



Response surface modeling and optimization of chromium(VI) removal from aqueous solution using Tamarind wood activated carbon in batch process

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ABSTRACT

The present paper discusses response surface methodology (RSM) as an efficient approach for predictive model building and optimization of chromium adsorption on developed activated carbon. In this work the application of RSM is presented for optimizing the removal of Cr(VI) ions from aqua solutions using activated carbon as adsorbent. All experiments were performed according to statistical designs in order to develop the predictive regression models used for optimization. The optimization of adsorption of chromium on activated carbon was carried out to ensure a high adsorption efficiency at low adsorbent dose and high initial concentration of Cr(VI). While the goal of adsorption of chromium optimization was to improve adsorption conditions in batch process, i.e., to minimize the adsorbent dose and to increase the initial concentration of Cr(VI). In the adsorption experiments a laboratory developed Tamarind wood activated carbon made of chemical activation (zinc chloride) was used. A 2⁴ full factorial central composite design experimental design was employed. Analysis of variance (ANOVA) showed a high coefficient of determination value ($R^2 = 0.928$) and satisfactory prediction second-order regression model was derived. Maximum chromium removal efficiency was predicted and experimentally validated. The optimum adsorbent dose, temperature, initial concentration of Cr(VI) and initial pH of the Cr(VI) solution were found to be 4.3 g/l, 32 °C, 20.15 mg/l and 5.41 respectively. Under optimal value of process parameters, high removal (>89%) was obtained for Cr(VI).

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1. Introduction

Chromium compounds are widely used in industries such as leather tanning, paints and pigments, mining, leather tanning, textile dyeing, electroplating, manufacturing of dye, paper, aluminum conversion coating operations, steel fabrication, plants producing industrial inorganic chemicals and wood treatment units. The pollution of water resources due to indiscriminate disposal of chromium metals has been causing worldwide concern for the last few decades. Chromium, an element which has been used by man for years, can be regarded as a longstanding environmental contaminant. It constantly released into the environment in a number of ways, like as leather tanning, electroplating, manufacturing of dye, paint and paper are just few examples [1–3] and also by natural processes, like as mainly by volcanic activity and weathering of rocks [4]. It is also added to cooling water to check corrosion. Overexposure of chromium workers to chromium dusts and mists

has been related to irritation and corrosion of the skin and the respiratory tract and, probably, to lung carcinoma. Chromium, especially in its VI oxidation state, is considered as a very toxic ion; thus, its elimination from aqueous solutions should be considered an environmental primary target. On the other hand, chromium is generally recognized as being essential to human health. However, hexavalent chromium compounds are also known to be significantly more toxic than the trivalent ones [5]. The hexavalent form has been considered to be more hazardous due to its carcinogenic properties [6]. Due to environmental concern, discharge limits of both Cr(III) and Cr(VI) have been instituted by most industrial countries. Their concentration in industrial wastewaters ranges from 0.5 to 270 mg/l. The tolerance limit for Cr(VI) for discharge into inland surface waters is 0.1 mg/l and in potable water is 0.05 mg/l [7,8]. The Ministry of Environment and Forest (MOEF); Government of India has set minimal national standards (MINAS) of 0.1 mg/l for safe discharge of effluent containing Cr(VI) in surface water [9]. The presence of high levels of chromium in the environment may cause long-term health risks to humans and ecosystems. It is therefore mandatory that their levels in drinking water, waste water and water used for agricultural and recreational purposes must be

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Nomenclature

C_0	initial concentrations of chromium solution (mg/l)
C_e	equilibrium concentrations of chromium solution (mg/l)
n	number of variables (dimensionless)
N	total number of tests (dimensionless)
V	volume of chromium solution (l)
W	weight of the adsorbent (g)
X_1	temperature ($^{\circ}\text{C}$)
X_2	pH (dimensionless)
X_3	initial feed concentrations of chromium (mg/l)
X_4	adsorbent dose (g/l)
X_i	variables of action called factors
Y	response of the system adsorption of chromium (%)

reduced to within the maximum allowable concentrations recommended by national and international health authorities such as World Health Organisation (WHO). Its removal from wastewater prior to discharge into environment is, therefore, necessary. The maximum contaminant level goal of chromium for the drinking water is 0.05 mg/l for the World Health Organization set standard [10].

The pollution of chromium metal in aqueous has become severe with the development of economy. People have paid attention to it which will make them sick such as cancer or even make them to die. In order to comply with this limit, it is essential that industries treat their effluents to reduce the Cr(VI) concentration in water and wastewater to acceptable levels before its transport and cycling into the natural environment. Therefore, the level of chromium in final effluent has to be reduced by the application of appropriate technology. There are many methods about how to deal with the chromium metal pollution, such as chemical precipitation [11], ion exchange [12], electrochemical precipitation [13], reduction [14], adsorption [15], solvent extraction [16], membrane separation [17], concentration [18], evaporation, reverse osmosis and bio-sorption [19,20] and emulsion per traction technology [21].

Adsorption is a versatile treatment technique practiced widely in fine chemical and process industries for wastewater and waste gas treatment. The usefulness of the adsorption process lies in the operational simplicity and reuse potential of adsorbents during long-term applications. Carbon adsorption has proved to be the least expensive treatment option, particularly in treating low concentrations of wastewater streams and in meeting stringent treatment levels. Activated carbon is a black solid substance resembling granular or powder charcoal and is carbonaceous material that has highly developed porosity, internal surface area and relatively high mechanical strength. Activated carbon based systems can remove a wide variety of toxic pollutants with very high removal efficiencies. For these reasons, activated carbon adsorption has been widely used for the treatment of chromium containing wastewaters [5,15,22,23]. However, commercially available activated carbons may be expensive and, for this reason, the knowledge of the optimal working conditions to maximize the sorbent capture capacity is required. The materials developed for this purpose range from agricultural waste products, biomass and various solid substances. Some examples are activated groundnut husk carbon, coconut husk and palm pressed fibers, coconut shell, wood and dust coal activated carbons, coconut tree sawdust carbon, used tyres carbon, fly ash, rice husk carbon, hazelnut shell carbon, almond shell carbon, agricultural wastes have been reported in literature [20,22–29].

