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Isotherm models for the nickel(II) biosorption using dead fungal biomass of *Aspergillus awamori*: comparison of various error functions

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ABSTRACT

In this research, the equilibrium sorption of nickel(II) by inexpensive dead fungal biomass of *Aspergillus awamori* was explained using the linear and nonlinear regression analysis of Freundlich, Langmuir, Temkin, and Redlich–Peterson isotherms. In the case of nonlinear regression method, the best fitting model was evaluated using six different error functions, namely coefficient of determination (r^2), chi-square test (χ^2), hybrid fractional error function (HYBRID), Marquardt's percent standard deviation (MPSD), average relative error (ARE), and sum of the errors squared (SSE). The r^2 function was found to be a better option to minimize the error distribution between the experimental equilibrium data and the predicted two-parameter isotherms. In the case of three-parameter isotherm, HYBRID was found to be the best error function to minimize the error distribution structure between experimental equilibrium data and theoretical isotherms.

Keywords: Biosorption; Nickel(II); Equilibrium isotherm; Error functions; Regression analysis

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1. Introduction

Toxic heavy metals are poisonous environmental contaminants, which can accumulate in living tissues, thus causing various diseases even in relatively lower concentrations [1,2]. Nickel(II) ions are of major concern because it is widely used in many industrial processes such as silver refineries, production of some alloys, electroplating, zinc base casting, storage battery industries, and printing [3,4]. The World Health Organization (WHO) has recommended the maximum acceptable concentration of Ni(II) ions in aqueous solution as only 0.02 mg/L. Higher concentration of nickel may cause poisoning effects such as nausea, headache, dizziness, tightness of the chest, vomiting, dry cough, shortness of breath, rapid respiration, cyanosis, and extreme weakness [5]. The international agency for research on cancer (IARC) has determined that some nickel compounds are human carcinogens [6]. The removal of hydrated nickel(II) ions due to its toxicological and biological effects is of great concern [1]. Chemical precipitation, ion exchange, filtration, electrochemical treatment, sludge separation, reverse osmosis, and evaporative recovery are the most commonly used techniques for heavy metals removal from wastewaters [7]. However, all these methods are either economically unfavorable or technically complicated and thus used in special cases [8]. Biosorption process

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is a effective, low-cost, and eco-friendly method for removal of toxic heavy metal ions from aqueous solutions by natural biosorbents [9,10]. Many microbial species such as algae, bacteria, fungi, yeast, activated sludge, and microbial biomass from fermentation and food industry are known to have high metal-adsorbing capacities [11,12]. Biosorption technology was used by a wide range of physicochemical mechanism, including physical adsorption, ion exchange, complexation, chelation, and surface microprecipitation [13]. Among the main microbial strains, fungi have been chosen for biosorption process because of their special physiology and their adsorbing capacity. Further, fungal biomass has a high percentage of cell wall material that shows excellent metal-binding capacity and is known to be more tolerant to metals and other factors such as low pH [14,15]. *Aspergillus* is a fungus commonly used in biosorption studies. Several *Aspergillus* species have been utilized for Ni(II) ions sorption including *Niger* [16], *Terreus*, *Flavus*, *Alternata* [17], and *Aspergillus* Spp. [18]. Equilibrium biosorption isotherms are the basic requirements for the proper analysis and efficient design of the biosorption separation processes. The isotherm models used to study of the biosorption process at equilibrium conditions and a constant temperature [19]. The different parameters of these equilibrium models help to understand the sorption mechanisms, the surface properties, and the affinity of the sorbent [20]. To determine the isotherm constants for any isotherm model, two methods are available: (i) fitting the isotherm equation to the data in its nonlinear form and (ii) converting the equation into a linear form [21]. Linear regression is frequently used to determine the most fitted sorption isotherm parameters [22]. The method of nonlinear regression involves the step of minimizing or maximizing the error distribution between the experimental data and the predicted isotherm. The coefficient of determination (r^2) is the most widely used error function. Recently, some of the researchers had used other error functions such as the chi-square test, Marquardt's percent standard deviation (MPSD), hybrid fractional error function (HYBRID), the average relative error (ARE), the sum of the absolute errors, and sum of the errors squared (SSE) to predict the optimum isotherm [23–27]. In the present study, a comparison of six different error functions, namely coefficient of determination (r^2), chi-square test (χ^2), HYBRID, MPSD, ARE, and SSE in minimizing the error distribution between the experimental and predicted isotherms is discussed using the experimental data of Ni(II) onto dead *Aspergillus awamori* biomass. The four isotherms, Freundlich, Langmuir, Temkin, and Redlich–Peterson isotherms, were applied to discuss this issue. The method of least squares was used to predict the isotherm by linear regression method. A trial and error method was used for nonlinear regression using the solver add-in with Microsoft Excel.

