

Full Length Research Paper

Biosorption of chromium by mangrove-derived *Aplanochytrium* sp.

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The microbial dried biomass of *Thraustochytrids* is used as bioadsorbent for the removal of the chromium in aqueous solution. In this investigation, three species of *Thraustochytrids* namely *Aplanochytrium* sp., *Thraustochytrium* sp. and *Schizochytrium* sp. were tested for the efficiency of chromium accumulation by culturing in chromium-incorporated medium at 30°C for one week incubation. The biomass was harvested by filtration through Whatman no.1 filter paper. The level of metal accumulation in the biomass was determined by using an inductively coupled plasma system (ICP- Optical Emission Spectrophotometer; Optima 2100DV). Finally, among the three strains, *Aplanochytrium* spp. was selected for the adsorption kinetics and optimization using response surface methodology. Optimization of chromium removal by dried microbial biomass was analyzed with important factors of different pH, adsorbent dosage (*Aplanochytrium* dried biomass), temperature and processing time with 30 batch experimental plan derived from the centre composite design (CCD) of response surface methodology. *Aplanochytrium* sp. dried biomass removed chromium of 69.4% in aqueous solution. Therefore, *Aplanochytrium* sp. dried biomass is potent for the removal of chromium in waste water treatment.

Key words: Mangroves, chromium removal, *Aplanochytrium* sp., biosorption, waste water treatment.

INTRODUCTION

Industrial effluents pose a potential threat to the environment of many countries. The major issue is disposal and degradation of the industrial effluents that contain toxic metals. The chemicals of the effluent are carcinogenic and mutagenic and their discharge affect the life cycle of flora and fauna. A combination of the toxic compounds varies, depending on the source of the industry. Majority of effluents have been dumped into the coastal environment without proper pretreatments and/or removal of toxic chemicals from the effluent. In general, the toxic levels of heavy metals such as lead, copper, aluminum, chromium and cobalt are present in the industrial effluents. Among these heavy metals, chromium is one of the major carcinogenic contaminant

in the industrial effluent waters of leather mining and textile industries (Costa, 2003). In general, chromium is the most stable forms but some binding site can be oxidized. Some of the oxidized compounds are carcinogenic and highly toxic to the flora and fauna (Tewari et al., 2005).

Increasing interest has been observed in the application of biological methods for removal of heavy metals. Thus far, many types of biological methods have been used. These methods are economically viable. Among these methods, bioadsorption is an ideal technique for the removal of the toxic metals from effluent (Basha and Murthy, 2007). Marine lower fungi and seaweeds are known to be biosorbents for the removal of chromium and other toxic metals (Babich and Stotzky, 1983; Vala et al., 2004). However, *Thraustochytrids* dried biomass has not been tested as a bioabsorbent for the removal of chromium. Hence, this study was aimed at

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selecting the potential *Thraustochytrids* for efficient bio-adsorption of chromium in aqueous solution and their adsorption kinetics, as well as factors influencing optimization process of chromium removal using statistical model response surface methodology.

MATERIALS AND METHODS

Selection of strains for removal of heavy metals and calcium

Three strains of *Thraustochytrids* namely: *Aplanochytrium* sp., *Thraustochytrium* sp. and *Schizochytrium* sp., were tested for their efficiency in removing chromium in aqueous solution at 30°C. After one week of incubation, the biomass was harvested by filtration through Whatman no.1 filter paper. The level of metal accumulation in the biomass was determined against known standard using an inductively coupled plasma system (ICP- Optical Emission Spectrophotometer; Optima 2100DV). The percentage of the accumulation was calculated.

Preparation of biosorbent biomass

Aplanochytrium sp. was cultivated in the production medium (50% seawater) at 28 ±2°C. After 7 days of incubation, the biomass was harvested and killed by boiling in 0.5 N NaOH solution for 15 min and then washed repeatedly with deionized water. After washing, the biomass was dried at 60°C for 24 h and powdered in a mortar and pestle. The dried biomass was stored in a desiccator and used for further experiments.

Preparation of the adsorbate (chromium) stock solution

The chromium stock solution was prepared using 1.4143 g of $K_2Cr_2O_7$ in 500 ml de-ionized water. The concentration of chromium solution was freshly diluted according to the experimental model derived from centre composite design (CCD) using stock chromium standard solution. The desired pH was maintained by the addition of 1 M HCl or NaOH at the beginning of the experiments and was not controlled further. The changes in the volume of the working solution due to the addition of HCl and NaOH were negligible.

Batch biosorption experiments

The adsorption experiments in this study were undertaken to investigate the effects of experimental conditions such as pH, temperature, biosorbent dosage and adsorption time, on the removal of chromium. The conditions that caused the maximum amount of chromium removal in aqueous solution were determined. The biosorption experiments were performed in 250 ml Erlenmeyer flasks by agitating specified amount of adsorbent in 100 ml of chromium solution of desired concentration at varying pH on a shaker for 120 min (Lab-Line Shaking incubator laboratory Equipment, India). The optimization of the biosorption of chromium was studied by varied important factors such as pH of 6.0 to 11.0, temperature at 20 to 60°C with an interval of 10°C and biosorbent dosage (biomass) of 0.2, 0.4, 0.6, 0.8 and 1.0 g.L⁻¹ was investigated. In all the experiments, at the end of the desired contact time, the residual chromium concentration in the solution was determined after filtering the samples using Whatman No. 1 filter paper and the biosorbent was successfully separated from aqueous solution. The filtrates were analyzed for residual chromium concentration using an inductively coupled plasma system Optical

Emission Spectrophotometer (Optima 2100DV) and quantified against known standard of chromium. The sample without biosorbent was run simultaneously as control. The kinetic and isotherm method was carried out and was followed by optimizing the condition for chromium removal using the central composite design of the response surface methodology (RSM).

