Journal of Hazardous Materials 161 (2009) 718–722

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Removal of Pb(II) from aqueous solution on chitosan/TiO_2 hybrid film

Yugui Tao [a,b,*], Lianbin Ye [a], Jun Pan [a], Yaoming Wang [a], Bin Tang [a,b]

[a] Engineering Technology Research Center of Microbial Fermentation, Anhui Province, China
[b] Department of Biochemical Engineering, Anhui University of Technology and Science, Wuhu 241000, China

ARTICLE INFO

Article history:
Received 7 November 2007
Received in revised form 5 April 2008
Accepted 7 April 2008
Available online 11 April 2008

Keywords:
Chitosan
Adsorption of Pb(II)
Box–Behnken design
Optimization

ABSTRACT

This paper presents the adsorption of Pb(II) from aqueous solution using chitosan/TiO_2 hybrid film (CTF) adsorbent. Batch experiments were carried out as a function of solution pH, adsorption time, Pb(II) concentration and temperature. The equilibrium data fitted well with the linear Freundlich model. The adsorption process was proved to be the second grade reaction and the theoretically maximum adsorption amount at equilibrium was 36.8 mg-Pb/g. The influence parameters were optimized by response surface method (RSM), such as initial metal concentration, pH and temperature. The extreme points were gained by the Statistical Analysis System software: initial metal concentration is 50–55 mg/l, pH is 3–4 and temperature is 60 °C. Very high regression coefficient (R^2 = 0.9689) indicates excellent evaluation of experimental data by second-order polynomial regression model. Under this condition the theoretical adsorption efficiency is 90.6%. It illuminates that this model is reliable to optimize the adsorption process and CTF is suitable for adsorbing Pb(II) from aqueous solution.

1. Introduction

The removal of heavy metal ions from aqueous solution has been taking on great importance in recent years, either for pollution control or for raw material recovery. Among the heavy metal ions, lead(II) holds a distinct position due to its long-term and widespread use. Lead enters into the environment as a result of both natural process and factitious activities [1–3]. Today, several methods have been developed for removing lead in aqueous solution such as chemical precipitation [4], adsorption [5], biosorption [6], electrodialytic process [7] and so on.

Adsorption has been shown to be an economically feasible alternative method for removing lead from wastewater and water supplies [8,9]. Several adsorbents, such as active carbon, herbaceous peat, fiber, rice husk ash, sawdust and starch have been used for removing heavy metal ions from aqueous solution. It has been well known that chitosan demonstrates the unique adsorption ability towards many metal cations. Now this material attracts growing attention in view of its utilization for removing heavy metals cations from diluted aqueous solution [10]. A great number of chitosan derivatives have already been obtained to adsorb metal ions by grafting new functional groups on the chitosan backbone. The new functional groups are incorporated with chitosan to increase the density of adsorption sites, to change the pH range for metal adsorption and to change the adsorption sites in order to increase adsorption selectivity for the target metal [11].

Chitosan/TiO_2 hybrid film (CTF) was synthesized by sol–gel method through 0.27 g chitosan and 11.6 ml acetic acid reaction with 0.54 ml tetrabutyl titanate and *n*-butyl alcohol mixture (molar ratio of them is 1:4). The as-obtained CTF is grafted Ti–O group on the chitosan backbone as reported in our former research [12]. Herein we investigate the adsorption ability of CTF towards Pb(II) from aqueous solution. The influence conditions on adsorption capacity of CTF were investigated, such as different concentration of Pb(II), pH value and temperature. Then those parameters were optimized by response surface method (RSM). This information will be useful for further applications in the treatment of wastewater.

The Box–Behnken model [13–15] was used to statistically design the experiments to evaluate the interactive effects of process parameters for optimizing adsorption. The Statistical Analysis System software (SAS Institute Inc., Cary, NC, USA, Version 8.0) was used to obtain optimal working parameters and to generate response surface graphs [16,17], which is widely used in statistics research and especially industry.

2. Experimental

2.1. Materials and instrument

Chitosan was obtained from ShangHai Fine Chemical Factory Co., Ltd. Its degree of deacetylation was 95%. Tetrabutyl titanate (TBT)

* Corresponding author at: Engineering Technology Research Center of Microbial Fermentation, Anhui Province, China. Tel.: +86 553 2871255; fax: +86 553 2871255.
E-mail address: taoyugui888@yahoo.com.cn (Y. Tao).

