

## Biosorption of chromium(VI) by coconut husk – optimization of adsorption variables and isotherm studies

N. Sameera,<sup>1,\*</sup> S. Kiran,<sup>1</sup> S.M. Desai,<sup>2</sup>

<sup>1</sup> Department of Biotechnology, Dayananda Sagar College of Engineering, Bangalore (INDIA)

<sup>2</sup> Department of Chemical Engineering, Dayananda Sagar College of Engineering, Bangalore (INDIA)

ORIGINAL RESEARCH ARTICLE

### ABSTRACT

Hexavalent chromium, present in industrial effluents, is a cause of great concern due to its carcinogenicity and toxicity even at trace levels. The present study aimed at determining the feasibility of using adsorption as a method of Cr(VI) removal by using easily and cheaply available agricultural waste such as coconut husk as the adsorbent. Based on Central Composite Design, values of independent variables viz. temperature, pH, initial metal ion concentration and adsorbent dosage were varied to study the Cr(VI) removal efficiency from aqueous solutions by three forms of the biomass – untreated, acid-treated and alkali-treated. The outcome was subjected to regression analysis and the second degree polynomial equation was found to fit the results to a great extent ( $R^2$  value > 0.9). The acid-treated form of coconut husk was found to be the best with maximum Cr(VI) removal capacity of 84.1% at 2.4 pH and 34.3 °C temperature, with highest initial metal concentration of 165.5 mg/L and lowest adsorbent usage of 4.89 g/100 mL. The impact of factors affecting the adsorption process, viz. temperature, pH, initial metal ion concentration and adsorbent dosage, was also studied. Further, isotherm studies were conducted which showed that the Langmuir Isotherm fitted the experimental data to a good extent with correlation coefficient  $R^2$  value  $\geq 0.87$ .

### KEYWORDS

ANOVA; Biosorption; Central Composite Design; Isotherm Study; Optimization; Regression Analysis

## 1. INTRODUCTION

Rapid and wide-spread industrialization has led to high degree of pollution by discharge of industrial waste-water into water bodies. One of the common heavy metals found in industrial effluents is chromium. It is widely used in industries such as electroplating, metal fabrication, mining, paints and pigments and varnishes, leather tanning etc. (Casarett and Doull, 1980; Nriagu and Nieboer, 1988; Arief et al., 2008). In solution forms, chromium exists in two valence states – trivalent chromium ions [Cr(III)] and hexavalent chromium ions [Cr(VI)]. Cr(III) is found to be relatively stable, unreactive and insoluble and an essential metal nutrient in trace quantities (Saner, 1980). On the other hand, Cr(VI) is relatively unstable and a very strong

oxidizing agent. It is known to be carcinogenic and highly toxic and, hence, is a cause of great concern (Cieslak-Golonka, 1995; Raji and Anirudhan, 1998).

Casarett and Doull (1980) have noted that the concentration of Cr(VI) in industrial effluents is found to be in the range of 0.5 to 270 mg/L, whereas the limits prescribed by statutory agencies is 0.05 to 0.1 mg/L. This necessitates the treatment of effluents to reduce the levels of Cr(VI) before letting them into water bodies. The conventional methods commonly employed for treatment of waste-water include chemical/ electrochemical precipitation, ion exchange, reduction, solvent extraction, membrane separation, evaporation, reverse osmosis, lime coagulation and adsorption (Rich and Cherry, 1987; Aksu and Kutsal, 1990; Lin et al., 1992; Zhou et al., 1993; Chakravarti

Corresponding author: N. Sameera

Tel: +91-9449171646

E. mail: k.sameera.n@gmail.com

Received: 22-03-2018

Revised: 15-05-2018

Accepted: 05-06-2018

Available online: 01-07-2018

et al., 1995; Aksu et al., 1996; Kongsricharoern and Polprasert, 1996; Tiravanti et al., 1997; Pagilla and Canter, 1999; Seaman et al., 1999; Calace et al., 2002).

The conventional treatment methods have many disadvantages such as high chemical and energy requirements, generation of toxic sludge or other waste products that require disposal or treatment (Ahalya et al., 2003). However, Adsorption has proved to be an effective method for removal of heavy metals and other contaminants from industrial effluents (Arief et al., 2008). It provides additional advantages such as easy sludge disposal and economic viability, especially when implemented with low-cost adsorbents in combination with proper regenerative techniques (Bailey et al., 1999).