Experimental setup by RSM for chromium removal

The experiments with different pH, adsorbent dosage (dried microbial biomass), temperature and processing time were tested for their interactive and individual effects on chromium removal by the central composite design. In order to describe the effects of pH, adsorbent dosage, temperature and processing time on percentage of chromium removal in 30 batch, experiments were conducted derived from CCD. The coded values of the process parameters were determined using Equation 1:

$$Y = \beta_0 + \sum_i \beta_i X_i + \sum_i \beta_{ii} X_i^2 + \sum_{ij} \beta_{ij} X_i X_j \quad (1)$$

Where, Y_i is the predicted response, $X_i X_j$ are independent variables, β_0 is the offset term, β_i is the i^{th} linear coefficient, β_{ii} is the i^{th} quadratic coefficient and β_{ij} is the ij^{th} interaction coefficient. The experiment design is presented in Table 1, along with experimental and predicted responses. In this study, the independent variables were coded as X_1 , X_2 , X_3 and X_4 . Thus, the second order polynomial equation can be presented as shown in Equation 2:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{44} X_4^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{14} X_1 X_4 + \beta_{23} X_2 X_3 + \beta_{24} X_2 X_4 + \beta_{34} X_3 X_4 \quad (2)$$

A statistical program package Design Expert 8.0.6, was used for the regression analysis of the data obtained and to estimate the coefficient of the regression equation, and to analyze the variance of selected factors and model significance.

Kinetic studies

Batch experiments were conducted for optimum adsorbent dosage and equilibrium time. The amount of adsorbed chromium was calculated using Equation (3) by the difference of initial and residuals amounts of chromium in solution divided by the mass of adsorbent (dried microbial biomass). The removal efficiency, R_e (determined as the chromium removal percentage relative to initial concentration) using Equation (4) of the system, was calculated as:

$$q_e = [C_0 - C_e] \times V / M \quad (3)$$

$$R_e = [(C_0 - C_e) / C_0] \times 100 \quad (4)$$

Where, q_e (mg.g⁻¹) is the amount of the chromium adsorbed per unit mass of dried *Aplanochytrium* sp. microbial biomass, C_0 and C_e are the initial and equilibrium (or at any time) ion concentration (mg.l⁻¹), respectively, V is the volume of chromium solution in liter of experimental solution and M is the mass (g) of *Aplanochytrium* sp.

Batch isotherms studies

After determining the optimum pH, temperature and equilibrium time, isotherm studies were conducted by varying the biomass of *Aplanochytrium* sp. and different concentrations of dried *Aplanochytrium* sp. biomass (0.2, 0.4, 0.6, 0.8 and 1 g.l⁻¹) containing 313.19 mg.l⁻¹ of chromium for 60 min in aqueous solution. The initial pH of the chromium solutions was adjusted to an optimum value of pH 9.

Table 1. Central composite design matrix for the experimental design and predicted responses for chromium removal.

| Standard order | Temperature (°C) | pH | Adsorbent dosage (mg.L ⁻¹) | Processing time (min) | Actual Value | Predicted value |
|----------------|------------------|----|--|-----------------------|--------------|-----------------|
| 1 | 20 | 7 | 0.2 | 30 | 65.81 | 43.09 |
| 2 | 60 | 7 | 0.2 | 30 | 48.57 | 30.48 |
| 3 | 20 | 11 | 0.2 | 30 | 27.70 | 19.36 |
| 4 | 60 | 11 | 0.2 | 30 | 25.16 | 21.37 |
| 5 | 20 | 7 | 1 | 30 | 15.63 | 20.45 |
| 6 | 60 | 7 | 1 | 30 | 21.53 | 21.40 |
| 7 | 20 | 11 | 1 | 30 | 23.50 | 11.61 |
| 8 | 60 | 11 | 1 | 30 | 21.47 | 27.18 |
| 9 | 20 | 7 | 0.2 | 120 | 68.63 | 58.42 |
| 10 | 60 | 7 | 0.2 | 120 | 28.28 | 31.39 |
| 11 | 20 | 11 | 0.2 | 120 | 23.95 | 15.29 |
| 12 | 60 | 11 | 0.2 | 120 | 12.23 | 2.90 |
| 13 | 20 | 7 | 1 | 120 | 58.44 | 53.44 |
| 14 | 60 | 7 | 1 | 120 | 36.15 | 39.98 |
| 15 | 20 | 11 | 1 | 120 | 11.62 | 25.20 |
| 16 | 60 | 11 | 1 | 120 | 12.44 | 26.37 |
| 17 | 0 | 9 | 0.6 | 75 | 0.096 | 17.65 |
| 18 | 80 | 9 | 0.6 | 75 | 10.47 | 6.20 |
| 19 | 40 | 5 | 0.6 | 75 | 32.04 | 47.58 |
| 20 | 40 | 13 | 0.6 | 75 | 12.49 | 10.24 |
| 21 | 40 | 9 | 0.0 | 75 | 10.09 | 42.45 |
| 22 | 40 | 9 | 1.4 | 75 | 62.36 | 43.29 |
| 23 | 40 | 9 | 0.6 | -15 | 0.44 | 21.01 |
| 24 | 40 | 9 | 0.6 | 165 | 42.81 | 35.53 |
| 25 | 40 | 9 | 0.6 | 75 | 59.49 | 64.43 |
| 26 | 40 | 9 | 0.6 | 75 | 59.50 | 64.43 |
| 27 | 40 | 9 | 0.6 | 75 | 59.73 | 64.43 |
| 28 | 40 | 9 | 0.6 | 75 | 69.41 | 64.43 |
| 29 | 40 | 9 | 0.6 | 75 | 69.38 | 64.43 |
| 30 | 40 | 9 | 0.6 | 75 | 69.10 | 64.43 |

