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# Full Factorial Design Applied to a Biosorption of Lead(II) Ions from Aqueous Solution Using Brewer's Yeast (*Saccharomyces cerevisiae*)

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**ABSTRACT:** The overall objective of this study is to model and optimize the elimination of lead ions from aqueous solutions by inactive brewer's yeast in a batch reactor. Optimization of the most important factors directly affecting the adsorption of lead onto the biosorbent was carried out by using a $2^k$ factorial experiment. This later is performed to ascertain the effect of solution pH, initial concentration of lead ions, inactive brewer's yeast dose, temperature, and their cross-influence on the lead adsorption yield. The results suggest that the most influential factor is the solution pH followed by the initial concentration of lead ions, inactive brewer's yeast dose, and temperature. The results have shown also the interaction between solution pH/initial lead concentration and initial lead concentration/inactive brewer's yeast dose with different degrees of importance. The optimal values of solution pH, initial concentration of lead ions, biosorbent dose, and temperature are 4, 53.75 mg·L$^{-1}$, 2.3 ≤ $m_{ads}$ ≤ 2.5 g·L$^{-1}$, and 305 ≤ $T$ ≤ 308 K, respectively. Adsorption parameters for the Langmuir and Freundlich isotherm models were determined at different temperatures between (298 and 308) K. According to the biosorption isotherm plots, the Freundlich model describes perfectly the sorption of lead onto inactive brewer's yeast.

## INTRODUCTION

There has been increasing concern over dangerous levels of heavy metals contaminating the aquatic environment and the source of drinking water. Heavy metals have been a major cause of concern over the last few decades because they are nonbiodegradable and hence are accumulated by living organisms.[1,2] The problem is aggravated by their high dispersion; they are widely spread in aquatic systems where they enter the food chain.[3,4] Conventional physicochemical methods like precipitation, adsorption, chemical reduction, electrochemical treatment, and ion exchange become inefficient when applied to metals present at low concentrations in aqueous solutions.[5] Among all of the methods, adsorption is highly effective and economical.[6,7] The use of commercial activated carbon is a well-known adsorbent for the removal of organic and inorganic compounds from water and wastewater, but the high cost of activated carbon limits its use as an adsorbent in developing countries.[8] Consequently, in the removal of pollutants from wastewaters, many investigators have studied the feasibility of various low-cost sorbents, which are defined as abundant materials in nature[9−12] or a byproduct or waste material from another industry.[12] A large number of microorganisms (bacteria, fungi, yeasts, cyanobacteria, and algae) may be employed as a potential alternative to remove heavy metals from aqueous solutions.[13−16]

Most of the biosorption studies reported in literatures have been carried out with living microorganisms.[17−19] However, due to certain inherent disadvantages, the use of living microorganisms for metal removal and recovery is not generally feasible in all situations. For example, industrial effluents contain high concentrations of toxic metals under widely varying pH conditions. These conditions are not always conducive to the growth and maintenance of an active microbial population. In the other hand, the use of dead or inactive biomass presents several advantages; the process is free from nutrient supply, there are no toxicity constraints in the organism employed, a wider range of operating conditions such as pH, temperature, and metal concentrations are possible, and aseptic operating conditions are not essential. Biosorption which is a property of certain types of inactive, dead microbial biomass to bind and concentrate heavy metals from even very dilute aqueous solutions is one of the most promising technologies which can be used for this purpose.[20,21] Therefore, the purpose of this work was to evaluate the sorption potential of biological waste obtained from brewer's yeast for lead. The technique of statistical design for experiments can be used for the process modeling and optimization of the operating parameters. It is widely accepted in manufacturing industry for improving the product performance and reliability, the process capability, and yield. In experimental statistical design, the factors involved at their respective levels can be simultaneously varied. Thus, a lot of information can be collected with a minimum number of experiment trials. Basically, the classical parameter design is complicated and not easy to use, especially when considering that a large number of experiments must be conducted when the number of the process parameters increased. For this reason, the experimental design is a useful tool to study the interactions between two or more variables at a reduced number of experimental trials. There is a collection of mathematical and statistical techniques useful for modeling and analysis in complex process optimization.[21−23] The optimization of experimental conditions using experimental design is widely applied in a large area of chemical processes. Many studies concerning the uptake of biosorption of lead(II) ions in aqueous solution have indicated that several parameters influence the yield of biosorption.[17,24−29] The individual and the interactive effects on the yield of the biosorption of lead of four operating

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parameters, mainly: pH, initial concentration of lead $[Pb^{2+}]_0$, adsorbent dose ($m_{ads}$), and temperature ($T$) are investigated. The equilibrium of the biosorption of lead onto inactive brewer's yeast process was also studied by using Langmuir and Freundlich models.

## MATERIALS AND METHODS

Brewer's yeast was collected from BSA Beer Company in the Bejaia city of Algeria. The brewer's yeast was first washed with distilled water to remove any impurities and then dried in an oven at 333 K for three days, crushed, and sieved to a particle size diameter less than 500 $\mu$m. The average diameter of the particle-size range used is estimated to be 246 $\mu$m. All reagents used in this study were analytical grade. The lead(II) solution was prepared from the dissolution of $Pb(NO_3)_2$ (100 % in mass purity) in distilled water, and the concentrations of metal solutions are varied between (53.75 and 151.25) mg·L$^{-1}$. The pH of each solution is adjusted to the required value by adding concentrated nitric acid ($HNO_3$; 52.5 % in mass purity).

The agitation speed, agitation time, and the volume solution were fixed to 480 rpm, 60 min, and 0.2 L, respectively. A Schimadzu AA6500 atomic absorption spectrophotometer (AAS), equipped with a Zeeman atomizer and a SSC-300 autosampler, is used to determine the concentration of unabsorbed Pb(II) in solution.