2. Materials and methods

2.1. Reagents and equipment

Ni(II) concentration in solution was determined by atomic absorption spectrophotometer (Varian-AA 240, Australia) with nickel hollow cathode lamp at a wavelength of 341.5 nm after biosorption. Samples of biosorbents were coated under vacuum with a thin layer of gold and examined by scanning electron microscopy (SEM) (∑ IGMA/VP-ZEISS, Germany) to study the surface texture morphology of the biomass before and after the biosorption. Further confirmation of the adsorption of Ni(II) ions onto *A. awamori* was done by energy dispersive X-ray (EDX, Oxford instruments) analysis.

2.2. Preparation of biomass

A. awamori (PTCC5097) that was obtained from the culture collection of Iranian Research Organization for Science and Technology (IROST) in the form of freeze dry was used. Sabouraud dextrose agar (SDA, Merck, Germany) was used for cultivation following incubation for 5 d at 30˚C (Fig. 1). The culture was prepared

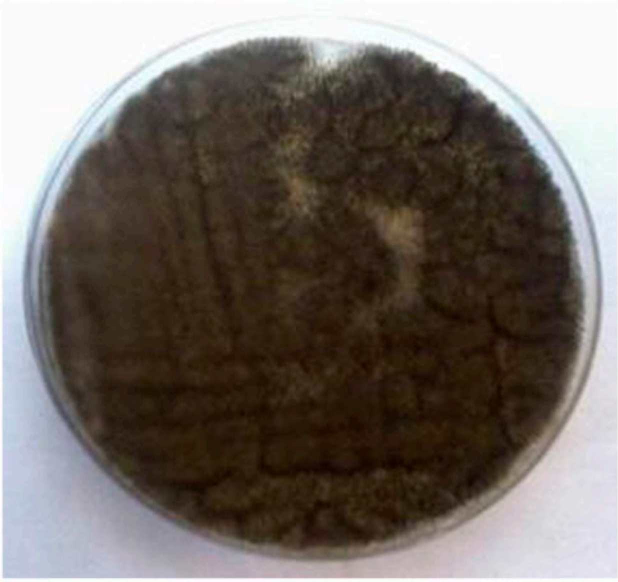

Fig. 1. Growth of *A. awamori* on SDA after incubation at 30˚C for 5 d.

in 1,000-mL Erlenmeyer flasks containing 250 mL of Sabouraud dextrose broth (SDB, Merck, Germany) growth medium and incubated on a rotary shaker (JalTajhiz, Iran) at 150 rpm at 30℃. The fungus cells were harvested after the end of exponential phase and washed with distilled water to remove the residual growth medium. The biomass was dried to a constant weight at 80℃ in an oven for 48 h and powdered to be used as a dead biomass in the biosorption experiments.

2.3. Batch studies of adsorption

The stock solution of Ni(II) (500 mg/L) was prepared by dissolving 0.24 g of analytical reagent grade $NiSO_4 \cdot 7H_2O$ (Merck) in 100 mL of deionized distilled water. Equilibrium isotherms were determined by shaking a fixed optimum biomass of *A. awamori* (0.25 g) with 100 mL of Ni(II) solutions in a 250-mL Erlenmeyer flask. A range of Ni(II) concentrations (25–75 mg/L) were tested at an initial optimum value of pH 6.0. Initial pH adjustments were carried out by adding 0.1 M HCl (Merck, Germany) and 0.01 M NaOH (Merck, Germany). After shaking the flasks for 3 h at constant temperature (25℃), Ni(II) solution was separated from biosorbent by filtration and the residual Ni(II) ion concentration in the solution was determined by atomic absorption spectrophotometer (Varian-AA 240, Australia) with nickel hollow cathode lamp at a wavelength of 341.5 nm. Metal uptake by biosorbent was calculated using the following equation:

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

where q_e is the equilibrium uptake in mg/g, C_0 and C_e are the initial and the equilibrium metal ion concentrations in mg/L, respectively, V is the volume of the solution in contact with the biosorbent in mL, and m is the mass of the added biosorbent in g [28].

3. Biosorption isotherm

3.1. Freundlich isotherm

In 1906, the German physicist Herbert Max Finlay Freundlich gave an empirical expression representing a relationship on energetically heterogeneous surfaces. The simplest and earliest known sorption equation can be expressed as follows:

$$q_e = k_f C_e^{\frac{1}{n}} \tag{2}$$

where q_e is the equilibrium uptake capacity (mg/g), k_f (L/mg) and n are Freundlich constants related to the biosorption capacity and sorption efficiency, respectively, and C_e is the equilibrium concentration [29–31].

3.2. Langmuir isotherm

The Langmuir isotherm model describes monolayer adsorption on homogeneous surface and obeys Henry's law by the following equation [32,33]:

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \tag{3}$$

where q_e is the equilibrium metal ions uptake (mg of adsorbate/g of dried adsorbent), q_m is the maximum monolayer uptake capacity (mg/g), K_a is the Langmuir constant or adsorption coefficient (L/mg) for binding of adsorbate on the biosorbent sites, and C_e is the equilibrium concentration (mg/L).