RESULTS AND DISCUSSION

In this study, three strains of the *Thraustochytrids* were tested for the biosorption of chromium. Among these strains tested, the *Aplanochytrium* sp. was found to be efficient for the removal of chromium and hence it was used for further kinetics and optimization study as a biosorbent. In general, chromium is a toxic chemical and its removal from industrial effluent is highly difficult. In this regard, the potential of *Aplanochytrium* sp. in chromium removal was proven in this study as the first report. The species used appeared to be tolerant to chromium toxicity. Although there is no earlier report to discuss this point, however, other fungal species are reportedly tolerant to the heavy metals by the way of the utilization, adsorption and uptake of the heavy metals and hence the fungal systems are suggested for bioremediation process in the sewage. Fungal species belonging to the genus

Fusarium have already been studied by other authors for their potential in biosorption of heavy metals and dyes (Delgado et al., 1993; Sen and Naskar, 2003).

Many seaweeds, bacteria, yeasts and filamentous fungi have also been investigated for their metal-binding capacities. Among these, fungi are the most promising since their cell wall surface contains many functional groups of carboxyl, hydroxyl, sulfhydryl, amino groups, phosphate group of lipids, proteins and polysaccharides. These functional groups have the ability to bind metal ions (Kumar et al., 2008; Sag et al., 2001). However the mechanism of biosorption of chromium in the present case of *Aplanochytrium* sp. is yet to be elucidated.

RSM approach for adsorption optimization

Center composite design (CCD) was used to statistically

Table 2. Analysis of variance table (ANOVA) for response surface methodology of main effects and interacting effects of parameters in quadratic model.

| Source | Sum of squares | df | Mean square | F-value | p-value (Prob > F) |
|---|----------------|----|-------------|----------|---------------------|
| Model | 11454.5 | 14 | 818.178 | 2.775 | 0.029** |
| X1-Temperature (°C) | 196.682 | 1 | 196.682 | 0.667 | 0.426 ^{NS} |
| X2-pH | 2091.814 | 1 | 2091.814 | 7.096 | 0.017** |
| X3-Adsorbent Dosage (mg.l ⁻¹) | 1.038 | 1 | 1.038 | 0.003 | 0.055* |
| X4-Processing time (min) | 316.002 | 1 | 316.004 | 1.072 | 0.316 ^{NS} |
| X1X2 | 214.038 | 1 | 214.038 | 0.726 | 0.007** |
| X1X3 | 183.963 | 1 | 183.963 | 0.624 | 0.041* |
| X1X4 | 207.485 | 1 | 207.485 | 0.703 | 0.014** |
| X2X3 | 221.599 | 1 | 221.599 | 0.751 | 0.399 ^{NS} |
| X2X3 | 376.089 | 1 | 376.089 | 1.275 | 0.276 ^{NS} |
| X3X4 | 312.089 | 1 | 312.089 | 1.058 | 0.319 ^{NS} |
| X1 ² | 4725.921 | 1 | 4725.92 | 16.033 | 0.001** |
| X2 ² | 2162.97 | 1 | 2162.97 | 7.338 | 0.016* |
| X3 ² | 797.131 | 1 | 797.131 | 2.704 | 0.120 ^{NS} |
| X4 ² | 2241.754 | 1 | 2241.754 | 7.605 | 0.014* |
| Residual | 4421.288 | 15 | 294.752 | | |
| Lack of Fit | 4279.27 | 10 | 427.92 | 15.06597 | 0.801 ^{NS} |
| Pure Error | 142.017 | 5 | 28.403 | | |
| Core Total | 15875.79 | 29 | | | |

Statistical significance: ***($P < 0.0001$), *($P < 0.05$). NS, Non-significant.

design the experiments and evaluate the interactive effects of parameters for optimizing adsorption of chromium onto the dead biomass of *Aplanochytrium* sp. The empirical relationship between the response and various input variables in the RSM approach obtained from the center composite model along with the predicted and experimental response of the chromium removal is presented in Table 1. The statistical significance was tested with the individual and interaction effects of variables at various levels of concentration on the chromium removal probability; values are shown in Table 2 based on Student's T- test and analysis of variance fitted to second order polynomial equation. The probability values of < 0.05 indicate that the variables are statistically significant. The highly significant parameters were detected based on the probability values for the variables (pH, adsorbent dosage). These were observed as significant parameters for the chromium removal. Regarding their interactions on the chromium removal, the parameters tested for interactions were: temperature and pH, temperature and adsorbent dosage, temperature and processing time. The interactive effects were significant indicating that the variables played important role on chromium biosorption process; the parameters were then fitted into second order polynomial equation as follows:

$$\text{Percentage of chromium removal} = 64.44 - 2.86X_1 - 9.34X_2 + 0.21X_3 + 3.63 + 3.66X_1X_2 + 3.39X_1X_3 - 3.60X_1X_4 + 3.72X_2X_3 - 4.80X_2X_4 + 4.42X_3X_4 \quad (5)$$

The model accuracy was tested by second order polynomial model and observed significant F-Value ($F = 2.77$, degree of freedom = 14, $P < 0.029$) and a low value of standard deviation (1.17) between the measured and modeled results which showed that the equation adequately represented actual relationship between chromium removal and significant variables. The high value of R^2 (0.82) was very close to the predicted value of R^2 and it indicated a high dependence and correlation between the observed and the predicted values of response. The lack-of-fit term was non-significant as it was desired. The non-significant value of lack of fit observed was 0.81 (which was more than 0.05), revealing that the quadratic model was valid for the present study.

