Statistical screening of hexavalent chromium biosorption by *Sargassum*

Hooshyar Hossini[1], Abbas Rezaee[*1], Seyedomid Rastegar[1]

1) *Department of Environmental Health, Faculty of Medical Sciences, Tarbiat Modares University, Tehran, Iran*

** Author for Correspondence: e-mail: rezaee@modares.ac.ir*

Received: 21 Oct. 2013, Revised: 02 Dec. 2013, Accepted: 30 Dec. 2013

ABSTRACT

The aim of this study was to investigate the statistical screening of hexavalent chromium, Cr (VI), from an aqueous solution using brown seaweed *Sargassum* as a biosorbent. The biosorption process conditions were evaluated with the statistical screening followed by Plackett-Burman design. The effect of solution pH, contact time, initial chromium and nitrate concentrations were studied. The experimental data were fitted to the Langmuir, Freundlich and Dubinin-Radushkevich isotherm models. Plackett-Burman design showed the contact time and pH are the most important parameters influencing the Cr (VI) biosorption onto *Sargassum*. The optimum pH, contact time, the initial biosorbent dosage and initial Cr (VI) and nitrate concentration were found to be 3, 120 min, 1.3 g, 50 mg/L and 1000 mg/L, respectively. The results indicated that the Freundlich model was the most suitable for Cr (VI) biosorption onto *Sargassum.*

Key words: Statistical screening, Hexavalent chromium, Plackett-Burman design, *Sargassum*, Biosorption, Isotherm

INTRODUCTION

Effluent issued from tanning, metallurgy, electroplating and other industries contain chromium ions that release in the environment such as water and soil [1]. Chromium is a heavy metal with various oxidation states; however, the Cr (VI) and Cr (III) are common in aqueous solutions. The two oxidation states have different properties. Cr (III) is relatively an essential micronutrient, while Cr (VI) is a contaminant because of its toxicity to humans and animal life. Chromium has been classified as a group I human carcinogen by the International Agency for Research on Cancer [2, 3]. Several treatment methods such as ion exchange, reduction, membrane technology electrochemical precipitation, and adsorption have been developed for chromium removal [4, 5]. Traditionally, the precipitation has been the most commonly used. Although chemical precipitation is good enough in terms of chromium removal from wastewater but it produces high sludge volume containing toxic metal ions which its disposal has relative high costs and possibility of ground water contamination [6]. Therefore, the development of a simple, robust, and cost-efficient technology for chromium removal is critical. Recent researches have been focused on use of non-conventional alternative including different biomaterials such as: waste sludge, algae, yeast and fungal biomass [7]. The removal of heavy metals by passive binding to non-living biomaterials, commonly referred to as biosorption, has gained a considerable amount of attention in recent decades because biosorption has many advantages over traditional methods when combined with appropriate regeneration steps. For example, biosorption is ecosystem friendly, cost efficient and highly selective [8, 9]. The use of biomaterials for chromium ions removal from industrial wastewater has become as an alternative technique to conventional techniques [10]. It has been reported in different studies that the seaweed *Sargassum* as biomaterial has a metal adsorption capacity superior to other biosorbents compared to the biosorption capacity of the other biomaterials. It is reported that *Sargassum* sp. is the best accumulator of heavy metal ions due to its powerful functional groups on surface [11]. Furthermore, application of dead biomaterial is nutrient independent, and it can be easily maintained in toxic environments [12]. Application of *sargassum* for biosorption of heavy metal ions such as chromium from aqueous solutions have been investigated by many researchers. They have evaluated chromium adsorption by *Sargassum* by investigating the influence of experimental parameters, such as pH, contact time, adsorbent dosage, metal ion concentration, and so on. In conventional method, one studied parameter set as variable at time while keeping the other parameters at fixed value. However, obtaining optimum value for each parameter is to some extend difficult. For solving this problem in term of process scale-up, statistical analysis offers several advantages over conventional method being rapid and reliable, helps understanding the interactions among the adsorbents and adsorbates and reduces the total

