

## WATER HYACINTH BIOMASS (WHB) FOR THE BIOSORPTION OF HEXAVALENT CHROMIUM: OPTIMIZATION OF PROCESS PARAMETERS

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Water hyacinth (*Eichhornia crassipes*) biomass has been used for many years for the remediation of heavy metals. The present study successfully utilizes the dried powdered biomass of the aerial part (stem and leaves) of water hyacinth for biosorption of hexavalent chromium. The effect of various parameters (viz. pH, initial metal ion concentration and temperature) on the removal of Cr(VI) was studied by conducting only 15 sets of sorption runs using Box-Behnken Design (BBD). The pH had a negative and temperature and concentration had positive effects on uptake of chromium. The predicted results (obtained using an empirical linear polynomial model) were found to be in good agreement ( $R^2 = 99.8\%$ ) with the experimental results. The predicted maximum removal of Cr(VI) (91.5181 mg/g) can be achieved at pH 2.0, initial metal ion concentration 300 mg/L, and temperature 40 °C. The sorption capacity of sorbent was also calculated using a Langmuir sorption isotherm model and was found to be 101 mg/g at 40 °C and pH 2.0.

*Keywords:* Water hyacinth biomass (WHB); hexavalent chromium; biosorption; Box-Behnken design; optimization

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### INTRODUCTION

Environmental contamination of the aquatic environment by toxic heavy metals is a serious problem. Chromium is one such heavy metal that has received widespread attention in the recent years because of its use in various industrial applications such as tanning, metallurgy, plating, and metal finishing (Karthikeyan et al. 2004; Das et al. 2004). The concentrations of Cr(VI) in these industrial wastewaters range from 0.5 to 270 mg/L. However, according to the United States Environmental Protection Agency (1990), the permissible limit of Cr(VI) for industrial effluents to be discharged to surface water is 0.1 mg/L and in potable water is 0.05 mg/L (Demirbas et al. 2004). Once chromium is introduced into the environment it can exist in two stable oxidation states, Cr(III) and Cr(VI) (Khezami and Capart 2005). The trivalent form is relatively innocuous, but hexavalent chromium is toxic, carcinogenic, and mutagenic in nature, highly mobile in soil and aquatic system, and also is a strong oxidant capable of being adsorbed by the skin (Bai and Abraham 2001; Ahalya et al. 2005). It is therefore essential to remove hexavalent chromium from industrial effluents before discharging them into aquatic environments or onto land. There are various tertiary treatment techniques for the removal of heavy metals from aqueous streams; however, these processes have technical

and/or economical constraints (Singh et al. 2005; Sumathi et al. 2005; Mungasavalli 2007). As an alternative to traditional methods, biosorption has been recognized as an effective technique for treatment of contaminated water. It can be defined as the passive uptake of toxicants by dead/ inactive biological materials or by materials derived from biological sources (Volesky and Holan 1995; Viera and Volesky 2000).

Water hyacinth (*Eichhornia crassipes*), a wild fern belonging to the family Pontederiaceae, is a submerged aquatic plant, found abundantly throughout the year; it is common in India (Mohanty et al. 2006; El-Khaiary 2007). One of the fastest growing plants known, water hyacinth reproduces primarily by way of runners or stolons, which eventually form daughter plants. It also produces large quantities of seeds, which are viable up to thirty years. It is a vigorous grower, known to double its population in two weeks and has been considered to be the least desirable aquatic plant (El-Khaiary 2007). It chokes the waterways and interferes with irrigation, fishing, recreation, and power generation by forming dense mats, which float on the water surface (El-Khaiary 2007). Water hyacinth has been shown to accumulate high concentrations of toxic metals (Hasan et al. 2007; Kelley et al. 1999; Schneider et al. 1995).