Validation of the model was also carried out by plotting standard error in response as a function of a pair of factors. A plot of the standard errors in biosorption of the metal as a function of temperature and pH is shown in Figure 1a to d. The shape of the standard error plot was not only found to fit on the design points but the polynomial also showed low and flat errors exhibiting circular contours and symmetrical shape around the centroid, representing best condition. A base standard deviation of 1.0 was used to generate the standard error plot for design evaluation. The actual magnitude of the plot would be a function of the standard deviation, which depends on the response data. Standard error value increased at the centroid as well as away from the optimization point. The standard error value around the

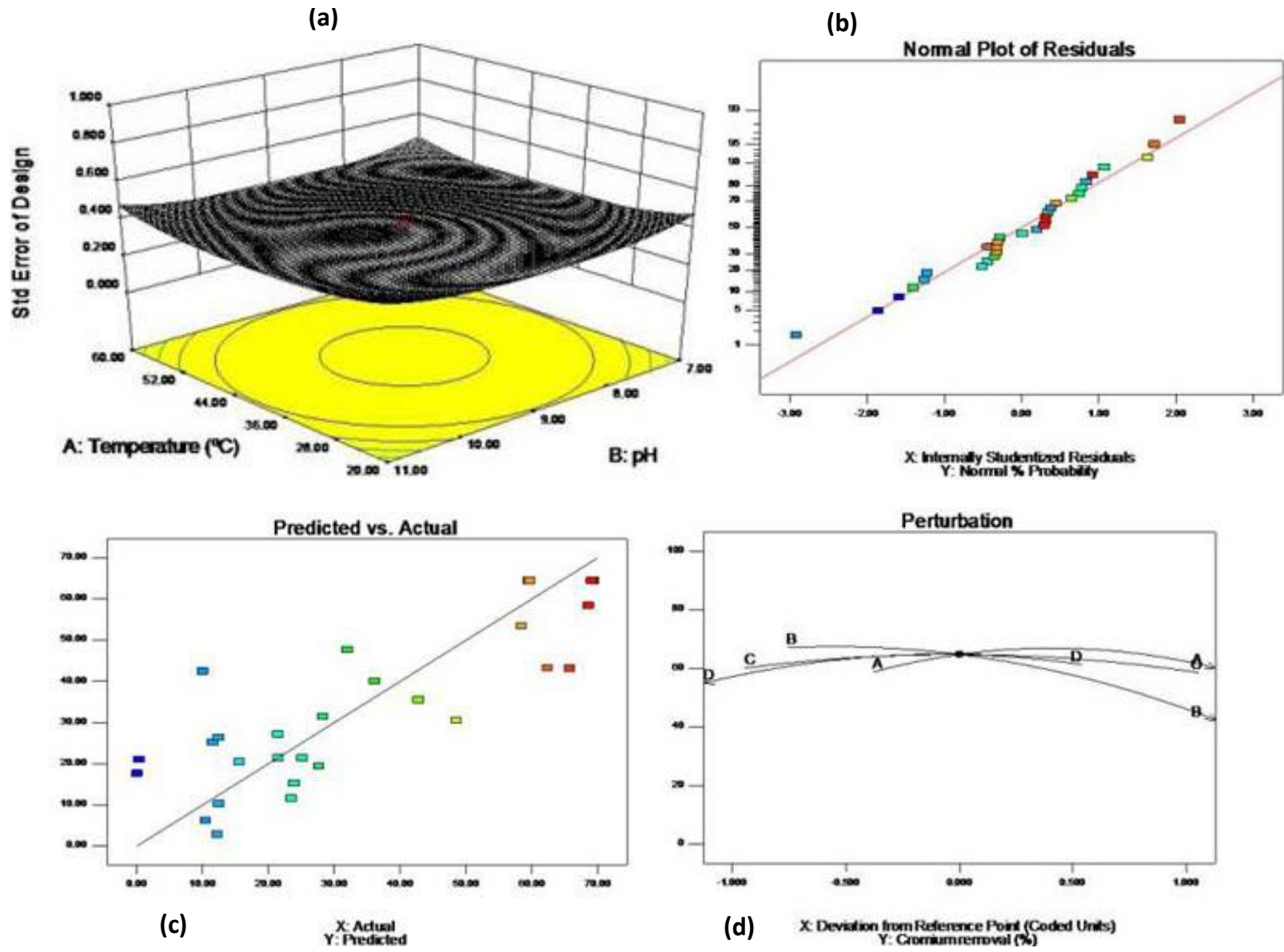


Figure 1. (a) Three-dimensional standard error plot for biosorption of chromium by *Aplanochytrium* sp. (b) Normal plot for the residuals and normal percentage of probability for the response of predicted and experimental values. (c) Predicted and actual experimental response for the chromium removal. (d) Perturbation plot for chromium removal.

centroid was 0.401, which was the best value. The inferences obtained from the experimental design model in relation to adsorption of chromium by the dried biomass of *Aplanochytrium* sp., with respect to each variable are as follows.