0304-3894/$ – see front matter
doi:10.1016/j.jhazmat.2008.04.012

was chemical grade obtained from Sinopharm Chemical Reagent Co., Ltd. Acetic acid and normal butyl alcohol were analytical reagent.

The CTF was synthesized with 0.27 g chitosan, 11.6 ml acetic acid and 0.54 ml mixture (tetrabutyl titanate and *n*-butyl alcohol). Lead nitrate was analytical reagent and it was used without further purification. Nitric acid was analytical reagent obtained from Nanjing Chemical Reagent No.1 Factory.

Pb(II) was measured by atomic absorption spectrometer (PerkinElmer AAnalyst 700), wave-length is 283.3 nm, lamp type is HCL, desired current is 8.

2.2. Removal studied by using CTF

2.2.1. Influence of pH on adsorption capacity

The adsorption experiments were followed batchwise in aqueous solutions of lead ion. 0.1 g CTF was dipped into 20 ml Pb(II) solution of concentration (20 mg/l). Solution pH was adjusted from 1 to 6 using either 1 M NaOH or 1 M HNO_3, for Pb(II) can occur precipitation when the solution pH is above 6. The experiment was controlled at 30 °C in an incubator. After adsorption sufficient (t = 300 min), the solution was percolated and the residual Pb(II) in the filtrate was measured. The content of remaining Pb(II) was checked by an atomic absorption spectrophotometer. All the experiments were performed in triplicates and their mean values are reported.

2.2.2. Kinetic experiments

The kinetic experiments were performed using Pb(II) concentration (200 mg/l) with 0.1 g CTF. The experiments were controlled at pH 3.0 and the adsorbent time varied from 30 to 300 min. The residual concentration of Pb(II) in the filtrate was measured similar to the above procedure described in Section 2.2.1.

2.2.3. Adsorption isotherm

The same procedure described for the influence of pH on adsorption capacity was used. Adsorption isotherm studies were carried out using 10 different initial Pb(II) concentrations varying from 10 to 500 mg/l. However, 50 ml Pb(II) solution of different concentration was added into the glass vessel respectively. The initial pH was adjusted to 3.0 and the temperature varying from 20 to 60 °C.

The measured liquid phase concentrations were then used to calculate the adsorption capacity, Q (mg/g) of the adsorption amount using the following mass balance equation [18]:

$$Q = \frac{V(C_1 - C_2)}{W} \quad (1)$$

Table 1
The range of full factorial value

Factors	Levels		
	−1	0	1
pH, X_1	2	3	4
Pb(II) concentration, X_2 (mg/l)	10	50	90
Temperature, X_3 (°C)	20	40	60

where Q is adsorption amount (mg/g), W is the weight of CTF (g), V is the volume of solution (l), and C_1 and C_2 are the concentrations of Pb(II) before and after adsorption, respectively (mg/l).

2.3. Optimization of adsorption parameters using RSM approach

Based on the above research, RSM was used to optimize the adsorption parameters. In the present study, Box–Behnken model for three variables (metal concentration, pH and temperature), each with two levels (the minimum and the maximum), was used as experimental design model. The model has the advantage that it permits the use of relatively few combinations of variables for determining the complex response function [19]. A total of 15 experiments are required to be performed to calculate 10 coefficients of second-order polynomial equation [20]. Through the experimental design model, pH (2–4), Pb(II) concentration (10–90 mg/l) and temperature (20–60 °C), were taken as input variables. The adsorption efficiency of Pb(II) from the aqueous solution was taken as response value of the design. The range of full factorial value was shown in Table 1. The experimental design matrix derived from the Box–Behnken model is shown in Table 2. The adsorption efficiency of Pb(II) by CTF in different experimental conditions based on the experimental design matrix was estimated, the results of which have also been included in the same table.

A second-order polynomial model where interaction terms have been fitted to the experimental data obtained from the Box–Behnken model experiment can be stated in the form of the following equation:

$$Y = a_o + \sum a_i x_i + \sum a_{ii} x_i^2 + \sum a_{ij} x_i x_j \quad (2)$$

where Y is the efficiency of Pb(II) adsorbed, a_o is offset term, a_i is first-order main effect, a_{ii} is second-order main effect and a_{ij} is the interaction effect. The data were subjected to analysis variance and the coefficient of regression (R^2) was calculated to find out the goodness of fit of the model [21].