**Modeling by Full Factorial Design.** To develop an adsorption process, a number of the operating parameters influencing the process such as pH, initial concentration of lead $[Pb^{2+}]_0$, adsorbent dose ($m_{ads}$), and temperature ($T$) are studied. But the study of the each and every factor is quite tedious and time-consuming. Thus, a factorial design can minimize the above difficulties by optimizing all of the affecting parameters collectively at a time. Factorial designs allow the simultaneous study of the effects that several factors may have on the optimization of a particular process. It determines which factors have the important effects on the response as well as how the effect of one factor varies with the level of the other factors. The effects are the differential quantities expressing how a response changes as the levels of one or more factors are changed. Also, factorial designs allow measuring the interaction between each different group of factors. The interactions are the driving force in many optimizations of the processes. Without the use of factorial experiments, some important interactions may remain undetected, and the overall optimization may not be attained. One of the simplest types of factorial designs used in experimental work is one having two levels ($2^k$). In a $2^k$ factorial design experiment, each factor may be assigned two levels: low ($-1$) and high ($+1$). If $k$ factors are considered, then $2^k$ measurements are required to perform a factorial design analysis.[30]

In this investigation, four operating factors were chosen as independent variables, namely: pH ($x_1$), initial concentration of lead ($x_2$), adsorbent dose ($x_3$), and temperature ($x_4$). Other variables such as a time of experiments, agitation speed, and solution volume were fixed at 60 min, 480 rpm, and 0.2 L, respectively. On the other hand, the yield of lead adsorption onto brewer's yeast ($y$) as da ependent output response variable which is expressed in percent:

$$y(\%) = \frac{[Pb^{2+}]_0 - [Pb^{2+}]_t}{[Pb^{2+}]_0} \cdot 100 \qquad (1)$$

**Table 1. Values and Levels of Operating Parameters**

| | levels | | |
|---|---|---|---|
| operating factors | −1 | 0 | 1 |
| $Z_1$: pH | 2 | 3 | 4 |
| $Z_2$: $[Pb^{2+}]_0$/ mg·L$^{-1}$ | 53.75 | 102.5 | 151.25 |
| $Z_3$: $m_{ad}$/ g·L$^{-1}$ | 0.3 | 0.4 | 0.5 |
| $Z_4$: $T$/K | 298 | 303 | 308 |

**Table 2. Full Factorial Design Matrix: Natural and Coded Values of Parameters**

| | natural values of parameters | | | | coded values of parameters | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| run no. | $Z_1$ | $Z_2$ | $Z_3$ | $Z_4$ | $x_0$ | $x_1$ | $x_2$ | $x_3$ | $x_4$ | $y$(%) |
| 1 | 2 | 53.75 | 0.3 | 25 | 1 | −1 | −1 | −1 | −1 | 5.30 |
| 2 | 2 | 53.75 | 0.3 | 35 | 1 | −1 | −1 | −1 | 1 | 11.97 |
| 3 | 2 | 53.75 | 0.5 | 25 | 1 | −1 | −1 | 1 | −1 | 16.48 |
| 4 | 2 | 53.75 | 0.5 | 35 | 1 | −1 | −1 | 1 | 1 | 23.34 |
| 5 | 2 | 151.25 | 0.3 | 25 | 1 | −1 | 1 | −1 | −1 | 15.20 |
| 6 | 2 | 151.25 | 0.3 | 35 | 1 | −1 | 1 | −1 | 1 | 18.06 |
| 7 | 2 | 151.25 | 0.5 | 25 | 1 | −1 | 1 | 1 | −1 | 12.21 |
| 8 | 2 | 151.25 | 0.5 | 35 | 1 | −1 | 1 | 1 | 1 | 15.42 |
| 9 | 4 | 53.75 | 0.3 | 25 | 1 | 1 | −1 | −1 | −1 | 90.39 |
| 10 | 4 | 53.75 | 0.3 | 35 | 1 | 1 | −1 | −1 | 1 | 93.86 |
| 11 | 4 | 53.75 | 0.5 | 25 | 1 | 1 | −1 | 1 | −1 | 95.41 |
| 12 | 4 | 53.75 | 0.5 | 35 | 1 | 1 | −1 | 1 | 1 | 96.20 |
| 13 | 4 | 151.25 | 0.3 | 25 | 1 | 1 | 1 | −1 | −1 | 73.20 |
| 14 | 4 | 151.25 | 0.3 | 35 | 1 | 1 | 1 | −1 | 1 | 67.64 |
| 15 | 4 | 151.25 | 0.5 | 25 | 1 | 1 | 1 | 1 | −1 | 73.96 |
| 16 | 4 | 151.25 | 0.5 | 35 | 1 | 1 | 1 | 1 | 1 | 79.10 |

where $[Pb^{2+}]_0$ and $[Pb^{2+}]_t$ are the initial lead concentration and lead concentration at a given time $t$.

The coded values of $x_j$ were obtained from the following relationship:[21−23]

$$x_j = \frac{Z_j - Z_j^0}{\Delta Z_j} \qquad j = 1, 2, \ldots, k \qquad (2)$$

with:

$$Z_j^0 = \frac{Z_{j\max} + Z_{j\min}}{2} \quad \text{and} \quad \Delta Z_j = \frac{Z_{j\max} - Z_{j\min}}{2\alpha}$$

where $x_j$ is the coded value of $j$th variable, $Z_j$ is the encoded value of $j$th variable, $Z_j^0$ is the value of $Z_j$ at the center point of the investigation domain, and $\Delta Z_j$ is the step size. Here, $Z_{j\max}$ and $Z_{j\min}$ represent the maximum and the minimum level of factor $j$ in natural unit; $\alpha$ is the distance of the axial point from the center domain ($\alpha = (2^k)^{1/4}$, $k$ is number of factors considered), respectively. The experimental data are analyzed by full factorial design to fit the following first-order polynomial equation:[21−23]

$$\begin{aligned}\hat{y} = {} & b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_4x_4 + b_{12}x_1x_2 \\ & + b_{13}x_1x_3 + b_{14}x_1x_4 + b_{23}x_2x_3 + b_{24}x_2x_4 \\ & + b_{34}x_3x_4 + b_{123}x_1x_2x_3 + b_{124}x_1x_2x_4 \\ & + b_{134}x_1x_3x_4 + b_{234}x_2x_3x_4 + b_{1234}x_1x_2x_3x_4 \end{aligned} \qquad (3)$$