Effect of pH and temperature on chromium removal

The interactions and individual effects of pH and temperatures were tested on chromium removal by the RSM model and the results are shown in the contours and 3D plots. The pH and temperature interaction was significant (F value - 0.726, P-0.007) and for statistical optimization of the parameters, the perturbation was observed by the way of increase and decrease in the levels of the parameters using the RSM model. The results indicate that the statistical optimum for the potential chromium removal was at pH 6.8 to 8.08 and temperature 27.03°C (Figure 2a). The results also suggest the active process at slightly acidic pH in biosorption of chromium. Such observations on enhanced biosorption at pH has been previously reported with other biosorbents such as bacteria (Zhou et al., 2007), fungi and milled peat (Sen and Ghosh-Dastidar, 2007). The reason for the enhanced adsorption of chromium at low pH is that negatively charged $[\text{HCrO}_4]^{2-}$, $[\text{Cr}_2\text{O}_7]^{2-}$, $[\text{Cr}_4\text{O}_{13}]^{2-}$ and $[\text{Cr}_3\text{O}_{10}]^{2-}$ ions are the dominant species under such conditions. The surfaces of yeast cell walls at low pH are surrounded by hydronium ions (H_3O^+). The negatively charged ion species are thus effectively adsorbed on the positively charged active sites on the biosorbent (Ozer et al., 1994). With an increase in pH, the binding of ions decreased on account of repulsive forces between the biosorbent (*Aplanochytrium* sp.) and chromium.

Effect of temperature and adsorbent dosage on chromium removal

The interactions and individual effects of the temperature and adsorbent dosage were tested on chromium removal by the RSM model and the results are shown in the contours and 3D plots. The adsorbent dosage and temperature interactions were significant (F value-0.624, P-0.041) and for the statistical optimization of the parameters, the perturbation was observed by the way of increasing and decreasing the levels of the parameters using the RSM model. The result indicates that the statistical optimum for the potential chromium removal was at adsorbent dosage 0.51 mg.L⁻¹ and temperature of 27.03°C (Figure 2b). The adsorption of chromium ions to cell wall functional groups in the fungus is an endothermic process and an increased temperature positively affects the metal uptake (Sudha and Abraham, 2001).

Effect of temperature and processing time on chromium removal

The interactions and individual effects of the temperature and processing time were tested on chromium removal by the RSM model and the results are shown in the contours and 3D plots. The processing time and temperature interactions were significant (F value- 0.703, P-0.014) and for statistical optimization of the parameters, the perturbation was observed by the way of increasing and decreasing the levels of the parameters using the RSM surface model. The result indicates that the statistical optimum for the potential chromium removal was at processing time of 79 h and at temperature of 27.03°C (Figure 2d). The results are presented in the contours and 3D plots (Figure 2d - f). Increased metal uptake at higher temperatures in bacterial biomass (*Bacillus licheniformis*) is reported to be due to a higher affinity of sites for metal or an increase in binding sites on the biomass (Zhou et al., 2007).

Kinetic and isotherm experiments

Isotherm and kinetic evaluations were tested using the first and second-order kinetic equation models and adsorption isotherm. Statistically optimized factors were used in kinetic studies. Optimized conditions for efficient chromium removal were at pH of 6.8 to 8.02 with known concentration of chromium of 313.19 mg.l⁻¹ and adsorbent concentration of 0.51 g.L⁻¹ at 27.03°C. The determination of the residual chromium concentration in aqueous solution was tested at definite intervals of 30 min over a period of 120 min.

Adsorption kinetics

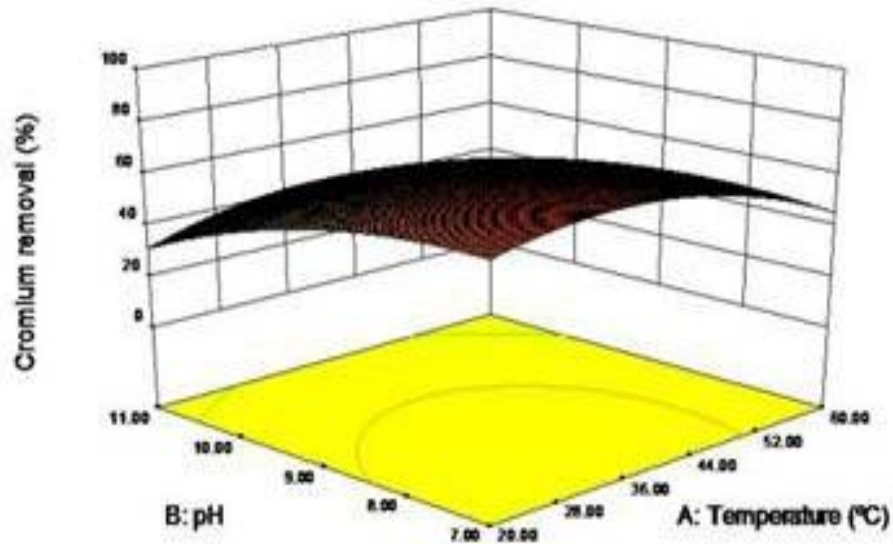
The kinetics of removal of chromium was explicitly explained in the literature using the first-order and second-order kinetic models. The adsorption of chromium was analyzed using Lagergran rate equation. The first order Lagergran model is given in Equation (6) (Gasser et al., 2007; Vasudevan et al., 2011) as:

