International Journal of Engineering Research
Volume No.3, Issue No.3, pp : 167-171
ISSN:2319-6890)(online),2347-5013(print)
01 March 2014

# Optimization of effect of pre-treatment on Chromium removal by algal biomass using Response Surface Methodology

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***Abstract*— *In this research work green algae was chemically treated with Calcium Chloride or Perchloric acid and Formaldehyde or only washed with distilled water. This pretreated algae was used for equilibrium sorption uptake studies with Cr(VI). The Box-Behnken Design in response surface methodology by MATLAB was used for modelling the experiments.***

Keywords- Green algae; pretreatment; biosorption; optimization; response surface methodology

## I. Introduction

Many industries discharge effluent contaminated with Chromium such as leather industry and electroplating industry (Bai and Abraham, 2001; Baral and Engelken, 2002; Costa, 2003). There are several technologies for treatment of waste water but biosorption has come up with an alternative treatment method for wastewater as is eco-friendly and cost effective as biological material is available is abundance (Srivastava and Majumder, 2008; Trivedi and Patel, 2007). Several biological materials have been investigated as bacteria, fungi, yeast and algae for treatment of wastewater containing heavy metal. Green algae have been found to be effective biosorbent for removing heavy metals due to their huge abundance and high metal uptake capacities (Chong et al, 2000; Mohanty et al 2005; Park et al 2004).

Metal sorption capacity of biosorbent can be altered by pretreatment. Various physical and chemicals pretreatment methods can be used for pretreatment (Gupta et al, 2001; Mohanty et al, 2006; Seki et al, 2005; Yang and Chen, 2008). The physical treatments include heating/boiling, freezing/thawing and drying. The various chemical treatments used for biomass modification include washing the biomass with detergents, cross-linking with organic solvents, and alkali or acid treatment (Barrera et al, 2006; Khezami and Capart, 2005; Mor et al, 2006). The pretreatment could modify the surface characteristics either by removing or masking the groups or by exposing more metal-binding sites (Donmez and Aksu, 2002; Dursun et al, 2003; Tunali et al, 2005; Park et al, 2006). Recently our group has used Calcium Chloride and formaldehyde and Perchloric acid to pretreat the green algae. Results showed that pretreated algae have much potential as a biosorbent for the removal of heavy metals from wastewater (Nakajima and Baba, 2004; Park et al, 2005; Zhou et al, 2007).

In this study, green algae was chemically modified by Calcium Chloride or Perchloric acid and Formaldehyde or only washed with distilled water. Effect of pretreatment on metal uptake capacity of biosorbent for the different pretreatment methods used has been studied. The objective of this work is to optimize the biosorption process using Response Surface Methodology (RSM) and Analysis of Variables (ANOVA) (Myer and Montogomery, 2002). In optimization of the sorption process parameters optimized were adsorption time, pH values, initial Chromium concentration, adsorbent dose. The biosorption capacities were evaluated using Langmuir and Freundlich isotherms and the results indicated that the pretreated algae are suitable materials for the development of high capacity biosorbents for heavy metal removal.

## II. Material and Methodology

**Biomass and pretreatment**

Green algae were sampled from water tank in the campus. Biomass was dried in an oven at 60 °C upto constant weight, ground and sieved with the help sieve of 85 BSS.

Calcium Chloride pretreatment (CC): 50 g screened algae was mixed with 500 mL solution of 1M $CaCl_2$ in 1000 mL beaker. The mixture was stirred with the help of magnetic stirrer for 8 hours and then washed with distilled water to remove excess Calcium ion. Treated algae were extracted with the help of centrifuge and it was dried for 12 hours at 60 °C, screened and kept for future use.

Raw algae (DW): Algae was washed with distilled water, dried at 60 °C upto constant weight, grinded and screened with 85 BSS Screen.

Perchloric acid and Formaldehyde pretreatment (PF): 100 g of screened algae was mixed with Perchloric acid ($HClO_4$) and Formaldehyde (HCHO). (25+25) mL equal v/v of $HClO_4$ and HCHO diluted to 1000 mL of distilled water. The mixture was stirred with the help of magnetic stirrer for 8 hours and then washed with distilled to remove excess $ClO_4^-$ and Aldehyde. Treated algae were extracted with the help of centrifuge and it was dried for 12 hours at 60 °C, dried and kept for future use.