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**Table 3. Results of Lead Biosorption at the Center Work Domain**

| | natural values of parameters | | | | coded values of parameters | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| run no. | $Z_1$ | $Z_2$ | $Z_3$ | $Z_4$ | $x_0$ | $x_1$ | $x_2$ | $x_3$ | $x_4$ | $y$(%) |
| 1 | 3 | 102.5 | 0.4 | 30 | 1 | 0 | 0 | 0 | 0 | 50.55 |
| 2 | 3 | 102.5 | 0.4 | 30 | 1 | 0 | 0 | 0 | 0 | 53.43 |
| 3 | 3 | 102.5 | 0.4 | 30 | 1 | 0 | 0 | 0 | 0 | 55.17 |
| 4 | 3 | 102.5 | 0.4 | 30 | 1 | 0 | 0 | 0 | 0 | 51.50 |
| 5 | 3 | 102.5 | 0.4 | 30 | 1 | 0 | 0 | 0 | 0 | 51.78 |

The natural values of each factor and their respective levels are presented in Table 1.

The full factorial design was composed of $2^4$ experiments of factorial design (Table 2) and 5 experiments realized at the center work domain (Table 3).[21−23]

## RESULTS AND DISCUSSION

**Characterization of Adsorbent.** *FTIR Spectrum of the Biosorbent.* Fourier transform infrared (FTIR) transmission spectra of samples were obtained on an IR Affinity-1 Shimadzu FTIR spectrometer. FTIR spectra of the brewer's yeast sample was obtained using an FTIR spectrometer over the wavenumber range of (4000 to 500) $cm^{-1}$. Brewer's yeast powder was mixed with potassium bromide at a ratio of roughly 2/100. The FTIR spectrum of the brewer's yeast displays a number of absorption peaks, indicating the complex nature of the brewer's yeast.

The spectrum displays the following bands:

- The broad absorption band around 3418 $cm^{-1}$ indicated the existence of O—H in the carboxyl groups and N—H groups of protein.[19,31]
- The absorption peak at 2924 $cm^{-1}$ can be assigned to C—H stretching,[11] and that at 1650 $cm^{-1}$ can be assigned to C═O stretching of carboxyl groups.[19]
- Peaks at 1053 $cm^{-1}$ to 1237 $cm^{-1}$ indicated the presence of aliphatic amines and/or halo compounds; the same results are reported by (Pratibha et al.[32]).

Therefore, it should be noted that the FTIR spectrum of the brewer's yeast supports the presence of amine and carboxyl groups.

*Brunauer—Emmett—Teller (BET) Surface Area of the Biosorbent.* The specific surface area of the resulting biomaterial was determined by nitrogen adsorption at 77 K (Quantachrome NOVA WIN2, Version 9.0). Prior to gas adsorption measurements, the sample was degassed at 373 K in a vacuum condition for a period of at least 3 h. The BET surface area was determined by means of the standard BET equation applied in the relative pressure range from 0.05 to 0.32.

The surface area of brewer's yeast sample was observed to be 35.13 $m^2 \cdot g^{-1}$.

**First-Order Model Using Full Factorial Design.** The results of the first-order model are collected in Tables 2 and 3. The model coefficients are estimated by the standard least-squares regression method using "Excel" software. Three tests are required to evaluate the adequacy of the model: Student's test, which is used to determine the significance coefficients and discarding the insignificant coefficients, *R*-square test, and Fisher tests.

*Student's Test.* To determine whether calculated effects were significantly (different from zero), Student's *t* test was employed. The estimated *t* values for particular process paramters can be calculated as follows:[33]

$$t_j = \frac{|b_j|}{\sigma_{bj}} \tag{4}$$

with

$$\sigma_{bj}{}^2 = \frac{\sigma_{\text{rep}}^2}{N} = 0.456 \quad \text{and}$$

$$\sigma_{\text{rep}}^2 = \frac{\sum_{i=1}^{n_0} (y_i - \bar{y}_0)^2}{n_0 - 1} = 3.328 \quad \text{and} \quad N = 16$$

where $\sigma^2{}_{bj}$ is the variance coefficients; $\sigma^2{}_{\text{rep}}$ the replication variance; $y_i$ the predicted values of lead removal yield for the *i*th central point; $\bar{y}_0$ the average value of lead removal yield for the central point; $n_0$ the repetition number of experiments at the center work domain, and *N* the total number of the experiments ($N = 16$) of the full factorial design. The tabulated *t* value for a 5 % level of significance and 4 degrees of freedom ($f = n_0 - 1 = 5 - 1 = 4$) is $t_{0.05}(f = 4) = 2.78$. It is found that all individual effects and only the interactions ($x_1x_2$) and ($x_2x_3$) are significant at a 5 % significance level, but the interactions ($x_1x_3$), ($x_1x_4$), ($x_2x_4$), ($x_3x_4$), ($x_1x_2x_4$), ($x_1x_3x_4$), ($x_2x_3x_4$), and ($x_1x_2x_3x_4$) are not significant. Therefore, they are eliminated from the regression equation.

*Reliability Test.* The test of reliability for predicting equations has been carried out by Fisher's variance ratio test, known as the *F*-test. The *F*-ratio is given by the following form:[33]

$$F = \frac{\sigma_{\text{res}}^2}{\sigma_{\text{rep}}^2} = 2.108 \quad \text{with}$$

$$\sigma_{\text{res}}^2 = \frac{\sum_{i=1}^{N} (y_i - \hat{y}_i)^2}{N - l} = 7.015 \tag{5}$$

where $\sigma^2{}_{\text{res}}$ is the residual variance; *N* the total number of the experiments of the full factorial design ($N = 16$); *l* the number of significant coefficients ($l = 8$); $y_i$ the observed values of lead removal yield for the *i*th observation, and $\hat{y}_i$ the predicted value of lead removal yield for the *i*th observation.