However, there are certain disadvantages in using the plants as such for remediation purposes. For example, it might be necessary to construct ponds if they are not available near the intended point of use. In addition, it has been reported that the heavy metals have phytotoxic effects on plants, which results in the inhibition of chlorophyll synthesis and necrosis. On the other hand, the use of dried plant biomass as biosorbent provides advantages in terms of transport and handling (Schneider et al. 1995). A few studies have been carried out which report the use of water hyacinth as biosorbent for the removal of various pollutants (Mohanty et al. 2006; El-Khaiary 2007; Kelley et al. 1999; Schneider et al. 1995; Low et al. 1995; Elangovan et al. 2008; Zheng et al. 2009). The present investigation is primarily aimed to utilize dried and powdered aerial parts (stem and leaves) of water hyacinth biomass (WHB) as a biosorbent for the removal of hexavalent chromium from water and to optimize the parameters affecting the sorption for its maximum removal via a three-level three-factor fractional factorial Box-Behnken design (BBD) for response surface methodology (RSM) with the help of the software MINITAB<sup>®</sup> Release 15. The application of RSM to the sorption process involves factorial search by examining simultaneous, systematic, and efficient variation of important components. It helps to predict a model for the process, identify possible interactions, higher order effects, and determine the optimum operational conditions.

## EXPERIMENTAL

### Preparation of Biosorbent (WHB)

Fresh plants of water hyacinth were collected from a pond within the university campus and then washed with water to remove dirt. The roots were cut out and disposed, then the leaves and stem were sun-dried for 48 h and then oven-dried at 60 °C for 48 h. After that, the biomass was reduced to powder form in a ball mill. The biomass was then sieved to particle size less than 300 microns (B.S.S. 52 mesh), stored in desiccator, and used for metal biosorption. The surface area of the dried powdered biomass of aerial part

of water hyacinth was determined by a three point  $N_2$  gas adsorption method using a Quantasorb Surface Area Analyzer (model Q5-7, Quanta chrome Corporation, USA), and it was found to be  $206 \text{ m}^2/\text{g}$ .

### Batch Sorption Experiment

The stock solution containing 1000 ppm of Cr(VI) was prepared by dissolving 2.8286 g of  $K_2Cr_2O_7$  in 1000 mL of deionized, double-distilled water. Required initial concentrations of Cr(VI) standards were prepared by appropriate dilution of the above stock Cr(VI) standard solution. Batch experiments were carried out in Erlenmeyer flasks by adding WHB (100 mg) in 50 mL of aqueous chromium solution of desired initial concentration. The pH of the solution was adjusted by adding 0.1 M HCl and 0.1 M NaOH solution as required. The flasks were gently agitated in an electrically thermostated reciprocating shaker at 200 rpm for a period of 140 mins. The content of each flask was separated from biosorbent by centrifuging at 15000 rpm and the supernatant solution was analyzed for remaining Cr(VI) concentration in the sample. The amount of Cr(VI) sorbed per unit mass of the biosorbent ( $q_t$  in mg/g) was evaluated by using following equations,

$$q_t = (C_i - C_t) \times V / W \quad (1)$$

where  $C_i$  and  $C_t$  are the Cr(VI) concentrations in mg/L initially and at a given time  $t$ , respectively,  $V$  is the volume of the Cr(VI) solutions in mL, and  $W$  is the weight of biosorbent in mg.

### Chromium Analysis in the Aqueous Solution

An atomic absorption spectrophotometer (Model no. AA 6300, Shimadzu, Japan) was utilized to determine total chromium (the sum of Cr(VI) plus the Cr(III) that had been oxidized) in the standard and unknown solution. Total Cr concentration in the solution was measured by first converting the Cr(III) species to Cr(VI) at high temperature (130 to 140 °C) by the addition of excess potassium permanganate (Park et al. 2005).

### Determination of Zero Point of Charge

The pH value, at which the charge of the solid surface is zero is referred to as the zero point of charge ( $pH_{zpc}$ ). For the determination of the  $pH_{zpc}$  of WHB, 45 ml of 0.1M  $KNO_3$  solution was transferred to a series of 100-ml Erlenmeyer flasks. A range of initial pH values of the metal solutions were adjusted at 2, 4, 6, 8, 10, and 12 by adding either 0.1N  $HNO_3$  or NaOH. The total volume of the solution in each flask was made up to exactly 50 ml by further addition of  $KNO_3$  solution of the same strength. The values of the initial pH of the solutions were then accurately noted, and 0.1 g of WHB was added to each flask, which was securely capped immediately. The suspensions were intermittently shaken manually and allowed to equilibrate for 48 h. The suspension was then centrifuged at 5000 rpm for 5 min, and the final pH values of the supernatant liquid ( $pH_f$ ) were recorded. The  $pH_{zpc}$  is the point where the curve pH final ( $pH_f$ ) versus pH

initial ( $\text{pH}_i$ ) crosses the line equal to  $\text{pH}_f$ . The point of zero charge ( $\text{pH}_{\text{pzc}}$ ) of WHB was experimentally found to be at pH 4.2 (Fig. 1).

