller particle size in order to get higher surface area to permit the adsorbate to accumulate deeply into the sewage in an elevated rate of adsorption. To avoid the color leaching effect, the grounded powder was soaked in water for 72 h, followed by filtration, and subsequent drying before subjecting to the adsorption process.

2.2. Biosorption batch experiments

The 0.1-M solutions of copper (II) and nickel (II) were prepared by dissolving 24.97-g of copper sulfate ($CuSO_4$ $5H_2O$) and 23.77-g of nickel chloride ($NiCl_2$ $6H_2O$) in distilled water, respectively. The various required concentration solutions were prepared from the stock solutions using the dilution formula $C_1V_1=C_2V_2$. In typical batch experiment, 100-mL capacity flasks were filled with 30 mL of the varying concentration of metal ions solutions and 20-mg *Nannorrhops ritchiana* (Mazri Palm) powder was added to each flask containing metal ions solutions. The flasks were potted to reduce evaporation and were shaken in wise bath water bath shaker at 180 rpm. The experiments were carried out at natural pH and at room temperature. After specific interval of time, sample aliquots were withdrawn and filtered to separate the metal-loaded biosorbent from metal ion-containing solution. The remaining concentration of metal ions was determined by Atomic Absorption Spectrophotometer.

Quantity of metal ions removed by the biomass of *Nannorrhops ritchiana* powder was determined using the Eq. (1)

$$N_f = (C_i - C_s)\frac{V}{m} \tag{1}$$

where N_f is the conc. of metal ions adsorbed (mmol/g), V is the volume of metal ions solutions (L), C_i is the initial conc. of metal ions (mmol/g), C_s is the final conc. of metal ions in aqueous phase (mmol/g), and m is the mass (g) of *Nannorrhops ritchiana* (Mazri Palm).

2.3. Analytical analysis of metal ions in solution

The concentration of each Cu(II) and Ni(II) in each sample after adsorption were analyzed with AA-7000 atomic absorption spectrophotometer. Firstly, the instrument was calibrated with standard solutions in the range covering the expected concentrations in diluted samples and then, the samples were analyzed in triplicate.

2.4. Biomass characterization

The chemical structure and nature of functional groups of biomass was studied using FTIR transmission spectra on a Perkin–Elmer Spectrum One. FTIR spectrum was recorded in the wave number range from 4,000 to 450 cm^{-1} with a resolution of 5 cm^{-1}.

2.5. Methods

2.5.1. Adsorption isotherm

The equilibrium relationship among the adsorbent and adsorbate is responsible for the studies of adsorptions procedure. Such separation processes have a thermodynamic background and easily find out the amount of material, which is capable of being adsorbed onto specific surfaces. To describe equilibrium relationships, two factor isotherms of Langmuir, Freundlich, and Temkin have been developed. Nevertheless, no single model is generally valid, all having some postulation that may or may not be applicable in a meticulous case.

2.5.2. Error functions

In order to assess the fit of an isotherm to the equilibrium data, an error function evaluation is necessary. For this purpose, various error functions, such as HYBRID, fractional error function, sum of absolute error, sum of the square of errors, average relative errors, chi-square test, and standard deviation of relative error have been adopted to conclude the best-fitting isotherm, among which the coefficient of determination (R^2) is possibly the most commonly applicable error function to forecast the optimum isotherm; and for the determination of the coefficient, the isotherm having R^2 value closest to unity is believed to be the best-fit isotherm.The Origin 6.1 version of software was used for the experimental data analysis. The equations used for linear and non-linear fitting of isotherm models has been given in Table 1.

3. Results and discussion

3.1. Characterization of adsorbent

The surface functional groups in biomass were determined using FTIR spectroscopy. The FTIR spectrum in Fig. 1 shows the functional groups in biomass. The peak at 3,443 cm^{-1} is assigned to the presence of –OH stretching vibration. It represents the presence of –0H group on the surface of biomass and chemisorbed water. The peak at 2,910 cm^{-1} showed the symmetric and unsymmetrical C–H stretching, due to the existence of –CH and C–H groups which are present in cellulose and lignin. The peak appeared at 2,834 shows CH stretch. The presence of adsorption peaks in region from 1,300 to 900 cm^{-1} represents the various carbonyl components such as alcohols, esters, carboxylic acid, or ethers. The peak at position 1,637 cm^{-1} is assigned to C=C. Additional peak at 1,227 cm^{-1} shows the C–O–C stretching. The peak associated at 1,016 cm^{-1} is assigned to C–N stretch. The absorption peak at 874.69 cm^{-1} is a prominent peak for the β-glucosidic linkage of cellulose in biosorbent [18]. The presence of these various nucleophilic groups represents that the biosorbent have potential to adsorb the metal ions effectively.