The higher level of freedom degrees is 8 ($f_1 = N - l = 16 - 8 = 8$), and the lower freedom degree level is 4 ($f_2 = n_0 - 1 = 5 - 1 = 4$). The tabulated value of *F* for the 5 % level of significance is 6.04. The estimated *F* value is much less than the tabulated value of *F* ($F_{0.05}$ (8, 4) = 6.04). It can be concluded that the two variances are equal and that most of the response variation can be explained by the regression.

*Test of Regression Significance.* This test calculates *F* by eq 6 and compares it to the tabulated *F* value for a 5 % level of significance and two degrees of freedom ($f_1 = l - 1, f_2 = N - 1$).[33]

$$F = \frac{\sum_{i=1}^{N} (\hat{y}_i - \bar{y})^2 / l - 1}{\sum_{i=1}^{N} (y_i - \hat{y}_i)^2 / N - l} = 409.143 \tag{6}$$

The tabulated value of *F* ($F_{0.95}$ ($f_1 = l - 1 = 7, f_2 = N - l = 8$) is equal to 3.50. The calculated *F* value ($F = 409.143$) is much


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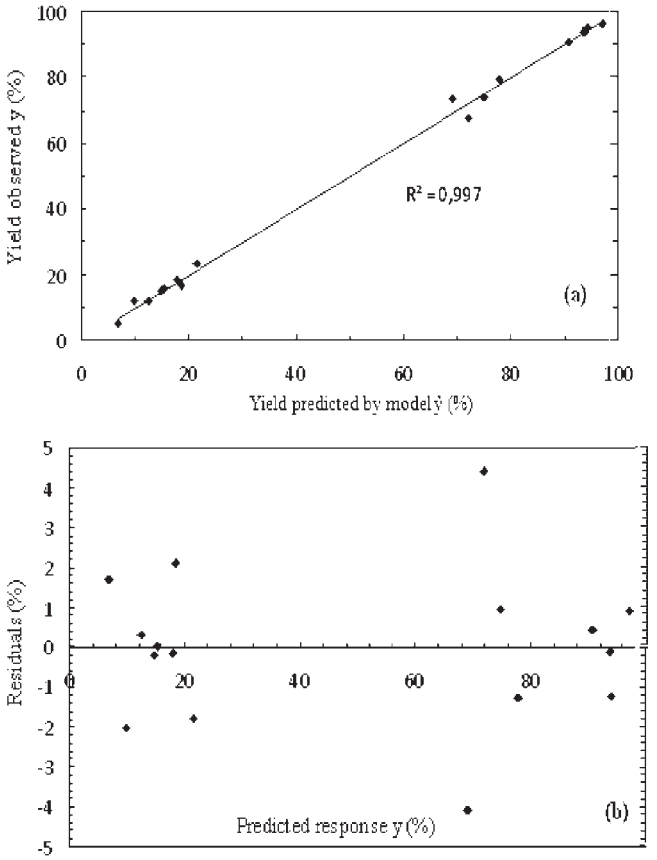


**Figure 1.** Analysis of quality of the model. (a) Comparison of experimental and predicted responses; (b) residual analysis for the estimated model.

higher than this interval. Hence, it can be concluded that the first-order model eq 7 is valid at 95 %.

$$\hat{y} = 49.234 + 34.486x_1 - 4.885x_2 + 2.281x_3 + 1.467x_4 - 5.36x_1x_2 - 1.458x_2x_3 + 2.065x_1x_2x_3 \quad (7)$$

The absolute value of the coefficient of a particular factor is the measure of its influence on the percentage removal of lead. The positive value of the coefficient indicates that a high level setting of the factor provides better adsorption than the low level setting and vice versa for the negative value of the coefficient.

The regression equation, eq 7, allows the prediction of pH ($x_1$), initial concentration of lead ($x_2$), adsorbent dose ($x_3$), and temperature ($x_4$) with a good accuracy (the correlation coefficient $R^2$ was found to be 0.997). A comparison of the experimental and calculated responses (Figure 1a) shows a clear agreement between the observed values and those predicted by the statistical model in eq 7. The random distribution of the residuals (Figure1b) shows the absence of a trend, indicating that the mathematical model was adequate and that there was no inconsistency between the experimental and the calculated values of the response.

The initial pH of the adsorbent solution is one of the most important parameters ($b_1$ = +34.486) controlling the removal of the metal ions by the biosorbent. The positive sign of the $b_1$ coefficient suggests that the increase of pH of lead solution increases the yield of biosorption of lead. A similar trend of the pH effect was observed for the biosorption of Pb(II), Ni(II), and

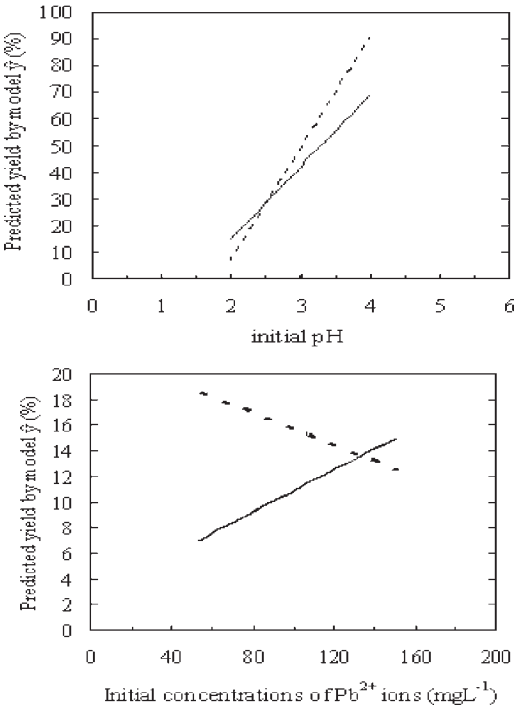


**Figure 2.** Significant interaction graphs. The symbols: ···, initial concentration of the lead(II) low level; —, initial concentration of the lead(II) high level; •••, adsorbent dose high level; —·—·—, adsorbent dose low level.

