



# On the optimal use of isotherm models for the characterization of biosorption of lead onto algae



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## ABSTRACT

For the first time we apply a new method based on the mathematical derivation of some known isotherm from the Burr function which describes many birth–death (sorption–desorption) phenomena in ecology and economy. Therefore, in this study the experimental isotherm data of biosorption of Pb(II) onto algae was modeled to Langmuir, Hill–Sips, Brouers–Sotolongo, Brouers–Gaspard, and Redlich–Peterson isotherm models. The parameters of each model were determined by nonlinear fitting algorithms using Mathematica program. The maximum Pb(II) removal rate increased with the increase of temperature and reached the maximum value (98%) at the temperature of 40 °C. The results showed that the Hill–Sips and the Brouers–Sotolongo isotherms were definitely the most suitable models to satisfactorily describe biosorption of Pb(II) on the algal biomass. In addition, as these two models gave very close results, the use of an intermediate one the Brouers–Gaspard isotherm model could also describe the sorption in most cases. High coefficient of determination values was obtained by using nonlinear methods and these findings are contrary to most works in this field that use linearization methods. Further, this study showed that a complete set of data is necessary to have a good representation of the isotherm and using only coefficient of determination is not always an adequate tool to compare the goodness of the nonlinear fit of an isotherm models.

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## 1. Introduction

Biosorption is a process which utilizes inexpensive dead biomass to sequester toxic pollutants [10,12,26]. Biosorption is proven to be quite effective at removing metal ions from contaminated solutions in a low cost and environment-friendly manner. Adsorbent comes under the following categories: algae; fungi; grass, agriculture waste, and nanomaterials [21,31,33,45,46,50,52]. These materials were used to remove pollutants in a batch and/or continuous systems [11,14,24,25,32]. The term algae refers to a large and diverse assemblage of organisms that contain chlorophyll and carry out oxygenic photosynthesis [10]. Algae are one of the most abundant and highly available natural resources in tropical ecosystems. Cyanophyta (blue-green algae), Chlorophyta (green algae), Rhodophyta (red algae), and Phaeophyta (brown algae) are the divisions of the largest visible algae. Many studies concluded that the algal biomass is a very promising material to be used as biosorbent to remove various kinds of pollutants from contaminated water and wastewaters [3,43,51]. This can be attributed that the algal biomass has many negative charge active groups on its surface cell wall such as hydroxyl, carboxyl, amino, sulfhydryl, and sulfonate [10].

The term isotherm is used for describing the retention of a substance on a solid at a constant temperature. The isotherm study is a major tool to predict the efficiency of a sorbent to remove a given pollutant from polluted water [15,22,38,39]. Analysis of isotherm data is an interesting mathematical approach for describing sorption isotherms at a constant temperature for water and wastewater treatment applications and to predict the overall sorption behavior under different operating conditions [13,34]. Hence, a large number of studies have been done to develop a mathematical isotherm models and to verify their suitability for describing the biosorption of heavy metals such as Pb<sup>2+</sup>; Cd<sup>2+</sup>, and Cr<sup>3+</sup> by as well as to understand the sorption isotherm phenomenon between the biomass surface and the metal molecules. Most of these models are empirical and bring little information on the physico-chemical processes responsible for the particular shape of the isotherm curves. Brouers [5] has shown that some of the most empirical models that can be used to describe the isotherm data were approximations of a generalized Brouers–Sotolongo model. This model is derived from the Burr–Maddala distribution which is itself solution of a birth and death differential equation which can describe sorption–desorption mechanisms [9,29]. The author concluded that only the Langmuir, the Hill–Sips and the Brouers–Sotolongo isotherms were genuine statistical functions and had the correct asymptotic limits for low and high concentrations. In addition, the author pointed out that a statistical analysis had a meaning only if the experimental data were complete until the

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saturation of the sorption. Furthermore, ion-exchange is an important concept in biosorption mechanisms using algae, because it explains many of the observations made during heavy metal uptake experiments. In this case, the ion exchange reaction type occurs between light metals already bound to the algae and other metals present in the aqueous solution [37]. The ion-exchange model is certainly a better representation of the biosorption process using algae since it reflects the fact that most algal biomass is either protonated or contains light metal ions such as  $K^+$ ,  $Na^+$  and  $Mg^{2+}$ , which are released upon binding of a heavy metal cation. It should be pointed out that the ion exchange model does not explicitly identify the binding mechanism [10]. Hence, verification of the various isotherm models is a growing area of study.

Despite the fact that linear regression is still frequently used [49], non-linear analysis of isotherm data is an interesting and useful mathematical approach for describing biosorption isotherms for water and wastewater treatment applications and to predict the overall sorption behavior under different operating conditions [20]. Indeed, the linearization of nonlinear isotherm equations has several disadvantages. This process implicitly alters their error structure and may also violate the error variance and normality assumptions of standard least squares [41]. In general, nonlinear regression gives a more accurate determination of model parameters than linear regression method. In recent years, several error analysis methods, such as the coefficient of determination ( $R^2$ ), the sum of the errors squared, a hybrid error function, Marquardt's percent standard deviation, the average relative error and the sum of absolute errors, have been used to determine the best-fitting isotherm [2,17]. [18,19] pointed out that using only  $R^2$  of linear regression analysis is not an appropriate tool to evaluate the goodness of the fit of an isotherm model. As different forms of the equations affected  $R^2$  values more significantly during the linear analysis, the non-linear analysis might be a method of avoiding such errors [27]. Additionally, Brouers [6] showed that the use of nonlinear programs allows an easy and precise fitting of the experimental data with the theoretical models.