3.3. Temkin isotherm

In 1940, Temkin and Pyzhev studied the Temkin isotherm firstly [34]. The Temkin isotherm model assumes that the heat of adsorption of all the molecules in the layer would decrease linearly with the increase in the coverage of adsorbent. The model is commonly used to describe adsorption process on heterogeneous surfaces and can be described by the following equation [28,35]:

$$q_e = \frac{RT}{b} \ln(K_T C_e) \tag{4}$$

where R is the universal gas constant, T represents the absolute temperature in Kelvin, K_T is the Temkin isotherm constant (L/mg), and b is the Temkin constant. The Temkin isotherm has the following formulation:

$$q_e = B_T \ln(K_T C_e) \tag{5}$$

where q_e is the amount of the equilibrium metal uptake (mg/g), C_e is the equilibrium metal concentration in solution (mg/L), and B_T is the constant related to the heat of sorption (J/mol) [35]. The nonlinear forms of Langmuir, Freundlich, Redlich–Peterson, and Temkin isotherms are shown in Table 1.

3.4. Redlich–Peterson isotherm

The Redlich–Peterson model is a combination of the Langmuir and Freundlich isotherms and the way to obtain the isotherm parameters is given by Eq. (6), where A (L/g), B (L/mmol), and g are Redlich–Peterson constants and g is the exponent, which lies between 1 and 0. For $g = 1$, the Redlich–Peterson is a special case of Langmuir isotherm [36,37]:

$$q_e = \frac{Ac_e}{1 + Bc_e^g} \tag{6}$$

4. Error functions

An error function assessment is required, in order to evaluate the fit of the isotherm models to the experimental results for the removal of Ni(II) onto *A. awamori*. In the present study, the following error functions were applied to confirm the best fitting isotherm. The error functions that produced minimum error distribution between the experimental and predicted isotherm models determined the best fitting model.

4.1. Coefficient of determination (r^2)

The coefficient of determination is perhaps the most commonly used error function to predict the optimum isotherm model in most studies [21]. It is expressed as:

$$r^2 = \frac{\sum(q_m - \overline{q_e})^2}{\sum(q_m - \overline{q_e})^2 + \sum(q_m - q_e)^2} \tag{7}$$

where q_m (mg/g) and q_e (mg/g) are the equilibrium capacities measured from the isotherm model and experimental data, respectively, and $\overline{q_e}$ (mg/g) is the average of q_e.

4.2. Chi-square test

The chi-square test (χ^2) is based on the sum of the squares of the differences between the experimental data and predicted isotherm models, with each squared difference divided by the corresponding data calculated using isotherm equation as presented in Eq. (8). The best-fit isotherm is selected based on the model that gives the smallest chi-square value:

$$\chi^2 = \sum \frac{(q_{e,meas} - q_{e,cal})^2}{q_{e,cal}} \tag{8}$$

where $q_{e,meas}$ (mg/g) and $q_{e,cal}$ (mg/g) are the equilibrium experimental adsorption capacity and the theoretically calculated adsorption capacity at equilibrium, respectively [24].

4.3. Sum of the squares of the errors

SSE is the most widely used technique and is defined as the sum of the squares of the difference between the calculated data by the experimental and predicted isotherms. It is expressed as [38]:

$$\text{SSE} = \sum_{i=1}^{n} (q_{e,cal} - q_{e,meas})_i^2 \tag{9}$$

Table 1
Isotherms and their linear form

Isotherm	Nonlinear isotherm	Linear isotherm	Plot
Langmuir	$q_e = \frac{q_m K_a c_e}{1 + K_a c_e}$	$\frac{c_e}{q_e} = \frac{c_e}{q_m} + \frac{1}{K_a q_m}$	$\frac{c_e}{q_e}$ vs. c_e
Freundlich	$q_e = K_f C_e^{\frac{1}{n}}$	$\ln(q_e) = \ln K_f + \frac{1}{n}\ln(c_e)$	$\ln q_e$ vs. $\ln c_e$
Temkin	$q_e = B_T \ln(K_T c_e)$	$q_e = B_T \ln K_T + B_T \ln c_e$	q_e vs. $\ln c_e$
Redlich–Peterson	$q_e = \frac{Ac_e}{1 + Bc_e^g}$	$\ln\left(\frac{Ac_e}{q_e} - 1\right) = g\ \ln(c_e) + \ln B$	$\ln\left(\frac{Ac_e}{q_e} - 1\right)$ vs. $\ln(c_e)$

4.4. Hybrid fractional error function

HYBRID method was developed in order to improve the fit of the SSE error function at low concentration values as follows:

$$\text{HYBRID} = \frac{100}{n-p}\sum_{i=1}^{n}\left[\frac{(q_{\text{e,meas}} - q_{\text{e,cal}})^2}{q_{\text{e,cal}}}\right]_i \tag{10}$$

where n is the number of experimental data points and p is the number of parameters in each isotherm model [27].