Cr(II) ions[24] and Ni(II) and Cd(II) ions[19] onto inactive *Saccharomyces cerevisiae*. This is partly due to the fact that the hydronium ions [$H_3O^+$] themselves are strong competing sorbates and that the solution pH influences the chemical speciation of lead ions and the charge of functional groups of the biomass. Lead(II) ions in solution at an acidic pH appear as divalent positive ions and are suitable to interact with negatively charged groups in biomass. Özer and Özer[24] reported that the outer layer of the cell wall of *S. cerevisiae* consists of a coat protein that can develop a charge by the dissociation of ionizable side groups of the constituent amino acids. The ionic state of ligands such as carboxyl, phosphate, imidazole, and amino groups will promote reactions with the positively charged metal ions. At a low pH, cell wall ligands were closely associated with the hydronium ions [$H_3O^+$] and restricted the approach of metal cations as a result of the repulsive force. The optimal pH for Pb(II), Ni(II), and Cd(II) removal by inactive *S. cerevisiae* is in the range 5.0 to 6.0.[19,24] The initial concentration of lead(II) was the second significant parameter with a negative effect ($b_2$ = −4.885) on the percentage uptake. In other words, the adsorption yield decreased with increasing initial lead(II) concentration. There was a decrease of lead removal (≅ 17 %) when the initial concentration was increased from (53 to 151) mg·L$^{-1}$ at pH = 4, $m_{ads}$ = 2.5 g·L$^{-1}$ and $T$ = 308 K. The third impacting factor was the adsorbent dose with a positive effect ($b_2$ = +2.281). This result suggests an increase in the percentage adsorption with increasing adsorbent dosage. There was an increase of lead removal (≅ 11%) when the biomass was increased from (1.5 to 2.5) g·L$^{-1}$ at pH = 4, $[Pb^{2+}]_0$ = 151.25 mg·L$^{-1}$, and $T$ = 308 K. This was due to the availability of more surface functional groups at higher biosorbent concentrations. The temperature had also a positive effect ($b_2$ = +1.467) on the percentage uptake.


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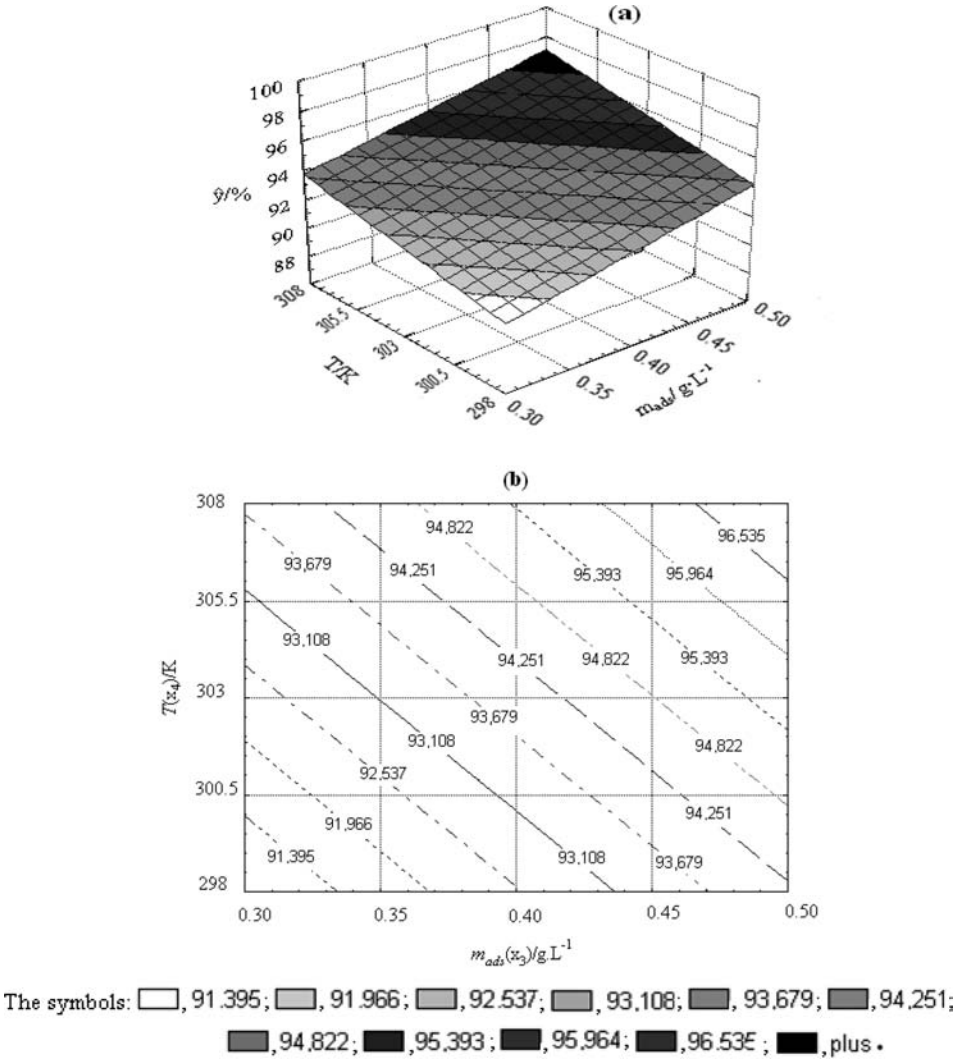


**Figure 3.** Response surfaces (a) and contour plots (b) showing the effect of adsorbent dose and temperature on the yield of biosorption of Pb(II). Conditions: pH = 4; $[Pb^{2+}]_0$ = 53.75 mg·$L^{-1}$.

