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Combination of Experimental Design and Desirability Function as a Genuine Method to Achieve Common Optimal Conditions for the Adsorption of Pb(II) and Cu(II) onto the Poplar Tree Leaves: Equilibrium, Kinetic and Thermodynamic Studies

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In this study, the ashes of poplar tree leaves are applied as an efficient, accessible and inexpensive biosorbent for the removal of heavy metals Pb^{2+} and Cu^{2+} in aqueous solutions. In the adsorption processes, the success of the ions removal highly depends on the level of several experimental factors such as pH, contact time, adsorbent dosage and temperature. Therefore, a genuine statistical experiment design method is required to achieve the common experimental conditions at which both ions have been removed from the aqueous solutions to a great degree. Here, the desired common optimal conditions are obtained by the combination of experimental design and desirability function methods. For a mixture of Pb^{2+} and Cu^{2+}, the following optimal conditions were achieved at: pH of 5.4, contact time of 23 min, adsorbent dosage of 0.14 g, and temperature of 28 °C; at 150 mg l^{-1} of Pb^{2+} and 120 mg l^{-1} Cu^{2+}. The removal efficiencies of Pb^{2+} and Cu^{2+} were 92.8% and 94.9%, respectively, indicating the applicability of this biosorbent for the ions removal. Moreover, the equilibrium and kinetic behavior of the adsorption processes are investigated and then thermodynamic parameters, $\Delta G°$ (kJ mol^{-1}), ΔH (kJ mol^{-1})°, and $\Delta S°$ (kJ mol^{-1}), are evaluated, revealing that both processes are endothermic and spontaneous.

Keywords: Desirability function, Biosorption, Heavy metals, Kinetic, Thermodynamic parameters

INTRODUCTION

Heavy metals are stable and persistent in environment because they are not degradable. They can endanger the environment and humans even in a small amount in water and waste waters [1] Pb(II) is one of the most hazardous materials whose toxicological effects in humans include inhibition of hemoglobin formation (anemia), sterility, hypertension, learning disabilities, abortion, kidney damage and mental retardation [1,2]. The permissible level of lead in drinking water is 0.05 mg l^{-1}; therefore, the removal of lead from water is crucial to protect human and environmental health [3,4]. Copper(II) is another heavy metal ion which is harmful to human as the accumulation of this ion in human body can cause liver and brain damage, stomach upset and ulcer, skin and heart diseases, and so on [5]. The acceptable concentration of copper in drinking water is 1.3 mg l^{-1}, so reduction of the ion concentration in aqueous solutions at least up to this acceptance level is crucial.

Several chemical, physicochemical and biological techniques including chemical precipitation [5], biosorption [6], microfiltration [4], coagulation [7], ion exchange [8], electrochemical [9] and adsorption [10] methods have been used to remove heavy metals from aqueous solutions. Among the mentioned techniques, adsorption is the most common method for the removal of organic and inorganic pollutants from aqueous solutions. This method benefits from advantages such as high capacity and large scale and ability to use generable non-toxic and cheap adsorbents.

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However, the success of adsorption process is highly dependent on the selection of experimental conditions leading to a maximum analyte adsorption. Additionally, the kinetic and thermodynamic studies of these processes depend on the optimal conditions of the process.

One-factor-at-a time (OFAT) is a traditional optimization method in which the effect of one factor at a time on an experimental response is monitored. Indeed, only one parameter is changed while keeping the other factors at fixed level. Its main drawback is that the interaction effects of the parameters are ignored among the factors studied. Therefore, this method does not depict the complete effects of the parameters on the response, which may lead to inaccurate optimal conditions. Another disadvantage of this technique is the large number of experiments needed to conduct the research. Indeed, it requires a lot of resources such as material, reagent and time. Experimental design methods and response surface methodology (RSM) [11,12] have been widely used to study the effects of factors simultaneously and to find the combination of factors producing the optimal conditions as well. Using these methods is advantageous, as it allows obtaining desirable condition with smaller number of systematic experiments; thus, saving time and expenses. However, when several responses of interest get involved in the analysis, the obtained results from response surface methodology are hardly analyzed. It is so because the optimal values for each response may be localized in different regions of the response surfaces; therefore it is difficult to find the conditions in which all responses are satisfied simultaneously. The more distant of these optimum regions is, the more difficulty is to find the common desirable conditions. An approach to overcome this problem is the use of a multi-criteria methodology. Harrington [13] introduced the desirability function as one of the multi-criteria approaches which was later improved and popularized by Derringer and Suich [14].

Recently, an immense research has focused on using different biomaterials as sorbents for the removal of heavy metals from aqueous solutions. Natural biomaterials are widely applied because of their relative abundance and low commercial value [15]. In addition, agricultural byproducts and plant wastes are used as biosorbents [16].

In this study, given that copper and lead are the common contaminants of wastewater from various industries [17], activated carbons obtained from poplar leaves as an efficient, accessible and inexpensive biosorbent is used for the removal of Pb^{2+} and Cu^{2+} from aqueous solutions for the first time. The adsorption process is monitored with flame atomic absorption spectrophotometry due to its low cost, operational facility and high sample throughout. The main goal is achieving the maximum removal of the ions by investigating the effective experimental variables such as pH, biosorbent dose, contact time and temperature. The central composite design (CCD) combined with response surface methodology (RSM) using the desirability function (DF) is used as an efficient statistical method to find the common optimal conditions of the analyte adsorption. This kind of optimization helps us overcome synergic effect between Pb^{2+} and Cu^{2+} if it occurs [17]. Moreover, if the analytes are optimized individually, the number of required experiments increases twice. Therefore, the applied statistical method allows us obtaining sufficient information about this system with low number of experiments. Finally, for a mixture of ions, the equilibrium, kinetic and thermodynamic of ions adsorption process are elucidated at the common optimal conditions.

EXPERIMENTAL

Instruments and Reagents

All the chemicals and reagents and nitrate ions used in the present study were of analytical grade and used without further purification. They were purchased from Merck (Darmstadt, Germany). The pH of solutions was adjusted by the addition of either 0.1 M HCl or 0.1 M NaOH solutions. Double distilled water was used throughout the experiments and the stock solutions 1000 mg l^{-1} of nitrate ions were subsequently diluted with distilled water.

FT-IR spectrophotometer using KBr pellets (FT-IR shimadzu 8400s, Japan) was used to record the adsorbent spectrum, in the wavenumber range 400-4000 cm^{-1}. A Phs-3PW (BEL Company, Italy) pH meter supplied with a glass combined electrode was used for pH measurements. A Shimadzu (AA680) atomic absorption spectrophotometer (AAS) with lead and copper hollow cathode lamps and air acetylene flame was used for determining Pb^{2+} and Cu^{2+} ions in solutions.