number of experiments. It can enormously save time and consumed chemical [13]. Initial screening of the ingredients is done to understand the significance of their effect on the product formation and then a few better ingredients are selected for further optimization [14]. Moreover, the design is orthogonal in nature and thus gives pure effect of each variable not confounded with interactions among variables. The Plackett–Burman design is a reliable method to understand the effective factors of the biosorption under a given set of conditions in a very small number of experiments. To the best of our knowledge, the use of Plackett–Burman design has not been investigated for the biosorption of heavy metal ions by *Sargassum*, thus, the main objective of the present investigation was to screen and optimize the studied parameters using Plackett–Burman experimental design for the biosorption of chromium (VI) from aqueous solution by *sargassum* algae.

MATERIALS AND METHODS

The biosorbent preparation

The biosorbent, *Sargassum sp*., was collected from the Persian Gulf. After collecting the material, s*argassum* was washed with distilled water to remove particulate material from its surface, and dried at 70°C in an oven for 24 h. Then, 1 kg of *Sargassum sp* was sub-sampled for use in the experiments. In order to ensure homogeneousity of the biosorbent, standard sampling was applied. Dried biosorbent was ground into a powder with a grinder and subsequently sieved using standard sieves to obtain particle size between 0.3–0.7 mm.

Preparation of chromium and nitrate solutions

Stock solutions of Cr (VI) and nitrate were made by adding the specific values of potassium dichromate ($K_2Cr_2O_7$) and potassium nitrate (KNO_3) in deionized water. These solutions stored at room temperature.

Batch adsorption experiments

Batch experiments were performed in 250 mL containing 100 mg/L of Cr (VI) solutions to explore the effects of solution pH, contact time, initial concentration of Cr (VI) and nitrate and adsorbent concentration on Cr (VI) biosorption by *sargassum* at room temperature (25±1°C). The pH value was adjusted to the desired value with 0.1 M HCl or 0.1 M NaOH throughout the experiment. A magnetic stirrer was used to agitate the solution continuously. After shaking, 1 mL sample was removed from the flasks and centrifuged at 15000 rpm for 5 min and the concentration of Cr (VI) in solution was determined. A control flask without *sargassum* was used to determine Cr (VI) biosorption in the absence of the biosorbent. All experiments were performed in triplicate to determine the precision of the results.

Analytical method

The residual concentration of Cr (VI) in solution was determined spectrophotometrically (Double Array Spectrophotometer, Ray UV 9200) by diphenyl-carbazide method [15]. Removal efficiency Cr (VI) was calculated according to the following equation:

$$\text{Removal efficiency}\,\% = \frac{(C_0 - C_f)}{C_0} \times 100 \qquad (1)$$

Where C_0 and C_f are the initial and final concentration of Cr (VI) as mg/L, respectively.

Statistical methodology by Plackett–Burman design

Plackett–Burman design was used as an appropriate screening method in order to choose the factors influencing removal efficiency. More details can be found in [16] and [17]. The model is a two factorial design (-1 for a low level and +1 for a high level), which identifies the critical factors during Cr (VI) biosorption onto sargassum, by screening of variables in the experiments (Table 1). The effect of initial concentration of nitrate was considered as anionic interfering agents.

Table1: Factors and levels used in the experimental Plackett-Burman design

Factors	Low (−1)	High (+1)
pH	3	8
Biosorbent dosage (g/L)	1	4
Initial concentration of Cr(VI)(mg/L)	50	300
Initial concentration of nitrate(mg/L)	500	1000
contact time (min)	15	120

Statistical model analyses the effect of each variable to identify those factors that had a significant effect, either positively or negatively on Cr (VI) biosorption is need. The effect of each variable was determined as the difference between the average value of the response for the six experiments at the high level (+1) and the average value for the experiments at the low level (-1) by below equation:

$$E(Xi) = \frac{\Sigma Rat(+1)}{n(+1)} - \frac{\Sigma Rat(-1)}{n(-1)} \qquad (2)$$