**Biosorption experiments**

All biosorption experiments were performed by the batch technique for Cr(VI) ions at various initial concentrations at 25°C and sorbent concentration. The stock solutions of 1000 ppm of Cr(VI) was prepared by dissolving analytical grade of $K_2Cr_2O_7$ in distilled water. The contact time was evaluated from kinetic experiments as 2 hours. The pH of each solution was adjusted with 0.1 mol $L^{-1}$ NaOH and HCl. The experiments were performed in 250 mL Erlenmeyer flasks containing 100 mL of Cr(VI) synthetic solutions in shaker at 150 rpm. The biomass was separated from the metal solution by filtration. Samples of sorbent suspension (5 mL) were taken to determine residual concentration of metal ions in the solution and analyzed for metal ions content using spectrophotometer.

**Response Surface Methodology**

Response surface method with Box-Behnken design (BBD) was applied to evaluate and determine the optimum operating conditions. The main effects of four independent factors: initial Concentration of Chromium(VI), pH, contact time and adsorbent dose were investigated. Removal efficiency of Chromium was selected as the dependent variables. For the evaluation of experimental data it was fitted to a second-order polynomial model and regression coefficients were obtained. The generalized Second-order polynomial model used for the response variable given by:

$$Y_n = b_0 + \sum b_i X_i + \sum b_{ii} X_i^2 + \sum\sum b_{ij} X_i X_j$$

Where Yn is the response variable to be modelled $X_i$ and $X_j$ are the independent variables. $b_0$, $b_i$, $b_{ii}$ and $b_{ij}$ are the regression coefficients for intercept, linear, quadratic and interaction terms respectively. The effects of independent variable on dependent variable are developed by volumetric slice plot. Additionally interactive response surface modelling is used for calculating optimum values of independent variable for favourable value of dependent.

## III. Results and Tables

**Identification of Algae**

The identification of fresh water algae samples was done using SEM and EDX. The comparison was made using the images available in the literature.

**Effect of Contact Time**

Contact time is one of the important parameters for successful biosorption application. The percentage removal increases as the time increases and becomes constant after a certain time period These changes in metal uptake may be due to the fact that, initially, all adsorbent sites were vacant and the solute concentration was high. The optimum contact time period for adsorption of chromium has been found to be 2 hours.

**Effect of pH**

The effect of pH on the biosorption of Cr(VI) ions was studied by changing pH values in the range, 2 to 6. Also the experiments were conducted for 5, 10, 15 g/L of algal dose. It was determined that at pH 2, we have maximum removal efficiency. This is due to the Cr(VI) is found in aqueous solution in $HCrO_4^-$ form. Increase in pH will shift the concentration of $HCrO_4^-$ to other forms $CrO_4^-$ and $Cr_2O_7^{2-}$.

**Effect of concentration of Chromium ion**

Effect of concentration was studied by varying the Chromium ion concentration by 10, 15, 20, 25, 30 ppm. The percentage removal of chromium decreases with increase in concentration of chromium keeping all other factors constant. This is due to the fact that the adsorbent has a definite capacity and can adsorb only a maximum specific amount. Therefore additional adsorbate does not get adsorbed and hence the percentage removal decreases.

**Effect of Pretreatment**

The effect of basic pretreatment using calcium chloride and acidic pretreatment using perchloric acid and formaldehyde for pretreatment of algae for the removal of chromium has been studied.

**Optimization by Response Surface Modeling**

The above equation has been used to visualize the effects of experimental factors on conversion percentage response. The model adequacy check is an important part of the data analysis procedure as the approximating model would give poor or misleading results if it were an inadequate fit. One of the main aims of this study was to find the optimum process parameters to maximize the adsorption of chromium, from the mathematical model equations developed in this study. The pure-quadratic model equation was optimized to maximize of adsorption of chromium within the experimental range studied. Three independent test variables are chosen for statistical experiment design as follows: adsorbent dose (X1, g/L), pH (X2) and initial feed concentrations of chromium (X3, mg/L). A 3-level four factor Box-Behnken experimental design has been used in this study. The Statistics Toolbox function rstool opens interactively investigating simultaneous one-dimensional contours of multidimensional response surface models. A sequence of plots is displayed, each showing a contour of the response surface against a single parameter with all other parameters held fixed. The ANOVA results are shown in Table 1 and Fig. 1, and RSM results are shown in Fig. 2, 3, 4, and 5.