4.5. Average relative error

ARE technique was developed as an attempt to minimize the fractional error distribution across the entire studied concentration range. It is defined as [39]:

$$\text{ARE} = \frac{100}{n}\sum_{i=1}^{n}\left|\frac{(q_{\text{e,meas}} - q_{\text{e,cal}})}{q_{\text{e,meas}}}\right|_i \tag{11}$$

4.6. Marquardt's percent standard deviation

MPSD error function is similar to the geometric mean error distribution which has been modified according to the number of degrees of freedom of the system. It is given as [40]:

$$\text{MPSD} = 100\sqrt{\sum_{i=1}^{n}\left[\frac{(q_{\text{e,meas}} - q_{\text{e,cal}})^2}{q_{\text{e,cal}}}\right]_i} \tag{12}$$

5. Results and discussion

5.1. SEM and EDX analysis of A. awamori

The SEM micrographs of the *A. awamori* biomass were compared before and after biosorption of Ni(II) onto the fungal biomass in Fig. 2. The structure of the biosorbents was at a constant condition: 0.05 g of the biosorbent, pH 6, 100 mL of Ni(II) with an initial concentration of 25 mg/L, a constant temperature of 25℃, a constant speed of 150 rpm, and 3 h for contact time. The results from Figs. 2a and 2b obviously show the difference between before and after loading of Ni(II) on the biomass surface. Following metal loading on biomass, some deformation and appearance of cavities onto the *A. awamori* surface were observed. This morphology may contribute to the relatively high surface area of the fungal biomass. Further confirmation of the adsorption of Ni(II) ions onto *A. awamori* was done by EDX analysis. Figs. 2c and 2d show the typical EDX (Oxford instruments) pattern for the biomass before and after the sorption of Ni(II), respectively. The difference in elemental peak intensities before and after the sorption process was as a result of binding of toxic metal ions onto the active sites on the surface of the *A. awamori* biomass.

5.2. Linear regression analysis

The widely used linearized form of Freundlich, Langmuir, Temkin, and Redlich–Peterson isotherms which are found to be the best-fit expressions in representing most of the experimental equilibrium data is shown in Table 1. Langmuir type 1 is most commonly applied compared with the other linearized Langmuir types by researchers due to the minimized deviations from the fitted equation resulting in the best error distribution [13]. The Freundlich, Langmuir, Temkin, and Redlich–Peterson constants can be obtained from the slope and intercept of plot between $\ln q_e$ vs. $\ln c_e$, c_e/q_e vs. c_e, q_e vs. $\ln c_e$, and $\ln(Ac_e/q_e - 1)$ vs. $\ln(c_e)$, respectively [23,24]. In the case of Redlich–Peterson isotherm, the constant A was obtained by maximizing the r^2 value between the theoretical data using the solver add-in function, Microsoft Excel, and Microsoft Corporation. Values of the isotherm constants are presented in Table 2 for the biosorption of Ni(II) ions onto *A. awamori* in a concentration range of 25–75 mg/L. Fig. 3 shows the experimental equilibrium data and the predicted theoretical isotherms using linear method for the sorption of Ni(II) onto *A. awamori*.

The predicted isotherm constants for the Ni(II) and their corresponding r^2 values by the linear method are shown in Table 2. The coefficient of determination values for the four models as shown in Table 2 showed that the Redlich–Peterson was found to be the best-fit isotherm for the equilibrium uptake of Ni(II) onto *A. awamori*.

Several researches suggested the nonlinear method as a better way to obtain the isotherm parameters. Previous studies showed that the linearization of a complex mathematical nonlinear isotherm expression produces different results and may alter the error distributions and violate the normality assumptions of the least square method [22,23,41]. Based on any of the error measures, nonlinear method can be useful to