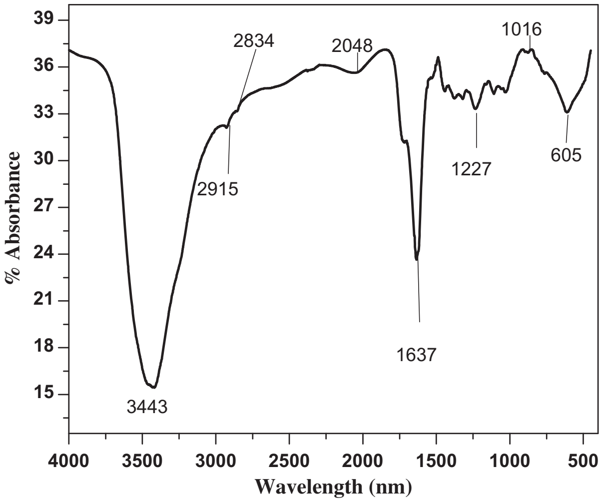


Fig. 1. FTIR spectrum of *Nannorrhops ritchiana* (Mazri Palm).

3.2. Linear method for adsorption isotherms

3.2.1. Langmuir linear adsorption isotherm

For the determination of isotherm parameters, the linear forms of the adsorption isotherms having best fit of an experimental data with various error functions were generally used. While analyzing the experimental data for the goodness of the Langmuir model, the equilibrium data were evaluated using the four linear forms of the Langmuir isotherm. To study the experimental data, Langmuir type (I) isotherm is the most commonly used linear expression and has been used by numerous researchers [19–22]. For one to four type linear form, Langmuir constants (sorption equilibrium constant) b, and the saturated monolayer sorption capacity N_s, the sorption of Cu^{2+} and Ni^{2+} onto *Nannorrhops ritchiana* (Mazri Palm) powder were determined from the slope and intercept of the plot between C_s and C_s/N_f, $1/N_f$ and $1/C_s$, N_f and N_f/C_s, and N_f/C_s and N_f, respectively as shown in Table 2. It is confirmed from the Table 2 that the calculated values for the Langmuir parameters for each type of linear Langmuir equation are different along with the different values for the co-efficient of determination (R^2) for each type of linear Langmuir equation. On the basis of the values for (R^2, Fig. 2(a) and (b)) and other error functions like squares of the errors and

Table 1
Equations for linear and non-linear of Langmuir, Freundlich, and Temkin isotherms

Isotherms	Linear form	Non-linear	Plot
Langmuir-1	$\frac{c_e}{q_e} = \frac{1}{bQ_e} + \frac{C_e}{Q_o}$	$q_e = \frac{Q_e b C_e}{1+bC_e} \frac{C_e}{q_e} vs. C_e$	
Langmuir-2	$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{bC_e Q_o}$		$\frac{1}{q_e}$ vs. $\frac{1}{C_e}$
Langmuir-3	$q_e = Q - \frac{q_e}{bC_e}$		q_e vs. $\frac{q_e}{C_e}$
Langmuir-4	$\frac{q_e}{c_e} = bQ_0 + qb_e$		$\frac{q_e}{c_e}$ vs. q_e
Freundlich	$\log q_e = \log K_f + \frac{1}{n} \log C_e$	$q_e = K_f q_e^{1/n}$	$\log q_e$ vs. $\log C$
Temkin	$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e q_e = \frac{RT}{b_T} \ln A_T C_e$		q_e vs. C_e

Table 2
Calculated values for Langmuir adsorption isotherm

	Cu(II)				
Isotherm	Constant	Type (1)	Type (II)	Type (III)	Type (IV)
Langmuir	N_f	1.1331	1.1331	1.1331	1.1331
	N_s	1.398601	1.77305	1.446	1.531834
	B	4.281437	2.611111	3.90625	3.424
	R^2	0.988	0.969	0.878	0.878
	SSE	0.047386	0.110965	0.048471	0.058332
	χ^2	0.025187	0.079668	0.024102	0.029497
	Ni(II)				
	N_f	0.6517	0.6517	0.6517	0.6517
	B	4.767677	3.431325	4.219409	2.591
	R^2	0.942	0.921	0.615	0.615
	SE	0.075925	0.076814	0.077017	0.082332
	χ^2	0.079345	0.080896	0.080348	0.092913

