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Response Surface Modeling of the High Concentration Pb^{2+} Adsorption onto Cross-linked Xanthated Chitosan

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Cross-linked xanthated chitosan was prepared as an adsorbent for removal of Pb^{2+} from aqueous solution. Adsorption of Pb^{2+} onto cross-linked xanthated chitosan was optimized using response surface methodology. A three level Box-Behnken design based on response surface methodology was employed to analyze the combined effect of pH, adsorbent dosage and contact time on adsorption capacity. The optimum values of the selected variables were determined to be: pH 5.66, adsorbent dosage 0.058 g and contact time 95 min for Pb^{2+} removal. In the optimal conditions, the corresponding Pb^{2+} adsorption capacity on cross-linked xanthated chitosan was found to be 446.8 mg/g.

Key Words: Chitosan, Cross-linked, Xanthation, Adsorption, Pb^{2+}, Response surface modeling.

INTRODUCTION

Heavy metals discharged from wastewater have posed direct or indirect threat to environment and public health because of their toxicity and bioaccumulation in the food chain and persistence in nature. Lead, one of the most common pollutants found in industrial effluents, is non-biodegradable and toxic even at low concentration[1]. Lead in the ecosystem has serious impacts on the environment and human health. Lead may cause mental disturbance, retardation, semi-permanent brain damage and it does not have an important biological activity[2]. It is classified as a persistent environmental toxic substance with a toxicity limit is < 0.05 µg/mL[3]. For the above reasons, strict environmental requirements and urgent treatment solutions are needed for lead removal from water and wastewater. Industrial wastewaters are often treated with chemical precipitation. However, with the development of electronic industry, plenty of high concentration heavy-metal wastewater is draining out of the manufacture world, which can not meet the emission regulation with traditional chemical precipitation and these processes involve the production of highly toxic sludge, which must be further treated before being environmentally safe[4]. In recent years, solid adsorbents have been widely used for the removal of heavy metals in low-cost wastewater treatment. Low-cost adsorbents may be used as an alternative in large scale wastewater treatment procedure. Usually, activated carbon is regarded as an effective adsorbent for removal of metal ions from water. However, due to its high cost and loss during regeneration, unconventional low-cost adsorbents such as the shell of *Pistacia vera* L[5], fly ash[6], chesnut shell[7], saw dust[8], red loess[9], chitosan[10], *etc.* have attracted the attention of more and more investigators in recent years.

Chitosan (CTS), a nitrogenous polysaccharide, is produced through the deacetylation of chitin, which is widely spread among marine and terrestrial invertebrates and in lower forms of the plant kingdom[11,12]. Chitosan is well established as an excellent natural adsorbent for metal ions due to the presence of the amino ($-NH_2$) and hydroxyl (-OH) groups[13,14]. However, there is limitation for the use of chitosan as adsorbent because it is easily dissolved in acid medium. In addition, adsorption capacity of chitosan to some metal ions is not satisfied. Fortunately, chitosan has high concentration of amine and hydroxyl groups and both its hydroxyl and amine groups can be chemically modified. They may increase the chemical stability of the adsorbent in acid media and, especially, decrease the solubility in most mineral and organic acids. Chemical modification of chitosan are performed such as crosslinking[15], carboxymethyl[16], acylation[17]. Among them, cross-linked modified chitosan is a convenient and effective way on improving its physical and mechanical properties for practical usages[18]. It enhances the resistance of chitosan against acid, alkai and chemicals, but cross-linked may reduce the adsorption capacity[17]. In order to deal with high concentration of Pb^{2+}, further chemical modification should be required to overcome the above deficiency. Sulphur has a very strong affinity for most heavy metals and the metal sulphur complex is very stable in acid conditions. Xanthation of chitosan has been reported to assist removal of metals from aqueous solutions. So, in this paper, sulphur groups were introduced onto glutaraldehyde cross-linked chitosan through a chemical reaction to get an adsorbent named cross-linked xanthated chitosan (CLXC). By now, there is no report about removal of Pb^{2+} from aqueous solution by cross-linked xanthated chitosan.