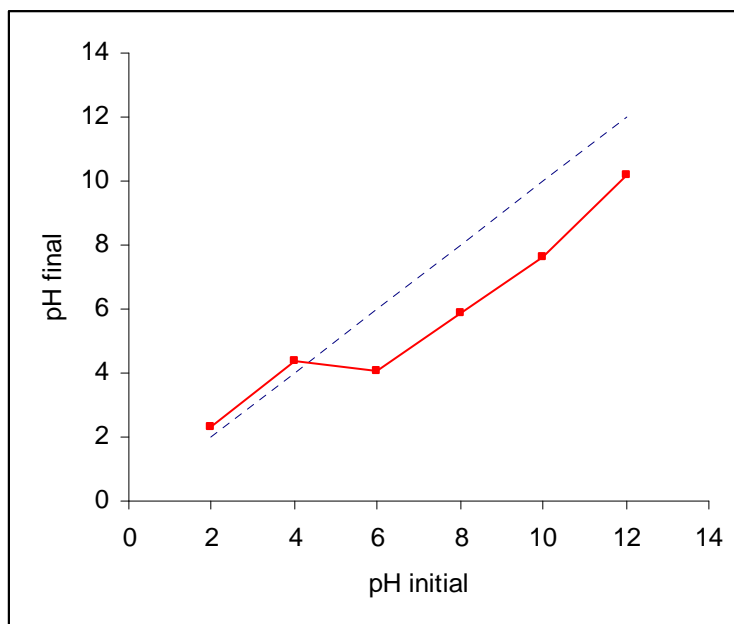


Fig. 1. Initial vs. final pH plot for the determination of  $\text{pH}_{\text{zpc}}$

### Response Surface Methodological Approach

Response Surface Methodology (RSM) is an empirical statistical technique employed for multiple regression analysis by using quantitative data. It solves multivariable data that are obtained from properly designed experiments to solve multivariable equations simultaneously (Tan et al. 2008; Annadurai et al. 1998). The graphical representation of their functions is called a response surface, and this approach was used to describe the individual and cumulative effects of the test variables and their subsequent effects on the response. An easy way to estimate a response surface is through a factorial design, which is one of the most useful schemes for the optimization of variables with a limited number of experiments. A variety of factorial designs are available to accomplish this task (Azargohar and Dalai 2005). In the present investigation a three-level, three-factor Box-Behnken Design (BBD) of response surface methodology was used. This design is suitable for exploring quadratic response surfaces and constructing second-order polynomial models (Nazzal and Khan 2002). BBD is a fractional factorial design consisting of a central point and the middle points of the edges of the cube circumscribed on the sphere. It has the advantage over other full factorial designs in that it requires relatively few combinations of variables for determining the complex response function. Another advantage of BBD is that it does not contain those combinations for which all variables are at their highest or lowest levels simultaneously. So these designs are useful in avoiding experiments performed under extreme conditions, for which unsatisfactory results might occur (Ferreira et al. 2007; Kiran et al. 2007; Hasan et al. 2009a).

Furthermore, the number of experiments (N) required for the development of BBD can be calculated from the following equation,

$$N = 2k(k-1) + C_o \quad (2)$$

where  $k$  is number of factors and  $C_o$  is the number of central points. Thus, for a three factor design, consisting of 3 central points, a total of 15 experimental runs are required (Ferreira et al. 2007).

Data from the BBD were subjected to a second-order multiple regression analysis to explain the behaviour of the system, using the least squares regression methodology to obtain the parameter estimators of the mathematical model (Kumar et al. 2008). The result may be expressed as,

$$Y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ii} X_{ii}^2 + \sum \beta_{ij} X_i X_j + \varepsilon \quad (3)$$

where  $Y$  is the response,  $\beta_0$  is a constant,  $\beta_i$  the slope or linear effect of the input factor  $X_i$ ,  $\beta_{ii}$  is the quadratic effect of input factor  $X_i$ ,  $\beta_{ij}$  the linear by linear interaction effect between the input factor  $X_i$ , and  $\varepsilon$  is the residual term.

MINITAB<sup>®</sup> Release 15, developed by Minitab Inc., USA, a statistical software package (Minitab, 2006), was used for this regression analysis of the data obtained and to estimate the coefficients of the regression equation.