Table 2
Box–Behnken design matrix for three variables along with observed response

Experimental run	Variables			Adsorption efficiency, Y%
	pH, X_1	Pb(II) concentration, X_2 (mg/l)	Temperature, X_3 (°C)	
1	−1	−1	0	30.84
2	−1	1	0	35.16
3	1	−1	0	55.80
4	1	1	0	59.06
5	0	−1	−1	61.56
6	0	1	−1	67.98
7	0	−1	1	71.12
8	0	1	1	76.52
9	−1	0	−1	40.39
10	1	0	−1	57.99
11	−1	0	1	52.86
12	1	0	1	88.21
13	0	0	0	81.80
14	0	0	0	80.94
15	0	0	0	79.99

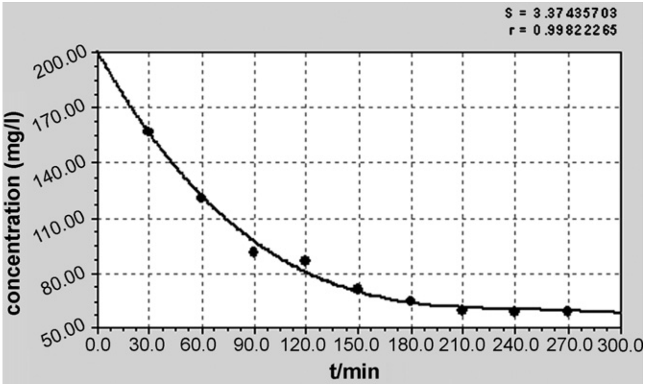

Fig. 1. The influence of solution pH on adsorption capacity (C_0 = 20 mg^{-1}/l, CTF 0.1 g, temperature 30 °C, t = 300 min).

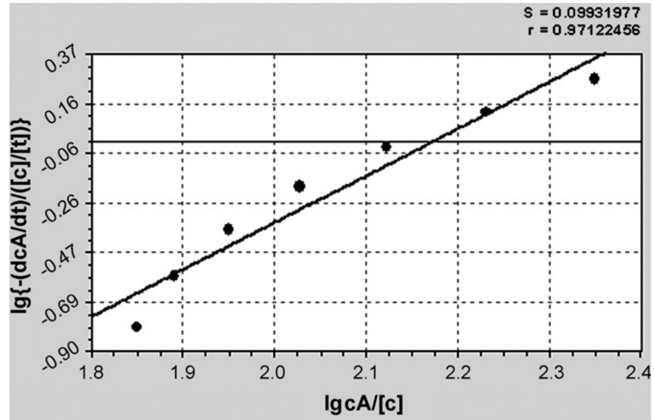

Fig. 2. The relation curve between concentration and t (C_0 = 200 mg^{-1}/l, CTF 0.1 g, t_0 = 0 min, t_{max} = 300 min, temperature 30 °C, pH 3.0).

3. Results and discussion

3.1. Influence of pH on adsorption capacity

The influence of solution pH on adsorption was investigated. When the initial pH increased to 3.0, the adsorption amount of Pb(II) by CTF increased. But when the initial pH increased from 3.0 to 6.0, the adsorption efficiency of Pb(II) decreased a little. For Pb(II) can exists in different form under different pH value, the adsorption efficiency of CTF changed. In addition, the adsorption efficiency was very slow at pH 1.0, as CTF can be dissolved in the high acidity solution. Pb(II) in aqueous solution may suffer solvation, hydrolysis and polymerization [22,23]. Through this processes the following cation could be formed:

$$M^{2+} + nH_2O \Leftrightarrow M(H_2O)_n{}^{2+};$$

$$M(H_2O)_n{}^{2+} \Leftrightarrow M(H_2O)^{n-1}(OH)^{+} + H^{+};$$

$$nM^{2+} + mH_2O \Leftrightarrow M_n(H_2O)m^{(2n-m)+} + mH^{+}$$

It has been reported that lead can form many polynuclear species such as $Pb_2(OH)^{3+}$, $Pb_3(OH)^{4+}$, etc. In dilute solutions the formation of Pb(II) hydrolysis products occurs at pH above 6. Therefore the higher the pH value is, the stronger the hydrolysis and polymerizing actions are. It affects CTF combination to Pb(II), so the adsorption capacity will descend.