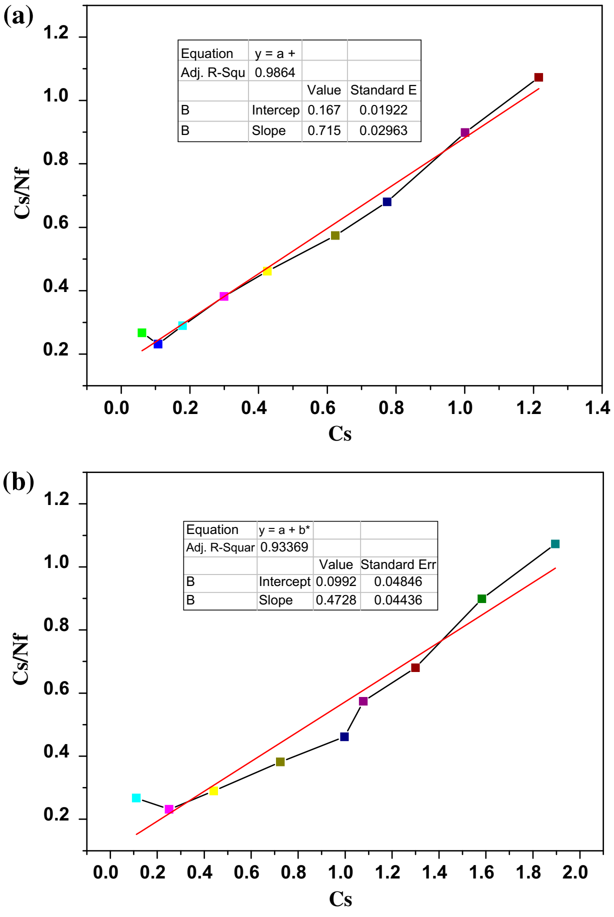
chi-square test (χ^2) obtained from Langmuir type I linear equation, it is concluded that Langmuir type I is the best fitting isotherm as compared to the other three Langmuir linear isotherms as the adsorption is monolayer and adsorption of each molecule on the biosorbent surface has an equal amount of activation energy as well negligible interaction among sorbate–sorbate.

3.2.2. Freundlich linear adsorption isotherm

The linear form of Freundlich adsorption isotherm was analyzed by plotting the graph between log N_f vs. log C_s (Eq. (2), Table 1). The applicability of Freundlich linear adsorption isotherm was judged from the coefficient of determination R^2.

$$\log N_f = \log K_f + \frac{1}{n} \log C_s \qquad (2)$$

The constants for Freundlich adsorption, K_f, and Freundlich exponent, $1/n$, were determined from the intercept and slope of plot as shown in Table 3 and Fig. 3(a) and (b). From Table 3, it was concluded that the error functions have higher values for Freundlich isotherm as compared to Langmuir type I isotherm, however, have least error functions than the other three types of linear Langmuir adsorption isotherms. The linear form of Langmuir adsorption type I is found to be more suitable for linking the experimental data than linear form of Freundlich adsorption isotherm. Nevertheless, in contrast with the error function of Freundlich isotherm with the other three linear



Equation	y = a +		
Adj. R-Squ	0.9864		
		Value	Standard E
B	Intercep	0.167	0.01922
B	Slope	0.715	0.02963

Equation	y = a + b*		
Adj. R-Squar	0.93369		
		Value	Standard Err
B	Intercept	0.0992	0.04846
B	Slope	0.4728	0.04436

Fig. 2. (a) Langmuir linear Type I for Cu(II); (b) Langmuir Type 1 for Ni(II).

Table 3
Calculated values for Freundlich and Temkin adsorption isotherms

Isotherm	Constant	Cu(II)	Ni(II)
Freundlich	K_f	1.104066	0.75654
	N	2.004008	2.631579
	R^2	0.903	0.809
	SE	0.164154	0.2608958
	χ^2	0.281038	0.626507
Temkin	K_T	97.54025	1987.661
	B (Kjol/mol)	3.65	10.92
	R^2	0.973	0.782
	SE	1.828989	1.314859
	χ^2	9.307584	7.379233