In this work it has been reported the results obtained on the preparation of activated carbon from Tamarind wood with zinc

chloride activation and their ability to remove chromium(VI) from waste water. The influence of several operating parameters, such as initial concentration, temperature, pH and adsorbent dose were investigated in batch mode. The published information in literature about adsorption of chromium in activated carbon is well detailed [5,15,21–23]. The conventional and classical methods of studying a process by maintaining other factors involved at an unspecified constant level does not depict the combined effect of all the factors involved. The conventional technique for the optimization of a multivariable system usually defines one-factor at a time. Such a technique needs to perform a lot of experiments and could not reveal the alternative effects between components. This method is also time consuming and requires a number of experiments to determine optimum levels, which are unreliable. Recently many statistical experimental design methods have been employed in chemical process optimization. Experimental design technique is a very useful tool for this purpose as it provides statistical models, which help in understanding the interactions among the parameters that have been optimized [30]. These methods involve mathematical models for designing chemical processes and analyzing the process results. Among them, response surface methodology (RSM) is one suitable method utilized in many fields. RSM is a collection of mathematical and statistical techniques useful for developing, improving and optimizing processes and can be used to evaluate the relative significance of several affecting factors even in the presence of complex interactions. The main objective of RSM is to determine the optimum operational conditions for the system or to determine a region that satisfies the operating specifications [31]. However, there is no information available in the literature regarding the optimization of chromium adsorption on activated carbon. Therefore, we decided to study more thoroughly the phenomenon of adsorption of chromium in Tamarind wood activated carbon. The effects of operating parameters such as initial feed concentration, temperature, pH and adsorbent dose were optimized using response surface methodology. The optimization of experimental conditions using RSM in adsorption of chromium in activated carbon are not available in literature.

2. Experimental technique

2.1. Adsorbate: chromium(VI)

A stock solution of Cr(VI) was prepared (1000 mg/l) by dissolving required amount of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) in distilled water. The stock solution was diluted with distilled water to obtain desired concentration ranging from 10 to 50 mg/l.

2.2. Adsorbent: Tamarind wood activated

The Tamarind wood was collected from Indian Institute of Technology campus of Kharagpur, West Bengal, India, and washed with deionized water four to five times for removing dirt and dust particles. The washed wood was cut into 50.8–76.2 mm pieces. The woods were sun dried for 20 days. Chemical activation of the precursor was done with ZnCl_2 . 10 g of dried precursor was well mixed with distilled water so that 100 ml concentrated solution contained 10 g of ZnCl_2 . The chemical ratio is defined as the ratio of chemical activating agent (ZnCl_2) to the precursor. The chemical ratio (activating agent/precursor) was 100% in this case. The mixing was performed at 50°C for 1 h. After mixing, the slurry was subjected to vacuum drying at 100°C for 24 h. The resulting chemical-loaded samples were placed in a stainless-steel tubular reactor and heated ($5^{\circ}\text{C}/\text{min}$) to the final carbonization temperature under a nitrogen flow rate of 150 ml/min STP. Samples were held at the final temperature (carbonization temperature) for carbonization times

of 40 min before cooling down under nitrogen. Nitrogen entering in the reactor was first preheated to 250–300 °C in a pre-heater. The products were washed sequentially with 0.5 N HCl, hot water and finally cold distilled water to remove residual organic and mineral matters, and then dried at 110 °C. In all experiments, heating rate and nitrogen flow was kept constant. The experiments were carried out for chemical ratio of (296%), activation time (40 min) and carbonization temperature (439 °C). Then carbon was dried to 60 °C. After this, carbon was crushed in a small ball mill with 50 numbers of small balls for 1 h. The powder from ball mill was collected and dried to remove the moisture. Then this powder carbon was kept in airtight packet for the experimental use.

2.3. Method of experiment

Jar tests were carried out to study the effect of various operating variables on the adsorption rate. Adsorption of Cr(VI) on developed activated carbon was conducted containing different weighted amounts of each sample with 200 ml solution of 10, 20 and 40 mg/l of initial concentration. The aqueous chromium solutions were prepared by dissolving known amount of corresponding potassium dichromate in 1 l of distilled water. The stock solution was diluted as required to obtain standard solutions of concentrations ranging between 10 and 50 mg/l. The experiments were performed in a thermal shaker at controlled temperature for a period of 24 h at 120 rpm using 250 ml Erlenmeyer flasks containing 100 ml of different Cr(VI) concentrations at different temperatures (10–50 °C). Samples were taken out at regular intervals and the residual concentration in the solution was analyzed using atomic absorption spectroscopy (AAS) after filtering the adsorbent with Whatmen filter paper to make it carbon free. The batch process was used so that there is no need for volume correction. Batch adsorption experiments were performed by contacting the selected activated carbon samples of different weights (0.1–0.5 g) with 100 ml of the aqueous solution of different initial concentrations (10, 20, 30, 40 and 50 mg/l) at solution pH (2–10) and at different temperatures (10, 20, 30, 40 and 50 °C). Continuous mixing was provided during the experimental period with a constant agitation speed of 120 rpm for better mass transfer with high interfacial area of contact. The remaining concentration of Cr(VI) in each sample after adsorption at different time intervals was determined by atomic absorption spectroscopy. The Cr(VI) concentration retained in the adsorbent phase was calculated according to

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations (mg/l) of chromium solution respectively; V is the volume (l) and W is the weight (g) of the adsorbent. Two replicates per sample were done and the average results are presented.

By knowing the chromium concentration at initial concentrations and equilibrium concentrations, the efficiency of adsorption of chromium by activated carbon can be calculated by using the following equation for efficiency of adsorption chromium:

$$\text{Adsorption (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

2.4. Multivariate experimental design

Response surface methodology (RSM) is a statistical method that uses quantitative data from appropriate experiments to determine regression model equations and operating conditions [30]. RSM is a collection of mathematical and statistical techniques for modeling and analysis of problems in which a response of interest is influenced by several variables [31]. A standard RSM design called central composite design (CCD) was applied in this work to study

the variables for adsorption of chromium from aqueous solution using prepared activated carbon in a batch process.

The central composite design was widely used for fitting a second-order model. By using this method, modeling is possible and it requires only a minimum number of experiments. It is not necessary in the modeling procedure to know the detailed reaction mechanism since the mathematical model is empirical. Generally, the CCD consists of a 2^n factorial runs with $2n$ axial runs and n_c center runs (six replicates). These designs consist of a 2^n factorial or fractional (coded to the usual ± 1 notation) augmented by $2n$ axial points ($\pm\alpha, 0, 0, \dots, 0$), ($0, \pm\alpha, 0, \dots, 0$), \dots , ($0, 0, \dots, \pm\alpha$), and n_c center points ($0, 0, 0, \dots, 0$) [32]. Each variable is investigated at two levels. Meanwhile, as the number of factors, n , increases, the number of runs for a complete replicate of the design increases rapidly. In this case, main effects and interactions may be estimated by fractional factorial designs running only a minimum number of experiments. Individual second-order effects cannot be estimated separately by 2^n factorial designs. Therefore, the central composite design was employed in this study. The responses and the corresponding parameters are modeled and optimized using ANOVA to estimate the statistical parameters by means of response surface methods.