3.2. Adsorption kinetics

The kinetics of the adsorption has to be determined in order to establish the time course of the metal uptake. Vasconcelos et al. [24] used chitosan and its modified new chelating polymer to study Cu(II) ion adsorption in aqueous solution. The results showed that the adsorption kinetics data were best fitted with the pseudo second-order model, which gave a correlation coefficient of 0.999 and a 1.53% deviation between experimental and calculated q_e values.

Time-dependent (30–300 min) adsorption of Pb(II) on CTF is shown in Fig. 1, as expected, the adsorption process was slow and a visible equilibrium reached within 240 min.

To study the adsorption kinetics, the kinetics reaction series should be confirmed first. The velocity equation can be depicted in one common formula:

$$-\frac{dc_A}{dt} = k_1 c_A^n \quad (3)$$

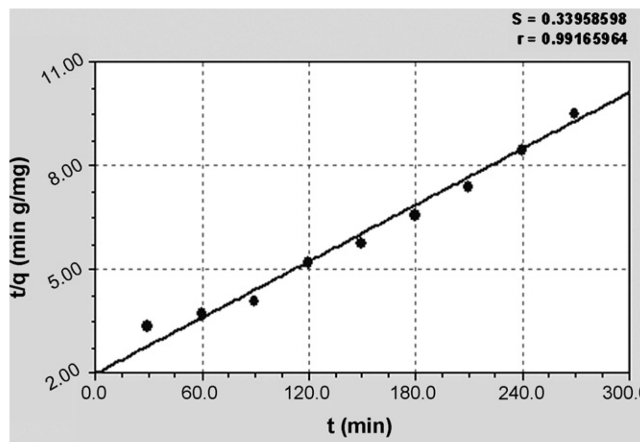

Fig. 3. Plot of $\lg\{-(dc_A/dt)/([c]/[t])\}$ vs. $\lg c_A/[c]$ (C_0 = 200 mg^{-1}/l, CTF 0.1 g, t_0 = 0 min, t_{max} = 240 min, temperature 30 °C, pH 3.0).

One new formula was formed after taken logarithm of Eq. (3):

$$\lg\left\{-\frac{(dc_A/dt)}{([c]/[t])}\right\} = \frac{\lg k_1}{[k_1]} + \frac{n \lg c_A}{[c]} \quad (4)$$

where c_A is the concentration of lead at time t (mg/l), k_1 is the velocity constant (mg^{-1} l min^{-1}), $[c]$, $[t]$ and $[k_1]$ are the dimensions of c, t, k_1, respectively. When temperature is determinate, k and n being constant, so $\lg\{-(dc_A/dt)/([c]/[t])\}$ versus $\lg c_A/[c]$ is linear as Fig. 2 shows, the gradient of the beeline is equal to the kinetics reaction series [25,26]. This linear of Fig. 2 fits the equation:

$$y = -4.3243572 + 2.0305639x \quad (5)$$

So the kinetics reaction series is second grade and data from the kinetics experiment were fitted to the equation [27] to determine Pb(II) sorption capacity (q_e) and rate constant (k_2). This model assumes that adsorption follows the Langmuir equation. The kinetic

Table 3
Adsorption isotherm parameters for metal adsorption on hybrid film at different temperature

Initial temperature (°C)	Langmuir equation			Freundlich equation		
	X_m (mg/g)	b (l mg^{-1})	r	k (mg/g)	$1/n$	r
20	145.53	0.01348	0.985	3.7376	0.6531	0.993
40	143.8	0.01611	0.983	4.2405	0.6345	0.992
60	163.34	0.01469	0.973	4.7239	0.636	0.996

Table 4
Mean square analysis of full factorial design experiment

Source	Degree freedom	Sum of square	Mean square	F value	Probability > F	R^2 value
Model	9	4252.706	472.5229	17.28525	0.002946	0.9689
Error	5	136.6838	27.33677			
Total	14	4389.39				

rate equations can be written as follows:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (6)$$

where q_t, and q_e are the amounts of lead adsorbed at time t, and at equilibrium (mg/g), respectively, and k_2 is the equilibrium rate constant for second-order sorption (g mg^{-1} min^{-1}). By integrating Eq. (6) for the boundary conditions (t = 0 to t = t; q_t = 0 to q_t = q_t) the following linearized form can be obtained:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

A plot of t versus t/q_t was used to determine values of k_2 and q_e. As Fig. 3 shows, the data was described adequately by this model (R^2 = 0.992). The adsorption capacity of CTF on Pb(II) at equilibrium (q_e) as determined using Eq. (6) was 36.8 mg-Pb/g.