The *Design-Expert*, a statistical package software version 7.0.0 was used for experimental design analysis and their subsequent regression analysis. In this software, the model-fitting is done by the QR decomposition algorithm [18] on the design matrix to compute model coefficients. It also employs Nelder-Mead Simplex method (McKinnon 1999) for the optimization.

The linear fitting of the kinetic and equilibrium data was carried out through the "*Linest*" function embedded in *Excel* software. This function helps us compute the linear parameters and their uncertainty as well [19].

Preparing and Characterizing the Adsorbent

Poplar autumnal leaves were collected from Semnan city and washed with tap water followed by distilled water to remove dirt. Then, they were dried in outdoors. Next, they were grinded and cut into small pieces (lower than 1 × 1 cm). Afterwards, they were put into an incinerator at 550 °C for 8 h to produce ashes. Finally, the ashes were washed with distilled water and dried in an oven at 90 °C for 24 h and kept for further studies.

To identify some characteristic functional groups which are responsible for the sorption of the metal ions, Fourier transform infrared spectrum of the ashes is recorded and illustrated in Fig. 1.

The broad band at 3431 cm^{-1} are assigned to the amine and hydroxyl groups. The strong peak at 1436 cm^{-1} is attributed to NH stretching vibrations [20]. As reported in [21], Pb and Cu form strong binding with the ligands containing OH and NH groups. In poplar leaves, OH and NH groups enhance the removal of Pb^{2+} and Cu^{2+} ions from aqueous solutions.

Batch Adsorption Studies

To optimize the experimental factors such as pH, contact time, sorbent dose, and temperature on the removal of the binary system of Pb^{2+} and Cu^{2+} ions, twenty nine experimental conditions were defined based on central composite design (CCD). By preliminary experiments, a mixture solution of Pb^{2+} (150 mg l^{-1}) and Cu^{2+} (120 mg l^{-1}) with 50 ml volume was selected and examined at 30 experimental conditions. The following procedure was for each experiment: (1) the pH of solution was adjusted using 0.1 M HCl or NaOH solutions, (2) the temperature of solution was adjusted, (3) a weighted amount of adsorbent was added to this solution, (4) the solution was transferred into 125 ml Erlenmeyer flasks, and was shaken in a thermostatic incubator at 200 rpm.

It should be mentioned that in the first step of the procedure, we do not conduct experiments in buffer media, because the cations of buffer may be adsorbed on the bioserbent leading to decrease the active surface of the biosorbent.At each experiment, the removal percentage of each ion, Pb^{2+} and Cu^{2+}, was calculated as follows:

$$\%\,\mathrm{Re}moval = \frac{(C_0 - C_e)}{C_0} \times 100 \qquad (1)$$

where C_0 (mg l^{-1}) and C_e (mg l^{-1}) are the initial and equilibrium ion concentrations.

The thermodynamic and isotherm parameters of the adsorption were determined by analyzing adsorbate concentration at various concentrations over different temperatures. The adsorption capacity at equilibrium state, q_e (mg g^{-1}), and time t, q_t (mg g^{-1}), were calculated as follows:

$$q_e = \frac{(C_0 - C_e)\,V}{W} \qquad (2)$$

where V (L) is the volume of the solution and W (g) is the mass of adsorbent. C_0 (mg l^{-1}) and C_e (mg l^{-1}) are the same as in Eq. (1),

$$q_t = \frac{(C_0 - Ct)\,V}{W} \qquad (3)$$

where C_t (mg l^{-1}) is the ion concentration at time t, and the other parameters are the same as in Eq. (2).

THEORETICAL BACKGROUND

Adsorption Isotherms

Adsorption isotherm models describe the capacities of the adsorbent and adsorbate which are usually the ratio between the quantity adsorbed and that remained in a solution at equilibrium at a fixed temperature. The most common adsorption isotherm models are Langmuir, Freundlich and Tempkin.

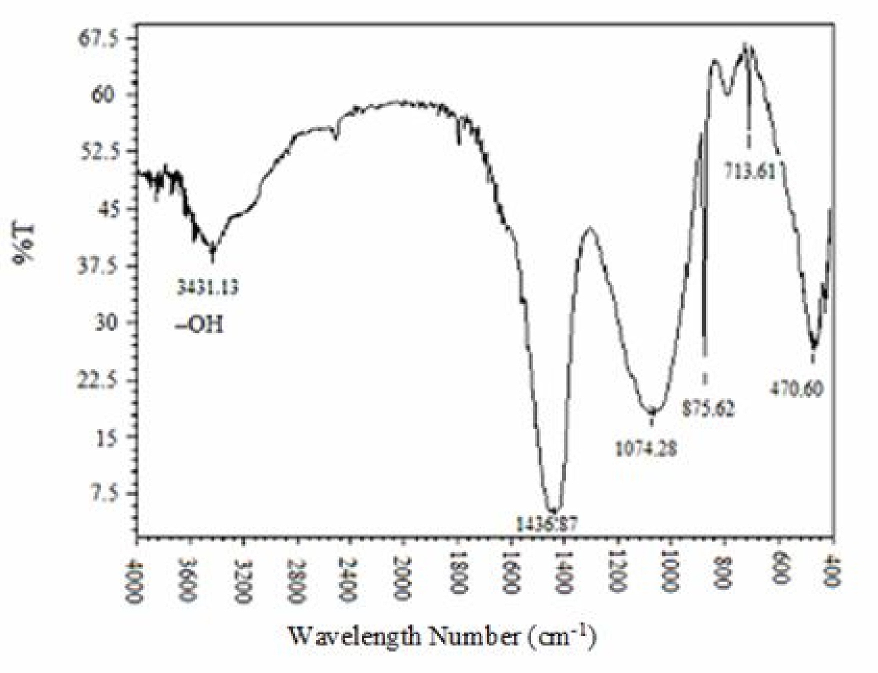

Fig. 1. The FT-IR spectrum of ashes of poplar tree leaves.

Langmuir Isotherm

The Langmuir adsorption, the monolayer adsorption, depends on these assumptions [22]:

Adsorption takes place at specific homogeneous sites within the adsorbent

Only, once an adsorbate molecule occupies a site without taking place a further adsorption at that site.

All sorption sites are the same and energetically equivalent.

The sorption of each sorbate molecule onto the surface equals to sorption activation energy.

The saturated or monolayer capacity can be expressed as the linear form of the Langmuir equation as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \tag{4}$$

where C_e is the equilibrium concentration of adsorbate (mg l^{-1}), q_e is the amount of the equilibrium adsorbate per unit weight of the adsorbent (mg g^{-1}), q_{max} is the monolayer capacity of the adsorbent (mg g^{-1}) and K_L is the Langmuir adsorption constant (l mg^{-1}). q_{max} and K_L can be computed by plotting C_e/q_e *vs*. C_e

The essential feature of the Langmuir isotherm can be shown by means of dimensionless equilibrium parameter R_L defined by:

$$R_L = \frac{1}{1 + K_L C_0} \tag{5}$$

where K_L (l mg^{-1}) is the Langmuir constant and C_0 (mg l^{-1}) is the initial ion concentration. Theoretically, $R_L > 1$ $R_L = 1$, $0 < R_L < 1$ and $R_L = 0$ show that an adsorption process is unfavorable, linear, favorable and irreversible, respectively.