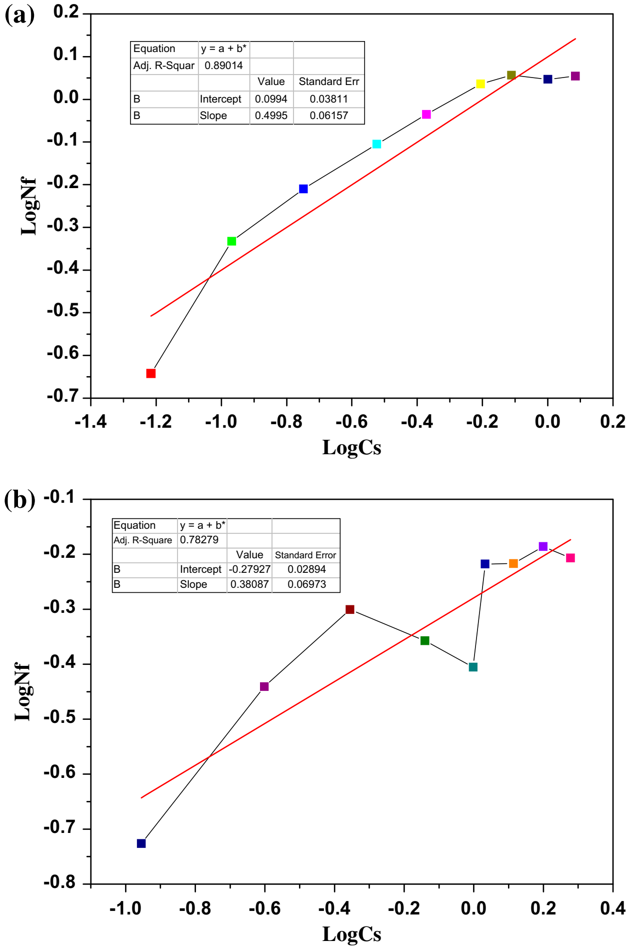


Fig. 3. (a) Freundlich isotherm for Cu(II); (b) Freundlich isotherm for Ni(II).

counterparts of Langmuir isotherm equation, the linear Freundlich isotherm is more appropriate in describing the biosorption process. Hence, in case of Langmuir type (I), the Langmuir theoretical postulation of monolayer coverage is valid for the biosorption of Cu(II) and Ni(II) onto *Nannorrhops ritchiana*, rather than the other three types of linear Langmuir adsorption isotherm.

3.2.3. Temkin linear adsorption isotherm

The equilibrium data for the biosorption of Cu(II) and Ni(II) onto *Nannorrhops ritchiana* was further analyzed using the linear form of Temkin adsorption isotherm. The mathematical form of Temkin linear isotherm is as following:

$$q_e = \frac{RT}{b_T} \ln \ A_T + \frac{RT}{b_T} \ln C_e \tag{3}$$

The Temkin parameters were calculated from slope and intercept of the graph plotted between N_f and ln C_s as evident from the Table 3 and Fig. 4(a) and (b). From the given Table 3 and Fig. 4(a) and (b), the values of various parameters and error functions obtained using Temkin adsorption isotherm parameters were found higher when compared to all other linear equations adsorption isotherms, hence the experimental data is not well represented by Temkin adsorption isotherm. The values of the error function in the current research data suggest that the Langmuir type (I) is the best representative of the experimental data for the biosorption of Cu(II) and Ni(II) onto *Nannorrhops ritchiana*, even though the Freundlich adsorption isotherm showed a good fitting to the experimental data.

3.3. Non-linear method for adsorption isotherms

In additional to linear, the non-linear methods were also applied for the experimental data. The linear method is used to evaluate the isotherm parameters in the three adsorption isotherm models for copper and nickel as shown in Table 4 and Fig. 5(a) and (b). The non-linear isotherm parameters and the error functions were determined through the origin version (6.0) software showing that the non-linear Langmuir isotherm parameters were quite close to the results of best fit linear Langmuir isotherm type (I).

Conversely, when the assessments of the different error functions regarding the non-linear Langmuir isotherm equation were evaluated (Table 4), it is observed that the values of the error functions are smaller in comparison to those of the four linearized types. These findings recommend that when applying the non-linear technique, there is no difficulty related with converting the non-linear Langmuir adsorption

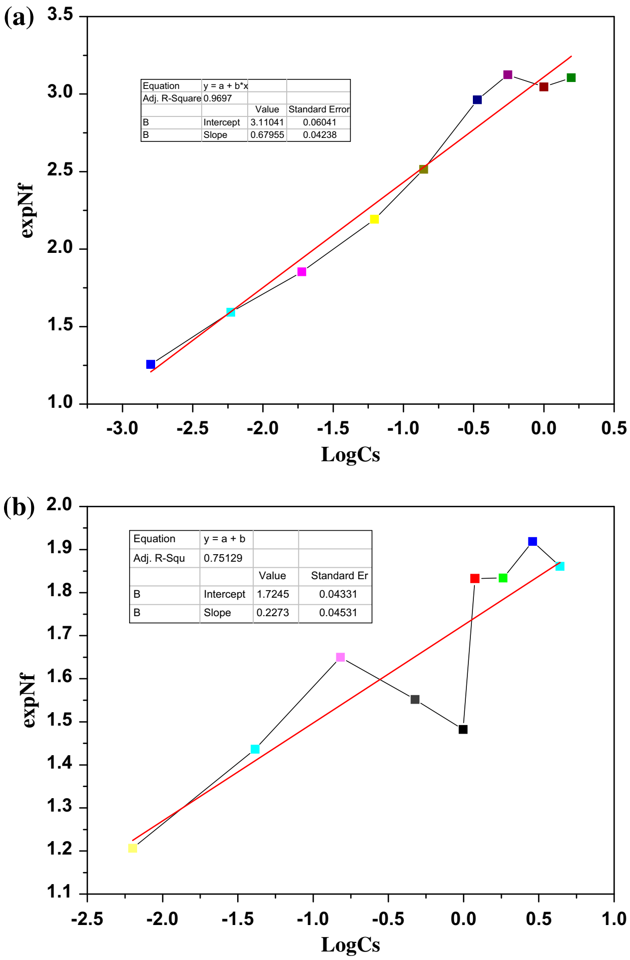


Fig. 4. (a) Temkin isotherm for Cu(II); (b) Temkin isotherm for Ni(II).

equation to its four different linearized forms. Additionally, it is to be renowned that the transformation of a non-linear isotherm equation to its linearized form may alter its error allocation.