## RESULTS AND DISCUSSION

### Optimization of Biosorption Process Using RSM Approach

In the present investigation the linear and interactive influences of three parameters (viz. pH, initial metal ion concentration, and temperature) on the biosorption of Cr(VI) on WHB were studied. The three different levels of pH studied were 2, 4, and 6; levels of initial metal ion concentration were 100, 200, and 300 mg/L, and that of temperature were 20, 30, and 40 °C. For the purpose of optimization of process parameters, 15 experimental runs were required as per three-level three-factor fractional factorial BBD. Experiments were performed according to the experimental plan (BBD), and the results thus obtained for each combination are given in Table 1. The results were also predicted with the help of Minitab software's Box-Behnken design, and are given in Table 1 itself. Significant changes in uptake of chromium were observed for all of the combinations, implying that all the variables were significantly affecting the sorption of chromium.

#### *Interpretation of the regression analysis*

The response surface regression results thus obtained from BBD, namely the  $T$  and the  $P$ -values, along with the constant and coefficients (estimated using coded values), are given in Table 2. The  $T$  value is used to determine the significance of the regression coefficients of the parameters, and the  $P$ -value is defined as the smallest level of significance leading to rejection of null hypothesis.

**Table 1.** Box-Behnken Design Matrix of Three variables (uncoded and coded values) along with Experimental and Predicted response (uptake) (mg/g)

Run Order	pH	Concentration (mg/L)	Temperature (°C)	Experimental (mg/g)	Predicted (mg/g)
1	2 (-)	300 (+)	30 (0)	82.135	81.9474
2	6 (+)	300 (+)	30 (0)	13.020	10.9664
3	2 (-)	100 (-)	30 (0)	43.600	45.6538
4	6 (+)	100 (-)	30 (0)	8.500	8.6878
5	2 (-)	200 (0)	40 (+)	79.210	78.7906
6	6 (+)	200 (0)	40 (+)	15.350	16.7971
7	2 (-)	200 (0)	20 (-)	59.940	58.4931
8	6 (+)	200 (0)	20 (-)	12.120	12.5396
9	4 (0)	300 (+)	40 (+)	39.560	40.1669
10	4 (0)	100 (-)	40 (+)	22.680	21.0458
11	4 (0)	300 (+)	20 (-)	26.420	28.0544
12	4 (0)	100 (-)	20 (-)	9.210	8.6033
13	4 (0)	200 (0)	30 (0)	30.300	30.3001
14	4 (0)	200 (0)	30 (0)	30.300	30.3001
15	4 (0)	200 (0)	30 (0)	30.300	30.3001

In general, the larger the magnitude of  $T$  and smaller the value of  $P$ , the more significant is the corresponding coefficient term (Ravikumar et al. 2007). The effects of all the linear, square, and interaction terms of pH, concentration and temperature ( $P < 0.05$ ), except for the quadratic term of temperature ( $P = 0.647$ ) and interaction term of concentration and temperature ( $P = 0.936$ ) were found to be highly significant on the removal of hexavalent chromium. A very high value of the parameter estimate for pH and relatively high values of coefficients of quadratic term of pH, concentration, and interaction term of pH and concentration show a high level of significance, indicating the importance of these variables in the biosorption process. A positive sign of the coefficient represents a synergistic effect, while a negative sign indicates an antagonistic effect. The variable pH had a negative significant relationship with the biosorption process, while the quadratic terms of initial metal ion concentration and interaction terms of pH and concentration and pH and temperature were significant but less affecting the process. The variables initial metal ion concentration, temperature, and the quadratic term of pH had positive and significant effects. A model is proposed based on the regression coefficients (Table 2) for the biosorption of hexavalent chromium.

$$Y = 30.300 - 26.9869 * \text{pH} + 9.6431 * \text{concentration} + 6.1387 * \text{temperature} + 11.8506 * \text{pH}^2 - 5.3369 * \text{concentration}^2 - 0.4956 * \text{temperature}^2 - 8.5038 * \text{pH} * \text{concentration} - 4.0100 * \text{pH} * \text{temperature} - 0.0825 * \text{concentration} * \text{temperature} \quad (4)$$

where  $Y$  is the response variable, the predicted amount of hexavalent chromium adsorbed (mg/g). The low value of standard deviation (1.956) between the measured and predicted results shows that the equation adequately represents actual relationship between the response and significant variables. High values of  $R^2$  (99.8%) and  $R^2(\text{adjusted})$  (99.3%)

indicate a high dependence and correlation between the observed and the predicted values of response. This model is valid only for the following conditions: pH=2-6; Cr=100-300 mg/L; and T=20-40 degrees C.