Many parameters may be responsible for the adsorption of Pb^{2+} ions from aqueous solution. The conventional methods of studying a process is time consuming and requires large number of experiments to determine optimum levels[19]. It is important to select a suitable experimentation technique, which will evaluate the effects of important parameters along with possible interactions with minimum number of experiments. Statistical experimental design such as response surface methodology is one of them. Response surface methodology is a collection of statistical and mathematical techniques which is widely used for developing, improving and optimizing processes[20,21].

In this study, the combined effect of adsorbent dose, pH and contact time on high concentration of Pb^{2+} removal from aqueous medium by cross-linked xanthated chitosan has been investigated using three level Box-Behnken design in response surface methodology by design 7.0.0 software (trial version).

EXPERIMENTAL

Chitosan with 92 % degree of deacetylation (Qingdao Jinhu Ocean Biology Co. Ltd., China), ethanol, acetic acid, glutaraldehyde, carbon disulfide, sodium hydroxide used in the experiment were of analytical and purchased from National Medicines Co. Ltd., China.

Preparation of cross-linked xanthated chitosan: Chitosan (1 g) was suspended in methanol (200 mL) and a 25 % (m/m) aqueous glutaraldehyde solution was added. After stirring at room temperature for 6 h, the product cross-linked chitosan were filtered. Cross-linked chitosan were treated with 50 mL of 14 % (m/m) NaOH and 2 mL of CS_2. The mixture was agitated at room temperature for 24 h. The obtained product, cross-linked xanthated chitosan were washed thoroughly with water and ethanol, then dried in vacuum and used for further experiments.

Characterization of cross-linked xanthated chitosan: IR spectra of the samples were recorded on a IR Prestige-21 spectrophotometer in KBr pellets. The power X-ray diffraction patterns of the samples were recorded on a D8 using CuK_α radiation in an operating mode of 40 KV and 30 mA. Data was collected from 10º to 80º in a step of 0.02 º/s.

Adsorption experiments: Adsorption of Pb^{2+} from aqueous solution on cross-linked xanthated chitosan was done in a static mode at room temperature (25 ºC). To each 50 mL solution of Pb^{2+} (1040 mg/L) in a flask, a desired quantity of the cross-linked xanthated chitosan was added in the flask and adjusted to desired pH. The mixture was agitated in a shaker at room temperature for predetermined time. The supernatant was separated by centrifugation at 4000 r/min for 10 min. All experiments were carried out in triplicate and the mean values are reported. The residual concentration in supernatant was determined by the methods of complexometric titration. The response was expressed as adsorption capacity calculated as the eqn. (1).

$$Q = V(C_0-C_1)/m \quad (1)$$

where, Q is the adsorption capacity (mg/g), V the volume of the solution (mL), m the amount of adsorbent (g), C_0, C_1 the before and after adsorbed concentration (mg/L) of Pb^{2+}.

Design of experiment using Box-Behnken design: Three factors such as pH, adsorbent dosage (m) and contact time (t) were chosen as independent variables and the adsorption capacity (q) as dependent output response variable. The experimental range and levels of independent variables for Pb^{2+} adsorption was presented as Table-1. The experimental design matrix which consists of 17 sets of coded conditions expressed in natural values resulted by three level Box-Behnken experimental design was shown in Table-2. The sequence of experiment was randomized in order to minimize the effects of uncontrolled factors. All the experiments were repeated three times.

TABLE-1
EXPERIMENTAL RANGE AND LEVELS OF INDEPENDENT VARIABLES FOR Pb^{2+} ADSORPTION

Factors	Range and levels (uncoded)		
	-1	0	1
pH (x_1)	2	3.75	5.5
Contact time (x_2, min)	20	70	120
Adsorbent dosage (x_3, g)	0.04	0.07	0.1

By the response surface methodology, a quadratic polynomial equation was developed to predict the response as a function of independent variables involving their interactions, the response (Y) for the quadratic polynomial is described in eqn. (2).

$$Y = \beta_0 + \sum\sum\beta_i x_i + \sum\beta_{ii} x_i^2 + \sum\sum\beta_{ij} x_i x_j + \varepsilon \quad (2)$$

where, Y is the process response or output (dependent variable), i and j are the index numbers for pattern; β_0 is the free or offset term called intercept term, x_1, x_2,.,x_i are the coded independent variables, β_i is the first order (linear) main effect, β_{ii} is the squared effect, β_{ij} is the interaction effect, ε and is the random error or allows for discrepancies or uncertainties between predicted and measured values.