Freundlich isotherm. The Freundlich equation is an empirical equation employed to describe the adsorption process. The linear form of the Freundlich equation can be represented as:

$$\ln q_e \ \ln K_F + \frac{1}{n} \ln C_e \tag{6}$$

where q_e is the equilibrium ion concentration on adsorbent (mg g^{-1}), C_e is the equilibrium ion concentration in solution (mg l^{-1}); K_F (l g^{-1}) and n are Freundlich constants. K_F and n indicate the adsorption capacity of the adsorbent and a measure of the deviation from linearity of the adsorption, respectively. When $\ln q_e$ is plotted *vs*. $\ln C_e$, K_F and n can be calculated from the intercept and slope of the regression model.

Tempkin isotherm. The Tempkin isotherm equation can be expressed as below:

$$q_e = B\ln(AC_e) \tag{7}$$

The linear form of it can be written as:

$$q_e = B\ln A + B\ln C_e \tag{8}$$

where B = RT/b and A (l mg^{-1}) are Tempkin constants representing the equilibrium binding and they can be determined from plotting of q_e *vs*. $\ln C_e$.

Adsorption Kinetics

While designing and optimizing a wastewater treatment, it is important to predict the removal rate of pollutants from aqueous solutions. There are four most common kinetic models for interpreting the adsorption process as described below.

Pseudo-first order kinetic model. In 1898, Lagergren proposed a pseudo-first-order equation, based on solid capaciy, for the sorption of liquid/solid systems. Accordingly, the rate of change occurred in sorbate uptake with the passage of time is directly proportional to the difference in the saturation concentration and the rate of solid uptake with time. The general Lagergren equation can be shown as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{9}$$

where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the same as in Eqs. (2) and (3). K_1 is the first-order rate constant. Using the linear plot of $\ln(q_e - q_t)$ against time't', the model parameters can be obtained.

Pseudo-second-order kinetic model. The sorption of Pb^{2+} and Cu^{2+} ions onto poplar leaves ashes following pseudo-second-order kinetics can be represented as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \tag{10}$$

where q_t and q_e are the same as in the above equation and k_2 (g mg^{-1} min^{-1}) is the pseudo-second- order rate constant for an adsorption process. The linear plot of $\ln(q_e - q_t)$ against time 't' gives the parameters of the model.

Elovich kinetic model. Elovich equation is expressed as follows:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \tag{11}$$

where α (mg g^{-1} min^{-1}) is the initial adsorption rate and β (g mg^{-1}) is the desorption constant related to the extent of surface coverage and activation energy for chemisorption. The slope and the intercept of the plot of q_t *vs*. lnt result in the determination of the kinetic constants, α and β.

Intraparticle diffusion kinetic model. To investigate the changes occurring in the concentration of sorbate onto sorbent with shaking time, the kinetic data of Pb^{2+} and Cu^{2+} ions sorption onto poplar leaves ashes were fitted into the following equation:

$$q_t = K_{id} t^{\frac{1}{2}} + C_i \tag{12}$$

where q_t is the same as mentioned previously. K_{id} is the rate constant of Morris-Weber transport calculated using the slope of the linear plot of q_t *vs*.. $t^{\frac{1}{2}}$.

Adsorption Thermodynamics

The dependency of the biosorption process to the temperature is associated with several thermodynamic parameters such as Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) which can be obtained from the following equations:

$$\Delta G° = -RT\ln K_c \tag{13}$$

$$K_c = CA_e/C_e \tag{14}$$

where K_c is the equilibrium constant, c_{Ae} (mg l^{-1}), and C_e (mg l^{-1}) are the equilibrium concentrations for the solute on the sorbent and in the solution, respectively. R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is temperature (K).

K_c can also be expressed in terms of ΔH° (kJ mol^{-1}) and ΔS° (J mol^{-1} K^{-1}) as a function of temperature:

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{15}$$

ΔH° and ΔS° can be estimated from the slope and intercept of the plot of $\ln K_c$ *vs*. 1/T.

RESULTS AND DISCUSSION

In this study, the ions adsorption process is optimized *via* statistical experimental design methods, and then the quilibrium, kinetic and thermodynamic behaviors of the system were investigated at the optimal conditions.

Achieving the Optimal Conditions of the Adsorption Process

To obtain the optimal experimental conditions for the simultaneous removal of Pb^{2+} and Cu^{2+} ions from aqueous solutions, two steps of statistical methods were used. First, twenty nine experiments were designed based on CCD, and then (RSM), the relationship between the factors and the removal percentage of each ion were investigated using response surface methodology. Although RSM can optimize univariate responses, it does not lead to common optimal conditions for multivariate responses. Therefore, multiple response surface methodology based on desirability function was used to obtain the common optimal condition of both ions removal.

Central composite design and response surface methodology. Several classes of RSM, such as central composite design (CCD), Box-Behnken design and three-level factorial design, have different properties and characteristics. Amongst the three, CCD is the most popular technique in the estimation and evaluation of the main and interaction effects of variables with the least number of experiments.

A central composite design (CCD) is composed of N experiments as in the following equation:

$$N = 2^k + 2k + k_0 \tag{16}$$

where k is the number of variables and k_0 is the number of center points [12] (Brown *et al.* 2009). In this work, according to the preliminary studies, four factors were considered in the optimization. The total experimental trials with one blocked design and 6 replicates was 30. The factors and their levels have been reported in Table 1.

The behavior of this system is explained by the following empirical second order polynomial model equation:

$$Y = \beta_0 + \sum_{i=1}^{k}\beta_i X_i + \sum_{i=1}^{k}\beta_{ii} X_i^2 + \sum_{i=1}^{k-1}\sum_{j=2}^{k}\beta_{ij} X_i X_j + \in \tag{17}$$

where Y is the response; *i.e.*, the removal percentage of each ion. x_is represent the variables, β_0 is the constant term; β_is and β_{ii}s show the coefficients of the linear and quadratic parameters, respectively. β_{ij}s are the coefficients of the interaction parameters x_i and x_j and ε is the residual associated to the experiments. The adequacy of the model is tested by the analysis of variance method (AVOVA). Based on ANOVA analysis, the following equations were defined to show the relationship between the removal percentage of each ion and experimental real factors:

$$Y_{pb} = 44.29 - 16.45X_1 - 0.35X_2 + 140.08X_3 + 0.87X_4 + 0.13X_1X_2 + 112.06X_1X_3 \tag{18}$$

$$Y_{Cu} = -55.38 + 38.11X_1 + 0.17X_2 + 442.6X_3 - 6.13X_4 - 8.12X_2X_3 + 0.05X_2X_4 + 31.62X_3X_4 - 3.57X^2_1 + 0.05X^2_4 \tag{19}$$

where Y_{pb} and Y_{cu} are the removal percentage of Pb^{2+} and Cu^{2+} ions, respectively. X_1, X_2, X_3 and X_4 are pH, contact time, adsorbent dosage and temperature, respectively.