## IV. Conclusion

The pretreated algae have much potential as a biosorbent for the removal of heavy metal ions from wastewaters. The coefficients of correlation as well as the kinetic parameters of chromium adsorption on algae are determined from the experimental kinetic data. The order of maximum metal uptakes for Cr(VI) was PF>DW>CC.

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Table 1. One way ANOVA for algal biomass

| Source | SS | df | MS | F | Prob>F |
|---|---|---|---|---|---|
| Columns | 10703.7 | 2 | 5351.84 | 24.07 | 9.9132e-009 |
| Error | 16011.4 | 12 | 222.38 | | |
| Total | 2671501 | 14 | | | |

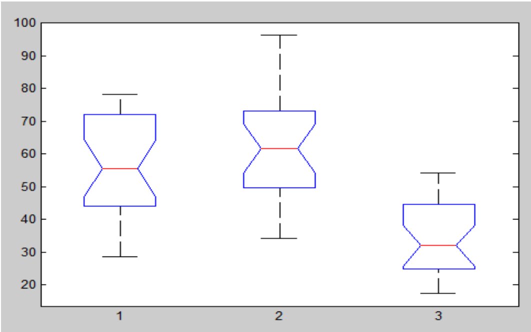

Fig. 1. One way ANOVA for alagal biomass

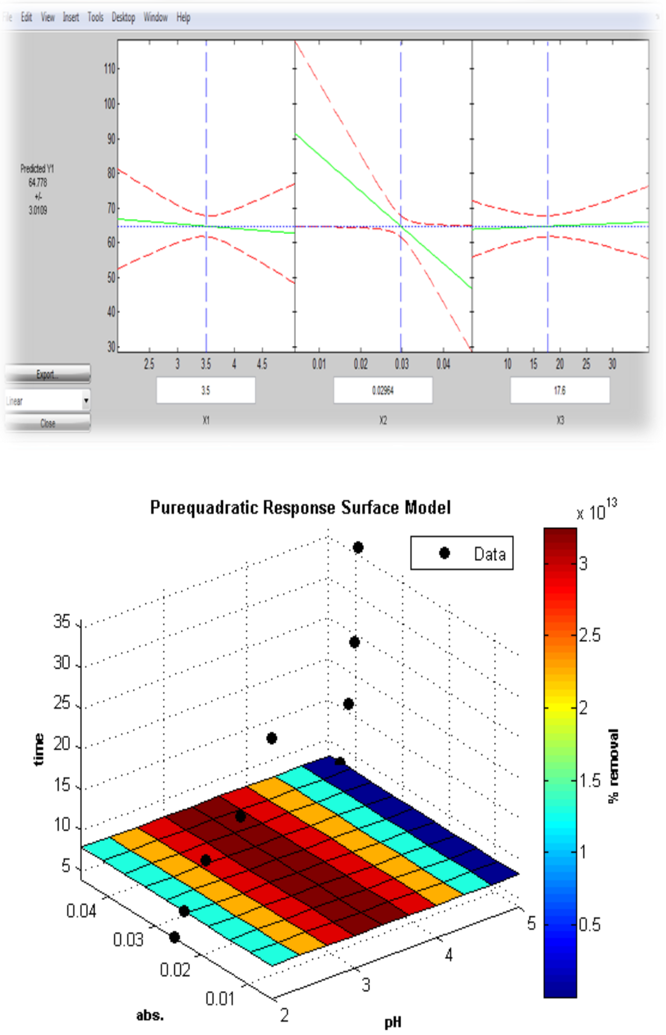


Fig. 2. Interactive RSM and 3-D plot showing effect of pH, time and absorbance on percentage removal of Cr(VI), $R^2$: 0.9908, Optimized data: pH: 3.5, Absorbance: 0.02964, Time (min.): 17.6, % removal: 64.775