**Table 2.** Estimated Regression Coefficients (using coded units) for Experimental uptake (mg/g)

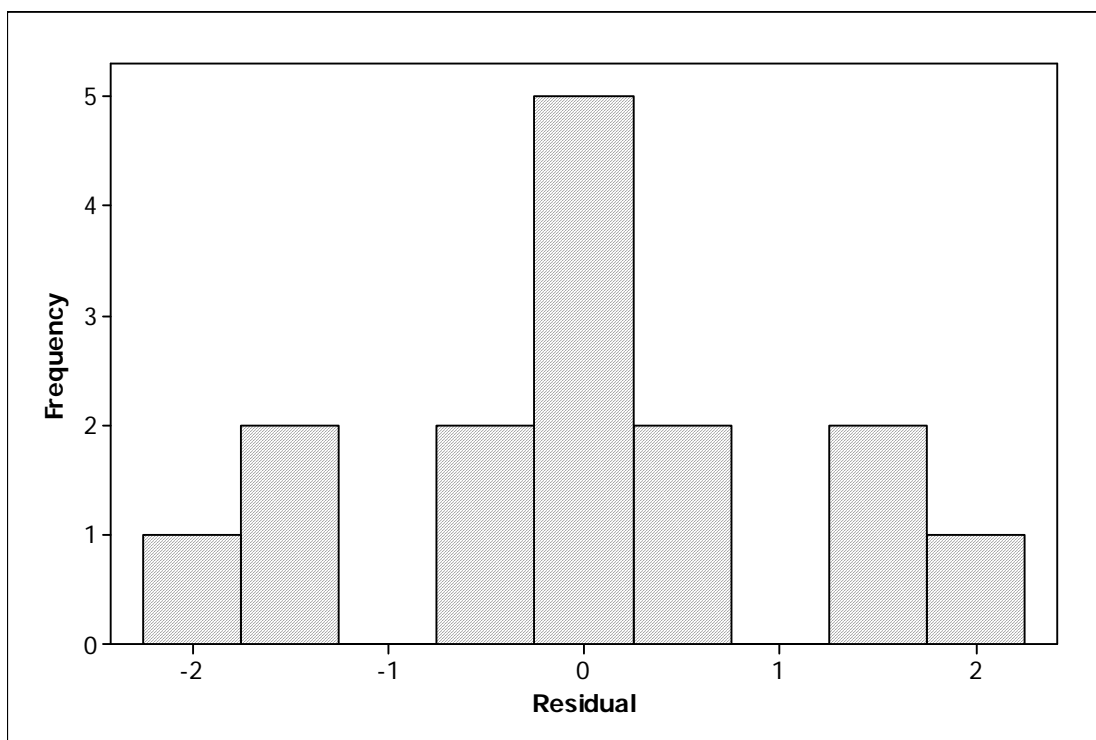
Term	Coef	SE Coef	T	P
Constant	30.3000	1.1291	26.835	0.000
pH	-26.9869	0.6914	-39.030	0.000
Concentration (mg/L)	9.6431	0.6914	13.946	0.000
Temperature (°C)	6.1387	0.6914	8.878	0.000
pH*pH	11.8506	1.0178	11.644	0.000
Concentration (mg/L)*Concentration (mg/L)	-5.3369	1.0178	-5.244	0.003
Temperature (°C)*Temperature (°C)	-0.4956	1.0178	-0.487	0.647
pH*Concentration (mg/L)	-8.5038	0.9778	-8.696	0.000
pH*Temperature (°C)	-4.0100	0.9778	-4.101	0.009
Concentration (mg/L)*Temperature (°C)	-0.0825	0.9778	-0.084	0.936

#### *Interpretation of residual graphs*

The normality of the data can be checked by plotting the histogram of the residuals. This is a graphical technique showing the distribution of the residuals for all observations and for assessing whether or not a data set is approximately normally distributed (Minitab 2006). The residual is the difference between the observed and the predicted value (or the fitted value) from the regression. Figure 2 shows a typical bell-shaped histogram (errors are normally distributed with mean zero) with no skewness (refers to a lack of symmetry) (Pokhrel and Viraraghvan 2006). It can be seen from the results that all the points of the residual were found to fall in the range of +2 to -2.