Over the past decade, several studies have been conducted to explore the possibility of using low-cost, easily available biomass, such as agricultural byproducts and waste materials, as adsorbent for removal of Cr(VI) from aqueous effluents. Materials which have been subjected to experiments include paper mill sludge, seaweed, sugar beet pulp, wheat bran, groundnut husk, coconut tree sawdust, shell and wood, spent tyre, cactus, wool, charcoal, rice husk, almond shell, cow dung etc. (Periasamy et al., 1991; Tan et al., 1993; Selomulya et al., 1994; Kratochvil et al., 1998; Low et al., 1999; Das et al., 2000; Hamadi et al., 2001; Selvi et al., 2001; Dakiky et al., 2002; Reddad et al., 2002; Dupond and Guillon, 2003).

In the present study, the feasibility of using one such easily and cheaply available biomass viz. coconut husk was explored. The study was designed using Response Surface Methodology (RSM). RSM consists of a group of statistical techniques, which are very effective in design of experiment, evaluation of dependent factors, optimization of operating variables, mathematical modeling etc. It is especially useful when the process under study involves multiple independent variables and the variables are spread over a wide range of values (Ravikumar et al., 2005; Aleboyeh et al., 2008; Korbathi, 2007).

The objective of the current study was to determine the factors affecting biosorption of Cr(VI) by coconut husk and to optimize the conditions for obtaining maximum removal of Cr(VI) in aqueous solutions. Further, the effect of pre-treatment processes on the performance of the biomass was evaluated. Isotherm studies were conducted to analyze the mechanism of adsorption by coconut husk.

## 2. MATERIALS AND METHODS

### 2.1. Preparation of biosorbent

Coconut husk, which is agro waste of the coconut industry, was collected from coconut market yards. It was dried in sun, and then crushed and powdered. The powdered material was then sieved to obtain biomass of uniform particle size. The biomass was split into three parts and they were subjected to different types of treatment, to obtain different forms of the biosorbent. One part was soaked in acid solution (0.2 N HCl) for 2 h while the other part was soaked in an alkali solution (0.2 N NaOH). The left-over portion of the biomass was soaked in distilled water. The mixture was filtered through Whatman Filter paper. The matter which got retained (treated biomass) was repeatedly washed with distilled water, followed by filtration, till the filtrate obtained was colorless. The biomass so obtained was dried in hot-air oven at 60 °C for 24 h and used as biosorbent for further studies.

### 2.2. Plotting standard calibration chart

Cr(VI) concentration was identified by colorimetric estimation method using diphenyl carbazide (DPC) as the coloring agent. Standard solutions of Cr(VI), with varying concentrations were prepared by dissolving known amount of potassium dichromate ( $K_2Cr_2O_7$ ) in double distilled water and diluting appropriately. The standard solution(s) were subjected to colorimetric estimation in Spectrophotometer and standard calibration chart was plotted for the absorbance of standard Cr(VI) solution(s) vs. their respective Cr(VI) concentration(s).

### 2.3. Initial study

Based on the preliminary studies, it was observed that following are the parameters and the range of values in which they predominantly affect biosorption of Cr(VI): biosorbent dosage (1 – 10 g/100 mL), pH (1 – 7), temperature (30 – 60 °C) and initial metal ion concentration (10 – 200 mg/L). Further studies were focused in the above mentioned range of values for the respective factors.

## 2.4. Experiment design by central composite design methodology

Central Composite Design (CCD) methodology was employed for design of the experiment. A statistical software MINITAB v16 was used for this purpose. Each of the four variables had 5 levels of values in the range mentioned. With 24 full-factorial experimental design for the above variables and 5 levels, total of 31 different combinations were obtained with 7 replicates at the center point. The design helps in analyzing the influence of the independent variables on Cr(VI) removal efficiency and, further, in obtaining the optimum conditions of these variables under which maximum removal of Cr(VI) can be achieved.