From Table 4, it is observed that there is a small variation between the Freundlich adsorption isotherm parameters calculated by non-linear and its linearized type. However, the values of the error functions determined by the non-linear form are much lower than the linear method. Additionally, the values of the error functions (Table 4), including the R^2 value, were quite close to those of the non-linear Langmuir adsorption isotherm suggesting that the Freundlich adsorption isotherm illustrates a reasonably good fit for relating the biosorption of Cu(II) and Ni(II) onto *Nannorrhops ritchiana*.

In case of the Temkin adsorption isotherm, the variation among the adsorption isotherm parameters acquired using the linearized and non-linearized forms is very large. Additionally, when evaluated with the R^2 value of the linear Temkin adsorption equation, the R^2 value of the non-linear Temkin adsorption equation was different. Furthermore, the values of the special error functions are much lesser than their linearized counterparts, suggesting that the experimental data-set should be calculated by the non-linear technique to improve the results. On the other hand, Temkin adsorption isotherm model is correspond to the least fit for experimental equilibrium data than the other two types of adsorption isotherm equations.

3.4. Comparison of non-linear vs. linear adsorption isotherms

In analyzing the experimental data for adsorption of metal ions and dyes, the linear methods have been generally used primarily due to its easiness and effectiveness. On the basis of the error functions that yield least error distribution among the experimental and calculated isotherms, the most excellent fit isotherm is favored. The optimum adsorption isotherm is usually selected through the error functions. In the current

Table 4
Calculated values for the three non-linear isotherms

Isotherm	Parameter	Cu(II)	Ni(II)
Langmuir	N_s	1.41162 ± 0.05468	0.69568 ± 0.07563
	B	4.32576 ± 0.52958	3.73333 ± 1.61016
	R^2	0.98344	0.78465
	χ^2	0.00209	0.00584
Freundlich	K	1.16879 ± 0.05519	0.52776 ± 0.02703
	N	2.59634 ± 0.37217	2.99788 ± 0.72087
	R^2	0.91277	0.78077
	χ^2	0.01103	0.00594
Temkin	K	38.97737 ± 6.71337	39.17337 ± 25.46372
	N	3.15466 ± 0.19451	6.8035 ± 1.29696
	R^2	0.97433	0.79881
	χ^2	0.00325	0.00545

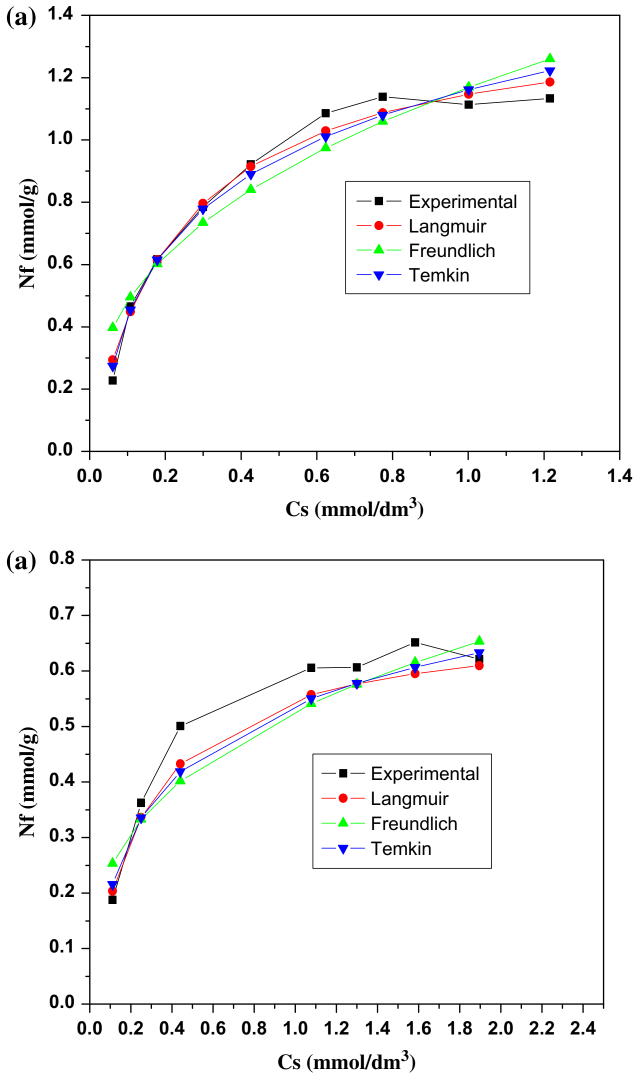


Fig. 5. (a) Comparison of the three non-linear isotherms for Cu(II); (b) comparison of three non-linear isotherms for Ni(II).