#### *Interpretation of contour plots and effect of various parameters*

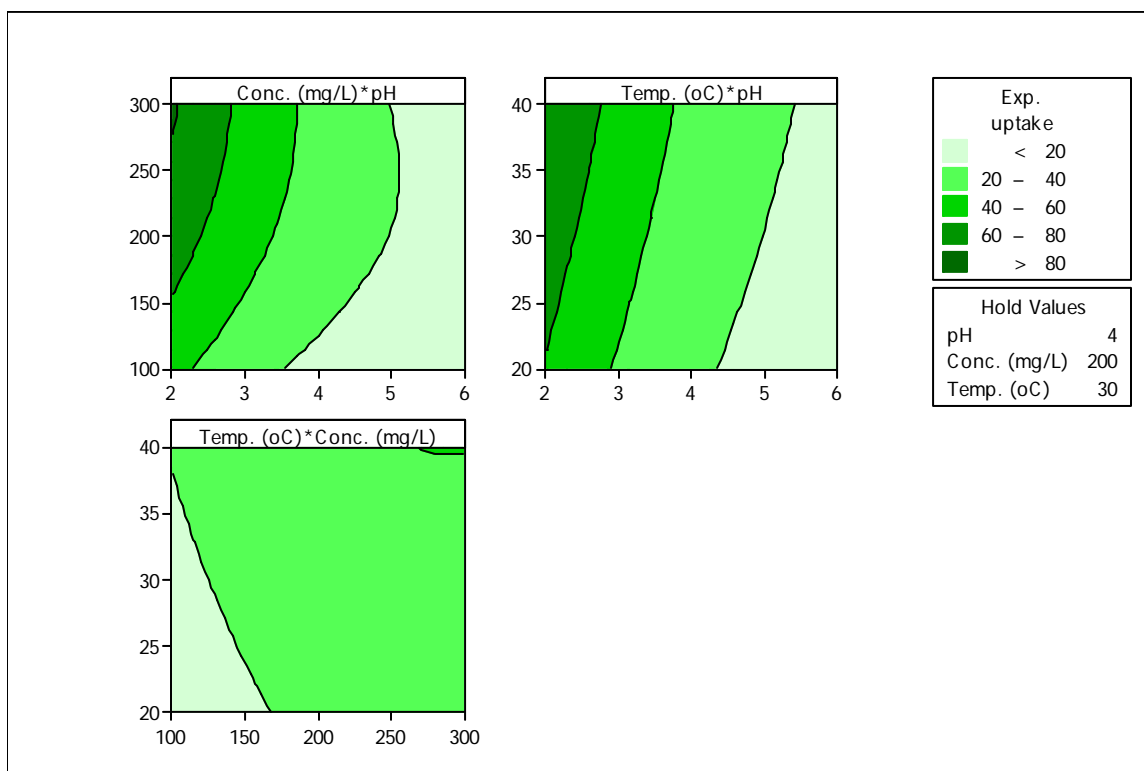
A contour plot is the projection of the response surface as a two-dimensional plane. This analysis gives a better understanding of the influence of variables and their interaction on the response (Chandran et al. 2002; Hasan et al. 2009b). To investigate the interactive effect of two factors on the removal of chromium, the RSM-BBD was used, and three dimensional and contour plots were drawn. The hold values of the remaining factors were set at their middle values (i.e. pH at 4.0, initial metal ion concentration at 200 mg/L, and temperature at 30 °C). Figure 3 represents three contour plots between the response i.e. uptake (mg/g) and the combined effect of pH of the system and initial metal ion concentration, pH and temperature, and initial metal ion concentration and temperature on the removal of Cr(VI). The figure shows that the uptake was decreased with the increase in pH and increased with an increase in initial metal ion concentration and temperature, reaching a maximum at pH 2.0, initial metal ion concentration 300 mg/L, and temperature 40 °C, confirming the experimental results as well.