Where E (Xi) is the main effect of the tested variable, and R is the measured response. When the sign is positive, the effect of the variable on Cr (VI) biosorption is greater at a high concentration, and the effect of the variable is greater at a low concentration when the sign be negative. Especially, this design is practical when the researcher is faced with large number of factors and is unconfident of which settings are probable to produce optimal responses [18]. Plackett-Burman

design model is based on the first order model as below equation:

$$Y = \beta_0 + \Sigma \beta_i X_i \qquad (3)$$

Where Y is removal efficiency of Cr (VI), β_0 is the model intercept and β_i is the variable estimations. The response for the selection of significant variables (pH, biosorbent dosage, initial Cr (VI) concentration, initial nitrate concentration and contact time) during Cr (VI) biosorption were tested and identified based on the Plackett–Burman design model. These variables will provide an appropriate estimation of the error. The standard error $(S.E.)_e$ which represents the experimental variability within the design was obtained according to below equations:

$$S^2 = \frac{\Sigma_{i=1}^{N} d_t^2}{2N} \qquad (4)$$

$$(S.E)_e = \sqrt{\frac{s^2}{N/2} + \frac{s^2}{N/2}} = \sqrt{\frac{4s^2}{N/2}} \qquad (5)$$

Where S^2 and d_i are the variance of each experiment determined by duplicated experiments and the difference between the duplicated experiments, respectively. The limit value is obtained from the t-test [19].

$$t = \frac{|E_X|}{(S.E)_e} \qquad (6)$$

RESULTS AND DISCUSSION

Screening of variables using Plackett–Burman design

Five variables were evaluated regarding their effect on Cr (VI) biosorption using a Plackett-Burman design. The design matrix selected for the screening of significant variables for Cr (VI) biosorption onto *sargassum* and the correlated responses are shown in Table 2. The acceptability of the model was calculated, and the variables with significant effects on Cr (VI) biosorption process evidenced by statistical analysis were screened via student's t-test for ANOVA (Table 3). Table 3 shows the model P-value in the ANOVA was lower 0.05. Therefore, it can be stated that there is a significant relationship between the variables at the 95% confidence level. The R-squared statistic demonstrates that the fitted model explains 90 % of the variability in Cr (VI) biosorption process. The results of the effect of each variable in Plackett–Burman experimental design are shown in Table 4.

Table 2: Placket–Burman matrix for evaluating factors influencing Cr (VI) biosorption

Run	pH	Dosage	$C_{Chromium}$	$C_{Nitrate}$	time	Removal efficiency (%)
1	+1	+1	-1	+1	+1	38.5
2	-1	+1	+1	-1	+1	50.75
3	+1	-1	+1	+1	+1	41
4	-1	+1	-1	+1	-1	52.5
5	-1	-1	+1	-1	+1	56
6	-1	-1	-1	+1	+1	63.5
7	+1	-1	-1	-1	-1	2
8	+1	+1	-1	-1	+1	36.5
9	+1	+1	+1	-1	-1	1
10	-1	+1	+1	+1	-1	10
11	+1	-1	+1	+1	-1	0
12	-1	-1	-1	-1	-1	20

Table 3: The ANOVA test for Cr (VI) biosorption response

Source	Sum of squares	df	Mean Square	F-value	p-value
Model	5226.7	5	1045.31	8.28	0.0115
Residual	757.49	6	126.25		
Total(corr.)	5984.06	11			
R-square=0.87	**Adj R-square=0.76**		**standard error = 3.24 df= Degree of fredoom**		

Table 4: Statistical analysis of the explicative factors on Cr (VI) biosorption via Plackett–Burman design

Variable	Term	Main effect	t-value	p-value	Confidence level (%)
A	pH	-22.2917	11.81	0.013	98.7
B	Dosage	1.125	0.03	0.8680	13. 2
C	C_0	-9.04167	1.94	0.2128	78.72
D	Nitrate	6.541667	1.02	0.3522	64.78
E	Time	33.45833	26.60	0.0021	99.79

The effect of variables can be estimated from their sign (+ or -) and their magnitude. Positive and negative signs indicate increasing or decreasing of the Cr (VI) biosorption, respectively. There are two potential variables (pH and initial Cr (VI) concentration), which have negative sign and other three variables (biosorbent dosage, contact time and initial nitrate concentration) have positive sign (Fig. 1).