$$dq_t / Dt = k_1 (q_e - q_t) \quad (6)$$

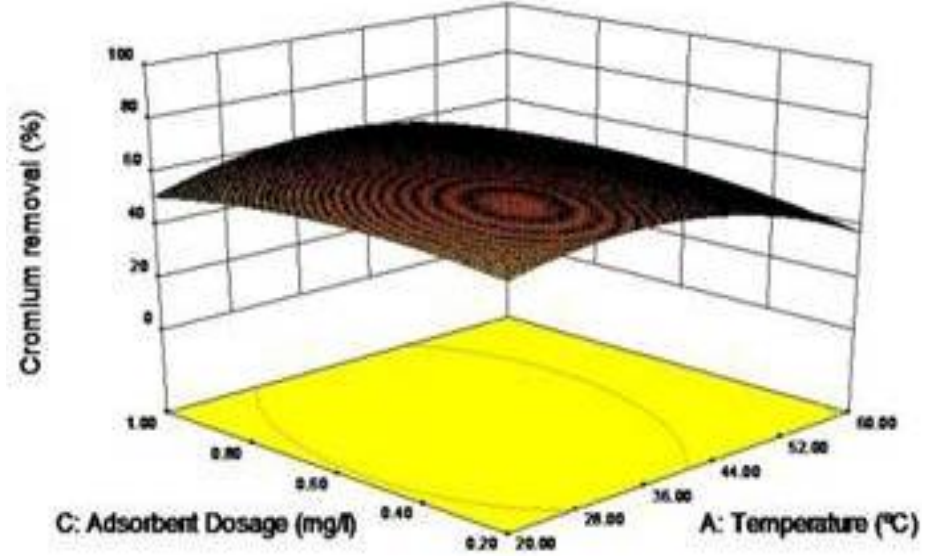
Where, q_t is the amount of chromium adsorbed on the adsorbent at time t (min) and k_1 (1/min) is the rate constant of first order adsorption. The incorporated form of the above equation with the state line conditions $t = 0$ to >0 ($q = 0$ to >0) and then rearranged gives the following time dependence function Equation (7):

$$\text{Log } (q_e - q_t) = \text{log } q_e - (k_1/2.303) t \quad (7)$$

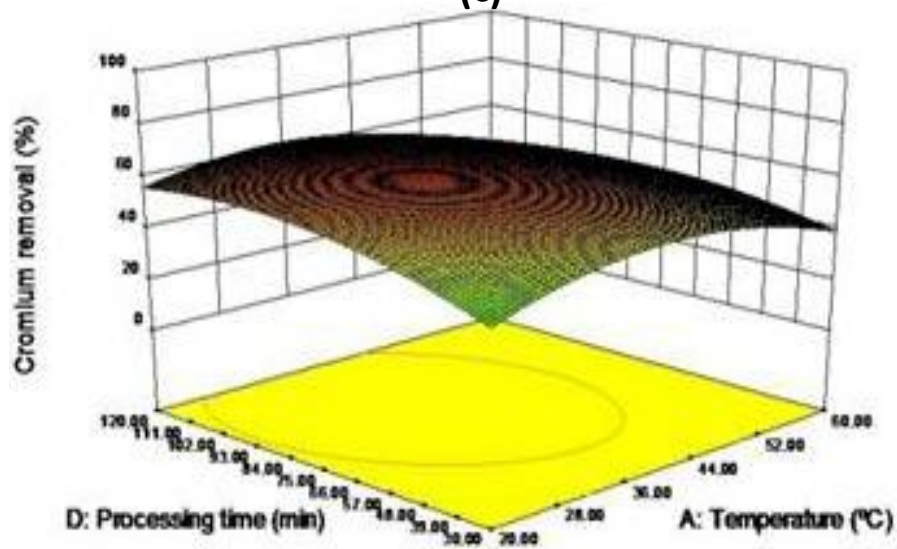
(a)



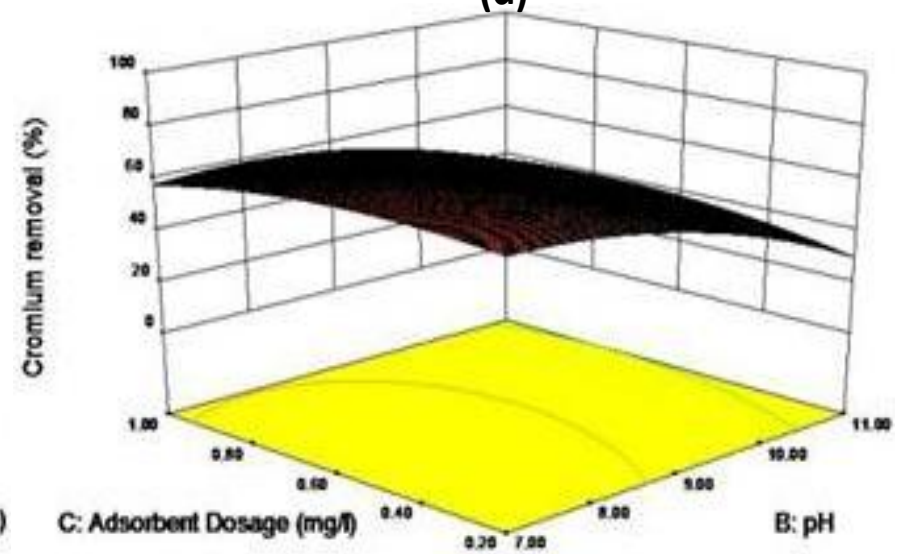
(b)



(c)



(d)