Tables 2 and 3 represent the results of ANOVA and the regression coefficients of Pb^{2+} and Cu^{2+} ions. The p-values of the regressions (significant with $p < 0.05$) were smaller than 0.05 for both Pb^{2+} and Cu^{2+}, indicating that either of the models were significant at a high confidence level (95%). The p-values of lack of fit for both ions were greater than 0.05, a fact which confirmed the models' significance.

The coefficient of determination R-square is used as the other parameter to express the quality of fit of polynomial model equation fitting. In this case, the R^2 coefficients of variation fitting for Y_{Pb} and Y_{Cu} were 0.73 and 0.88,

Table 1. Factors and Their Levels in CCD Design with α = 2

Factors	Real levels and their coded values in parenthesis				
	Axial (-α)	Low (-1)	Central (0)	High (+1)	Axial (+α)
X_1: pH	2.00	3.05	4.40	5.15	6.20
X_2: Time (min)	10	30	50	70	90
X_3: Adsorbent dose (g)	0.040	0.065	0.090	0.115	0.140
X_4: Temperature (°C)	5	11	18	24	30

Table 2. Analysis of Variance (ANOVA) Result for the Model of Pb^{2+}

Source of variation	Sum of square	Df[a]	P-value
Model	7933.79	6	<0.0001
X_1	2.45	1	0.08921
X_2	313.82	1	0.1343
X_3	4730.48	1	<0.0001
X_4	633.04	1	0.0380
X_1X_2	176.23	1	0.2565
X_1X_3	198.32	1	0.2296
Residuals	3263.92	23	
Lack of fit (LOF)	2796.01	18	0.3456
Pure error	467.91	5	
Total	11366.51	29	

[a] Df: degrees of freedom.

indicating a reasonable correlation between the response and the independent variables for both analytes. Although for both analytes, R^2 values are not high, they are still reasonable. Also, adjusted regression coefficients R^2_{adj} = 0.66 and 0.83 for Pb^{2+} and Cu^{2+}, respectively, are in reasonable agreement with their counterparts R^2, indicating the significance of the proposed model.

The normality the residuals plots of (Fig. 2) of responses for both ions as a diagnostic test confirmed both the suggested models.

Table 3. Analysis of Variance (ANOVA) Result for the Model of Cu^{2+}

Source of variation	Sum of square	Df[a]	P-value
Model	10785.53	9	<0.0001
X_1	2193.80	1	<0.0001
X_2	948.14	1	0.0025
X_3	5253.96	1	<0.0001
X_4	807.39	1	0.0045
X_2X_3	267.47	1	0.0796
X_2X_4	677.25	1	0.0083
X_3X_4	424.45	1	0.0308
X^2_1	546.01	1	0.0159
X^2_4	69.66	1	0.3564
Residuals	1481.72	20	
Lack of fit (LOF)	1335.05	15	0.0998
Pure error	146.67	5	
Total	12267.25	29	

To portray the interaction effects in the models of ions, the three-dimensional (3D) response surfaces were plotted based on Eqs. (18) and (19) for Pb^{2+} and Cu^{2+}, respectively; when the amount of two factors are fixed at the central point and the others are allowed to vary. For example, Fig. 3a shows a 3-D plot of Pb^{+2} removal versus pH and time other factors are fixed: the adsorbent dose = 0.09 g l^{-1} and temperature = 18 °C. Figures 3 and 4 illustrate the different response surfaces of Pb^{2+} and Cu^{2+}, respectively. In these figures, the curvatures of the plots indicate the interaction between the factors. The existence of interaction means that the factors may affect the response interactively and not independently. So their combined effect is greater or less sharper than that of what is expected for the straight addition of the effects.

As seen in Figs. 3 and 4, the shapes of the responses of analytes are different, so the conditions where the maximum recovery of the analytes occurs cannot be achieved by RSM. Also, according to Tables 2 and 3, and model Eqs. (18) and (19), number of the significant factors is not the same for the analytes. Moreover, the effect of the factors and their interactions are different. So it is not supposed the individual optimization to be equivalent to simultaneous optimization. Here, the goal of this study is finding experimental conditions in which both Pb^{2+} and Cu^{2+} ions can be removed from aqueous solutions with high efficiency, a fact which is not possible using RSM. This problem can be overcome by using multiple response surface methodology (MRS) as will be described in the following section.

Multiple response surface methodology. One of the most widely used methods in MRS for optimization studies is desirability function [12-14] in which multiple responses ae reduced to a single aggregated function and then solved as a single objective optimization.

Desirability Function (DF)