Basically this optimization process involves three major steps, which are, performing the statistically designed experiments, estimating the coefficients in a mathematical model and predicting the response and checking the adequacy of the model.

$$Y = f(X_1, X_2, X_3, X_4, \dots, X_n) \quad (3)$$

where Y is the response of the system and X_i is the variables of action called factors. The goal is to optimize the response variable (Y). It is assumed that the independent variables are continuous and controllable by experiments with negligible errors. It is required to find a suitable approximation for the true functional relationship between independent variables and the response surface [33].

The experimental sequence was randomized in order to minimize the effects of the uncontrolled factors. The response was used to develop an empirical model that correlated the response to the adsorption of chromium from aqueous solution using prepared activated carbon in a batch process variable using a second-degree polynomial equation as given by Eq. (4)

$$Y = b'_0 + \sum_{i=1}^n b_i X_i + \sum_{i=1}^n b_{ii} X_i^2 + \sum_{i=1}^n \sum_{j>1}^n b_{ij} X_i X_j \quad (4)$$

where Y is the predicted response, b'_0 the constant coefficient, b_i the linear coefficients, b_{ij} the interaction coefficients, b_{ii} the quadratic coefficients and x_i, x_j are the coded values of the adsorption of chromium on prepared activated carbon variables. The number of tests required for the CCD includes the standard 2^n factorial with its origin at the center, $2n$ points fixed axially at a distance, say α from the center to generate the quadratic terms, and replicate tests at the center; where n is the number of variables. The axial points are chosen such that they allow readability, which ensures that the variance of the model prediction is constant at all points equidistant from the design center [34]. Replicates of the test at the center are very important as they provide an independent estimate of the experimental error. For four variables, the recommended number of tests at the center is six [35]. Hence, the total number of tests (N) required for the four independent variables is

$$N = 2^n + 2n + n_c = 2^4 + (2 \times 4) + 6 = 30 \quad (5)$$

Once the desired ranges of values of the variables are defined, they are coded to lie at ± 1 for the factorial points, 0 for the center points and $\pm\alpha$ for the axial points.

3. Results and discussions

3.1. Physical and chemical characterization of the adsorbent

3.1.1. Chemical properties

Adsorbent pH may influence the removal efficiency. Distinctly acidic adsorbent may react with the material to be removed and may hamper the surface properties of the adsorbent. The pH of activated Tamarind wood was measured, for our experiment the pH of activated Tamarind wood was found 6.77.

Ash content of the activated carbon is the residue that remains when the carbonaceous portion is burned off. The ash consists mainly of minerals such as silica, aluminum, iron, magnesium and calcium. Ash in activated carbon is not required and considered to be an impurity. As the ash content is 4.55% it resembles good adsorbent.

The spectra of the Tamarind wood, prepared activated carbon (under the optimum preparation conditions) and adsorbed Cr(VI) activated carbon were measured by an FTIR spectrometer within the range of 400–4000 cm^{-1} wave number. The FTIR spectrum plot obtained for the Tamarind wood, prepared activated carbon and adsorbed Cr(VI) activated carbon was shown in Fig. 1.

3.1.2. Physical properties

The smaller the particle sizes of a porous carbon, the greater the rate of diffusion and adsorption. Intraparticle diffusion is reduced as the particle size reduces, because of the shorter mass transfer zone, causing a faster rate of adsorption. Since we have prepared our carbon in a powdered form so it has a great efficiency of removal. The

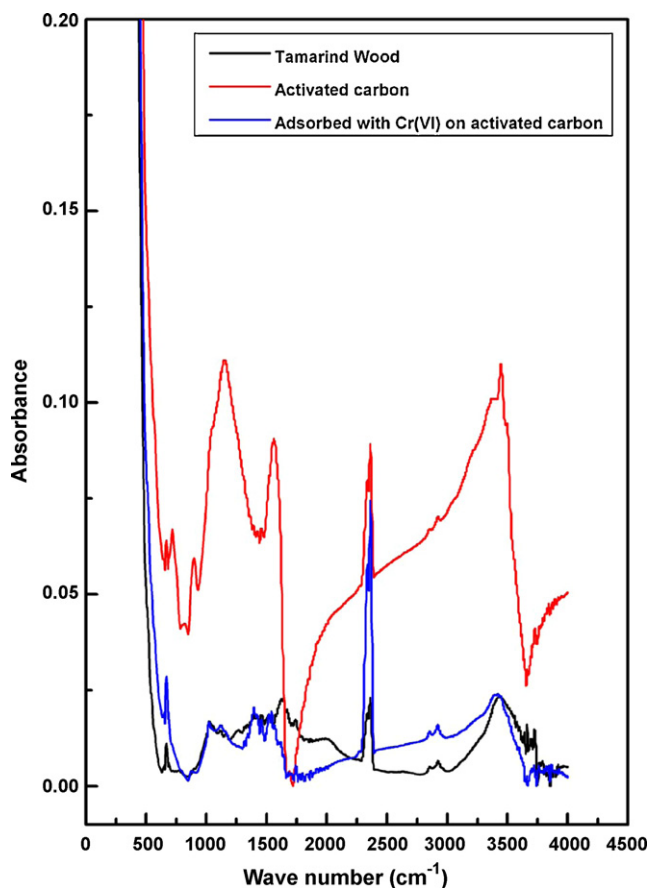


Fig. 1. FTIR result of Tamarind wood, prepared activated carbon and adsorbed with Cr(VI).

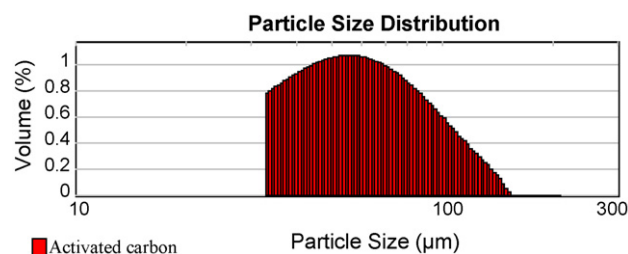


Fig. 2. Particle size distribution of activated Tamarind wood measured using Malvern master size.

particle size analysis of the prepared activated carbon was done using Malvern analyzer. From Fig. 2 it shows that there are no particles above the size of 150 μm .