This parameter is important in the context of adsorption on solid phase. The temperature has two main effects on the sorption processes. Increasing the temperature is known to increase the diffusion rate of the sorbate within the pores as a result of decreasing solution viscosity, and it also modifies the equilibrium capacity of the sorbent for a particular sorbate. In the present case the effect of temperature was investigated between (298 and 308) K. As the temperature increases, the yield of the adsorbed quantity slightly increases. There was an increase of lead removal (≅ 5 %) when the temperature was increased from (298 to 308) K at pH = 4, $[Pb^{2+}]_0$ = 151.25 mg·$L^{-1}$, and $m_{ads}$ = 2.5 g·$L^{-1}$. Özer and Özer[24] reported 298 K as the optimal temperature for the biosorption of Pb(II), Ni(II), and Cr(II) ions onto inactive *S. cerevisiae*.

All significant interactions found by the model are displayed in Figure 2. According to the interaction graphs (Figure 2), the strongest interaction was between the initial concentration of Pb(II) and the adsorbent dose.

**Optimization.** The model equation obtained by full factorial design was used to determine the optimal values of the operating parameters to obtain the highest yield of biosorption of Pb(II) ions. The response surface and contour plots (Figure 3 a and b) were drawn using STATISTICA software. An analysis of these figures clearly indicated that the optimal conditions found for the yield of biosorption of Pb(II) were: pH 4, $[Pb^{2+}]_0$ = 53.75 mg·$L^{-1}$, 2.33 ≤ $m_{ads}$ ≤ 2.5 g·$L^{-1}$, and (305 ≤ $T$ ≤ 308) K. Under these conditions, the obtained biosorption yield of Pb(II) ions was 96 %.

**Biosorption Isotherms.** Since the adsorption isotherm provides important information about the working mechanism,[17] the biosorption equilibrium of lead ions on dead brewer's yeast at three different temperatures, (298, 303, and 308) K, are presented in Figure 4. The experiments are performed with 2.5 g·$L^{-1}$ of dead brewer's yeast at pH 4, agitation time of 60 min, and agitation speed of 480 rpm, in a shake-flask system.

The classic models of Langmuir and Freundlich were used to fit this type of adsorption isotherm. The Langmuir model is valid for monolayer adsorption onto a surface with a finite number of identical sites which are homogeneously distributed over the adsorbent surface. It is expressed as follows:[6,34]

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \quad (8)$$


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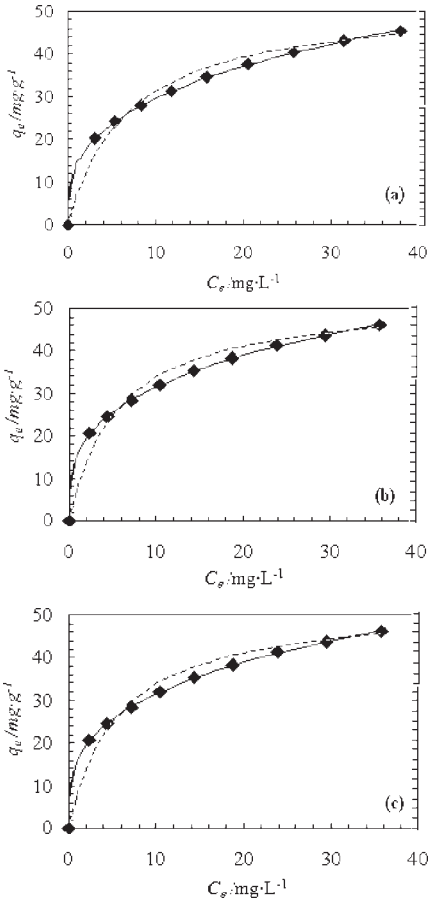


**Figure 4.** Adsorption isotherms of lead ions onto brewer's yeast at different temperatures Conditions: pH = 4, agitation speed = 480 rpm, and $t$ = 60 min; (a) $T$ = 298 K, (b) $T$ = 303 K, (c) $T$ = 308 K. The symbols: ◆ experimental points; ···, Langmuir isotherm; —, Freundlich isotherm.

where $q_e$, the lead concentration retained in the adsorbent phase, was calculated according to:

$$q_e = \frac{(C_0 - C_e)}{m} V \tag{9}$$

$C_0$ is the initial lead concentration (mg·L$^{-1}$), $C_e$ the equilibrium lead concentration (mg·L$^{-1}$), $V$ the volume of the solution (L), and $m$ the mass of the brewer's yeast (g).

$q_m$ and $k_L$ are the Langmuir parameters related to the maximum adsorption capacity and bonding energy of adsorption, respectively.

The Langmuir equation can be linearized as shown:

$$C_e/q_e = \left(\frac{1}{q_m}\right) C_e + \frac{1}{k_L q_m} \tag{10}$$

$k_L$ and $q_m$ are calculated by plotting $C_e/q_e$ versus $C_e$.

The Freundlich model is based on sorption onto a heterogeneous surface, suggesting that binding sites are not equivalent. It is characterized by the following equation[6] where $k_F$ and $n$ are Freundlich parameters indicating the adsorption capacity and the adsorption intensity, respectively:

$$q_e = k_F C_e^{1/n} \tag{11}$$

**Table 4. Langmuir and Freundlich Constants for Lead Sorption at Three Temperatures**

| | Freundlich | | | | | Langmuir | | | |
|---|---|---|---|---|---|---|---|---|---|
| $T$/K | $k_F$ | $1/n$ | $n$ | $R^2$ | $D$ (%) | $q_m$/ mg·g$^{-1}$ | $k_L$ | $R^2$ | $D$ (%) |
| 298 | 13.999 | 0.33 | 3.077 | 0.999 | 0.47 | 51.81 | 0.148 | 0.992 | 1.14 |
| 303 | 15.768 | 0.30 | 3.322 | 0.999 | 0.44 | 51.54 | 0.183 | 0.991 | 8.78 |
| 308 | 18.047 | 0.27 | 3.704 | 0.997 | 1.13 | 51.28 | 0.233 | 0.989 | 8.05 |

From the linear plot (eq 12) of ln $q_e$ versus ln$C_e$, $k_F$, and $1/n$ values can be determined.