In this method, each individual response predicted is

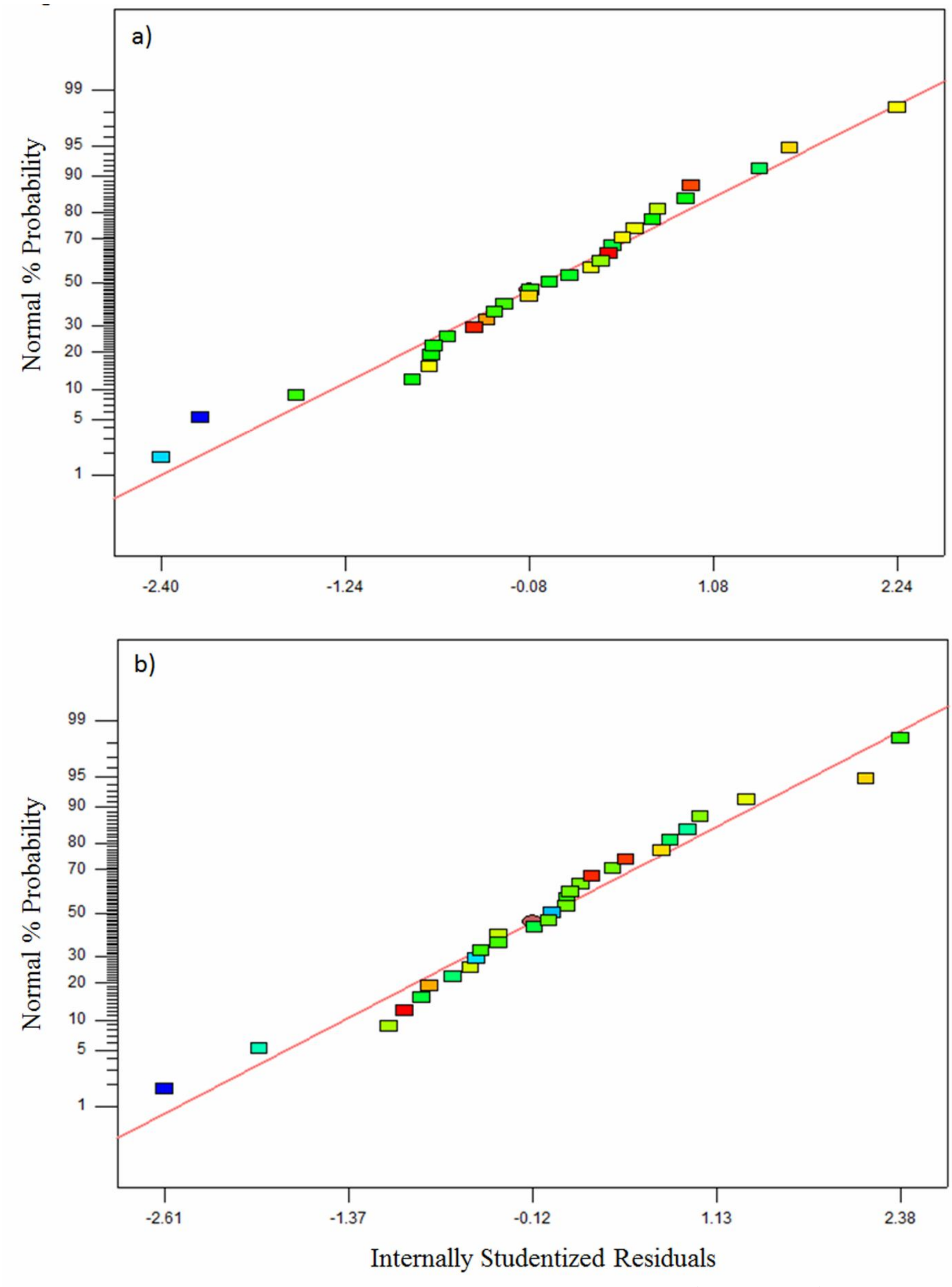

Fig. 2. The normality plot of the residuals for the models of Pb^{2+} (a) and Cu^{2+} (b).

transformed to a partial desirability function (df_i) which varies from zero (undesirable response) to one (optimal response) based on the Derringer and Suich equation as follows (Derringer 1980) [14]:

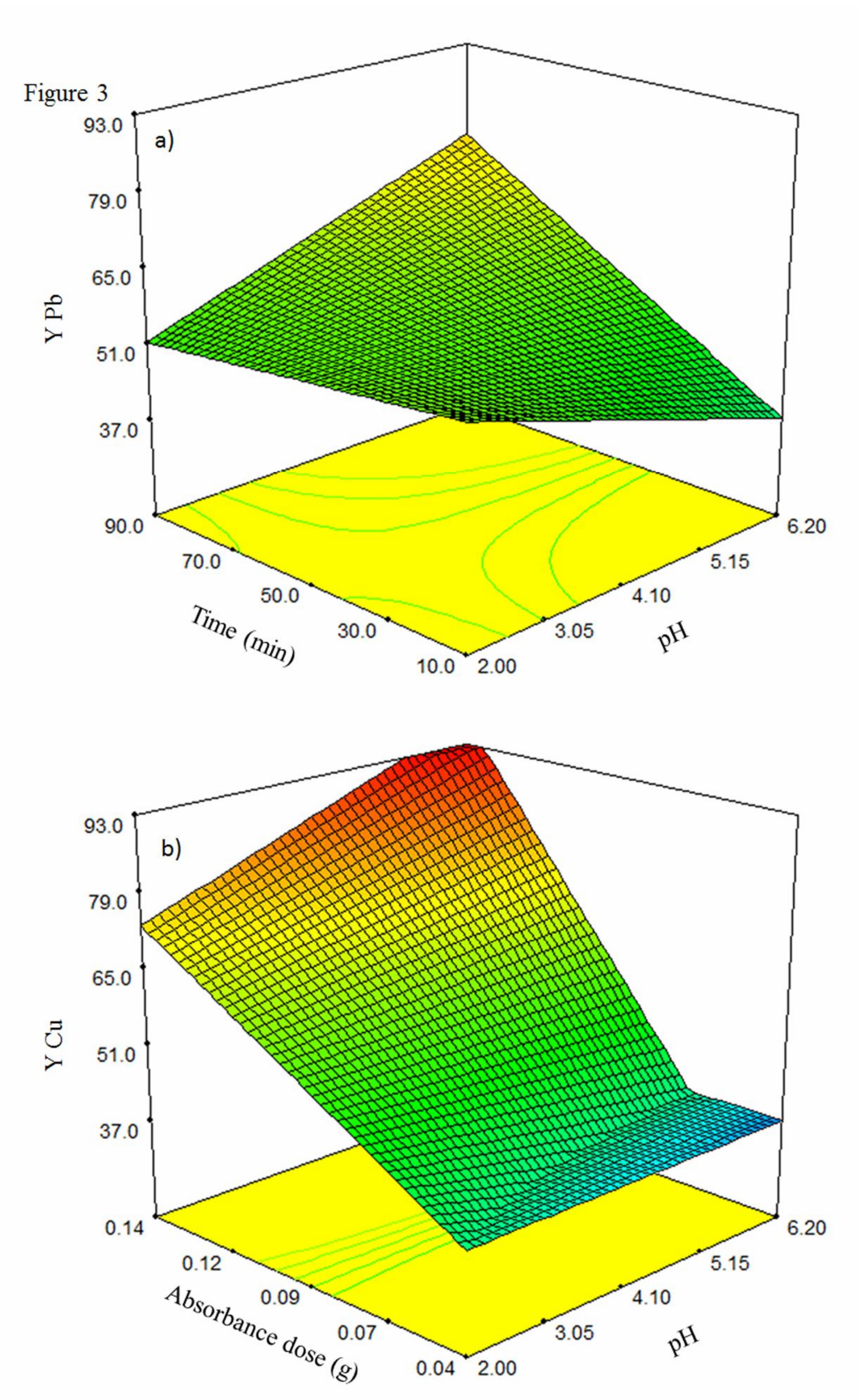

Fig. 3. The 3-D response surface plots of Pb^{2+}, when two factors are fixed at central point and the others are variables.