3.3. Adsorption isotherms

Adsorption characteristics can be depicted by an adsorption isotherm. Adsorption isotherm is the presentation of the amount of solute adsorbed per unit weight of adsorbent as a function of the equilibrium concentration in the solution at constant temperature. Boddu et al. [28] described the equilibrium adsorption of chitosan-coated biosorbent removal of arsenic(III) and arsenic(V) with three models, such as Langmuir, Freundlich, and Redlich–Peterson adsorption models. All three models represented the experimental data well. The monolayer adsorption capacity of the sorbent, as obtained from the Langmuir isotherm, was 56.50 and 96.46 mg/g of chitosan for As(III) and As(V), respectively. Two of the most commonly used isotherm theories have been adopted in this research, namely, the Langmuir and Freundlich isotherm theories [29]. The form of Langmuir equation can be expressed by the following Eq. (8):

$$\frac{C_e}{q_e} = \frac{1}{bX_m} + \frac{C_e}{X_m} \quad (8)$$

where C_e is the equilibrium concentration of remaining metal in the solution (mg/l), q_e is the amount of metal adsorbed per unit weight of adsorbent (mg/g of CTF), X_m is the amount of adsorption capacity (mg/g), b is a constant that relates to the heat of adsorption (l mg^{-1}). Freundlich isotherm model can be represented by Eq. (9):

$$\log q_e = \log k_3 + \frac{1}{n}\log C_e \quad (9)$$

where k_3 (mg/g) and $1/n$ are the constant characteristics of the system [30].

As Table 3 shows, both the models adequately predicted adsorption of Pb(II) on CTF, however, only the Freundlich equation yielded a better fit. This suggests that CTF has characteristics with several possible functional groups responsible for adsorption of Pb(II). In addition, the parameter k of Freundlich model increased as the temperature enhanced, so did the adsorption amount of Pb(II). The increase in metal uptake with increasing temperature may be due to either higher affinity of sites for metal or an increase in the number of binding sited on CTF [31].

3.4. RSM approach for adsorption optimization

The empirical relationship between the response and various input variables obtained from the Box–Behnken model are shown in Table 3. It shows distinct response pattern in terms of percent lead under different combinations of initial metal concentration, pH and temperature.

Table 4 displays the retrogressive mean square analysis. The probability is 0.002946 (**P < 0.01) which indicates that the prominence and reliability of retrogressive equation are so high. High value of R^2 (0.9689) indicates a high dependence and correlation between the observed and the predicted values of response. After retrogressive analysis, one quadratic model equation was established as follows:

$$\begin{aligned} Y_1 = {} & 80.91 + 12.72625X_1 + 3.21X_2 + 6.81375X_3 - 22.56375X_1X_1 \\ & - 0.265X_1X_2 + 4.4375X_1X_3 - 13.13125X_2X_2 \\ & - 0.255X_2X_3 + 1.51625X_3X_3 \end{aligned}$$

The response surface figures of regression equation are shown in Fig. 4, from which some interactions between the three factors could be found. First it indicates that pH value was prominent to the effect of adsorption efficiency and the maximum adsorption efficiency was got around pH 3.0. Second it shows that adsorption

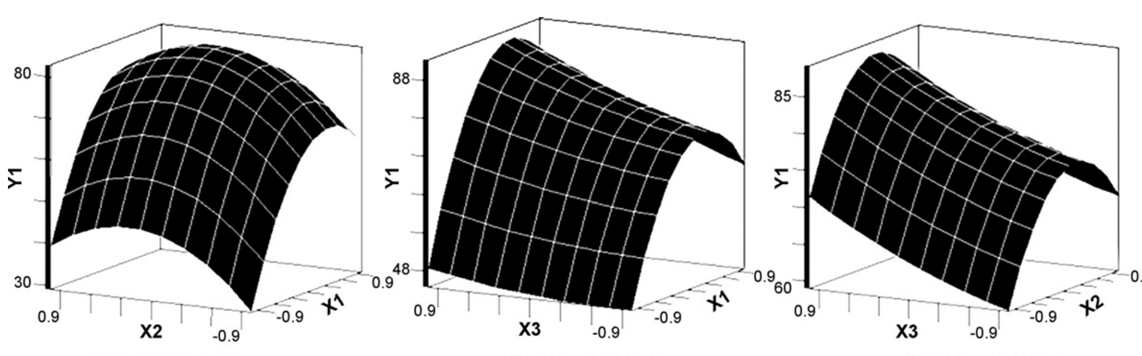

Fig. 4. Langmuir kinetics curve of adsorption lead on CTF (C_0 = 200 mg^{-1}/l, CTF 0.1 g, temperature 30 °C, pH 3.0).