Density is particularly important in removal. If two carbons differing in bulk density are used at the same weight per liter, the carbon having higher bulk density will be able to remove more efficiently. Average bulk density can be calculated by water displacement method. In this method, volume of water displaced is observed by a particular amount of carbon. The average bulk density was found to be 0.791 g/ml.

The BET surface area of activated Tamarind wood was measured from Fig. 3 and it was found 1322 m^2/g . The average pore diameter was found as 5.3 Å. This shows that activated Tamarind wood is reasonably good for adsorption. The DFT result shows that the activated carbons consists mainly pore width from 5 to 60 Å.

Fig. 4 shows the scanning electron microscope (SEM) image of the activated carbon obtained under the optimum preparation conditions. There were very little pores available on the surface of the precursor. However, after ZnCl_2 treatment under the optimum preparation conditions, many large pores in a honeycomb shape were developed on the surface of the activated carbon and a smooth melt surface appeared, interspersed with generally large pores due to some of the volatiles being evolved as shown in Fig. 4.

3.2. Development of regression model equation

CCD was used to develop correlation between the adsorption of Cr(VI) from aqueous solution variables to the adsorption of chromium(VI) in activated carbon. Runs 25–30 at the center point were used to determine the experimental error. According to the sequential model sum of squares, the models were selected based on the highest order polynomials where the additional terms were significant and the models were not aliased. The quadratic model was selected as suggested by the software. Experiments were planned to obtain a quadratic model consisting of 2^4 trials plus a star configuration ($\alpha = \pm 2$) and there replicates at the center point. The design of this experiment is given in Table 1, together with the experimental results. The maximum adsorption of Cr(VI) was found to be >89%. Regression analysis was performed to fit the response function of adsorption of chromium (%). The model expressed by Eq. (4), where the variables take their coded values, represents adsorption (Y) as a function of temperature (X_1), pH (X_2), initial feed concentrations of chromium (X_3) and adsorbent dose (X_4). The final empirical model in terms of coded factors for adsorption of chromium (Y) is given in Eq. (6):

$$Y = 79.19 + 4.53X_1 - 9.62X_2 - 2.92X_3 + 10.02X_4 - 2.84X_1X_2 + 0.37X_1X_3 - 2.75X_1X_4 + 3.76X_2X_3 + 5.03X_2X_4 - 6.09X_3X_4 + 0.804X_1^2 - 14.77X_1^2 - 8.23X_2^2 - 3.61X_3^2 - 6.57X_4^2 \quad (6)$$

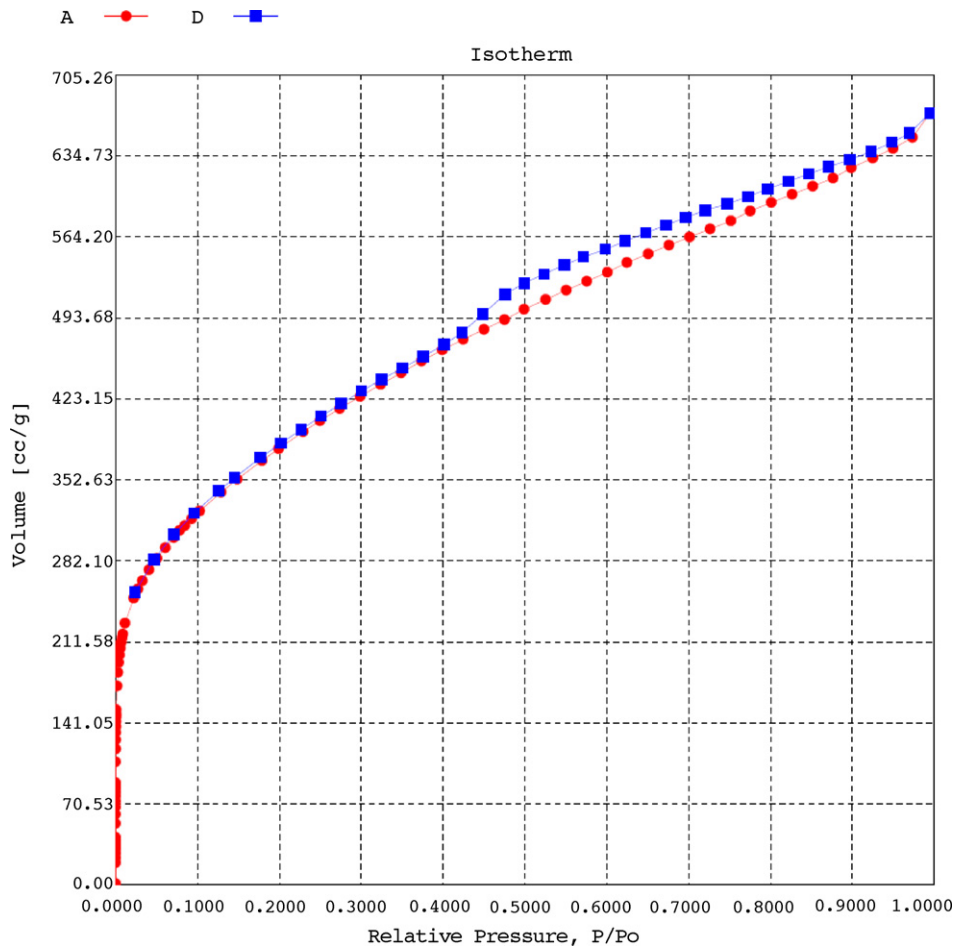


Fig. 3. N₂ adsorption/desorption isotherm of prepared activated carbon.

3.3. Statistical analysis

Eq. (6) has been used to visualize the effects of experimental factors on conversion percentage response in Figs. 5–11. The actual and the predicted adsorption of chromium percent are shown in Fig. 5. Actual values are the measured response data for a particular run, and the predicted values are evaluated from the model and are generated by using the approximating functions. In Fig. 5, the values

of R^2 and R^2_{adj} were found to be 0.888 and 0.785, respectively. The fair correlation coefficients might have resulted by the insignificant terms in Table 2, and most likely due to four different variables selected in wide ranges with a limited number of experiments as well as the nonlinear influence of the investigated parameters on process response.