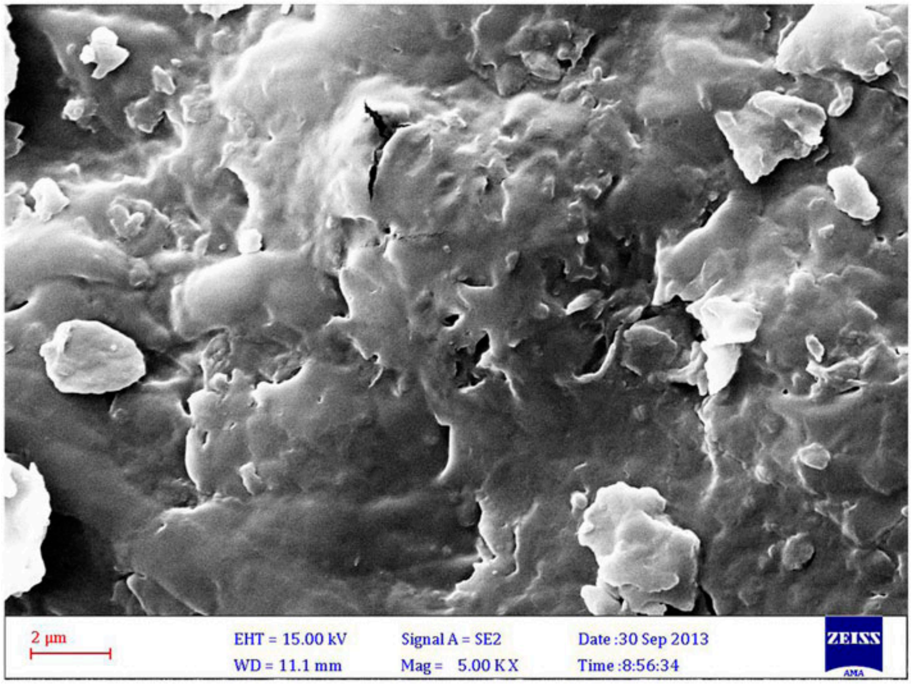

Fig. 2a. Micrograph of *A. awamori* before biosorption of nickel(II).

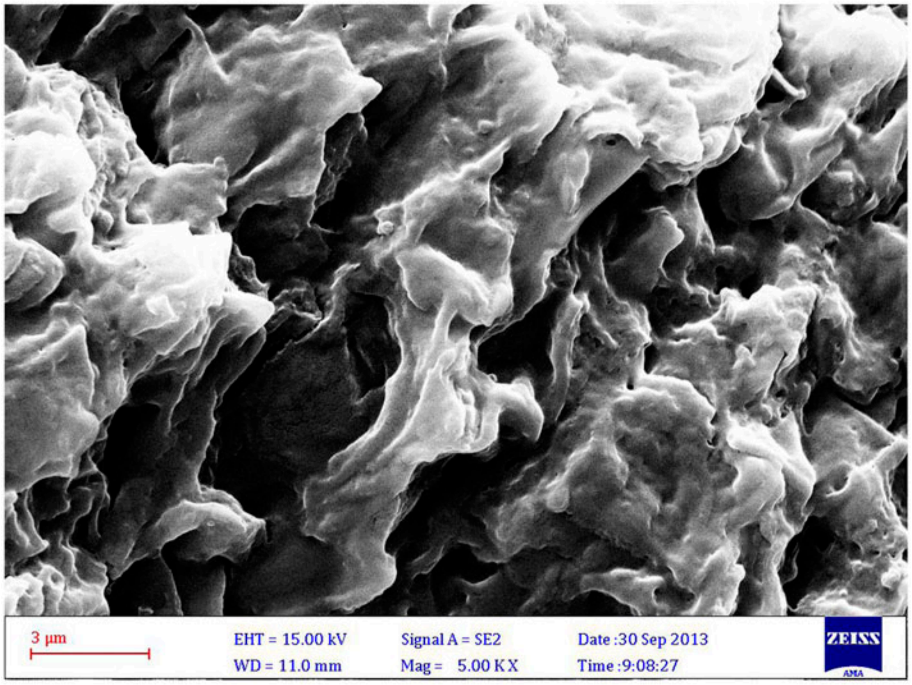

Fig. 2b. Micrograph of *A. awamori* after biosorption of nickel(II).

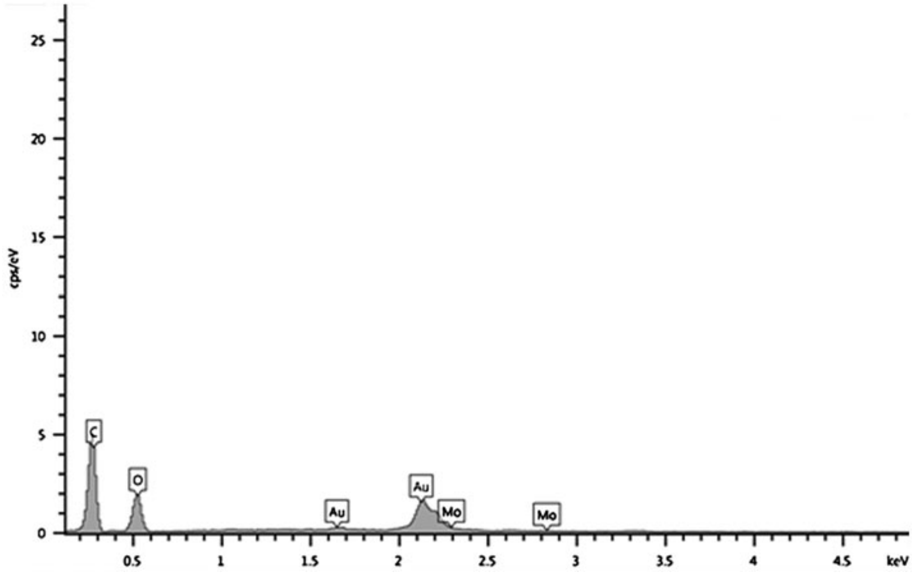

Fig. 2c. EDX spectra of *A. awamori* before Ni(II) biosorption.