efficiency increases with increasing Pb(II) concentration and afterwards shows a slight decrease. Finally it also illuminates that the adsorption efficiency increases with increasing temperature as it has been described above. The extreme points were also gained from the SAS software: initial metal concentration is 50–55 mg/l, pH value is 3–4 and temperature is 60 °C. Under this condition the theoretical adsorption efficiency is 90.6%. It illuminates that this model is reliable to optimize the adsorption parameters and CTF is more useful for adsorbing Pb(II) from aqueous solution.

4. Conclusions

The removal of lead ions from aqueous solution is carried out using chitosan/TiO_2 hybrid film. The CTF exhibited high sorption capacity, and it was found that it is favorable adsorbent for Pb(II) removal from aqueous solution. The Pb(II) uptake performance was strongly affected by pH. Optimal conditions for Pb(II) adsorption were found using Box–Behnken model to be pH 3–4, temperature 60 °C and metal concentration 50–55 mg/l. It indicates the reaction parameter optimization using response surface method is scientific and valid. This work shows some importance in removing metal cations. And our current research is using CTF as an imprinted plate to selectively adsorb metal cations.

Acknowledgements

This research was supported by the National Nature Science Foundation of China (no. 20276001). We thank Wuhu Entry-Exit Inspection and Quarantine of China for inspection.