exploration, it was experienced that the error functions values for all the four types of Langmuir linear isotherm equations are different, while comparing the error functions values for all the four linear forms of Langmuir adsorption isotherm. These are due to the variation in giving out of the error arrangement for different linear equations. As a result, in a linear investigation the calculations for the parameter are significantly affected by different linear types of the same isotherm model. Accordingly, by applying the linearized process the different values reveal the actual complication in approximating the isotherm parameters. From these results, it is clear that error allocation get distorted the better or worse during the linearization of the equation. The experimental data was best fitted to the Langmuir linear isotherm type (I) in contrast to the other three counterparts of Langmuir isotherm. Due to the alteration in error distribution of different linear equations for Langmuir isotherm, the other linear forms of Langmuir isotherm equation have comparatively higher error functions values [23,24]. The alteration in the allocation of errors is dependent of different axial locations. The final finding of parameters is considerably exaggerated by the dependent variables which are distorted to different axial locations. Different axial locations also change the outcome of the regression; thus, manipulate the accurateness as well as stability which leads to the breaking of such assumptions which are followed by the isotherms [25]. Additionally, the linearized method follow the postulation that, the dispersed vertical positions nearby the line follows a Gaussian distribution and at every point of the x-axis, the distribution of the error functions is identical [23]. This assumption is rarely true or practically impossible, as most of the adsorption isotherms are non-linear due to different mechanism. Accordingly, on changing a non-linear isotherm equation to its linearized counterpart, the error allocation gets distorted. Furthermore, the equilibrium data is not assessed by the linear method, as an alternative, it supposes that the known data-set is linear and presents a straight line that forecasts the righteousness of fit for the experimental data. The linearized form only determines the intercept and slope for a straight line, which only calculate the y-value for a particular x. In linear method, the various results because of linearized form obviously indicate that all the ambiguity is in y-value, whereas x-value is known accurately. So it confirms that, the normality assumption behind the linear regression method is possibly been disobeyed. Accordingly, different parameters are obtained for the various forms of linear Langmuir adsorption isotherm from the identical equilibrium experimental data results. Besides, the linear methods have higher values for the error functions than the non-linear methods for all the three isotherms. Therefore, it is unsuitable in forecasting the righteous fit for a particular exits linearized form. In contrast, the shortcomings of the linearized technique may be evaded by taking the non-linear technique for analyzing the experimental equilibrium data due to the reason that in the non-linear method, the isotherms and the experimental data are in fixed y- and x-axis, that is the non-linear investigation is carried out on the identical ordinate and abscissa, consequential in the identical error allocation and arrangement [26]. Therefore, it is logical for the use of non-linear method to represent adsorption isotherm model capably and efficiently. As a result, the use of non-linear method than the

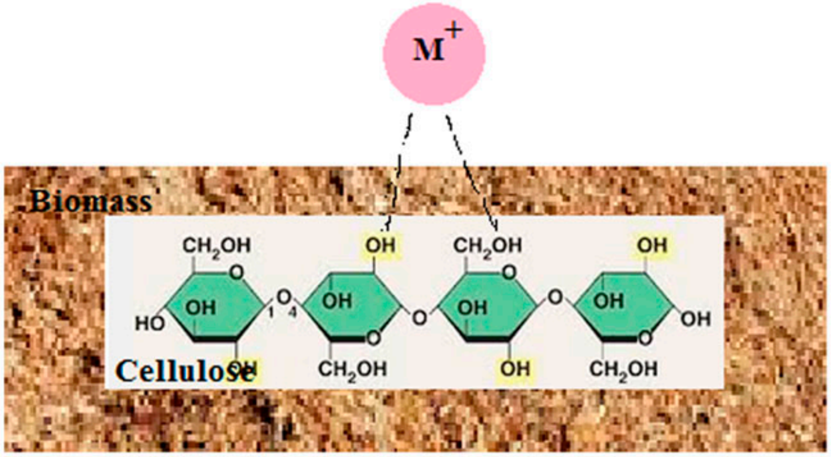


Fig. 6. Adsorption mechanism of metal ions on *Nannorrhops ritchiana*.

linearized method is more appropriate to approximate the parameters concerned with the adsorption isotherm model.