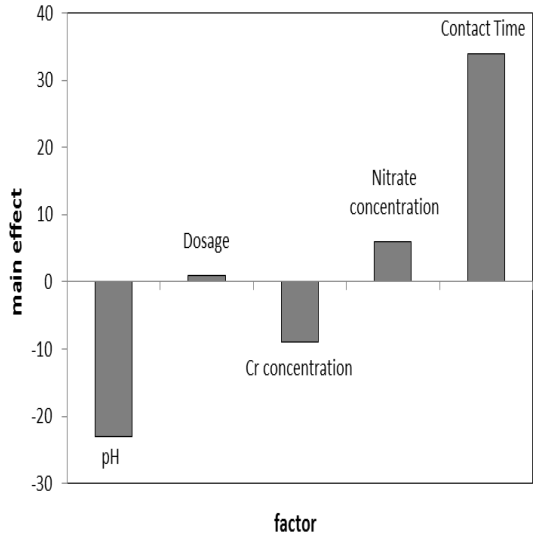

Fig. 1: Effect of mean factors on the Cr (VI) biosorption onto *Sargassum* sp. based on the results of Plackett-Burman design

Plackett–Burman design succeeded in classified factors to understand the Cr (VI) biosorption process better than conventional analysis without application of design model. The results of this study showed the potential variables (contact time and pH) have p-value < 0.05 that is lower than the level of the other variables (Table 4). Using the Pareto chart is an appropriate procedure to regard the results obtained by Plackett-Burman design. The Pareto chart illustrates the order of significance of the variable affecting the Cr (VI) biosorption. Fig. 2 shows the contact time and pH parameters have the highest degree of significance as demonstrated by Pareto chart.

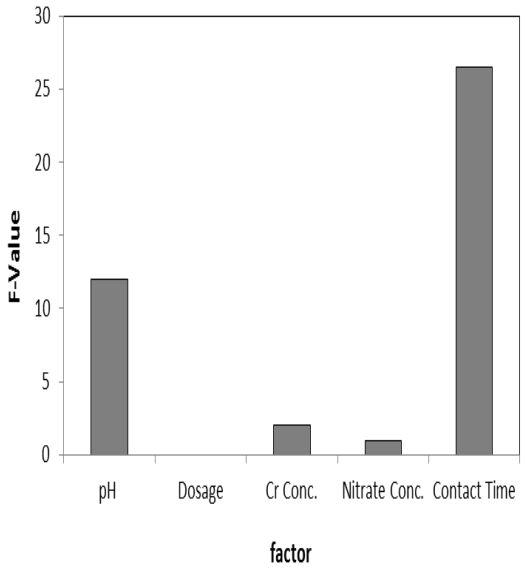

Fig. 2: Pareto plot of Plackett-Burman design model based on different parameters

Isotherm study

The Langmuir isotherm model

The Langmuir isotherm model is valid for monolayer adsorption which is presented as below equation:

$$q_e = \frac{q_m K_L C_e}{(1+K_L C_e)} \qquad (7)$$

where q_e (mg/g) is the amount of metal adsorbed per unit weight of biosorbent, C_e (mg/L) is concentration of free metal ions in solution, and q_m (mg/g) is the maximum amount of metal per unit weight of biosorbent that is required to form a monolayer on the surface of the biosorbent and *K* (L/mg) is related to the affinity of the binding sites. The values of q_m and K_L can be determined from the linear plot of C_{eq}/q_{eq} versus C_{eq} (Fig. 3).