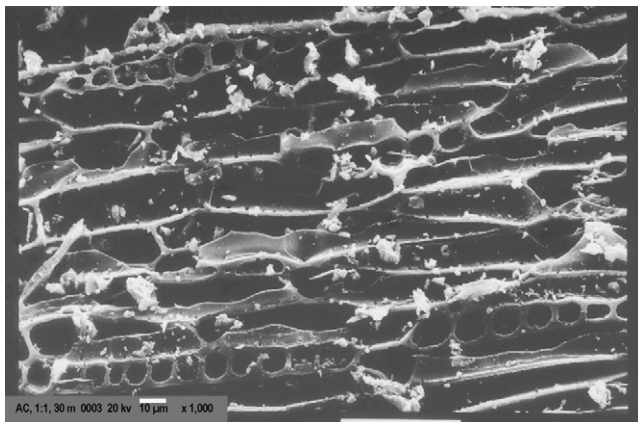


Fig. 4. Scanning electron micrograph of prepared activated carbon.

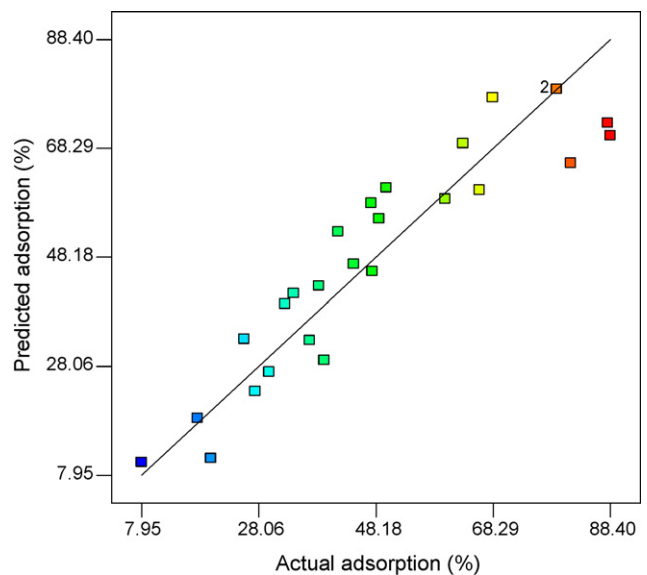


Fig. 5. The actual and predicted plot of adsorption of chromium(VI).

Table 1
Experimental design matrix and results.

Run	Actual level of variables				Adsorption, Y (%)
	X ₁ (°C)	X ₂	X ₃ (mg/l)	X ₄ (g/l)	
1	20	4	20	2	34.05
2	40	4	20	2	49.95
3	20	8	20	2	7.95
4	40	8	20	2	17.55
5	20	4	40	2	32.55
6	40	4	40	2	65.92
7	20	8	40	2	27.45
8	40	8	40	2	25.55
9	20	4	20	4	63.13
10	40	4	20	4	68.24
11	20	8	20	4	47.35
12	40	8	20	4	48.70
13	20	4	40	4	38.37
14	40	4	40	4	41.67
15	20	8	40	4	44.35
16	40	8	40	4	47.55
17	10	6	30	3	19.83
18	50	6	30	3	39.30
19	30	2	30	3	81.64
20	30	10	30	3	29.83
21	30	6	10	3	88.40
22	30	6	50	3	60.06
23	30	6	30	1	36.80
24	30	6	30	5	87.93
25	30	6	30	3	79.20
26	30	6	30	3	79.19
27	30	6	30	3	79.19
28	30	6	30	3	79.19
29	30	6	30	3	79.19
30	30	6	30	3	79.20

3.4. Adsorption capacity of chromium(VI)

To investigate the effects of the four factors on the adsorption of chromium, the response surface methodology was used, and three-dimensional plots were drawn. Based on the ANOVA results obtained, adsorbent dose and pH were found to have significant effects on the adsorption of chromium, with adsorbent dose imposing the greatest effect on the adsorption of chromium. Initial feed concentration of Cr(VI) and temperature, on the other hand, imposed the least effect on the response. The quadratic effects of initial feed concentration of Cr(VI) as well as the interaction effects between X₁X₂, X₁X₃, X₁X₄, X₂X₃ and X₂X₄ were considered moderate. The adsorption of chromium percent response surface graphs is shown in Figs. 6–11.

Table 2
Analysis of variance (ANOVA) for response surface quadratic model for of adsorption of Cr(VI).

Source	Sum of squares	Degree of freedom	Mean square	F-value	Prob > F	Remarks
Model	14,242.93	14	1017.352	8.575847	<0.0001	Significant
X ₁	493.8464	1	493.8464	4.162915	0.0593	
X ₂	2224.626	1	2224.626	18.75265	0.0006	Significant
X ₃	205.1888	1	205.1888	1.729654	0.2082	
X ₄	2413.252	1	2413.252	20.34268	0.0004	Significant
X ₁ X ₂	129.0212	1	129.0212	1.087594	0.3135	
X ₁ X ₃	2.261264	1	2.261264	0.019061	0.8920	
X ₁ X ₄	121.0825	1	121.0825	1.020674	0.3284	
X ₂ X ₃	226.4649	1	226.4649	1.909002	0.1873	
X ₂ X ₄	405.0659	1	405.0659	3.414533	0.0844	
X ₃ X ₄	593.4705	1	593.4705	5.002703	0.0409	Significant
X ₁ ²	5987.407	1	5987.407	50.47129	<0.0001	Significant
X ₂ ²	1858.608	1	1858.608	15.66728	0.0013	Significant
X ₃ ²	357.2216	1	357.2216	3.011225	0.1032	
X ₄ ²	1185.635	1	1185.635	9.9944	0.0065	Significant
Residual	1779.45	15	118.63	–	–	
Lack of fit	1779.449	10	177.9449	11,718,326	<0.0001	Significant
Pure error	7.59E–05	5	1.52E–05	–	–	
Correlation total	16,022.38	29	–	–	–	

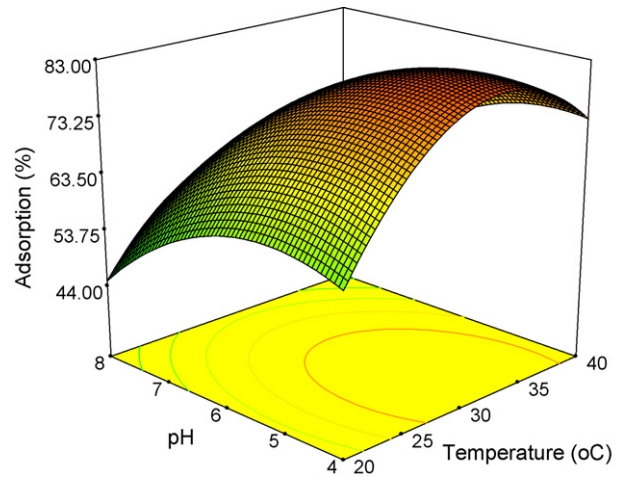


Fig. 6. The combined effect of temperature and pH on adsorption of chromium(VI) at constant initial concentration of Cr(VI) (30 mg/l) and adsorbent dose (3 g/l).