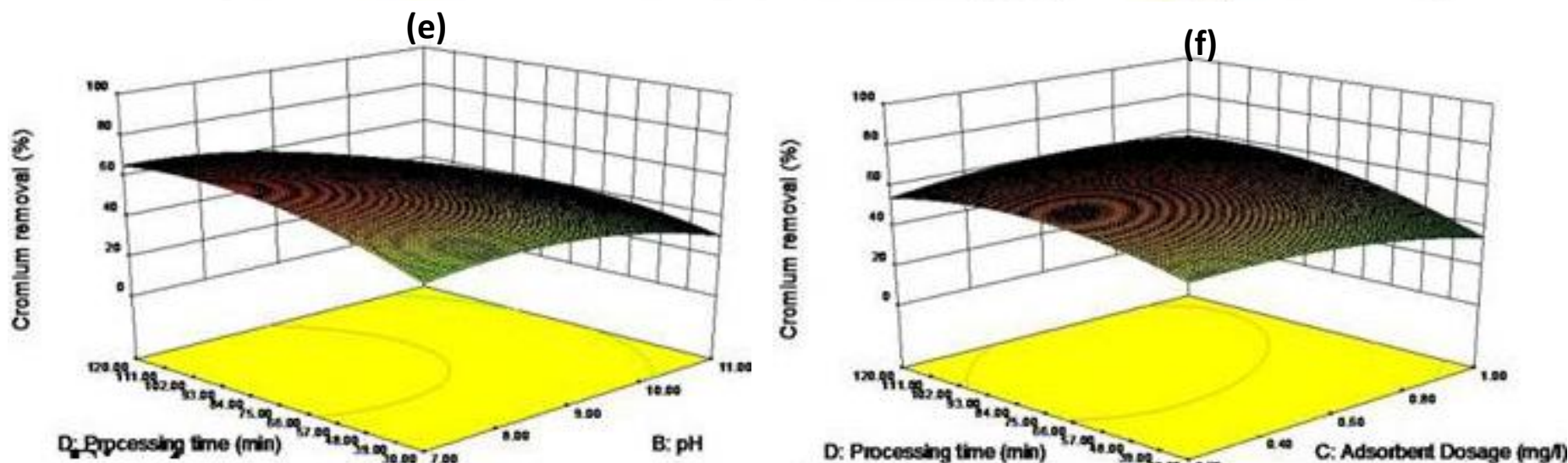


Figure 2. Three-dimensional response surface plot for the (a) Effect of temperature and pH, (b) Effect of temperature and adsorbent dosage ($\text{mg}\cdot\text{L}^{-1}$), (c) Effect of temperature and processing time, (d) Effect of pH and adsorbent dosage, (e) Effect of pH and processing time and (f) Effect of adsorbent dosage and processing time, on biosorption of chromium by *Aplanochytrium* sp.

Where, q_e is the amount of chromium adsorbed at equilibrium. The q_e and rate constant (k_1) were calculated from the slope of the plots of $\log(q_e - q_t)$ versus time (t) (Figure 3). It was found that the calculated q_e value did not agree with the experimental q_e values. The second order kinetic model is expressed as shown in Equation (8) (Vasudevan et al., 2011):

$$(dq_t / Dt) = k_1 (q_e^2 - q_t^2) \tag{8}$$

Where, k_2 is the rate constant of second order adsorption. The integrated form of Equation (9) with the boundary condition $t = 0$ to >0 ($q=0$ to >0) is:

$$t / q_t = [(1 / k_2 q_e^2) + (1/t)] t \tag{9}$$

Equation 9 can be rearranged and linearized as,

$$h = k_2 q_e^2 \tag{10}$$

The plot t/q_t versus time (t) (Figure 4) shows the straight line. The second order kinetic values of q_e and k_2 were calculated from the slope and intercept of the plots t/q_t versus t . Table 3 depicts the computed results obtained from first and second order kinetic model. The calculated q_e values agreed well with the experimental q_e values for second order kinetics model better than the first order kinetics model for adsorption capacity of adsorbent. These results indicate that the adsorption system belongs to both kinetic model of first second order kinetics.

Adsorption isotherm

The equilibrium adsorption isotherm is of importance

in the design of adsorption systems (Wang et al., 2005). Several isotherm equations are available and the Langmuir isotherm was selected in this study.

The Langmuir adsorption isotherms assumes that adsorption takes place at specific homogeneous sites within the adsorbent and has found successful application to many sorption process of monolayer adsorption. The Langmuir adsorption isotherm can be written as:

$$q_e = (q_m b C_e) / (1 + b C_e) \tag{11}$$

The Langmuir parameters were obtained by fitting the experimental data to the linearized equation derived from Equation (9):