$$\ln q_e = \ln k_F + (1/n) \ln C_e \tag{12}$$

It is generally stated that values of $n$ in the range 2 to 10 represent good, 1 to 2 moderately difficult, and less than 1 poor sorption characteristics.[35] In the last case, impractically large adsorbent dosages may be required for the appreciable fractional removal of solute.[36] Table 4 shows the values of Langmuir and Freundlich constants and the related correlation coefficients ($R^2$). The Freundlich isotherm model yielded a better fit with the higher $R^2$ value compared to the Langmuir model. Hamdaoui and Naffrechoux[37] reported that linear correlation coefficient ($R^2$) showed the fit between experimental data and the linearized form of isotherm equation, while the average percentage error ($D$(%)) obtained from eq 13 indicated the fit between the experimental $q_e^{exp}$ and predicted $q_e^{th}$ values of sorption equilibrium capacity used for plotting isotherm curves. It is not appropriate to use the coefficient of correlation of linear regression method for comparing the best-fitting isotherms.

$$D(\%) = \frac{1}{P} \sum_{i=1}^{P} \left( \frac{|q_e^{exp} - q_e^{th}|}{q_e^{exp}} \right)_i \tag{13}$$

where $P$ is the number of experimental data.

Then, to check the validity of the two models, it is interesting and essential to recalculate the adsorbed amount using the calculated constant parameters determined using the linearized forms and the average percentage errors ($D$ (%)).

The average percentage errors and the simulated curves at (298, 303, and 308) K using Freundlich and Langmuir models are given. In Figure 4, the points represent experimental data, and the lines represent Freundlich and Langmuir isotherm models. It is clear from the average percentage errors shown in Table 4 that the Freundlich model provides a better fit to the experimental data.

The values of $n$ shown in Table 4 are greater than 2, indicating that lead is favorably biosorbed by brewer's yeast.

## CONCLUSION

The present study shows that dead biomass (*S. cerevisiae*) obtained from BSA Beer Company in Bejaia city, Algeria, can be used as an adsorbent for the removal of lead from aqueous solutions. Optimum biosorption conditions were determined by using a full factorial design (FFD). The model equation obtained led to a classification of the parameters based on their level of significance, namely, the solution pH > the initial concentration of lead(II) > the adsorbent dose > the temperature. In addition, two relevant interactions were found: initial concentration of Pb(II)/adsorbent dose and solution pH/initial concentration of Pb(II). In the optimal conditions determined by response surface and contour plots (pH = 4, $[Pb^{2+}]_0$ = 53.75 mg·L$^{-1}$,

($2.33 \leq m_{ads} \leq 2.5$) $g \cdot L^{-1}$, and ($305 \leq T \leq 308$) K) the biosorption yield reached 96 %. The model was tested under optimal conditions (pH 4, $[Pb^{2+}]_0 = 53.75$ $mg \cdot L^{-1}$, $m_{ads} = 2.5$ $g \cdot L^{-1}$, and $T = 308$ K). A good adequacy between the experimental (94.8 %) and theoretical (96 %) biosorption yields was found. Langmuir and Freundlich isotherm models were determined at different temperatures, $T = (298$ to $308)$ K. According to the biosorption isotherm plots, the Freundlich model describes perfectly the sorption of lead onto dead brewer's yeast. It can be concluded that dead biomass tested can be used as an alternative biosorbent to treatment wastewater containing lead ions, since dead *S. cerevisiae* is low-cost biomass and has a high biosorption capacity.

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## REFERENCES

(1) Hasan, S. H.; Srivastava, P.; Talat, M. Biosorption of Pb(II) from water using biomass of Aeromonas hydrophila: central composite design for optimization of process variables. *J. Hazard. Mater.* **2009**, *168*, 1155–1162.

(2) Hasan, S. H.; Srivastava, P.; Talat, M. Biosorption of lead using immobilized Aeromonas hydrophila biomass in up flow column system: Factorial design for process optimization. *J. Hazard. Mater.* **2010**, *177*, 312–322.

(3) Pardo, R.; Herguedas, M.; Barrado, E. Biosorption of cadmium, copper, lead and zinc by inactive biomass of Pseudomonas Putida. *Anal. Bioanal. Chem.* **2003**, *376*, 26–32.

(4) Fergusson, J. E. *The heavy elements: chemistry, environmental impact and health effects*; Pergamon: Exeter, 1990.

(5) Aksu, Z.; Egretli, G.; Kutsal, T. A comparative study for the biosorption characteristics of chromium(VI) on Ca-alginate, agarose and immobilized C. vulgaris in a continuous packed bed column. *J. Environ. Sci. Health* **1999**, *34*, 295–316.

(6) Boudrahem, F.; Aissani-Benissad, F.; Aït-Amar, H. Batch sorption dynamics and equilibrium for the removal of lead ions from aqueous phase using activated carbon developed from coffee residue activated with zinc chloride. *J. Environ. Manage.* **2009**, *90*, 3031–3039.

(7) Imran, A.; Gupta, V. K. Advances in water treatment by adsorption technology. *Nat. Protocols* **2007**, *1*, 2661–2667.

(8) Dursun, G.; Çiçek, H.; Dursun, A. Y. Adsorption of phenol from aqueous solution by using carbonised beet pulp. *J. Hazard. Mater. B* **2005**, *125*, 175–182.

(9) Gupta, V. K.; Carrot, P. J. M.; Ribeiro-Carrpt, M. M. L.; Suhas Low-cost adsorbents: growing approach to wastewater treatment-a review. *Crit. Rev. Environ. Sci. Technol.* **2009**, *39*, 783–842.

(10) Gupta, V. K.; Rastogi, A. Biosorption of hexavalent chromium by raw and acid-treated green alga *Oedogonium hatei* from aqueous solutions. *J. Hazard. Mater.* **2009**, *163*, 396–402.

(11) Gupta, V. K.; Rastogi, A.; Nayak, A. Biosorption of nickel onto treated alga (Oedogonium hatei): Application of isotherm and kinetic models. *J. Colloid Interface Sci.* **2010**, *342*, 533–539.