Statistical analysis: The significance of independent variables and their interactions were tested by means of the analysis of variance (ANOVA). An alpha (α) level of 0.05 was used to determine the statistical significance in all analyses. Results were assessed with various descriptive statistics such as p value, F value, degrees of freedom (df), determination coefficient (R^2), adjusted determination coefficient (R^2adj), correlation coefficient (R), sum of squares, mean sum of squares.

The standardized effects of the independent variables and their interactions on the dependent variable were investigated by preparing a Pareto chart.

RESULTS AND DISCUSSION

IR analysis: IR spectra of chitosan (CTS) and cross-linked xanthated chitosan (CLXC) are shown in Fig. 1. Compared with the IR spectra of chitosan, IR spectra of cross-linked xanthated chitosan showed new characteristic absorption-SH bands at 2380 cm^{-1} and the stretching vibrations of C=S groups (1657 cm^{-1}) after xanthation. In addition, some peaks disappeared after modification such as the stretching vibration of the NH-CO group (1652 cm^{-1}), the bending vibration of N-H group (1592 cm^{-1}) and the stretching vibration of the O-H group (1024 cm^{-1}).

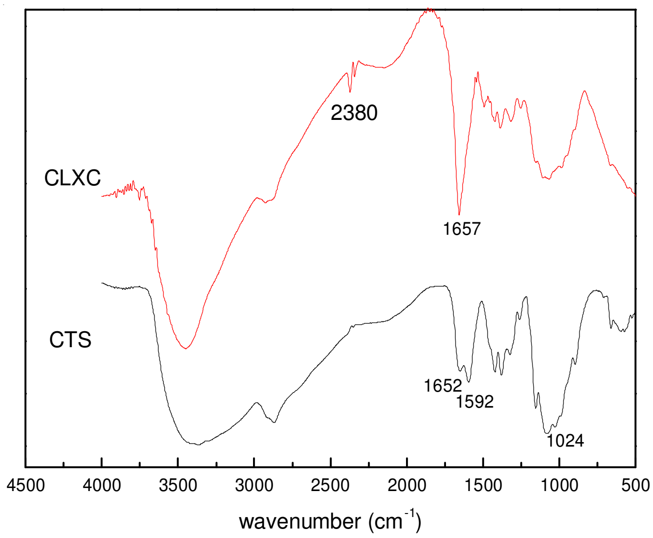

Fig. 1. IR spectra of chitosan and cross-linked xanthated chitosan

XRD analysis: XRD of chitosan (CTS) and cross-linked xanthated chitosan (CLXC) are shown in Fig. 2. For the chitosan, the strongest reflection appears at 20º, which correspond to crystal forms, cross-linked xanthated chitosan shows a less intense peak at 20º and this peak further broadens showing a decrease in the crystallinity of the substituted chitosan, which is in accordance with the literature[15]. It also had shown that decreasing the crystallinity results in an improvement in metal ion adsorption capacity.

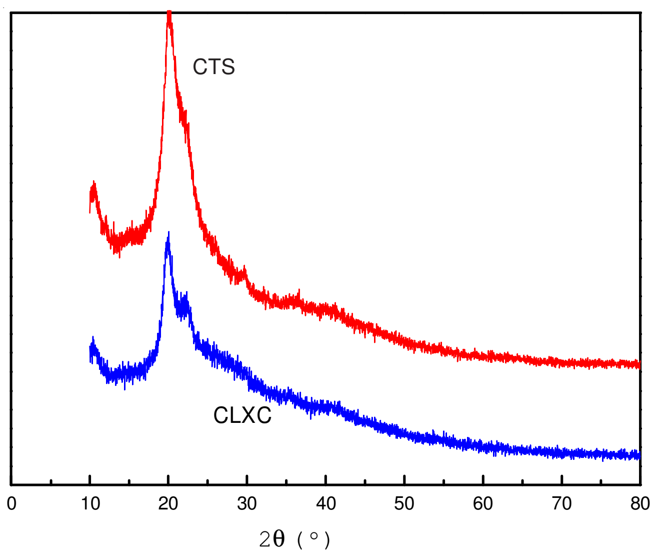

Fig. 2. XRD spectra of chitosan and cross-linked xanthated chitosan

Response surface methodological approach: The results for each trial performed as per the experimental plan are given in Table-2. The application of the response surface methodology based on the estimates of the parameters indicated an empirical relationship between the response and input variables expressed by the following quadratic model (eqn.3).