$$C_e / Q_e = (1 / b q_m) + (C_e / q_m) \tag{12}$$

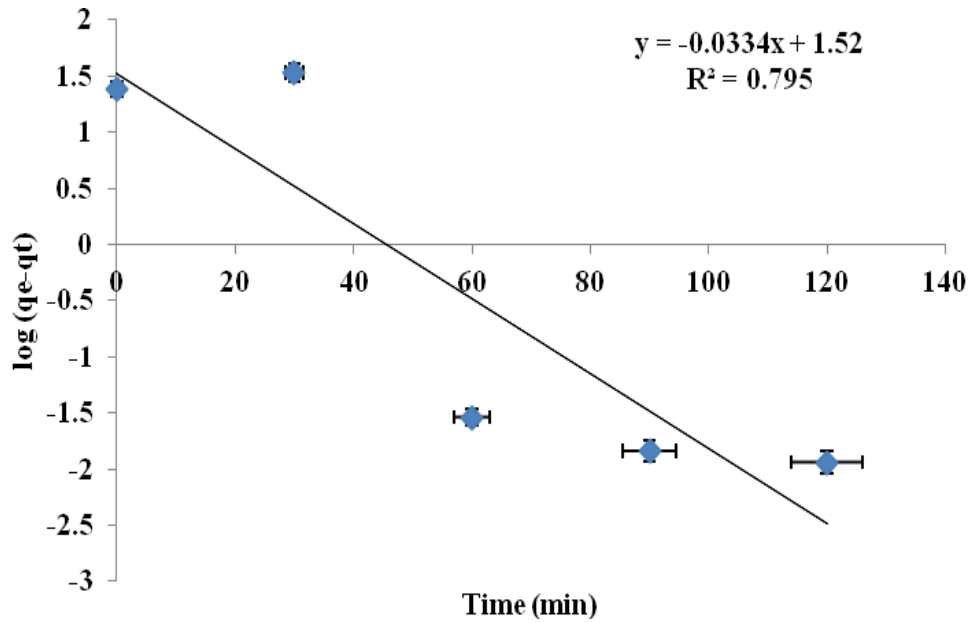


Figure 3. Kinetics analysis of chromium adsorption by linear plots of pseudo first-order rate equations.

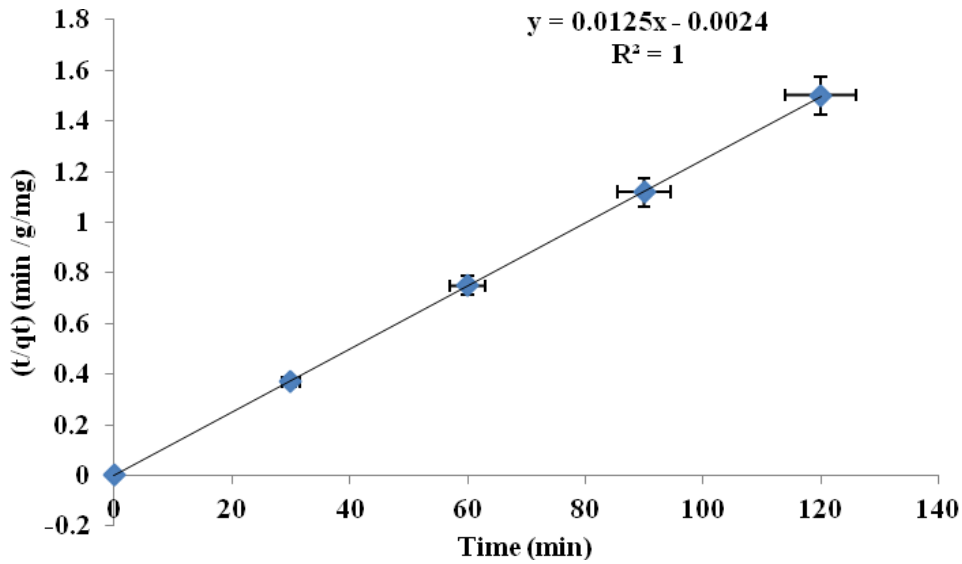


Figure 4. Kinetics analysis of chromium adsorption by linear plots of pseudo second-order rate equations.

Table 3. Lagergran constants and Pseudo second-order rate constants for chromium.

| Chromium (mg.L ⁻¹) | Lagergran constants | | | | | |
|--------------------------------|---------------------|-----------------------------------|----------------|----------------|-----------------------------------|----------------|
| | q _{exp} | K ₁ X 10 ⁻³ | R ² | Q _e | K ₂ X 10 ⁻³ | R ² |
| 313.19 | 300.09 | 0.033 | 0.79 | 9.86 | 0.012 | 1 |

$$1/q_e = [(1/bq_m) X (1/q_m) + (1/q_m)] \tag{13}$$

Where, q_e is the adsorbent amount (mg.g⁻¹) of the

Table 4. Langmuir isotherm constant for adsorption of chromium by *Aplanochytrium* sp.

| Langmuir isotherm parameters | C _e /q _e | 1/q _e |
|--------------------------------------|--------------------------------|------------------|
| q _m (mg.g ⁻¹) | 72.56 | 72.56 |
| b (L.mg ⁻¹) | 0.18 | 0.21 |
| R ² | 1 | 2.12 |

chromium, C_e is the equilibrium concentration of the chromium in solution (mg.L⁻¹), q_m is the monolayer adsorption capacity (mg.g⁻¹) and b is the constant related to the free energy of adsorption (L.mg⁻¹). Based on Equations 10 and 12, the isotherms were fitted to the adsorption data obtained. From the Langmuir adsorption exponents for Equations 12 and 13, the q_m and b were determined from the linear plots of C_e/q_e versus C_e and 1/q_e versus 1/C_e and correlation coefficients calculated for these isotherms are shown in Table 4. The values of the Langmuir constant were calculated from the slopes and intercepts of the plots. The magnitude of Langmuir constant b was small (0.18 mg L⁻¹) and the adsorption capacity q_m was determined as 72.56 mg.g⁻¹. The biological process of the bioadsorption capacity was studied using the kinetic model, and the results show that the maximum adsorption capacity of 72.56 mg.L⁻¹ was by 0.51 g of absorbent biomass of *Aplanochytrium* sp.

Conclusion

The highest percentage removal of chromium from aqueous solution (69.4%) was recorded in the statistically optimized condition of pH of 6.8 to 8.2 and temperature of 27°C within 79 h, and an adsorbent dosage (*Aplanochytrium* dried biomass) of 0.51 g.L⁻¹. The adsorption data fitted well to the Langmuir and the adsorption isotherms. Thus, the biomass of *Aplanochytrium* sp. could be able to remove toxic chromium. This study proves that mangrove derived lower fungi dried microbial biomass is a potent adsorbent for the removal of the chromium in the waste water treatment, with eco-friendly technique and economically viable.

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