**Fig. 2.** Histograms of residuals

The maximum uptake at the lowest pH studied (pH 2) can be explained with the help of the  $pH_{zpc}$  of the WHPP, which was found to be 4.2, and the aqueous chemistry of the chromium ion. At acidic pH, the predominant species of chromium will be  $Cr_2O_7^{-2}$ ,  $HCrO_4^-$ ,  $Cr_3O_{10}^{-2}$ , and  $Cr_4O_{13}^{-2}$ , and at higher pH (pH 8) the presence of  $CrO_4^{-2}$  is reported (Mor et al. 2007). At  $pH < pH_{zpc}$  (i.e. below 4.2), the surface of the adsorbent is positively charged, while the chromium ions are in the negatively charged species. This results in an electrostatic attraction between the negatively charged adsorbate species and the positively charged WHB, resulting in higher uptake of Cr(VI). At  $pH > pH_{zpc}$  (i.e. above 4.2), the adsorbent is negatively charged and the adsorbate species are also negatively charged. Such a situation enhanced the electrostatic repulsion between the negatively charged adsorbate species and the negatively charged adsorbent (WHB) surface, which ultimately resulted in a decrease in the adsorption of metal ions. The increase in adsorption capacity of biomass with the increase of initial concentration may be attributed to a lack of sufficient available sites present on the biomass surface to accommodate much more metal in the solution. At lower concentration levels the biosorption capacity showed a decreasing trend due to decreased diffusion coefficient and decreased mass transfer coefficient of chromium species. With the increase of initial concentrations, the mass transfer driving force of the metal ion species between the aqueous solution and biosorbent phases would increase, which would lead to an increase in chromium biosorption (Salinas et al. 2000). The increase in adsorption capacity of WHB with increasing temperature may be explained as due to either creation of some new sorption sites on the sorbent surface or the increase in the intraparticle diffusion rate of the sorbate, so that greater biosorption would be observed at higher temperature.





**Fig. 3.** Contour plot for uptake (mg/g)

#### *Interpretation of process optimization curve*

Response optimization helps to identify the factor settings that optimize a single response or a set of responses. It is useful in determining the operating conditions that will result in a desirable response (Minitab 2006). In the present study the goal for Cr(VI) uptake using WHB was to obtain a value at or near the target value of 92.0 mg/g. Uptake values less than 8.0 and greater than 100 mg/g were unacceptable. Both weight and importance were set at 1. The global solution (optimum condition), which is defined as the best combination of factor settings for achieving the optimum response, was found to be pH (2.0), initial metal ion concentration (300 mg/L), and temperature (40 °C) for a predicted response of 91.5181 mg/g with a desirability score of 0.99426 (Fig. 6). There are many advantages of an optimization plot so as to achieve predicted response with higher desirability score, lower-cost factor settings with near optimal properties, to study the sensitivity of response variables to changes in the factor settings, and to get required responses for factor settings of interest.

#### *Langmuir sorption isotherm*

The Langmuir sorption isotherm describes that the uptake that occurs on a homogeneous surface by monolayer sorption without interaction between sorbed molecules (Langmuir 1918). The linear form of the Langmuir isotherms may be represented as:

$$C_e/q_e = 1/Q^o b + C_e/Q^o \quad (7)$$

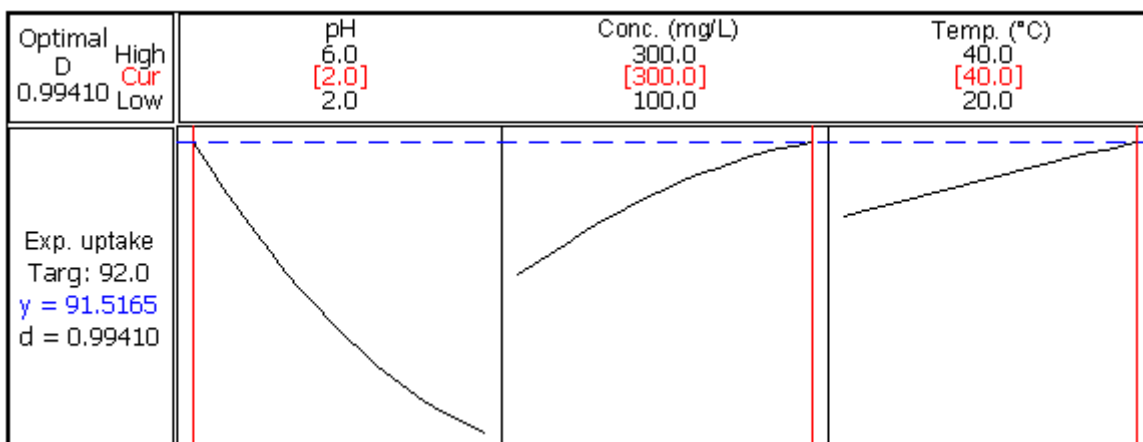


Fig. 4. Process optimization curve for a target value of 92.0 mg/g.