$$q(Pb^{2+}) = 412.46 + 34.27x_1 + 89.23x_2 - 59.91x_3 - 9.2x_1x_2 + 57.15x_1x_3 - 29.62x_2x_3 - 26.86x_1^2 - 98.44x_2{}^2 - 89.44x_3^2 \quad (3)$$

TABLE-2
BOX-BEHNKEN EXPERIMENTAL DESIGN FOR THE THREE INDEPENDENT VARIABLES

No	Coded values of the variables			Pb^{2+} adsorbed (mg/g)	
	x_1	x_2	x_3	Exp.	Pred.
1	0	1	-1	358.8	403.45
2	1	1	0	395.8	401.46
3	0	0	0	412.6	412.46
4	1	-1	0	200.2	241.39
5	0	-1	-1	156.6	378.93
6	0	-1	1	149.6	105.05
7	0	0	0	412.6	412.46
8	-1	1	0	392.5	351.31
9	1	0	-1	383.4	333.18
10	-1	0	-1	382.3	403.35
11	0	0	0	411.9	412.46
12	-1	-1	0	160.1	154.43
13	0	1	1	233.3	224.28
14	-1	0	1	94.6	112.46
15	1	0	1	324.3	327.66
16	0	0	0	412.6	412.46
17	0	0	0	412.6	412.46

Statistical analysis of response surface quadratic model for Pb^{2+} adsorption was tested by the analysis of variance (ANOVA) and the results were presented in Table-3. The significant of each coefficient was determined by F value and P value. The larger the value of F and the smaller the value of P, the more significant is the corresponding coefficient term. The results show that the regression model for removing Pb^{2+} are statistically significant with F value of 18.17 and P value of 0.0005. By analyzing the F value and P value, it is observed that x_1, x_2, x_3, x_1^2, x_2^2 and x_3^2 are the significant model terms for Pb^{2+} removal, while x_1x_3, x_1x_2 and x_2x_3 are the unsignificant terms. The coefficient of determination (R^2) of the model was 0.94, which indicated that the model adequately represented the relationships among the selected parameters. The analytical results showed that the experimental values were significantly in agreement with the predicted values and also suggested that the model of eqn. (3) was satisfactory and accurate.

The normal probability and studentized residuals plot were shown in Fig. 3 for the adsorption capacity of Pb^{2+}. As can be seen from Fig. 3, residuals showed the model satisfies the assumptions of ANOVA where the studentized residuals measured the number of standard deviations separating the actual and predicted values[22]. It also showed that neither response transformation needed nor there was apparent problem with normality.

By analyzing Fig. 4, it can be observed that the importance of the factors was different. The absolute value in the Fig. 4 indicates the standardized effect of the factor on the response. The positive values of effects meant that an increase in their levels lead to an increase in the metallic ion adsorption by the cross-linked xanthated chitosan. On the other hand, the negative values of the effects result to a decrease of the response (q) when their levels were increased. The fact that the absolute value for x_1 in compared to other terms indicated that this term contributes the least in prediction of the Pb^{2+} adsorption. The positive coefficients for the model components (x_1, x_2, x_2x_3) indicate favourable effect on the Pb^{2+} adsorption capacity, while the other negative coefficients for the model components show unfavourable effect on the Pb^{2+} adsorption capacity.