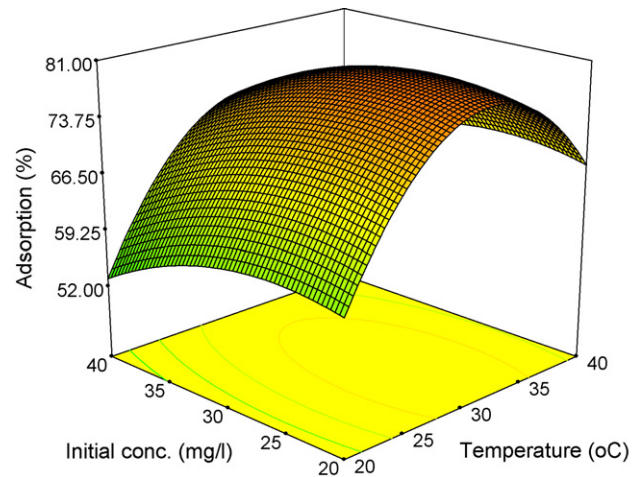


Fig. 7. The combined effect of temperature and initial concentration of Cr(VI) on adsorption of chromium(VI) at constant pH (6) and adsorbent dose (3 g/l).

Fig. 6 shows the three-dimensional response surfaces, the combined effect of temperature and pH on adsorption of Cr(VI) at constant initial feed concentration of Cr(VI) (30 mg/l) and adsorbent dose (3 g/l). Increasing the temperature from 25 to 45 °C facili-

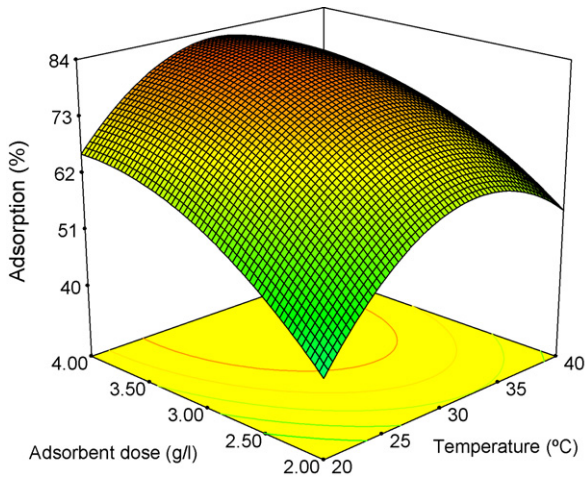


Fig. 8. The combined effect of temperature and adsorbent dose on adsorption of chromium(VI) at constant pH (6) and initial concentration of Cr(VI) (30 mg/l).

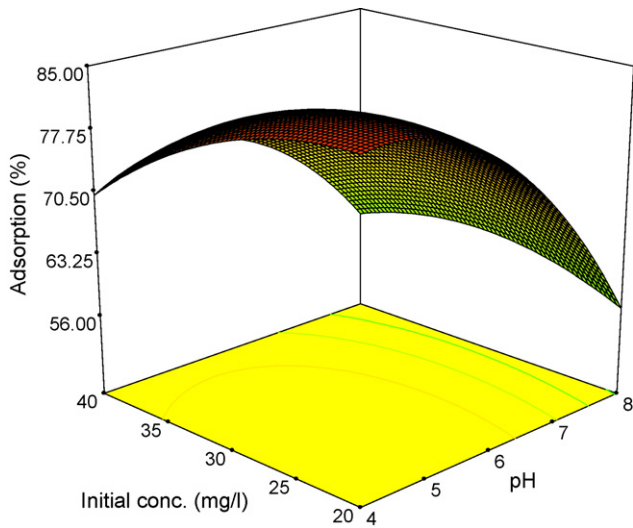


Fig. 9. The combined effect of initial concentration of Cr(VI) and pH on adsorption of chromium(VI) at constant adsorbent dose (3 g/l) and temperature (30 °C).

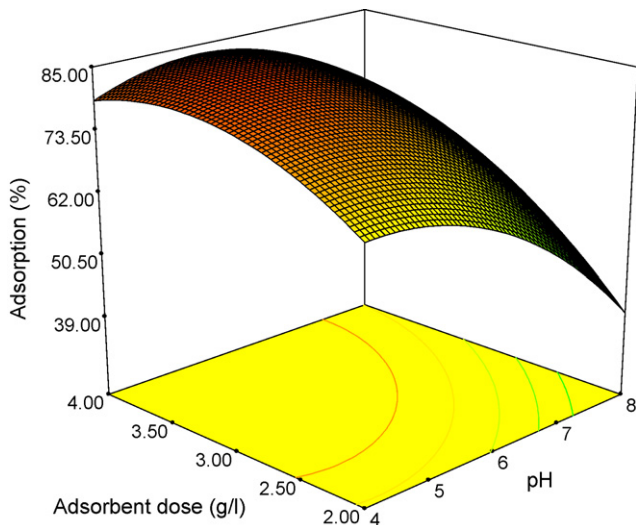


Fig. 10. The combined effect of pH and adsorbent dose on adsorption of chromium(VI) at constant temperature (30 °C) and initial concentration of Cr(VI) (30 mg/l).