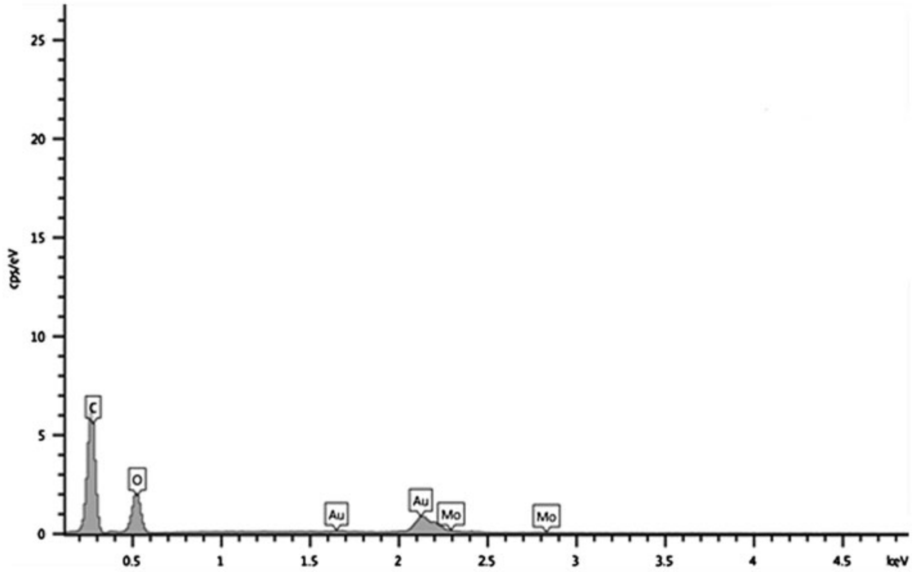

Fig. 2d. EDX spectra of *A. awamori* after Ni(II) biosorption.

Table 2
Isotherm parameters obtained using the linear method

Langmuir		Freundlich		Temkin		Redlich–Peterson	
$q_{\max}$ (mg/g)	9.520	$1/n$	0.333	K_T (L/mg)	0.641	A (L/g)	4.250
K_a (L/mg)	0.800	K_f (mg/g) $(\text{L/g})^{1/n}$	1.840	B_T (J/mol)	1.960	B (L/mg$^{(1/A)}$)	1.930
r^2	0.920	r^2	0.891	r^2	0.851	g	0.700
						r^2	0.970

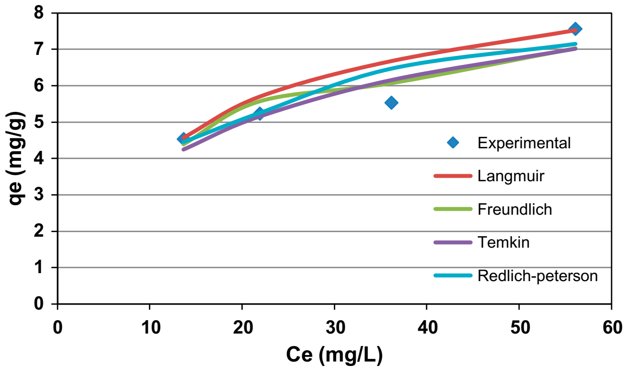

Fig. 3. Experimental equilibrium data and isotherm by linear regression method for the sorption of Ni(II) onto *A. awamori*.

realize that one might obtain a good fitting model. Thus, in the present study, nonlinear regression method was used to determine the optimum isotherm using the four isotherm models (Freundlich, Langmuir, Temkin, Redlich–Peterson) studied.

5.3. Nonlinear method

In the case of nonlinear method, previous research showed that the predicted isotherms were varying with respect to the error function applied, while minimizing the error distribution between the experimental data and predicted isotherms [24,41–43]. Thus, in order to analyze the impact of various error functions on the predicted isotherms, six error functions r^2, χ^2, HYBRID, MPSD, ARE, and SSE were applied (Table 3).

From Table 3, it is found that the coefficient of determination values for the four models shows that all models are applicable in describing the data ($r^2 > 0.90$) with the Redlich–Peterson and Temkin models being more appropriate. As can be seen from Table 3, all the error functions studied except (r^2) method suggested Freundlich model as the best-fit isotherm. Figs. 4a–4d shows the experimental and predicted Freundlich, Langmuir, and Temkin isotherms for Ni(II) onto *A. awamori* by minimizing the error distribution between the experimental data and the theoretical isotherms using various error functions. From Figs. 4a–4d, it is clear that the predicted theoretical isotherm was found to be varying with the error functions used.