## 2.5. Batch adsorption study

Based on the Central Composite Design Matrix obtained, batch adsorption studies were conducted to determine the percentage removal of Cr(VI) by the biosorbent. 100 mL of synthetically prepared Cr(VI) solution with different known concentration(s) were taken in 250 mL conical flasks. The conditions of temperature, pH and biosorbent dosage were maintained as per the design obtained from CCD. The flasks were shaken in a rotary shaker incubator. 1 mL of sample was obtained from each of the flasks at regular intervals of time and analyzed in spectrophotometer using DPC method to determine the equilibrium concentration of Cr(VI) in the solution. Based on this, the percentage removal of Cr(VI) was calculated.

## 2.6. Optimization of parameters affecting biosorption

Response Surface Methodology was employed for analyzing the results obtained in batch adsorption studies. Regression analysis was performed on the response variable and the independent variables, which yielded a second degree polynomial equation. For regression analysis of the data and determining the values of coefficients, MINITAB v16 was employed. Further, using the Response Optimizer in MINITAB v16, the second degree polynomial equation was solved to obtain the optimum values of the parameters.

## 2.7. Study of adsorption isotherms under optimum conditions

Biosorption process is often described by adsorption equilibrium isotherm models. The two widely accepted

and linearized isotherm models for single solute system are – Langmuir isotherm model and Freundlich isotherm model. Suitability of these isotherm models to the experimental values of Cr(VI) removal was studied.

The Langmuir model suggests, as a hypothesis, that uptake occurs on a homogeneous surface by monolayer adsorption without interaction between adsorbed molecules. This model is described by the equation,

$$q_{eq} = Q_o b C_{eq} / (1 + b C_{eq}) \quad (1)$$

where  $q_{eq}$  and  $C_{eq}$  are the amount of adsorbed metal per unit weight of biosorbent and un-adsorbed metal ion concentration in solution at equilibrium respectively.  $Q_o$  is the maximum amount of metal per unit weight of biomass to form a complete monolayer on the surface bound.  $Q_o$  and  $b$  are constants related to the affinity of the sites. A plot of  $1/q_{eq}$  against  $1/C_{eq}$  yields a straight line, from which the value of  $Q_o$  and  $b$  can be determined.

The Freundlich model proposes a monolayer adsorption with a heterogeneous energetic distribution of active sites, and with interactions between adsorbed molecules, as described by the equation,

$$q_{eq} = K_F C_{eq}^{1/n} \quad (2)$$

where  $K_F$  and  $n$  are the Freundlich constants; they are characteristics of the system and are called as adsorption capacity and adsorption intensity, respectively. A plot of  $\ln q_{eq}$  against  $\ln C_{eq}$  yields a straight line, the slope and intercept of which can be used to determine the Freundlich constants.

# 3. RESULTS AND DISCUSSION

## 3.1. Batch adsorption study

From batch adsorption study, % removal of Cr(VI) was determined for each of the set of conditions obtained from CCD. The theoretical response was calculated by performing regression analysis. The values obtained are tabulated against the corresponding experimental data, in Table 1.

## 3.2. Regression analysis by Response Surface Methodology

Regression analysis was performed on the experimental

**Table 1.** Full-factorial Central Composite Design (CCD) matrix of design specifications along with observed response for removal of Cr(VI) by different pre-treated forms of coconut husk (Exp and Thr denote experimental and theoretical/ predicted values respectively)