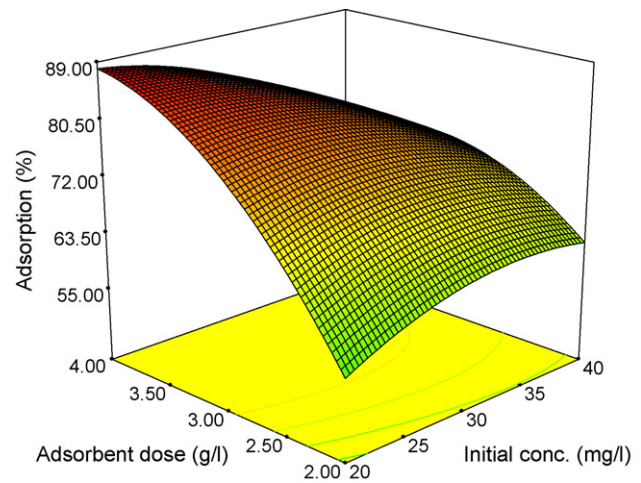


Fig. 11. The combined effect of initial concentration of Cr(VI) and adsorbent dose on adsorption of chromium(VI) at constant pH (6) and temperature (30 °C).

tated the removal of Cr(VI) ions. The increase in metal uptake with increasing temperature may be due to either higher affinity of sites for metal or an increase in number of binding sites on activated carbon. It is clear from this figure that the percent adsorption of Cr(VI) decreases with increase in pH from 2.0 to 6.0 and after pH 6.65 (natural pH), no adsorption takes place at all. It is important that the maximum adsorption at all the concentrations takes place at pH 2.0. A maximum adsorption of chromium >81% was determined at constant initial feed concentration of Cr(VI) (30 mg/l) and adsorbent dose (3 g/l).

The interactive effect of temperature and initial concentration of Cr(VI) of the solution on percent adsorption of Cr(VI) onto activated carbon is shown in Fig. 7. It shows that adsorption increases with increasing metal concentration up to 25–30 mg/l and afterwards shows a slight decrease. A maximum adsorption of chromium >73% was determined at constant pH (6) and adsorbent dose (3 g/l).

The combined effect of temperature and initial feed concentration of Cr(VI) on adsorption of chromium(VI) at constant pH (6) and adsorbent dose (3 g/l) is shown in Fig. 8, the three-dimensional response surfaces. A maximum adsorption of chromium >79% was determined at constant pH (6) and adsorbent dose (3 g/l).

The three-dimensional response surfaces of the combined effect of initial concentration of Cr(VI) and pH on adsorption of Cr(VI) at constant adsorbent dose (3 g/l) and temperature (30 °C) is shown in Fig. 9. A maximum adsorption of chromium >76% was determined at constant adsorbent dose (3 g/l) and temperature (30 °C).

Fig. 10 shows the three-dimensional response surfaces which were constructed to show the most important two variables (pH and adsorbent dose) on the adsorption of chromium(VI) at constant temperature (30 °C) and initial concentration of Cr(VI) (30 mg/l). It can be seen from the figure that initially the percentage removal increases very sharply with the increase in adsorbent dosage but beyond a certain value 0.25–0.30 g, the percentage removal reaches almost a constant value. This trend is expected because as the adsorbent dose increases the number adsorbent particles increases and thus more Cr(VI) is attached to their surfaces. A maximum adsorption of chromium >84% was determined at constant temperature (30 °C) and initial concentration of Cr(VI) (30 mg/l).

It can be clear from Fig. 11 that there is a combined effect of initial feed concentration of Cr(VI) and adsorbent dose on adsorption of chromium(VI) at constant pH (6) and temperature (30 °C). It can be also seen that the maximum adsorption of chromium >84% was determined at constant pH (6) and temperature (30 °C).

Table 3
Model validation.

Temperature, X_1 ($^{\circ}\text{C}$)	pH, X_2	Initial feed concentration, X_3 (mg/l)	Adsorbent dose, X_4 (g/l)	Adsorption of Cr(VI), Y (%)	
				Predicted	Experimental
32	5.57	20.15	5.41	89.94	90.82

3.5. Optimization by response surface modeling

One of the main aims of this study was to find the optimum process parameters to maximize the adsorption of chromium from the developed mathematical model equations. The quadratic model equation was optimized using quadratic programming (QP) to maximize adsorption of chromium within the experimental range studied. The optimum adsorption conditions determined for a new adsorbent activated Tamarind wood in batch process were temperature 32 $^{\circ}\text{C}$, initial feed concentration of Cr(VI) 20.15 mg/l, pH 5.41 and adsorbent dose 5.41 g/l. The model validations have been determined as optimum levels of the process parameters to achieve the maximum adsorption of chromium of 89.94%, compared to 90.82% which was maximum adsorption of chromium in the tests conducted (Table 3).

4. Conclusions

The objective of the present study was to find out and optimize the chromium(VI) adsorption capacity of a new adsorbent activated Tamarind wood. The response surface methodology based on five variables central composite design was used to determine the effect of temperatures (ranging 10–50 $^{\circ}\text{C}$), pH (ranging 2–10), initial feed concentrations of Cr(VI) (ranging 10–50 mg/l) and adsorbent doses (ranging 1–5 g/l) on the adsorption of chromium. The regression analysis, statistical significance and response surface were done using Design Expert Software for predicting the responses in all experimental regions. Models were developed to correlate the adsorption variables to the responses. Through analysis of the response surfaces derived from the models, adsorbent dose was found to have the most significant effect on adsorption of chromium. Process optimization was carried out and the experimental values obtained for the adsorption of chromium are found to agree satisfactorily with the values predicted by the models. The optimal adsorption of chromium was obtained as adsorbent dose, temperature, initial concentration of Cr(VI) and initial pH of the Cr(VI) solution and these were found to be 4.3 g/l, 32 $^{\circ}\text{C}$, 20.15 mg/l and 5.41 respectively resulting in 89.94% of adsorption of chromium.