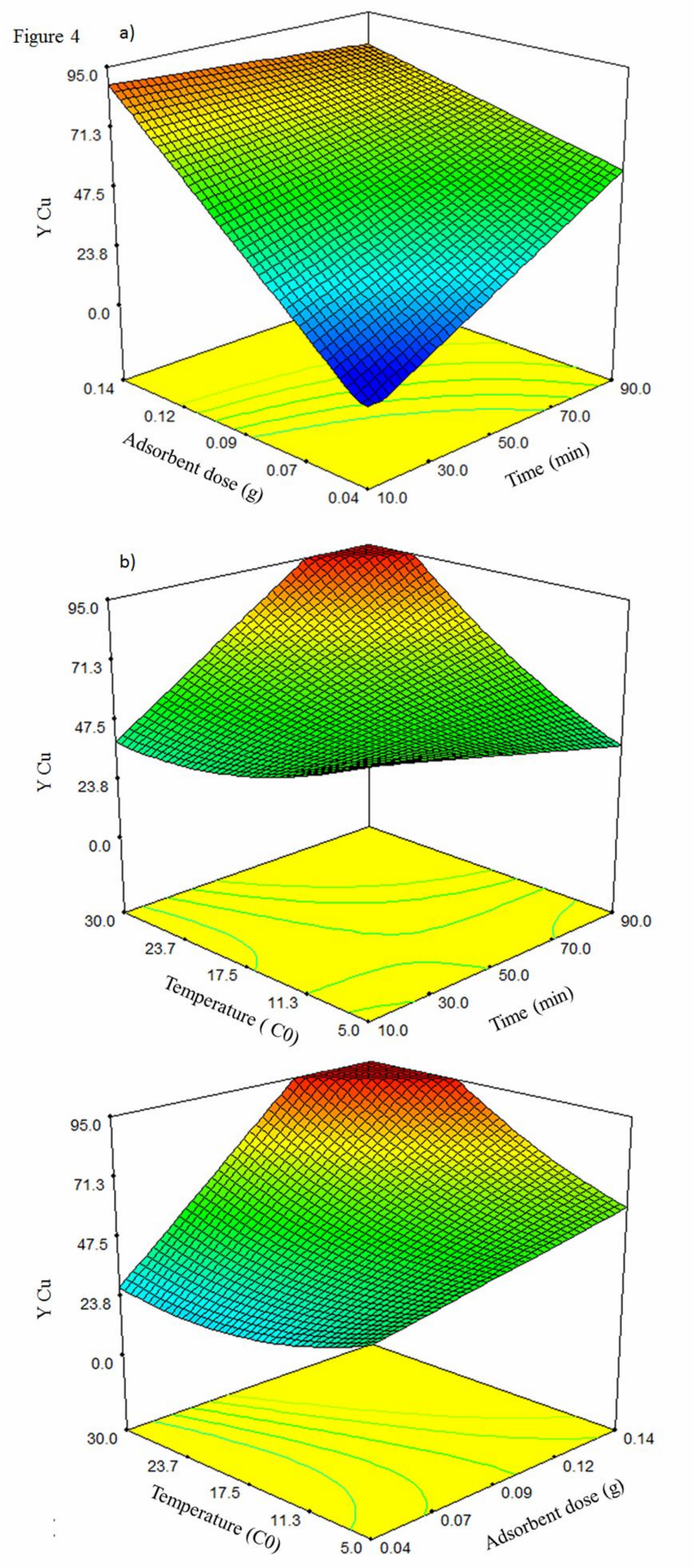

Fig. 4. The 3-D response surface plots of Cu^{2+}, when two factors are fixed at central point and the others are variables.

$$df_i \left(\frac{R-\alpha}{\beta-\alpha}\right)^{wi}, \qquad \alpha \le R \le \beta$$

$$df_i = 1, R > \beta$$

$$df_i = 0, R < \alpha \tag{20}$$

where α and β are the lowest and highest values of ith response, respectively, and w_i is the weight of each response. DF as the overall optimization function is computed by geometric mean of different df_i values as follows:

$$DF = \left[df_1^{v1} \times df_2^{v2} \times ... \times df_n^{vn}\right]^{\frac{1}{n}}, \; 0 \le vi \le 1 \; (i = 1,2,...,n) \tag{21}$$

$$\sum_{i=1}^{n} \upsilon i = 1$$

where df_i indicates the individual desirability of the response R_i (i = 1,2,3, ... ,n) and v_i shows the importance of ith response. Indeed, DF is the collected measure of all responses R_i's and it is optimized over the independent variable domain by any existing univariate search technique.

Here, the goal of optimization is finding the conditions in which the maximum removal of both Pb^{2+} and Cu^{2+} occurs; therefore, the desirability function was maximized. Figure 5 illustrates the desirability plot as a function of time (min) and pH at a fixed level of adsorbent dose=0.14g, corresponding to (+α) level of this factor, and temperature = 28 °C for the simultaneous removal of Pb^{2+} and Cu^{2+}. Finally, the optimal experimental conditions for simultaneous removal of Pb^{2+} and Cu^{2+} was achieved at factor vales: pH = 5.43, contact time = 23 min, adsorbent dosage = 0.14 g and temperature 28 °C.

This condition was used to investigate the equilibrium and kinetic models of the adsorption process of metal ions to determine the thermodynamic and kinetic parameters of the system.

Adsorption Isotherms

In this study, the equilibrium experimental data for adsorbed Pb^{2+} and Cu^{2+} on poplar leaves ashes were analyzed using three isotherm models (Eqs. (4)-(8)). Each model was examined at four levels of temperature to find the most superior and robust model.

Isotherm constants and R^2 of each model were calculated and reported in Table 4. As seen in this table, Freundlich and Tempkin isotherms represent low value of R^2 indicating that none of the adsorption processes can be interpreted by this models. However, a high R^2 value of Langmuir isotherms shows the superiority of this model to interpret the adsorption processes of Pb^{2+} and Cu^{2+} ions. Moreover, the values of R_L varies between 0 and 1, indicating a favorable adsorption for Pb^{2+} and Cu^{2+} onto the poplar leaves ashes. Meantime, the results showed that the maximum adsorption capacity can vary in the range of 67.11-70.13 mg g^{-1} and 52.25-6273 mg g^{-1} for Pb^{2+} and Cu^{2+}, respectively. Alslaibi applied olive stone activated carbon (OSAC) for the removal of heavy metals that the highest value of adsorption capacity on the OSAC was obtained 23.47 mg g^{-1} and 22.73 mg g^{-1} for Cu^{2+} and Pb^{2+}, respectively [23]. Moreover, in our work, the removal efficiencies of Pb^{2+} and Cu^{2+} were 92.8% and 94.9%, respectively, which are in good agreement with the reported results in [23]. Their results showed 98.55% removal of Cu^{2+} and 98.83% of Pb^{2+}. The comparison of the present results with the previous ones indicated the successful application of poplar leaves ashes as a biosorbent for the removal of Cu^{2+} and $Pb^{2+.}$

Adsorption Kinetics

To study the robust kinetic models of the adsorption process of Pb^{2+} and Cu^{2+} onto poplar leaves ashes, the experimental data were obtained at the optimum concentration of the ions and four levels of temperature. 50 ml of solution of Pb^{2+} (150 mg l^{-1}) and Cu^{2+} (120 mg l^{-1}), in optimal conditions (pH = 5.68, dose of adsorbent = 0.14) was shaken for 3, 6, 9, 12, 15, 18, 21, 24, 28, 30, 40, 50, 60, 80 and 90 min in a thermostatic incubator at 200 rpm. These batch experiments were conducted at four temperatures 284.15 K, 291.15 K, 297.15 K and 303.15 K, and the corresponding data are shown in Figs. 6a and b for Pb^{2+} and Cu^{2+}, respectively.