TABLE-3
ANOVA FOR SECOND-ORDER MODEL OF Pb^{2+} ADSORPTION

Source	Sum of squares	df	Mean square	F Value	*p*-value prob > F
Model	15733.8	9	1748.2	18.17	0.0005
x_1	2838.058	1	2838.05	29.49	0.0010
x_2	4537.23	1	4537.23	47.157	0.0002
x_3	1177.09	1	1177.09	12.23	0.0100
x_1x_2	148.23	1	148.23	1.54	0.2545
x_1x_3	10.98	1	10.99	0.114	0.7453
x_2x_3	94.96	1	94.96	0.987	0.3536
x_1^2	773.091	1	773.09	8.035	0.0252
x_2^2	2633.73	1	2633.73	27.37	0.0012
x_3^2	2851.84	1	2851.8	29.64	0.0010
Residual	673.50	7	96.21		
Lack of Fit	607.84	3	202.6	12.34	0.0172
Pure Error	65.66	4	16.41		

$R^2 = 0.94$; $Radj^2 = 0.89$

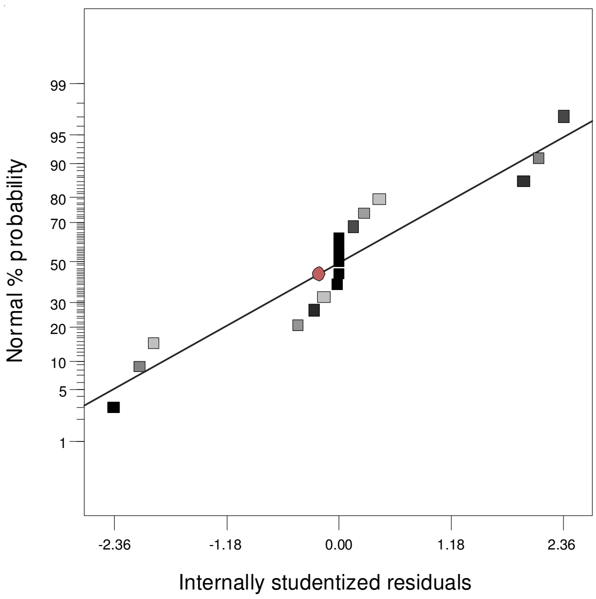

Fig. 3. Normal % probability and studentized residual plot for Pb^{2+} adsorption

Perturbation plot (Fig. 5) shows the comparative effects of all factors on adsorption capacity of Pb^{2+}. In Fig. 5, a steep curvature in q curve shows that the response of Pb^{2+} adsorption was very sensitive to factor B(contact time) and C(adsorbent dosage). The relatively flat lines of A(pH) show insensitivity of the responses to change in this factor.

To investigate the interactive effect of factors on the adsorption capacity of the Pb^{2+} on cross-linked xanthated chitosan, the response surface methodology was used and three dimensional plots were drawn. The three dimensional response surface plots (Fig. 6) were represented as a function of two factors at a time, holding other factor at the center level. As can be seen from Fig. 6, the response surfaces of mutual interactions between the variables were found to be nonlinear which indicates the interaction for factors. Furthermore, it can also be concluded that a strong interation between factors from the contour plots with elliptical shape.

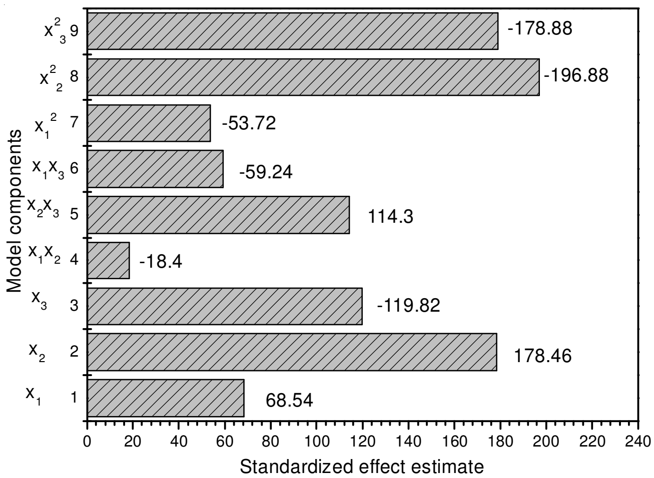

Fig. 4. Pareto chart showing the standardized effect (absolute value)