where  $Q^{\circ}$  and  $b$  are the Langmuir constants related to the monolayer sorption capacity (mg/g) and free sorption energy (L/mg), respectively. The isotherm constants  $Q^{\circ}$  and  $b$  are calculated from the slope and intercept of plot between  $C_e/q_e$  and  $C_e$  (Fig. 5), respectively. The isotherm showed a good fit to the experimental data with good correlation coefficients (Table 3). The sorption capacity of WHB was found to be 101 mg/g at 40 °C and pH 2.0.

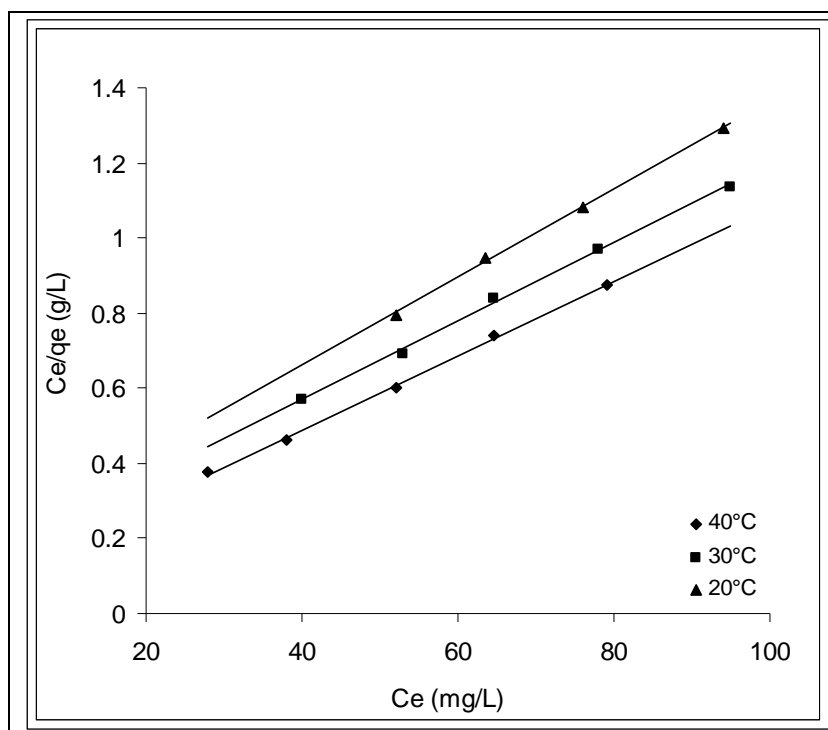


Fig. 5. Langmuir isotherm plot for Cr(VI) biosorption using WHB. Conditions: pH 2.0; temperature 20, 30, and 40 °C.

**Table 3.** Parameters of Langmuir Isotherm for Biosorption of Cr(VI) on WHB at Various Temperatures

Temperature (°C)	$Q^o$ (mg/g)	$b$ (L/mg)	$R^2$
20	85.47	0.064	0.9987
30	96.15	0.069	0.9976
40	101.01	0.107	0.9984

## CONCLUSIONS

1. Water hyacinth biomass (WHB) was found to have high potential for the removal of hexavalent chromium from aqueous solution. A Box-Behnken RSM design was employed successfully to develop a mathematical model for the prediction of hexavalent chromium removal from aqueous solution using WHPP. The  $R^2$  value for the predicted model was found to be 99.8%, which means there was a high correlation between the experimental and predicted values.
2. The uptake of chromium was found to be very sensitive to the initial pH of the solution, and was found to decrease with an increase in the pH in the present study. However, there was a positive effect of initial metal ion concentration and temperature on the uptake; i.e., there was an increase in uptake with increase in these variables. With the help of the developed model and the optimization curve the predicted maximum removal of Cr(VI) (91.5181 mg/g) was found to be achieved at pH (2.0), initial metal ion concentration (300 mg/L), and temperature (40 °C).
3. The sorption of Cr(VI) on WHB was found to follow a Langmuir isotherm, suggesting monolayer sorption on homogeneous energetic active sites on the surface of the sorbent. The sorption capacity of WHB was found to be 101 mg/g at 40 °C and pH 2.0.

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