The current research corroborates the non-linear method than the linear method as an appropriate method to calculate the most complimentary adsorption isotherm. The present equilibrium data gives the Langmuir isotherm model as the most excellent appropriate isotherm for both linear and non-linear analyses. The values of the various error functions obtained from linear and non-linear methods for the three isotherm representation suggest the use of the non-linear method for the determination of isotherm parameters. Ho [27] match up to the linear technique and a non-linear technique of three familiar isotherms, including Langmuir isotherm to the experimental adsorption data of Pb(II) on to peat. The parameters calculated from the four Langmuir linear equations using the linearized technique were differed from each other, while they were matching when the non-linear technique was applied. Therefore, it was declared that the non-linear technique is an improved method to calculate the isotherm parameters. Additionally, using the linearized technique the best fit isotherm is obtained, the Langmuir type (I) equation, as it has the highest value for the coefficient of determination (R^2). Several researchers reported the same observation [23,25,28,29]. The researchers recommended that the linear equations for isotherms in fact cause actual tribulations and miscalculations occurring from the difficulties for simultaneous conversion of data, directing to the contravention of assumption followed by the isotherm model. In such circumstances, it probably is more reasonable and reliable to construe experimental equilibrium data through processes of non-linear regression.

3.5. Mechanism of metal adsorption

To understand the mechanism of adsorption of metal ions on the adsorbent is the main and important task. To study and understand the mechanism of adsorption, it is very necessary and important to know structure and surface of adsorbent. FTIR result (Fig. 1) shows that the biosorbent have –OH, COOH, and ketonic groups, which are more exposed and have strong chemical interaction between metal ions and adsorbent and mechanical interaction because of easy penetration of metal ions to microstructure of adsorbent.

The mechanism for adsorption of metal ions on adsorbent involving the migration of dye molecules: In this step, the passage of metal ions from bulk of the solution occurred to the surface of the adsorbent. In next step, diffusion of metal ions can take place through the boundary layer to the surface of the adsorbent. In third step, there is formation of surface hydrogen bonding between the metal ions and hydroxyl group of biomass. The proposed possible mechanism for adsorption of metal ions on the surface of biomass is shown in (Fig. 6).

$$\text{Biosorbent-OH-----------Biosorbent-O}^- + \text{M}^+$$

$$\text{Biosorbent-O}^- + \text{M}^+\text{-----------Biosorbent} - \text{O} - \text{M}^+$$

In this final step, the intraparticle diffusion of metal ions occurs. Metal ions get approached inside the pores of adsorbent.

4. Conclusions

Observing all these features in sight, our recent study indicated that *Nannorrhops ritchiana* is found to be effective for the removal of Cu(II) and Ni(II) from aqueous solutions. Freundlich isotherms indicated that the sorption capacities on the biomass surfaces increased with increasing initial concentrations of both metals. The equilibrium adsorption data were analyzed using Freundlich, Langmuir, and Temkin. Langmuir type I was found as the best fitting isotherm for adsorption of both Cu^{2+} and Ni^{2+} ions when compared to the other three Langmuir linear isotherms. Non-linear methods for the three isotherms suggested that the use of the non-linear method is more effective when compared to the linear methods, for the determination of isotherm parameters for adsorption of Cu (II) and Ni(II) on *Nannorrhops ritchiana.*

Acknowledgements

The authors are very thankful to Higher Education Commission of Pakistan for providing financial support for the current study under National Research Program for universities.

References

[1] M. Martín-González, O. González-Díaz, P. Susial, J. Araña, J. Herrera-Melián, J.M. Doña- Rodríguez, J. Perez-Peña, Reuse of phoenix canariensis palm frond mulch as biosorbent and as precursor of activated carbons for the adsorption of imazalil in aqueous phase, Chem. Eng. J. 245 (2014) 348–358.

[2] M.A. Abdullah, A.U. Rahmah, Z. Man, Physicochemical and sorption characteristics of malaysian ceiba pentandra (L.) Gaertn. as a natural oil sorbent, J. Hazard. Mater. 177 (2010) 683–691.

[3] K. Vijayaraghavan, Y.S. Yun, Bacterial biosorbents and biosorption, Biotechnol Adv. 26 (2008) 266–291.

[4] M.N. Zafar, I. Aslam, R. Nadeem, S. Munir, U.A. Rana, S.U.-D. Khan, Characterization of chemically modified biosorbents from rice bran for biosorption of Ni(II), J. Taiwan Inst. Chem. Eng. doi: 10.1016/j.jtice.2014.08.034.

[5] R.H. Vieira, B. Volesky, Biosorption: A solution to pollution? Int. Microbiol. 3 (2010) 17–24.

[6] A. Esposito, F. Pagnanelli, A. Lodi, C. Solisio, F. Veglio, Biosorption of heavy metals by Sphaerotilus natans: An equilibrium study at different pH and biomass concentrations, Hydrometallurgy 60 (2001) 129–141.

[7] S. Silver, T.K. Misra, Plasmid-mediated heavy metal resistances, Annu. Rev. Microbiol. 42 (1988) 717–743.

[8] P.X. Sheng, Y.-P. Ting, J.P. Chen, L. Hong, Sorption of lead, copper, cadmium, zinc, and nickel by marine algal biomass: Characterization of biosorptive capacity and investigation of mechanisms, J. Colloid. Interface 275 (2004) 131–141.