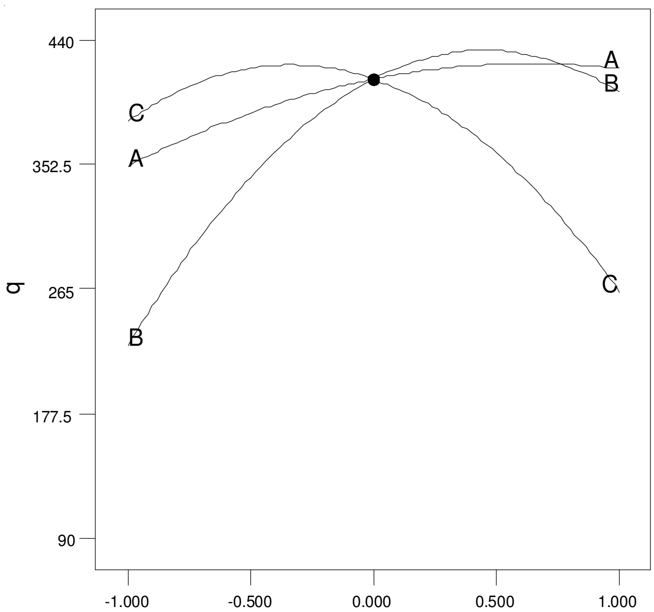

Fig. 5. Perturbation plot for Pb^{2+} adsorption

The three-dimensional response surfaces of the combined effect of adsorbent dosage and pH on adsorption of Pb^{2+} at contact time (70 min) and temperature (30 ºC) is shown in Fig. 6(a). It can be seen from the Fig. 6(a), that adsorption capacity decrease slowly at adsorbent dosage of 0.04-0.07 g and then decreases sharply with the increase in adsorbent dosage. This may be explained when the adsorbent dose increases, the number of adsorbent particles increases, but also, the denominator of eqn. (2) increased more leading to the decrease of adsorption capacity. A maximum adsorption capacity of Pb^{2+} > 419.9 mg/g was determined at adsorbent dosage 0.06 and pH 5.7.

In Fig. 6(b), adsorbent dosage is fixed at 0.07 g. The contact time effect on Pb^{2+} adsorption is reached equilibrium at 2 h. Adsorption capacity increased from 241.4 mg to 401.46 mg when the pH increased from 2 to 5.5 at 2 h. The precipitation occurrence simultaneously at pH beyond 6.5 for Pb^{2+} ions[26] and it while, at higher pH value, the adsorption of Pb^{2+} increases due to the weaker electrostatic repulsion could lead to the decrease of the adsorption capacity. A maximum adsorption capacity of Pb^{2+} > 423.9 mg/g was determined at contact time 71 min and pH 5.6.