Each experimental kinetic data was analyzed by the presented kinetic models in Eqs. (9)-(12). Forboth ions, the kinetic parameters and R^2 of each model were calculated

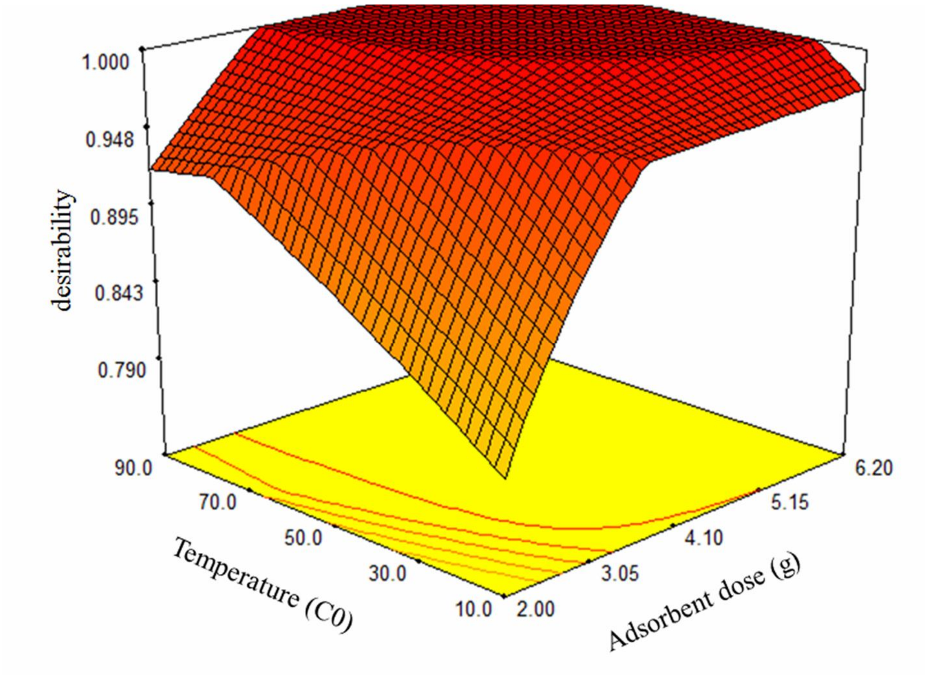

Fig. 5. The 3-D plot of desirability function, when pH and time vary at adsorbent dose = 0.14 g and temperature = 28 °C.

and reported in Table 5.

Based on the R^2 coefficient values, it can be inferred that the pseudo-second-order model agrees with the experimental data. The kinetic parameters, q_e and k_2 and their uncertainties were calculated and reported in Table 6 for Pb^{2+} and Cu^{2+}. The uncertainty of q_e was computed based on the standard deviation of the slope, while the uncertainty of k_2 was calculated based on the standard deviation of slope and intercept because of the error propagation. Moreover, It can be seen that for both analytes calculated q_e and experimental q_e are in good agreement, further evidencing that the analytes adsorptions obey the pseudo-second-order kinetic model.

The rate constant of this model can be expressed as a function of temperature by the following Arrhenius relationship:

$$\ln k_2 = \ln A - \frac{E_a}{RT} \qquad (22)$$

where E_a (kJ mol^{-1}) is the Arrhenius activation energy of adsorption, A is the Arrhenius factor, R and T are the same as in Eq. (19). The linear plots of $\ln k_2$ *vs.* 1/T for the adsorption of Pb^{2+} and Cu^{2+} ions onto poplar leaves ash were constructed to generate the activation energies from the slope (-Ea/R). The calculated E_a (kJ mol^{-1}) values were 0.57 (±0.16) and 0.62 (±0.13) for Pb^{2+} and Cu^{2+}, respectively.

The chemical (chemisorption) or physical (physisorption) adsorption mechanisms are often important indicator to explain the type of interactions between adsorbate and adsorbent. The magnitude of an activation energy is indicative of the nature of adsorption, whether physical or chemical. Activation energies ranging between 5-40 kJ mol^{-1} and 40-800 kJ mol^{-1} are attributed to the physisorption and chemisorption, respectively. The result obtained for the adsorption of Pb^{2+} and Cu^{2+} ions onto poplar leaves ash indicate that the adsorption has a low potential barrier and it may correspond to a physisorption mechanism for both analytes.

Adsorption Thermodynamics

The experimental results at different temperatures for both analytes showed that the higher temperature, leads to

Table 4. Isotherm Constant Parameters and Correlation Coefficients for the Adsorption of Pb^{2+} and Cu^{2+} at Different Temperatures

Isotherm models	Parameters	Pb^{2+}				Cu^{2+}			
	Temp. (K)	284.15	291.15	297.15	303.15	284.15	291.15	297.15	303.15
Freundlich	R^2	0.9742	0.8805	0.7492	0.6960	0.9162	0.9165	0.9299	0.8885
Tempkin	R^2	0.9779	0.8957	0.7751	0.7242	0.8754	0.9248	0.9417	0.9024
Langmuir	R^2	0.9978	0.9982	0.9984	0.9982	0.9809	0.9945	0.9989	0.9994
	K_L	0.526	1.644	2.854	9.714	0.547	1.049	2.733	23.143
	q_{max} (calc.)	67.11	69.93	72.99	73.53	55.25	58.82	60.98	61.73
	R_L	0.011	0.003	0.002	0.001	0.013	0.007	0.003	0.0003

Table 5. Correlation Coefficients (R^2) in Pb^{2+} (150 mg l^{-1}) and Cu^{2+} (120 mg l^{-1}) Adsorption for Different Kinetic Models at Different Temperatures

Kinetic models		R^2 at different temperature (K)			
		284.15	291.15	297.15	303.15
Pb^{2+} adsorption	Pseudo-first order	0.9109	0.9595	0.8875	0.7645
	Pseudo-second order	0.9904	0.9992	0.9994	0.9998
	Elovich	0.9671	0.9116	0.8310	0.8191
	intraparticle diffusion	0.8981	0.5976	0.5010	0.4142
Cu^{2+} adsorption	Pseudo-first order	0.9133	0.9105	0.9269	0.7870
	Pseudo-second order	0.9938	0.9976	0.9998	0.9999
	Elovich	0.9609	0.8812	0.7562	0.7636
	intraparticle diffusion	0.8540	0.6777	0.4339	0.3980

the more biosorption capacity for poplar leaves ash (Table 4). It might be due to either increase in the number of active sites present on the surface of the biosorbent or the increase of the attractive forces between the metal ions and the biosorbent. The correlation between temperature and the biosorption capacity indicates that adsorption of Pb^{2+} and Cu^{2+} are endothermic in nature.