[9] S. Peyman, A. Behvar, M. Fatemeh, Biosorption of Ni(II), Cu(II) and Pb(II) by Punica gerana-tum from aqueous solutions, J. Water Res. Prot. 2 (2010) 701–705.

[10] M. Şener, D.H.K. Reddy, B. Kayan, Biosorption properties of pretreated sporopollenin biomass for lead (II) and copper(II): Application of response surface methodology, Ecol. Eng. 68 (2014) 200–208.

[11] L. Addour, D. Belhocine, N. Boudries, Y. Comeau, A. Pauss, N. Mameri, Zinc uptake by *Streptomyces rimosus* biomass using a packed-bed column, Chem. Technol. Biotechnol. 74 (1999) 1089–1095.

[12] Y. Xia, C. Liyuan, Study of gelatinous supports for immobilizing inactivated cells of *Rhizopus oligosporus* to prepare biosorbent for lead ions, Int. J. Environ. Stud. 5 (2002) 1–6.

[13] D. Reddy, K. Seshaiah, A. Reddy, S. Lee, Optimization of Cd(II), Cu(II) and Ni(II) biosorption by chemically modified Moringa oleifera leaves powder, Carbohydr. Polym. 88 (2012) 1077–1086.

[14] E. Sala Cossich, C.R. Granhen Tavares, T.M. Kakuta Ravagnani, Biosorption of chromium (III) by *Sargassum* sp. biomass, Electron. J. Biotechnol. 5 (2002) 6–7.

[15] M.N. Vara Prasad, H.M. De Oliveira Freitas, Metal hyperaccumulation in plants: Biodiversity prospecting for phytoremediation technology, Electron. J. Biotechnol. 6 (2003) 285–321.

[16] B. Volesky, Z. Holan, Biosorption of heavy metals, Biotechnol. Prog. 11 (1995) 235–250.

[17] P.D. Saha, K. Sinha, Natural dye from bixa seeds as a potential alternative to synthetic dyes for use in textile industry, Desalin. Water Treat. 40 (2012) 298–301.

[18] R. Krishni, K. Foo, B. Hameed, Adsorption of methylene blue onto papaya leaves: Comparison of linear and non-linear isotherm analysis, Desalin. Water Treat. 52 (2014) 34–36.

[19] P. Saha, S. Chowdhury, S. Gupta, I. Kumar, R. Kumar, Assessment on the removal of malachite green using tamarind fruit shell as biosorbent, Clean Soil Air Water 38 (2010) 437–445.

[20] S. Liang, X. Guo, N. Feng, Q. Tian, Isotherms, kinetics and thermodynamic studies of adsorption of Cu^{2+} from aqueous solutions by Mg^{2+}/K^{+} type orange peel adsorbents, J. Hazard. Mater. 174 (2010) 756–762.

[21] H.S. Altundogan, N.E. Arslan, F. Tumen, Copper removal from aqueous solutions by sugar beet pulp treated by NaOH and citric acid, J. Hazard. Mater. 149 (2007) 432–439.

[22] M. Mohapatra, S. Khatun, S. Anand, Kinetics and thermodynamics of lead (II) adsorption on lateritic nickel ores of Indian origin, Chem. Eng. J. 155 (2009) 184–190.

[23] K.V. Kumar, Optimum sorption isotherm by linear and non-linear methods for malachite green onto lemon peel, Dyes Pigm. 74 (2007) 595–597.

[24] Z.L. Yaneva, B.K. Koumanova, N.V. Georgieva, Linear and Non-linear regression methods for equilibrium modelling of p-nitrophenol biosorption by *Rhizopus oryzae*: Comparison of Error analysis criteria, J. Chem. ID 517631 (2013) 1–10.

[25] K.V. Kumar, Comparative analysis of linear and non-linear method of estimating the sorption isotherm parameters for malachite green onto activated carbon, J. Hazard. Mater. 136 (2006) 197–202.

[26] K.V. Kumar, S. Sivanesan, Isotherm parameters for basic dyes onto activated carbon: Comparison of linear and non-linear method, J. Hazard. Mater. 129 (2006) 147–150.

[27] Y.S. Ho, Isotherms for the sorption of lead onto peat: Comparison of linear and non-linear methods, Pol. J. Environ. Stud. 15 (2006) 81–86.

[28] M.I. El-Khaiary, Least-squares regression of adsorption equilibrium data: Comparing the options, J. Hazard. Mater. 158 (2008) 73–87.

[29] K.V. Kumar, K. Porkodi, F. Rocha, Isotherms and thermodynamics by linear and non-linear regression analysis for the sorption of methylene blue onto activated carbon: Comparison of various error functions, J. Hazard. Mater. 151 (2008) 794–804.