Run order	Temperature (°C)	pH	Biosorbent dosage (g/100 mL)	Initial concentration (mg/L)	Response (% Cr(VI) removal)					
					C		CH		CN	
					Exp	Thr	Exp	Thr	Exp	Thr
1	37.5	2.5	3.25	152.5	56.94	56.78	58.7	58.53	55.23	55.91
2	37.5	5.5	3.25	152.5	52.96	52.82	54.6	54.45	51.37	50.3
3	52.5	2.5	7.75	57.5	52.09	51.03	53.7	52.6	50.53	47.9
4	45	4	5.5	105	67.42	67.43	69.5	69.51	65.4	65.41
4	30	4	5.5	105	71.3	80.14	73.5	82.61	69.16	77.84
5	45	4	5.5	105	67.12	67.43	69.2	69.51	65.11	65.41
6	45	4	5.5	105	67.42	67.43	69.5	69.51	65.4	65.41
7	52.5	2.5	3.25	57.5	47.72	47.01	49.2	48.47	46.29	44.46
8	52.5	5.5	3.25	152.5	34.73	33.79	35.8	34.83	33.69	32.29
9	52.5	5.5	7.75	152.5	39.96	46.92	41.2	48.37	38.76	46.55
10	45	1	5.5	105	70.52	70.81	72.7	73	68.4	67.7
12	37.5	5.5	3.25	57.5	76.92	67.45	79.3	69.53	74.61	65.36
13	52.5	2.5	3.25	152.5	37.35	37	38.5	38.14	36.23	34.57
14	45	4	5.5	105	67.71	67.43	69.8	69.51	65.68	65.41
15	37.5	2.5	7.75	152.5	78.28	78.35	80.7	80.77	75.93	76.38
16	37.5	5.5	7.75	57.5	78.76	77.91	81.2	80.32	76.4	75.77
17	45	7	5.5	105	59.46	62.19	61.3	64.11	57.68	61.09
18	60	4	5.5	105	34.63	28.81	35.7	29.7	33.59	27.62
19	45	4	5.5	105	67.42	67.43	69.5	69.51	65.4	65.41
20	45	4	5.5	200	50.83	43.33	52.4	44.66	49.31	41.71
21	52.5	5.5	3.25	57.5	44.62	43.35	46	44.69	43.28	43.08
22	37.5	5.5	7.75	152.5	74.5	73.4	76.8	75.67	72.27	71.14
23	45	4	5.5	105	67.51	67.43	69.6	69.51	65.48	65.41
24	45	4	5.5	10	47.34	57.86	48.8	59.65	45.92	56.23
25	52.5	5.5	7.75	57.5	48.02	46.37	49.5	47.8	46.58	46.89
26	52.5	2.5	7.75	152.5	43.46	51.12	44.8	52.7	42.16	48.45
27	37.5	2.5	3.25	57.5	80.03	71.87	82.5	74.09	77.63	70.09
28	45	4	10	105	76.44	70.36	78.8	72.53	74.15	68.35
29	45	4	1	105	36.67	45.77	37.8	47.18	35.57	44.08
30	37.5	2.5	7.75	57.5	84.2	83.33	86.8	85.9	81.67	80.11
31	45	4	5.5	105	67.42	67.43	69.5	69.51	65.4	65.41

observations recorded during batch adsorption studies by Response Surface Methodology (RSM) using MINITAB v16. The value of the response variable Y as a quadratic function of the independent variables for the three different forms of biosorbent C, CH and CN are given in equations (3), (4) and (5) respectively.

$$Y = 67.43 - 12.83X_1 - 2.16X_2 + 6.15X_3 - 3.63X_4 - 3.24X_1^2 - 0.23X_2^2 - 2.34X_3^2 - 4.21X_4^2 + 0.19X_1X_2 - 1.86X_1X_3 + 1.27X_1X_4 - 0.25X_2X_3 + 0.11X_2X_4 + 2.53X_3X_4 \quad (3)$$

$$Y = 69.51 - 13.23X_1 - 2.22X_2 + 6.34X_3 - 3.75X_4 - 3.34X_1^2 - 0.24X_2^2 - 2.42X_3^2 - 4.34X_4^2 + 0.19X_1X_2 - 1.92X_1X_3 + 1.31X_1X_4 - 0.26X_2X_3 + 0.12X_2X_4 + 2.61X_3X_4 \quad (4)$$

$$Y = 65.41 - 12.55X_1 - 1.65X_2 + 6.07X_3 - 3.63X_4 - 3.17X_1^2 - 0.25X_2^2 - 2.30X_3^2 - 4.11X_4^2 + 0.83X_1X_2 - 1.65X_1X_3 + 1.07X_1X_4 + 0.09X_2X_3 - 0.22X_2X_4 + 2.61X_3X_4 \quad (5)$$

where  $X_1$  = temperature ( $^{\circ}\text{C}$ ),  $X_2$  = pH,  $X_3$  = biosorbent dosage (g/100 mL) and  $X_4$  = initial concentration of metal ion (mg/L).