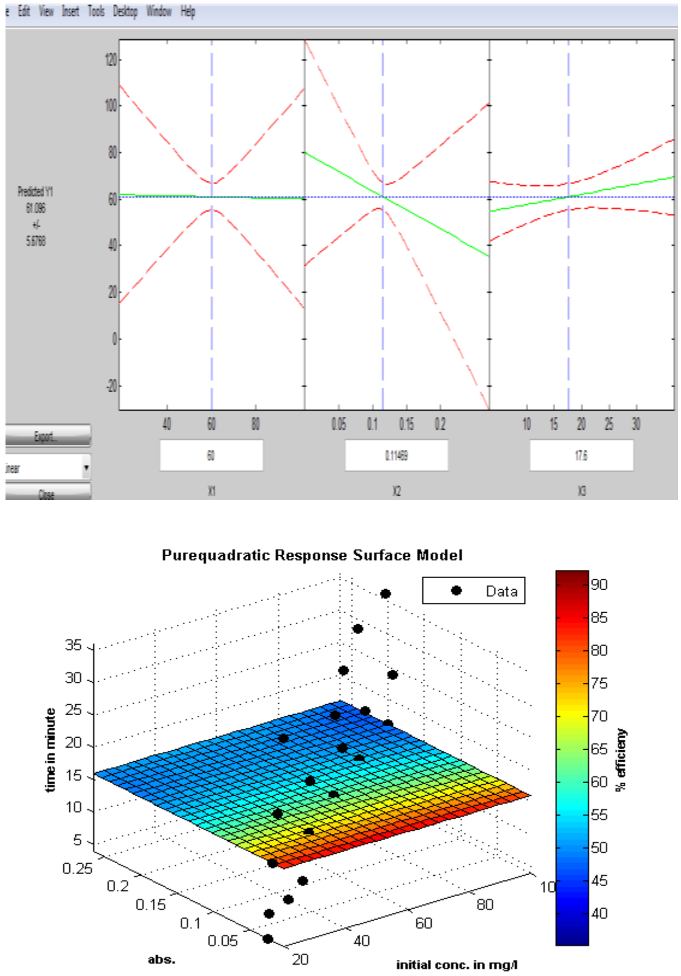


Fig. 3. Interactive RSM and 3-D plot showing effect of absorbance, time and initial concentration on percentage removal of Cr(VI), R2: 0.8328, Optimized data: Initial conc.(mg/L): 60, Absorbance: 0.11469, Time (min.): 17.6, % removal: 61.6007