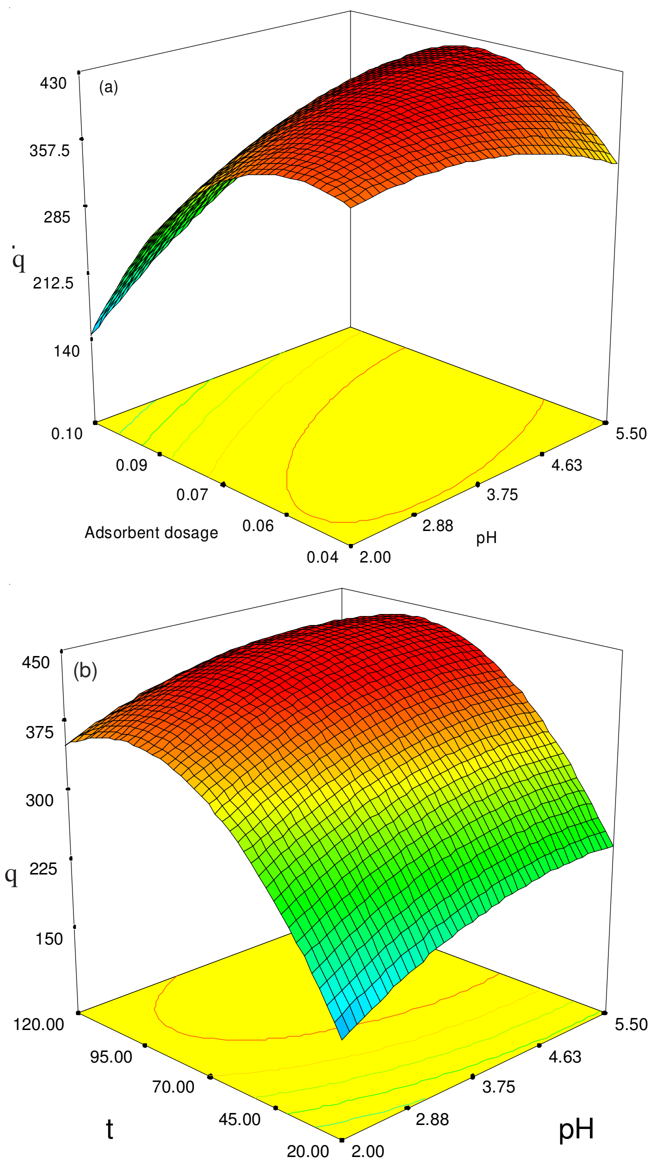

Fig. 6. Three-dimensional response surface plots and two-dimensional contour plots for Pb^{2+} by cross-linked xanthated chitosan showing variable interactions of: (a) adsorbent dosage and pH; (b) contact time and pH

Optimization process was carried out to determine the optimum value of adsorption capacity for Pb^{2+} using the Design expert 7.0.0 software. According to the software optimization step, the desired goal for each operational condition (pH, contact time and adsorbent dosage) was chosen within the range, while the response was defined as maximize to achieve highest performance. Accordingly, the optimum working conditions and respective adsorption capacity were established and the results are presented in Table-4. To verify the validity of the proposed model, several additional batch experiments were carried under the optimized conditions. The confirmatory experiments were conducted with the parameters as suggested by the model and adsorption capacity was found to be 446.8 mg/g for Pb^{2+} adsorbed, which is in agreement with the predicted ones, indicating suitability of the model.

TABLE-4
OPTIMUM VALUES OF THE PROCESS PARAMETER FOR MAXIMUM ADSORPTION CAPACITY Pb^{2+}

Parameter	Optimum value for adsorption capacity
x_1 (time, min)	95.00
x_2 (pH)	5.66
x_3 (adsorbent, g)	0.058
Adsorption capacity (mg/g)	448.5

Comparison study: A comparison of several adsorbents employed for Pb^{2+} adsorption is presented in Table-5. As can be seen from Table-5, cross-linked xanthated chitosan are within the range of sorption capacity of several adsorbents. These adsorbents present lower adsorption capacities than cross-linked xanthated chitosan, indicating cross-linked xanthated chitosan is promising adsorbent for Pb^{2+} than those reported previously.

TABLE-5
COMPARISON OF DIFFERENT ADSORBENTS FOR Pb^{2+} ADSORPTION

Adsorbent	q (mg/g)	Ref.
Tripolyphosphate-modified kaolinite clay	78.74	[2]
Sulfured orange peel	164.00	[23]
Orange peel xanthate	204.50	[24]
Bentonite	14.60	[25]
N-succinyl-chitosan	353.60	[26]
Living bio-sludge	250.00	[27]
Chitosan	141.10	[28]
Cyanobacterium Gloeocapsa sp	232.56	[29]
Clinoptilolite	27.70	[30]
Chitosan functionalized with xanthate	332.60	[31]

Conclusion

Response surface methodology was applied successfully for the optimization of operational conditions to the adsorption process of Pb^{2+} on cross-linked xanthated chitosan. The present study clearly demonstrated the applicability of cross-linked xanthated chitosan for Pb^{2+} adsorbed. Under the optimized conditions of pH 5.66, adsorbent dosage 0.058 g and time 95 min, the experimental response values (446.8 mg/g) agreed with the predicted ones(448.5 mg/g), indicating suitability of the model and the success of response surface methodology in optimizing the conditions of adsorption of Pb^{2+} on cross-linked xanthated chitosan. Comparison study clearly showed that cross-linked xanthated chitosan was one of the suitable adsorbents for Pb^{2+} adsorption process.

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