References

- [1] M.J. Udy, Chromium, Reinhold Publishing Corporation, New York, 1956.
- [2] L.J. Casarett, J. Dou, Toxicology, The Basic Science of Poisons, Macmillan, New York, 1980.
- [3] J.O. Nriagu, E. Nieboer, Chromium in the Natural and Human Environment, Wiley, New York, 1988.
- [4] N. Serpone, E. Borgarello, E. Pelizzetti, E. Schiavello (Eds.), Photocatalysis and Environment, Kluwer Academic, The Netherlands, 1988.
- [5] S.B. Lalvani, T. Wiltowski, A. Hubner, A. Weston, N. Mandich, Removal of hexavalent chromium and metal cations by a selective and novel carbon adsorbent, Carbon 36 (7–8) (1998) 1219–1226.
- [6] J.L. Gardea-Torresdey, K.J. Tiemann, V. Armendariz, L. Bess-Oberto, R.R. Chianelli, J. Rios, J.G. Parsond, G. Gamez, Characterization of Cr(VI) binding and reduction to Cr(III) by the agricultural by products of *Avena monida* (Oat) biomass, J. Hazard. Mater. B80 (2000) 175–188.
- [7] World Health Organization, Guidelines for Drinking-Water Quality, 3rd ed., World Health Organization, Geneva, Switzerland, 2006, p. 54.
- [8] EPA (Environmental Protection Agency), Environmental Pollution Control Alternatives. EPA/625/5-90/025, EPA/625/4-89/023, Cincinnati, US, 1990.
- [9] Indian Standard, Drinking Water Specification (First Revision), IS 10500, 1991.
- [10] MINAS, Pollution control acts, rules, and notification there under Central Pollution Control Board, Ministry of Environment and Forests, Government of India, New Delhi, 2001.
- [11] X. Zhou, T. Korenaga, T. Takahashi, T. Moriwake, S. Shinoda, A process monitoring/controlling system for the treatment of wastewater containing chromium(VI), Water Res. 27 (1993) 1049–1054.
- [12] G. Tiravanti, D. Petruzzelli, R. Passiono, Pretreatment of tannery wastewaters by an ion exchange process for Cr(III) removal and recovery, Water Sci. Technol. 36 (1997) 197–207.
- [13] N. Kongsricharoern, C. Polprasert, Chromium removal by a bipolar electrochemical precipitation process, Water Sci. Technol. 34 (1996) 109–116.
- [14] J.C. Seaman, P.M. Bertsch, L. Schwallie, In situ Cr(VI) reduction within coarse-textured, oxide-coated soil and aquifer systems using Fe(II) solutions, Environ. Sci. Technol. 33 (1999) 938–944.
- [15] N. Calace, D.A. Muro, E. Nardi, B.M. Petronio, M. Pietroletti, Adsorption isotherms for describing heavy metal retention in paper mill sludges, Ind. Eng. Chem. Res. 41 (2002) 5491–5497.
- [16] K. Pagilla, L.W. Canter, Laboratory studies on remediation of chromium contaminated soils, J. Environ. Eng. 125 (1999) 243–248.
- [17] A.K. Chakravarti, S.B. Chowdhury, S. Chakrabarty, T. Chakrabarty, D.C. Mukherjee, Liquid membrane multiple emulsion process of chromium (VI) separation from wastewaters, Colloids Surf. A: Physicochem. Eng. Aspects 103 (1995) 59–71.
- [18] C.F. Lin, W. Rou, K.S. Lo, Treatment strategy for Cr(VI) bearing wastes, Water Sci. Technol. 26 (1992) 2301–2304.
- [19] Z. Aksu, T. Kutsal, A comparative study for biosorption characteristics of heavy metal ions with *C. vulgaris*, Environ. Technol. 11 (1990) 979–987.
- [20] D. Mohan, K.P. Singh, V.K. Singh, Removal of hexavalent chromium from aqueous solution using low-cost activated carbons derived from agricultural waste materials and activated carbon fabric cloth, Ind. Eng. Chem. Res. 44 (4) (2005) 1027–1042.
- [21] I. Ortiz, M.F.S. Roman, S.M. Corvalan, A.M. Eliceche, Modeling and optimization of an emulsion pertraction process for removal and concentration of Cr(VI), Ind. Eng. Chem. Res. 42 (2003) 5891–5899.
- [22] E. Demirbas, M. Kobya, E. Senturk, T. Ozkan, Adsorption kinetics for the removal of chromium(VI) from aqueous solutions on the activated carbons prepared from agricultural waste, Water SA 30 (2004) 533–539.
- [23] C. Selomulya, V. Meeyoo, R. Amal, Mechanisms of Cr(VI) removal from water by various types of activated carbons, J. Chem. Technol. Biotechnol. 74 (1994) 111–122.
- [24] C.P. Dwivedi, J.N. Sahu, C.R. Mohanty, B. Raj Mohan, B.C. Meikap, Column performance of granular activated carbon packed bed for Pb(II) removal, J. Hazard. Mater. 156 (1–3) (2008) 596–603.
- [25] C.K. Singh, J.N. Sahu, K.K. Mahalik, C.R. Mohanty, B. Raj Mohan, B.C. Meikap, Studies on the removal of Pb(II) from wastewater by activated carbon developed from Tamarind wood activated with sulphuric acid, J. Hazard. Mater. 153 (2008) 221–228.
- [26] J.N. Sahu, S. Agarwal, B.C. Meikap, M.N. Biswas, Performance of a modified multi-stage bubble column reactor for lead(II) and biological oxygen demand removal from wastewater using activated rice husk, J. Hazard. Mater. 161 (2009) 317–324.
- [27] K. Rastogi, J.N. Sahu, B.C. Meikap, M.N. Biswas, Removal of methylene blue from wastewater using fly ash as an adsorbent by hydrocyclone, J. Hazard. Mater. 158 (2008) 531–540.
- [28] J. Goel, K. Kadirvelu, C. Rajagopal, V.K. Garg, Removal of mercury(II) from aqueous solution by adsorption on carbon aerogel: response surface methodological approach, Carbon 43 (2005) 195–213 (Letters to the Editor).
- [29] U.K. Garg, M.P. Kaur, V.K. Garg, D. Sud, Removal of Nickel(II) from aqueous solution by adsorption on agricultural waste biomass using a response surface methodological approach, Bioresour. Technol. 99 (2008) 1325–1331.
- [30] M.Z. Alam, S.A. Muyibi, J. Toramae, Statistical optimization of adsorption processes for removal of 2,4-dichlorophenol by activated carbon derived from oil palm empty fruit bunches, J. Environ. Sci. 19 (2007) 674–677.
- [31] D.C. Montgomery, Design and Analysis of Experiments, 5th ed., John Wiley and Sons, New York, USA, 2001.
- [32] R.H. Myers, Response Surface Methodology, Allyn and Bacon, New York, 1971.
- [33] V. Gunaraj, N. Murugan, Application of response surface methodologies for predicting weld base quality in submerged arc welding of pipes, J. Mater. Process. Technol. 88 (1999) 266–275.
- [34] G.E.P. Box, J.S. Hunter, Multi-factor experimental design for exploring response surfaces, Ann. Math. Stat. 28 (1957) 195–241.
- [35] G.E.P. Box, W.G. Hunter, The 2^{k-p} fractional factorial designs, parts I and II, J. Technometr. 3 (1961) 311–458.