Figs. 5a and 5b show the experimental equilibrium data and predicted isotherms for the sorption of Ni(II) onto *A. awamori* by maximizing r^2 function and minimizing the MPSD error function, respectively. From Figs. 4a and 4b, it can be observed that Redlich–Peterson isotherm overlaps the Freundlich isotherm. Thus, the Redlich–Peterson is a special case of Freundlich when the constant A and $B >> 1$. The similar findings have been reported by other researchers as well [22]. A similar effect was observed for the predicted isotherms by minimizing the error functions HYBRID, SSE, ARE, and χ^2 (not shown). Both the size of error function and also the determined isotherm parameters should be investigated to select the optimum model due to the theory behind the isotherm [44]. Thus, in order to study which error function minimizes the error distribution between the experimental

Table 3
Predicted isotherm by minimizing the error distribution using different error functions

Error functions		r^2	χ^2	HYBRID	MPSD	ARE	SSE
Langmuir	$q_{\max}$	9.160	8.590	8.590	8.180	8.180	9.010
	K_a	0.062	0.072	0.072	0.083	0.080	0.060
	OF[a]	0.992	0.159	7.950	11.320	6.700	0.950
Freundlich	$1/n$	0.360	0.340	0.340	0.320	0.300	0.360
	K_f	1.660	1.780	1.780	1.880	2.044	1.680
	OF[a]	0.995	0.095	4.750	8.870	4.520	0.560
Temkin	K_T	0.650	0.780	0.780	0.950	1.560	0.650
	B_T	1.960	1.830	1.830	1.710	1.470	1.960
	OF[a]	0.999	0.120	6.200	9.960	5.102	0.750
Redlich–Peterson	A	4.250	127.600	126.700	128.460	128.480	125.090
	B	1.930	68.800	70.750	67.650	67.620	74.010
	g	0.710	0.660	0.650	0.670	0.670	0.630
	OF[a]	0.999	0.095	9.530	8.884	4.620	0.600

[a] Objective function for the minimum error distribution between experimental and predicted isotherms.

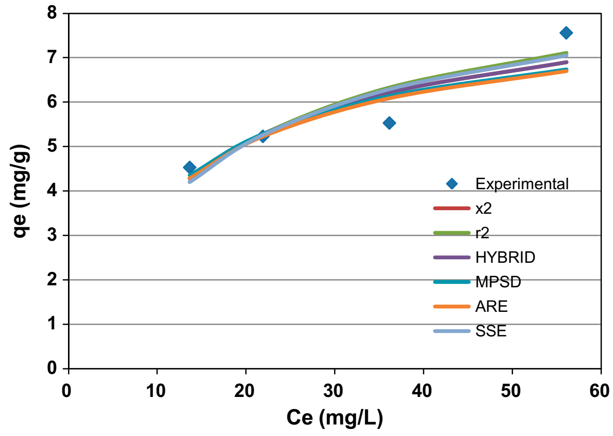

Fig. 4a. Langmuir isotherm plots for Ni(II) onto *A. awamori* using various error analysis methods.

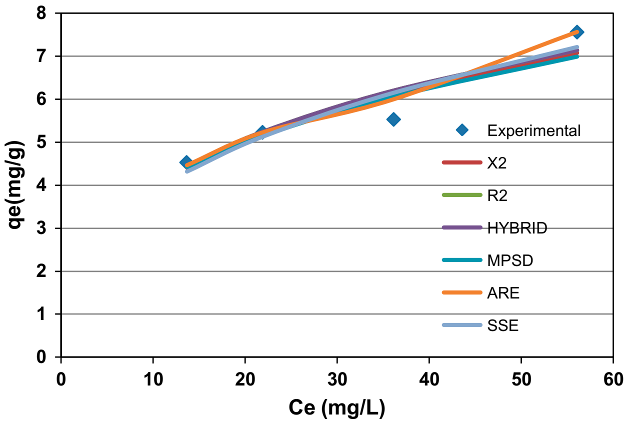

Fig. 4d. Redlich–Peterson isotherm plots for Ni(II) onto *A. awamori* using various error analysis methods.

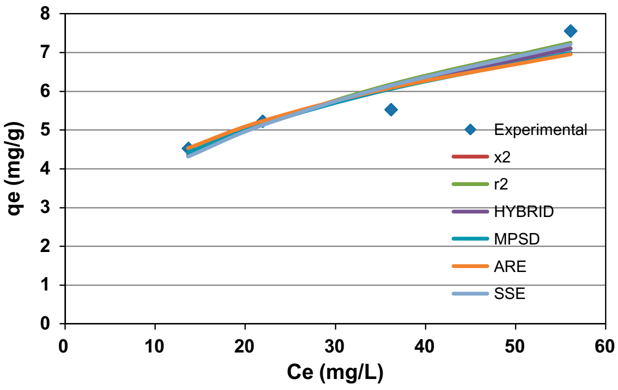

Fig. 4b. Freundlich isotherm plots for Ni(II) onto *A. awamori* using various error analysis methods.

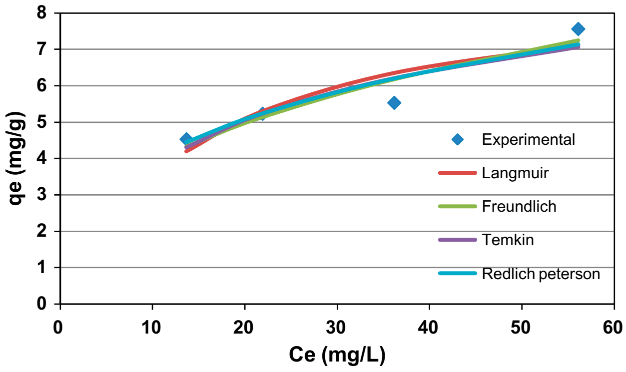

Fig. 5a. Isotherms by maximizing r^2 function for Ni(II) onto *A. awamori*.