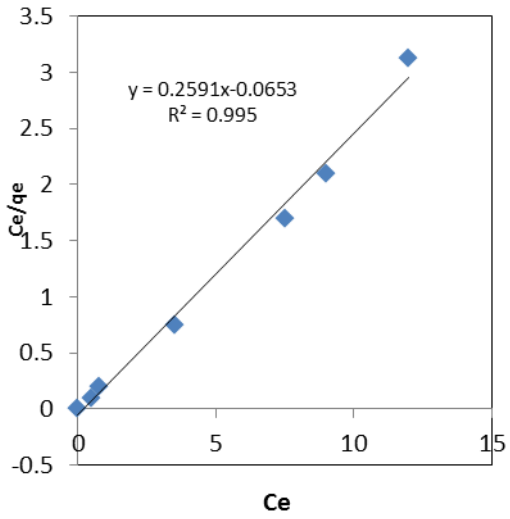

Fig. 3: Langmuir isotherm of Cr (VI) biosorption onto *Sargassum* sp

Eq. (8) illustrates the linear form of the Langmuir isotherm model:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \qquad (8)$$

The K_L and q_m were calculated from the slope and intercept of the plot between C_e/q_e and C_e, respectively [7]. The slope of the line is negative, so this equation is not suitable for correlating the obtained data.

The Freundlich isotherm model

Freundlich isotherm assumes that the uptake of adsorbate occurs on a heterogeneous surface by multilayer adsorption. The Freundlich isotherm is expressed as below equation:

$$q_e = K_F (C_e)^{1/n} \qquad (9)$$

Where K_F and n are Freundlich constants, and are correlated to adsorption capacity and intensity, respectively. The linear form of the Freundlich isotherm model is shown in Eq. (10):

$$log(q_e) = log(K_F) + \frac{1}{n} log(C_e) \qquad (10)$$

The slope and the intercept of the line correspond to (1/n) and K_F, respectively. The linearized isotherm for Cr (VI) ions biosorption was shown that the plot of *log* q_e versus *log* C_e yields a suitable straight line (Fig. 4).

The Freundlich isotherm model provides a more realistic description of adsorption by organic biosorbent. This model accounts for different types of binding sites, surface heterogeneity and the energy of the biosorbent surface [9, 12, 20].

The Dubinin–Radushkevick isotherm model

To identify the nature of the biosorption process, the equilibrium data were also correlated to the Dubinin–Radushkevich (D–R) model.

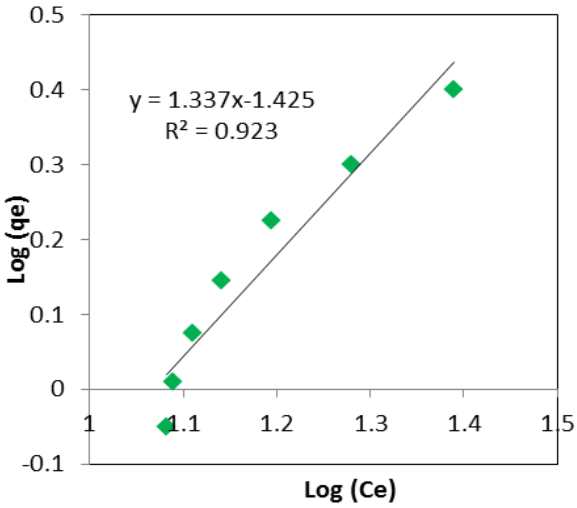

Fig. 4: Freundlich isotherm of Cr (VI) biosorption onto *Sargassum* sp

The linear form of this model can be written as:

$$\ln Q = \ln Q^o - k\varepsilon^2 \qquad (11)$$

Where Q is the amount of metal ions adsorbed per unit weight of adsorbent (mol/g), k is a constant related to the adsorption energy (mol^2kJ), ε is the Polanyi potential and Q^o is the adsorption capacity (mol/g), and ε is the Polanyi potential described as below equation:

$$\varepsilon = RT \ln\left[1 + \left(\frac{1}{C_e}\right)\right] \qquad (12)$$

As shown in Fig. 5, the values of k and Q° were determined by the slope and intercept of the linear plot [12, 21].