Using the above equations, the predicted response for each set of experimental conditions were calculated. These values were plotted against the experimental values of Cr(VI) removal to obtain the parity plots.

From the parity plots, it was observed that there was good correlation between the experimental and predicted values of Cr(VI) removal. The Regression coefficient ( $R^2$ ) determines the fitness of the model to the data, and value closer to 1 indicates that the statistical model fits the data well. The value of  $R^2$  obtained for C, CH and CN were 0.87, 0.90 and 0.84 respectively, which clearly indicated that the model was apt for the experimental data.

### 3.3. Analysis of Variance (ANOVA)

ANOVA of the regression model was performed and the outcome has been tabulated in Table 2. From Table 2, it can be observed that the Fischer value 'F' was highest for CH (18.58). This, combined with the lowest probability value ( $P = 0.004$ ) indicated that the model was strongly significant for CH, while it was comparatively less significant for the other forms (C and CN). It is evident from the probability values that the regression model was strongly significant for all the three adsorbents (C, CH and CN). Also, the linear and square effect of the variables was significant while the interaction effect was non-significant in the case of all the three adsorbents.

### 3.4. Optimization of parameters affecting biosorption

The second degree polynomial equations (1, 2 and 3) were solved by using the Response Optimizer to determine the optimum value of the independent variables for extracting maximum response from the biosorbent. The results are tabulated in Table 3.

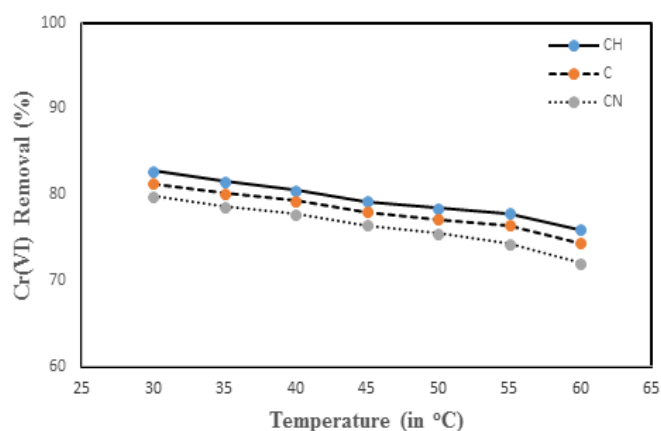
From Table 3, it is clear that out of the three forms of coconut husk tested for Cr(VI) adsorption, the acid-treated form (CH) was found to be the most desirable due to highest Cr(VI) removal efficiency at low adsorbent dosage and high metal ion concentration. % removal of Cr(VI) from the aqueous solution was highest

in the case of CH (84.06%) at the lowest adsorbent dosage of 4.89 g/100mL and highest initial metal ion concentration of 165 mg/L. Moreover, it was found to be more suitable for large-scale operations compared to other forms, since the optimum temperature was nearer to ambient temperature ( $34.3^{\circ}\text{C}$ ) and optimum pH was higher (2.35), which is less acidic compared to the other forms.

### 3.5. Effect of independent variables on adsorption

#### 3.5.1. Effect of temperature

The effect of temperature on the adsorption of Cr(VI) by the biosorbent was studied by varying temperature between  $30^{\circ}\text{C}$  and  $60^{\circ}\text{C}$  keeping other conditions at optimum values. The response obtained (% Cr(VI) removal) was plotted against temperature and is shown in Figure 1. From the figure, it is clear that as the temperature was increased, % removal of Cr(VI) decreased. Maximum Cr(VI) removal observed was 82.76% at a temperature of  $30^{\circ}\text{C}$  for HCl treated coconut husk. Hence, low temperature condition aided removal of Cr(VI) by coconut husk. This indicates that adsorption by coconut husk might be a spontaneous and exothermic reaction, as reported by few researchers (Sekar et al., 2004; Israel and Eduok, 2012).