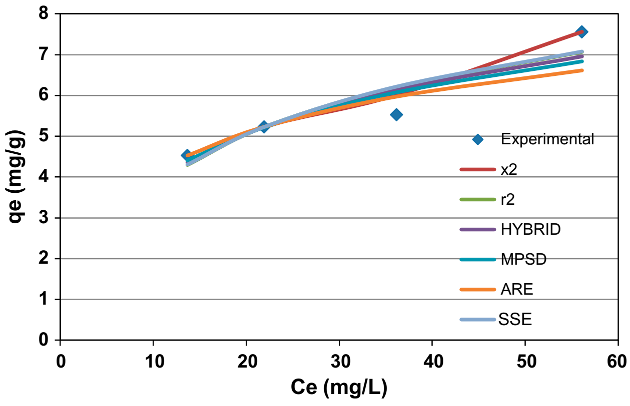

Fig. 4c. Temkin isotherm plots for Ni(II) onto *A. awamori* using various error analysis methods.

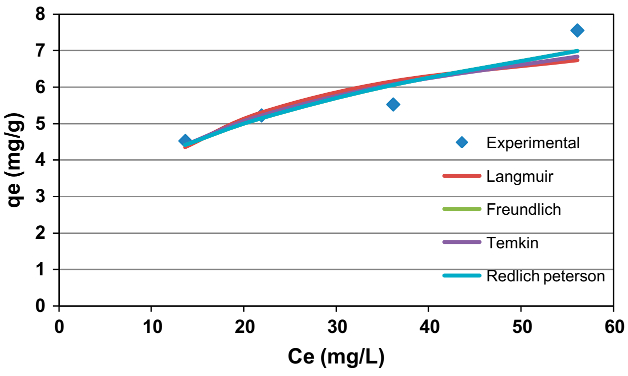

Fig. 5b. Isotherms by minimizing MPSD function for Ni(II) onto *A. awamori*.

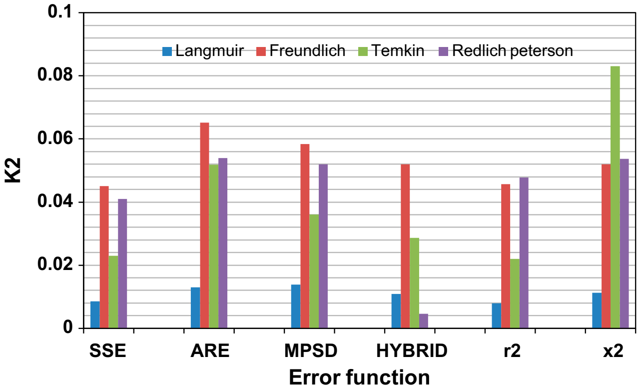

Fig. 6. Coefficient of nondetermination for isotherms of Ni (II) onto *A. awamori*.

data and predicted isotherms, another statistical function, namely coefficient of nondetermination (K^2) was used [23] as:

$$K^2 = \frac{\text{unexplained variance}}{\text{total variance}} = 1 - \frac{\text{explained variance}}{\text{total variance}} = 1 - r^2 \tag{13}$$

Fig. 6 shows the calculated K^2 values for the isotherms predicted by minimizing or maximizing the various error functions for Ni(II) onto *A. awamori*. From Fig. 5, it is observed that r^2 function least unexplained the two-parameter isotherm, suggesting this function as the best function to minimize the error distribution between the experimental and predicted two-parameter isotherms, namely the Freundlich, Langmuir, and Temkin isotherms. Thus, the results of r^2 can be useful in predicting the optimum isotherm based on the two-parameter isotherms in this study. In the case of three-parameter Redlich–Peterson isotherm, it can be observed that HYBRID was found to be the best error function in minimizing the error distribution between the experimental equilibrium data and the predicted isotherms (Fig. 4). Thus, the results of HYBRID can be useful in predicting the optimum isotherm based on the three-parameter Redlich–Peterson isotherm.

6. Conclusion

The equilibrium sorption of Ni(II) by *A. awamori* was explained using the Freundlich, Langmuir, and Temkin isotherms. The coefficient of determination (r^2) was used to select the best-fit linear theoretical isotherm. In the case of nonlinear regression method, six error functions were used to predict the parameters involved in the two-parameter and three-parameter isotherms and also to predict the optimum isotherm. For the two-parameter isotherms, r^2 function and for the three-parameter isotherms, HYBRID function was found to be a better option to minimize the error distribution between the experimental and predicted isotherms. The coefficient of nondetermination was found to be a more useful statistical term in determining the best error function while selecting the optimum isotherm.

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