For both ions, the equilibrium constants K_cs, were calculated at different Ts and ΔG° (kJ mol^{-1}) based on Eqs. (13) and (14), as reported in Table 7. The negative values of

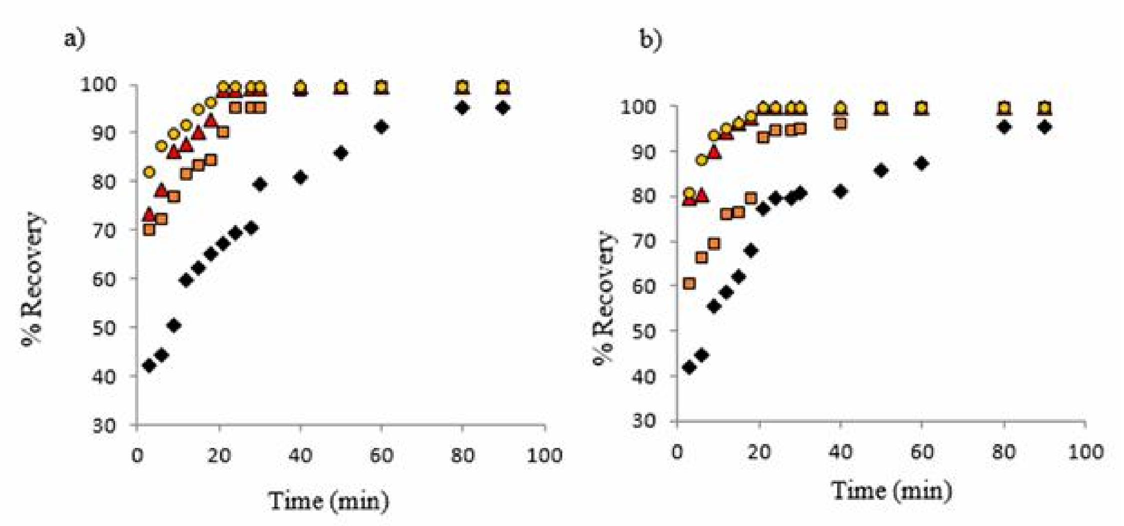

Fig. 6. Experimental data for the kinetic adsorption of (a) Pb^{2+} (150 mg l^{-1}) and (b) Cu^{2+} (120 mg l^{-1}), at different temperatures.

Table 6. Parameters of Pseudo-second Order Kinetic Model in Pb^{2+} (120 mg l^{-1}) and Cu^{2+} (120 mg l^{-1}) Adsorption at Different Tempretures

Ions	Parameters	Temperature (K)			
		284.15	291.15	297.15	303.15
	k_2	0.0133 (±0.0047)	0.0187 (±0.0047)	0.0341 (±0.0094)	0.1700 (±0.0450)
Pb^{2+}	q_e (exp.)	51.50	53.30	53.70	53.80
	q_e (calc.)	43.81 (±0.32)	43.89 (±0.21)	43.59 (±0.18)	43.25 (±0.04)
	k_2	0.0031 (±0.0030)	0.0065 (±0.0042)	0.0302 (±0.0076)	0.0334 (±0.0052)
Cu^{2+}	q_e (exp.)	41.70	42.80	43.00	43.20
	q_e (calc.)	43.53 (±0.99)	44.83 (±0.63)	43.67 (±0.17)	43.7 (±0.10)

ΔG° reveal that the sorption of Pb^{2+} and Cu^{2+} onto the poplar leaves ash is a spontaneous process and thermodynamically favorable under the experimental conditions. The Gibbs free energy (ΔG°) is small and negative, but it increases with the raising temperature.

ΔH° and ΔS° were estimated from the slope and intercept of the plot of $\ln K_c$ *vs*. 1/T (Eq. (15)), as reported in Table 8. The positive values of ΔH° suggest that the biosorption of Pb^{2+} and Cu^{2+} onto the poplar leaves ash are endothermic. The negative values of ΔS° indicate the decreased randomness of adsorbate ions on the solid surface than in solution.

Poplar tree leaves as an inexpensive, accessible and suitable adsorbent were successfully used for the simultaneous removal of Pb(II) and Cu(II) from aqueous solutions in a batch system. The simultaneous optimization

Table 7. Equilibrium Xonstants K_c and $\Delta G°$ (kJ mol^{-1}) for the Adsorption Processes of Pb^{2+} and Cu^{2+} on Poplar ash Leaves at Different Temperatures

Ions	Parameter	Temperature (K)			
		284.15	291.15	297.15	303.15
Pb^{2+}	K_c	9.70	35.67	71.67	216.00
	$\Delta G°$ (kJ mol^{-1})	-2.33	-3.75	-4.58	-5.88
Cu^{2+}	K_c	7.36	25.38	59.67	89.67
	$\Delta G°$ (kJ mol^{-1})	-2.04	-3.40	-4.39	-4.92

Table 8. Thermodynamic Parameters for the Adsorption of Pb^{2+} and Cu^{2+} onto Poplar Leave Ash

Thermodynamic parameters	Metal ions	
	Pb^{2+}	Cu^{2+}
R^2	0.9728	0.9930
ΔS (K mol^{-1})	0.02 ($\pm 2 \times 10^{-4}$)	0.04 ($\pm 1 \times 10^{-4}$)
ΔS (K mol^{-1})	-0.60 ($\pm$0.07)	-0.72 ($\pm 2.7 \times 10^{-3}$)

of the ions adsorption process was performed by means of the CCD and RSM methods coupled with desirability function. Different equilibrium and kinetic models were evaluated for the processes at the optimal conditions obtained from the experimental design. Equilibrium data showed that the adsorption process of both ions follow the Langmuir model and kinetic studies suggested pseudo-second-order kinetic model as the best model for describing the adsorption process. In addition, thermodynamic parameters such as ΔG^o, ΔH^o and $\Delta S°$ were calculated. The ΔG^o values were negative, meaning that the processes were spontaneous in nature. The positive values of ΔH^o revealed that the adsorption process of both analytes were physiosorption and endothermic in nature. The negative values of $\Delta S°$ implied decreased randomness of adsorbate ions on the solid surface than in solution.

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