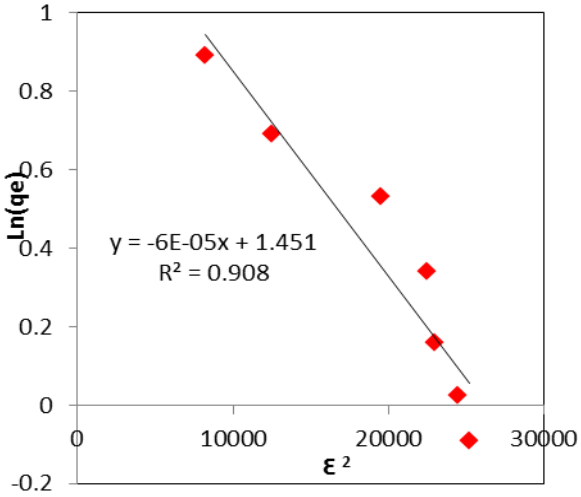

Fig5: D-R isotherm of Cr (VI) biosorption onto *Sargassum* sp

The obtained parameters related to studied isotherms are given in Table 5. As our results show, biosorption of Cr (VI) by *Sargassum* can be fitted using Freundlich equation according to high correlation coefficient. Similarly [22] showed that

the biosorption of Cr (VI) by *Synechococcus sp*. obeys the Freundlich model. Moreover about the biosorption of different metal ions onto different biosorbents, it was shown the fitting experimental data to Freundlich model [7].

Table5: Obtained isotherm parameters for Cr (VI) biosorption onto *Sargassum* algae.

biosorbent	Langmuir isotherm			Freundlich isotherm			D–R isotherm		
Sargassum	q_{max}	K	R^2	K_f	n	R^2	k	Q°	R^2
	3.86			0.03	0.75	0.923	-6×10^{-5}	0.162	0.908

Validation conditions optimized to removal efficiency

The validation of the statistical data based on the studied model and regression equation were performed by taking 4 g of adsorbent, 50 mg/L of Cr (VI), 1000 mg/L of nitrate ,120 min contact time and pH 3. Under these optimized conditions, the predicted response for chromium biosorption was 81 %, and the observed experimental value was 83%. The results indicate that the Plackett–Burman design is a powerful tool for determination of studied variables, which had a significant influence on Cr (VI) biosorption. This obtained data according to the model shows a much higher level of Cr (VI) biosorption with compared to other adsorbents.

CONCLUSION

In the present study, the five variables were tested using the Plackett–Burman design, and two variables (pH and contact time) had significant effects on Cr (VI) biosorption by *sargassum* algae as a cost-efficient biosorbent. This study showed the optimum value for each parameters, including solution pH 3, contact time of 120 min, initial Cr (VI) concentration of 50 mg/L, the biosorbent dosage of 1.3 g and nitrate concentrations of 1000 mg/L. At the optimum conditions maximum removal efficiency is 83%. Among isotherm models, the Freundlich isotherm best fit the experimental data, compared to the Langmuir and D-R models.

REFERENCES

[1] Tor A, Arslanb G, Muslub H, Celiktasb A, Cengeloglub Y, Ersozb M. Facilitated transport of Cr(III) through polymer inclusion membrane with di(2-ethylhexyl)phosphoric acid (DEHPA). J Membrane Sci. 2009; 329(1):169-174.

[2] Park D, Lim S-R, Yun Y-S, Park JM. Development of a new Cr (VI)-biosorbent from agricultural biowaste. Bioresource Technol. 2008; 99(18): 8810-8818.

[3] Lakshmanraj L, Gurusamy A, Gobinath MB, Chandramohan R. Studies on the biosorption of hexavalent chromium from aqueous solutions by using boiled mucilaginous seeds of Ocimum americanum. J Hazard Mater. 2009 ; 169(1): 1141–1145.

[4] Baig SA, Qian W, Xiaoshu L, Xinhua X. Removal of hexavalent chromium by limonite in aqueous solutions. Hydrometallurgy. 2013; 138: 33-39.

[5] Önal S, Baysal, ŞH, Ozdemir G. Studies on the applicability of alginate-entrapped Chryseomonas, luteola TEM 05 for heavy metal biosorption. J Hazard Mater. 2007; 146(1): 417–420.