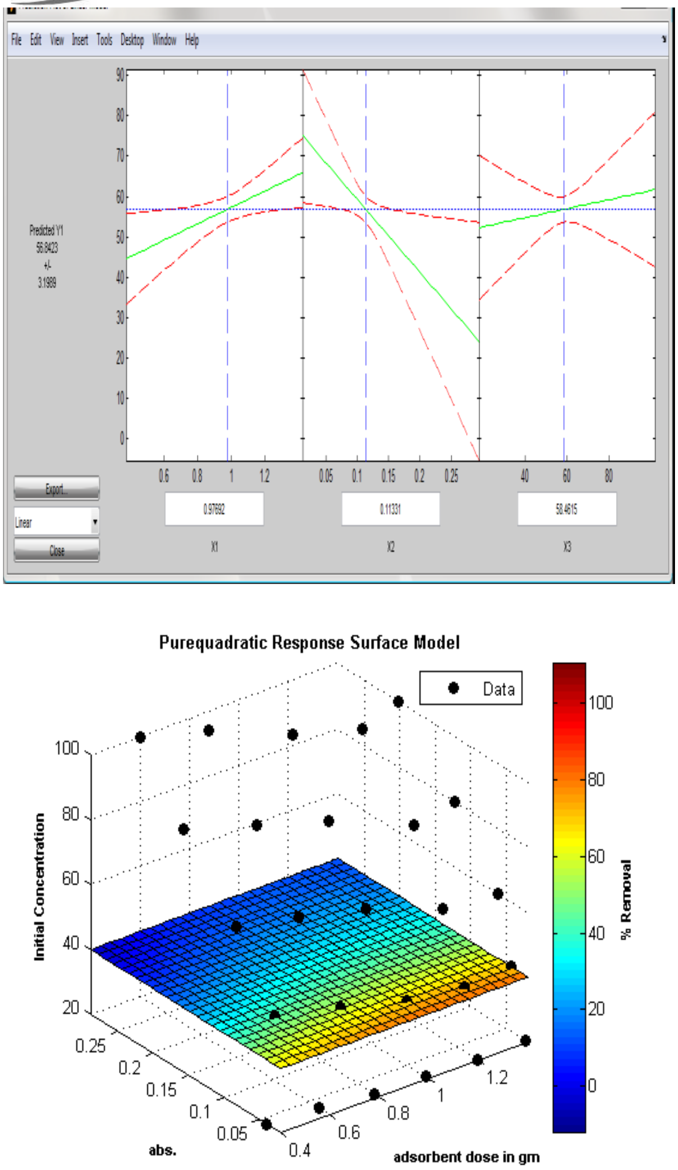


Fig. 4. Interactive RSM and 3-D plot showing effect of initial concentration, absorbance and adsorbent dose on percentage removal of Cr(VI), R2: 0.9770, Optimized data: Adsorbent Dose (g): 1.19, Absorbance: 0.03, initial concentration (mg/L): 59.74, % removal: 84.36

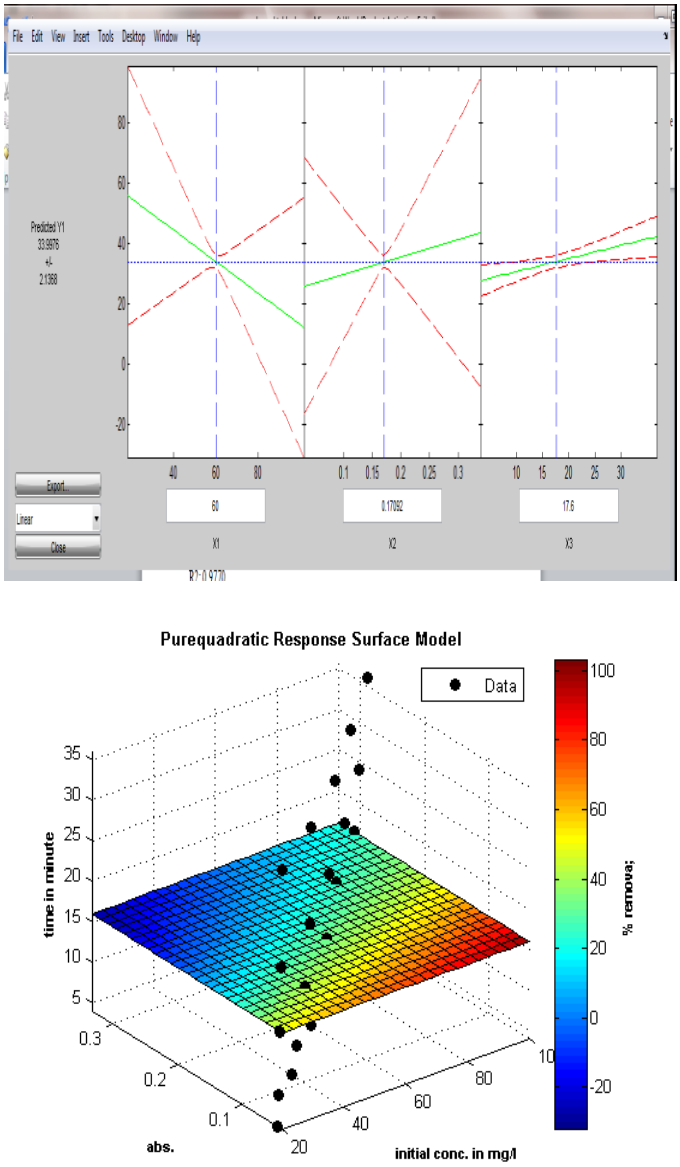


Fig. 5. Interactive RSM and 3-D plot showing effect of initial concentration, time and absorbance on percentage removal of Cr(VI), R2: 0.9850, Optimized data: Initial concentration (mg/L): 60, Absorbance: 0.0294, Time (min.): 17.6, % removal: 41.09