The aim of this paper is to apply and demonstrate the interest of new methodology introduced by Brouers [4,5] on the isotherm data for the biosorption of Pb(II) in aqueous solution using algae. The nonlinear method of five isotherm models, Langmuir, Hill–Sips, Brouers–Sotolongo, Brouers–Gaspard, and Redlich–Peterson models, was compared with the experimental data. A trial-and-error procedure was used for the non-linear analysis method using the Mathematica 9 program and based on the Burr–Maddala distribution function introduced by Burr [9].

## 2. Materials and methods

### 2.1. Materials

Fresh mixture of green and blue-green algae was used in this study as a biosorbent. This material was collected from the artificial irrigation canal in Baghdad University, Iraq. It was mainly a mixture of three species of algae. Blue-green *Oscillatoria princeps* alga was the highest percentage (88%), green *Spirogyra aequinoctialis* alga was (9%), and blue-green *Oscillatoria subbrevis* alga was (3%). And to make it user friendly the collected algae were not separated. The foreign matters were removed manually from the collected algae, then rinsed with tap and distilled water to remove dirt, sands, and external salts. Afterward, the washed algae were kept in air for removing water and dried at an oven temperature of 65 °C for 48 h. The dried biomass was roughly chopped, grounded into powder, sieved, and kept in air-tight polyethylene container at room temperature. An average size of 0.54 mm was used for experiments with required amounts. A sample of algal biomass was analyzed for the physico-chemical properties and the results were listed in Table 1. The surface area was determined from  $N_2$  adsorption isotherm using a Micrometrics Nano Porosity System. Point of zero charge ( $pH_{pzc}$ ) of used biosorbents was determined by conventional

**Table 1**  
Properties of the algal biomass and Pb(II) salt used in this study.

Algal biomass	Pb(II)		
Real density (g/cm <sup>3</sup> )	1.120	Salt	PbCl <sub>2</sub>
Surface area (m <sup>2</sup> /g)	1.880	Appearance	White
Total exchange capacity (mEq/g)	1.240	Solubility (g/100 ml)	52
Micropore volume (cm <sup>3</sup> /g)	0.713	Density (g/l)	4.530
Point of zero charge, $pH_{pzc}$	5.500	Company	Fluka

method [23]. Briefly, initial pH values of 50 ml of 0.1 M NaCl were adjusted in a pH range of 2 to 12 using 1 M NaOH or H<sub>2</sub>SO<sub>4</sub> solutions. Afterward, a 0.5 g of algal biomass was added to each solution and the obtained suspensions were shaken for 48 h. The algal biomass was filtered and the final pH of the solution was measured. The value of  $pH_{pzc}$  of algal biomass was found from the intersection of the curve of final vs. initial pH. The micropore volume was evaluated by the t-plot method. Total exchange capacity was measured using atomic absorption spectrophotometer (type: SHIMADZU, AAS 7200, Japan).

All the chemicals used in this work are analytical grade reagents with deionized water used for solutions preparation. Stock solution (1000 mg/l) of Pb(II) was prepared by dissolving the appropriate weight of lead chloride in distilled water and kept in glass container at room temperature. The desired concentrations were prepared by diluting the stock solution in accurate proportions to different initial concentrations. The initial pH of the working solutions was adjusted by addition of 1 mol/l NaOH or HCl using a pH meter (WTW, inoLab 720, Germany). All the glassware used for dilution, storage and experimentation were cleaned with detergent, thoroughly rinsed with tap water, soaked overnight in a 20% HNO<sub>3</sub> solution and finally rinsed with distilled water before use. Table 1 listed the properties of Pb(II) salt used in this study.

### 2.2. Methods

#### 2.2.1. Experiments

Isotherm experiments were carried out in 250 ml stoppered conical flasks containing 0.05, 0.1, 0.3, 0.5, 0.8, 1, 2, and 3 g of algal biomass and 100 ml of Pb(II) solution. These experiments were performed at the same initial concentration (50 mg/l) for Pb(II) and repeated for temperature range from 10 to 40 °C. According to the previous studies, the optimum pH for Pb(II) removal using algae is in the range between pH 2 and pH 4 [10,50]. In addition, several authors showed that further increases in temperature (above 40 °C) lead to a decrease in the percentage of removal. This may be attributed to an increase in the relative desorption of the metal from the solid phase to the liquid phase, deactivation of the biosorbent surface, destruction of active sites on the biosorbent surface [30,44]. Hence, in this study all the isotherm experiments were conducted at temperature below 40 °C and the pH solution was adjusted to 3. The flasks were placed in a shaker (Edmund Buhler, 7400 Tubingen Shaker–SM 25) with constant shaking at 200 rpm for 4 h. After equilibrium condition, the sorbent was separated from aqueous solution by using filter paper (WHATMAN, No.42, diameter 7 cm). The Pb(II) concentrations in both initial and withdrawn samples were determined using atomic absorption spectrophotometer (type: SHIMADZU, AAS 7200, Japan). Each sample was measured thrice and the results were given as the average value. Biosorption capacity  $q(x)$  at equilibrium conditions and the percentage of removal (%) were calculated using Eqs. (1) and (2), respectively.

$$q(x) = \frac{(C_0 - C_e)V}{m} \quad (1)$$

$$\% \text{ Removal efficiency} = \frac{q(x)}{q_{\max}} \times 100 \quad (2)$$

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