[6] Gao P, Chen X, Shen F, Chen G. Removal of chromium (VI) from wastewater by combined electrocoagulation–electroflotation without a filter. Separ Purif Technol. 2005; 43(2): 117-123.

[7]. Soltani RDC, Rezaee A, Khorramabadi G S, Yaghmaeian K. Optimization of lead (II) biosorption in an aqueous solution using chemically modified aerobic digested sludge. Wat Sci Technol. 2011; 63(1):129–135.

[8] Mohan D, Singh KP, Singh VK. Trivalent chromium removal from wastewater using low cost activated carbon derived from agricultural waste material and activated carbon fabric cloth. J Hazard Mater. 2006; 135(1): 280-295.

[9] Gok C, Aytas S. Biosorption of uranium (VI) from aqueous solution using calcium alginate beads. J Hazard Mater. 2009; 168(1): 369–375.

[10] Agarwala GS, Bhuptawatb HK, Chaudhari S. Biosorption of aqueous chromium(VI) by Tamarindus indica seeds. Bioresource Technol . 2006; 97(7): 949-956.

[11] Chen JP, Yang L. Study of a heavy metal biosorption onto raw and chemically modified Sargassum sp. via Spectroscopic and modeling analysis. Langmuir. 2006; 22(21): 8906–8914.

[12] Nadavala SK, Swayampakula K, Boddu V M, Abburia K. Biosorption of phenol and o-chlorophenol from aqueous solutions on to chitosan– calcium alginate blended beads. J Hazard Mater. 2009 ; 162(1): 482–489.

[13] Kazemi SY, Ahamidib A-S, Asanjaranib N, Zolgharneinb J. Optimization of a new polymeric chromium (III) membrane electrode based on methyl violet by using experimental design. Talanta. 2010 ; 81(4):1681–1687.

[14] Reddy LVA, Wee Y-J, Yun, J-S, Ryu H-W. Optimization of alkaline protease production by batch culture of Bacillus sp. RKY3 through Plackett–Burman and response surface methodological approaches. Bioresource Technol. 2008; 99(7): 2242–2249.

[15] APHA, AWWA, WEF. Standard methods for the examination of water and wastewater. 4th ed. Washington DC; 2005.
[16] Gunasundari D, Muthukumar K. Simultaneous Cr (VI) reduction and phenol degradation using Stenotrophomonas sp. isolated from tannery effluent contaminated soil. Environ Sci Pollut Res 2013; 20: 6563–6573.
[17] Massart DL, Vandeginste BGM, Buydens LMC, Jong SD, Lewi PJ, Smeyers-Verbeke J. Handbook of Chemometrics and Qualimetrics, Part A. Elsevier. Amsterdam. 2003
[18] Adbel-Fattah Y R, Soliman N A, Gaballa A A, Sabry S A, Ei-Diwany A I. Lipase production from a novel thermophilic Bacillus sp: Application of Placket-Burman design for evaluating culture conditions affecting enzyme formation. Acta Microbial Pol. 2001; 51(4): 353-366.
[19] Jiang Y, Ji B, Wong RNS, Wong MH. Statistical study on the effects of environmental factors on the growth and microcystins production of bloom-forming Cyanobacterium Microcystis aeruginosa. Harmful Algae. 2008; 7(2):127-136.
[20] Aksu Z, Açıkel U, Kabasakal E, Tezer S. Equilibrium modelling of individual and simultaneous biosorption of chromium(VI) and nickel(II) onto dried activated sludge. Wat Res. 2002 ; 36 (12): 3063–3073.
[21] Ghazy SE, Ragab AH. Removal of copper fromwater samples by sorption onto powdered limestone. Indian J Chem Technol. 2007;14: 507-514.
[22] Li H, Li Z, Liu T, Xiao X, Peng Z, Deng L. A novel technology for biosorption and recovery hexavalent chromium in wastewater by bio-functional magnetic beads. Bioresour Technol. 2008; 99(14): 6271–6279.