(12) Gupta, V. K.; Rastogi, A. Equilibrium and kinetic modelling of cadmium(II) biosorption by nonliving algal biomass *Oedogonium* sp. from aqueous phase. *J. Hazard. Mater.* **2008**, *153*, 759–766.

(13) Gupta, V. K.; Mohan, D.; Sharma, S.; Park, K. T. Removal of chromium(VI) from electroplating industry wastewater using bagasse fly ash-a sugar industry wast material. *The Environmentalist* **1999**, *19*, 129–136.

(14) Gupta, V. K.; Rastogi, A. Sorption and desorption studies of chromium(VI) from nonviable cyano bacterium Nostoc muscorum biomass. *J. Hazard. Mater.* **2008**, *154*, 347–354.

(15) Gupta, V. K.; Sharma, S. Removal of zinc from aqueous solutions using bagasse fly ash - a low cost adsorbent. *Ind. Eng. Chem. Res.* **2003**, *42*, 6619–6624.

(16) Gupta, V. K.; Rastogi, A.; Diwivedi, M. K.; Mohan, D. Process Development for the Removal of Zinc and Cadmium from Wastewater using Slag -A Blast-Furnace Waste Material. *Sep. Sci. Technol.* **1997**, *32*, 2883–2912.

(17) Çabuk, A.; Akar, T.; Tunali, S.; Gedikli, S. Biosorption of Pb(II) by industrial strain of Saccharomyces cerevisiae immobilized on the biomatrix of cone biomass of Pinus nigra: Equilibrium and mechanism analysis. *Chem. Eng. J.* **2007**, *131*, 293–300.

(18) Baysal, Z.; Cinar, E.; Bulut, Y.; Alkan, H.; Dogru, M. Equilibrium and thermodynamic studies on biosorption of Pb(II) onto Candida albicans biomass. *J. Hazard. Mater.* **2009**, *161*, 62–67.

(19) Cui, L.; Wu, G.; Jeong, T. Adsorption performance of nickel and cadmium ions onto brewer's yeast. *Can. J. Chem. Eng.* **2010**, *88*, 109–115.

(20) Volesky; B. Biosorption for the next century. *International Biohydrometallurgy symposium*; El Escorial: Escorial, Spain, 1999.

(21) Box, G. E. P.; Hunter, W. G.; Hunter, J. S. *Statistics for experimenters*; Wiley: New York, 1978.

(22) Goupy, J. *Experimental designs for response surfaces*; Dunod: Paris, 1999.

(23) Yahiaoui, I.; Aissani-Benissad, F.; Fourcade, F.; Amrane, A. Response surface methodology for the optimization of the electrochemical degradation of phenol on $Pb/PbO_2$ electrode. *Environ. Prog. Sustainable Energy* **2011**, DOI 10.1002/EP.10572.

(24) Özer, A.; Özer, D. Comparative study of the biosorption of Pb(II), Ni(II) and Cr(VI) ions onto S. cerevisiae: determination of biosorption heat. *J. Hazard. Mater. B* **2003**, *100*, 219–229.

(25) Göksungur, Y.; Üren, S.; Güvenç, U. Biosorption of cadmium and lead by ethanol treated waste baker's yeast biomass. *Bioresour. Technol.* **2005**, *96*, 103–109.

(26) Gupta, V. K.; Rastogi, A. Biosorption of lead(II) from aqueous solutions by non-living algal biomass Oedogonium sp. and Nostoc sp.-A comparative study. *Colloids Surf., B* **2008**, *64*, 170–178.

(27) Gupta, V. K.; Rastogi, A. Biosorption of lead from aqueous solutions by green algae *Spirogyra* species: Kinetics and equilibrium studies. *J. Hazard. Mater.* **2008**, *152*, 407–414.

(28) Gupta, V. K.; Mohan, D.; Sharma, S. Removal of lead from wastewater using bagasse fly ash-a sugar industry waste material. *Sep. Sci. Technol.* **1998**, *33*, 1331–1343.

(29) Gupta, V. K.; Singh, P.; Rahman, N. Adsorption behavior of Hg(II), Pb(II) and Cd(II) from aqueous solution on duolite C-433: a synthetic resin. *J. Colloid Interface Sci.* **2004**, *275*, 398–402.

(30) Yahiaoui, I.; Aissani-Benissad, F.; Ait-Amar, H. Optimization of silver cementation yield in fixed bed reactor using factorial design and central composite design. *Can. J. Chem. Eng.* **2010**, *6*, 1099–1106.

(31) Ashkenazy, R.; Gottlieb, L.; Yannail, S. Characterization of acetone-washed yeast biomass functional groups involved in lead biosorption. *Biotechnol. Bioeng.* **1997**, *55*, 1–10.

(32) Pratibha, R.; Malar, P.; Rajapriya, T.; Balapoornima, S.; Ponnusami, V. Statistical and equilibrium studies on enhancing biosorption capacity of Saccharomyces cerevisiae through acid treatment. *Desalination* **2010**, *264*, 102–107.

(33) Djoudi, W.; Aissani-Benissad, F.; Bourouina-Bacha, S. Optimization of copper cementation process by iron using central composite design experiments. *Chem. Eng. J.* **2007**, *133*, 1–6.

(34) Argun, M. E.; Dursun, S.; Ozdemir, C.; Karatas, M. Heavy metal adsorption by modified oak sawdust: Thermodynamics and kinetics. *J. Hazard. Mater.* **2007**, *141*, 77–85.

(35) Treybal, R. E. *Mass-transfer operations*; McGraw Hill: New York, 1980.

(36) Annadurai, G.; Juang, R. S.; Lee, D. L. Adsorption of heavy metals from water using banana and orange peels. *Water Sci. Technol.* **2002**, *47*, 185–190.

(37) Hamdaoui, O.; Naffrechoux, E. Modeling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon Part I. Two-parameter models and equations allowing determination of thermodynamic parameters. *J. Hazard. Mater.* **2007**, *147*, 381–394.