References

[1] D.C. Adriano, Trace Elements in the Terrestrial Environment, Springer-Verlag, New York, 1986.
[2] D.M. Heil, Z. Samani, A.T. Hanson, B. Rudd, Remediation of lead contaminated soils by EDTA. I. Batch and column studies, Water Air Soil Pollut. 13 (1999) 77–95.
[3] M.J. Eick, J.D. Peak, P.V. Brady, J.D. Pesek, Kinetics of lead sorption and desorption on goethite: residence time effect, Soil Sci. 164 (1999) 28–39.
[4] S.K.A. Solmaz, G.E. Üstün, A. Birgül, Y. Taşdemir, Treatability studies with chemical precipitation and ion exchange for an organized industrial district (OID) effluent in Bursa, Turkey, Desalination 217 (2007) 301–312.
[5] M.M. Matlock, B.S. Howerton, D.A. Atwood, Irreversible precipitation of mercury and lead, J. Hazard. Mater. 84 (2001) 73–82.
[6] J.T. Matheickal, Q.M. Yu, Biosorption of lead(II) and copper(II) from aqueous solutions by pre-treated biomass of Australian marine algae, Bioresour. Technol. 69 (1999) 223–229.
[7] C. Ferreira, P. Jensen, L. Ottosen, A. Ribeiro, Removal of selected heavy metals from MSW fly ash by the electrodialytic process, Eng. Geol. 77 (2005) 339–347.
[8] M. Dakiky, M. Khamis, A. Manassra, M. Mer'eb, Selective adsorption of chromium(VI) in industrial wastewater using low-cost abundantly available adsorbents, Adv. Environ. Res. 6 (2002) 533–540.
[9] W.S. Peterlene, A.A. Winkler-Hechenleitner, E.A.G. Pineda, Adsorption of Cd(II) and Pb(II) onto functionalized formic lignin from sugar cane bagasse, Bioresour. Technol. 68 (1999) 95–100.
[10] A.V. Kucherov, N.V. Kramareva, E.D. Finashina, A.E. Koklin, L.M. Kustov, Heterogenized redox catalysts on the basis of the chitosan matrix 1. Copper complexes, J. Mol. Catal. A: Chem. 198 (2003) 377–389.
[11] R. Jayakumar, M. Prabaharan, R.L. Reis, J.F. Mano, Graft copolymerized chitosan-present status and applications, Carbohydr. Polym. 62 (2005) 142–158.
[12] Y.G. Tao, J. Pan, S.L. Yan, B. Tang, L.B. Zhu, Tensile strength optimization and characterization of chitosan/TiO2 hybrid film, Mater. Sci. Eng. B-Solid 138 (2007) 84–89.
[13] G.E.P. Box, W.G. Hunter, J.S. Hunter, Statistics for Experimenters: An Introduction to Design, Data Analysis and Model Building, John Wiley & Sons, New York, 1978.
[14] S.L.C. Ferreira, W.N.L. dos Santos, C.M. Quintella, B.B. Neto, J.M. Bosque-Sendra, Doehlert matrix: a chemometric tool for analytical chemistry, Talanta 63 (2004) 1061–1067.
[15] A.S. Souza, W.N.L. dos Santos, S.L.C. Ferreira, Application of Box–Behnken design in the optimisation of an on-line pre-concentration system using knotted reactor for cadmium determination by flame atomic absorption spectrometry, Spectrochim. Acta B: At. Spectrosc. 60 (2005) 737–742.
[16] G.A. Corte's, M.Y. Salinas, S.E. Martı'n-Martinez, Stability of anthocyanins of blue maize (Zea mays L.) after nixtamalization of separated pericarp-germ tip cap and endosperm fractions, J. Cereal Sci. 43 (2006) 57–62.
[17] T.J. Vyn, D.C. Hooker, Assessment of multiple- and single-factor stress impacts on corn, Field Crop Res. 75 (2002) 132–137.
[18] R. Coskun, C. Soykan, Lead(II) adsorption from aqueous solution by poly(ethyleneterephthalate)-g-acrylamide fibers, J. Polym. Res. 13 (2006) 1–8.
[19] M. Muthukumar, D. Mohan, M. Rajendran, Optimization of mix proportions of mineral aggregates using Box–Behnken design of experiments, Cem. Concr. Res. 25 (2003) 751–758.
[20] C.A. Toles, W.E. Marshell, M.M. Johns, GAC from nutshells for the uptake of metal ions and organic compounds, Carbon 35 (1997) 1414–1470.
[21] B. Kiran, A. Kaushik, C.P. Kaushik, Response surface methodological approach for optimizing removal of Cr(VI) from aqueous solution using immobilized cyanobacterium, Chem. Eng. J. 126 (2007) 147–153.
[22] B.M. Babic, S.K. Milonjic, M.J. Polovina, S. Cupic, B.V. Kaludjerovic, Adsorption of zinc, cadmium and mercury ions from aqueous solutions on an activated carbon cloth, Carbon 40 (2002) 1109–1115.
[23] V. Gomez-Serrano, A. Macias-Garcia, A. Espinosa-Mansilla, C. Valenzuela-Calahorro, Adsorption of mercury, cadmium and lead from aqueous solution on heat-treated and sulphurized activated carbon, Water Res. 32 (1998) 1–4.
[24] H.L. Vasconcelos, T.P. Camargo, N.S. Goncalves, A. Neves, Chitosan crosslinked with a metal complexing agent: synthesis, characterization and copper(II) ions adsorption, React. Funct. Polym. 68 (2008) 572–579.
[25] S. Glasstone, K.J. Laidler, H. Eyring, The Theory of Rate Processes the Kinetics of Chemical Reactions, Viscosity, Diffusion and Electrochemical Phenomena, McGraw-Hill Book Company, New York, 1941.
[26] R.W. Haywood, Equilibrium Thermodynamics, John Wiley & Sons, New York, 1980.
[27] Y.S. Ho, G. McKay, The kinetics of sorption of divalent metal ions onto sphagnum peat moss, Water Res. 34 (2000) 735–742.
[28] V.M. Boddu, K. Abburi, J.L. Talbott, E.D. Smith, R. Haasch, Removal of arsenic(III) and arsenic(V) from aqueous medium using chitosan-coated biosorbent, Water Res. 42 (2008) 633–642.
[29] V. Chantawong, N.W. Harvey, V.N. Bashkin, Comparison of heavy metal adsorptions by thai kaolin and ballclay, Water Air Soil Pollut. 148 (2003) 111–125.
[30] S.D. Faust, O.M. Aly, Adsorption Processes for Water Treatment, Butterworth Publishers, Boston, 1987.
[31] A.M. Marques, X. Raca, M.D. Simon-Pujol, M.C. Fuste, F. Congregado, Uranium accumulation by *Pseudomonas* sp. eps-5028, Appl. Microbiol. Biotechnol. 35 (1991) 406–410.