**Figure 1.** Graph of % Cr(VI) removal vs. temperature ( $^{\circ}\text{C}$ )

#### 3.5.2. Effect of pH

The effect of pH on the adsorption of Cr(VI) by the biosorbent was determined by varying pH between 1.0 and 7.0 while other conditions were kept at the optimum values. The % removal of Cr(VI) was plotted against respective pH values and the graph is shown in Figure

**Table 2.** Analysis of Variance (ANOVA) for quadratic model for Cr(VI) removal by pre-treated forms of coconut husk ('F' is the Fischer value which is the ratio of mean square of the term to the mean square of the residual, 'P' is low-probability value and DF is Degrees of freedom; \* denotes significant values)

Source	DF			Sum of Squares			F			P		
	C	CH	CN	C	CH	CN	C	CH	CN	C	CH	CN
Regression	14	14	14	6293.55	6688.64	6014.44	15.08	18.58	10.37	0.004*	0.012*	0.015*
Linear	4	4	4	5287.44	5619.31	5047.85	31.12	35.11	30.47	0.018*	0.014*	0.023*
Square	4	4	4	820.99	872.56	783.73	4.83	5.23	4.73	0.10*	0.11*	0.15*
Interaction	6	6	6	185.12	196.76	182.86	0.73	0.73	0.74	0.635	0.635	0.628
Residual Error	16	16	16	679.64	722.39	662.71	--	--	--	--	--	--
Total	30	30	30	6973.19	7411.02	6677.15	--	--	--	--	--	--

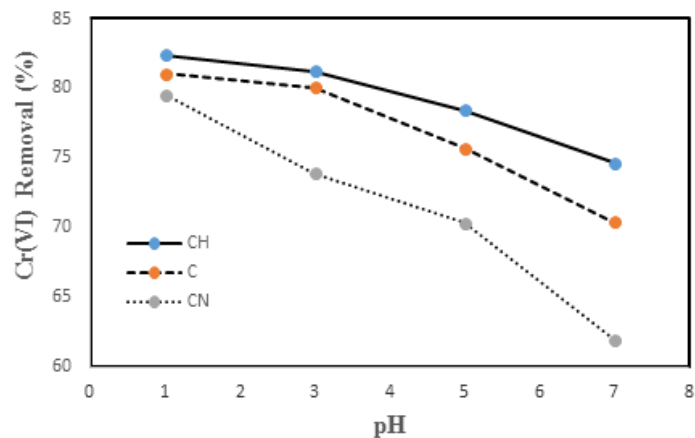
**Table 3.** Optimized values of operational variables for obtaining maximum biosorption of Cr(VI) from the pre-treated forms of coconut husk

Biosorbent	Temperature (°C)	pH	Biosorbent dosage (g/100mL)	Initial metal ion concentration (mg/L)	Predicted response (% Cr(VI) removal)
C	32.8	1.87	7.23	117	83.12
CH	34.3	2.35	4.89	165	84.06
CN	31.4	1.32	8.75	83	80.20

2. It was observed that % removal of Cr(VI) decreased with increase in pH. The maximum removal observed was 82.38% at a pH of 1.0 for HCl treated coconut husk. Hence, it can be concluded that for Cr(VI) adsorption by CH, low pH condition was favorable compared to higher pH. The effect of pH on the adsorption of Cr(VI) by coconut husk can be explained on the basis of the composition of coconut husk biomass and the form(s) in which Cr(VI) exists in aqueous solutions.

Research on the chemical composition of coconut husk, by Israel and Eduok (2012), revealed that it contains lignin and cellulose to a large extent (53.5 and 35.9%, respectively). Cukierman (2007) reported, based on FTIR (Fourier transform infrared) spectroscopic studies, that the surface functional group(s) predominant in ligno-cellulosic biomass are -OH group and the C-O, C-C and C-OH bonds. The mechanism of Cr(VI) adsorption at low pH has been explained, by Dave et al. (2012), on the basis of protonation of adsorbent surface. In aqueous solutions, hexavalent chromium exists as  $\text{CrO}_4^{2-}$ ,  $\text{HCrO}_4^-$ ,  $\text{HCr}_2\text{O}_7^-$  or  $\text{Cr}_2\text{O}_7^{2-}$ , depending on the pH of the medium and the total Cr(VI) concentration. At low pH conditions,  $\text{HCrO}_4^-$  is the prevalent form, which subsequently shifts to other forms such as  $\text{CrO}_4^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$ , as the pH increases. The acidic pH also causes the surface of the adsorbent to be protonated to a higher extent.

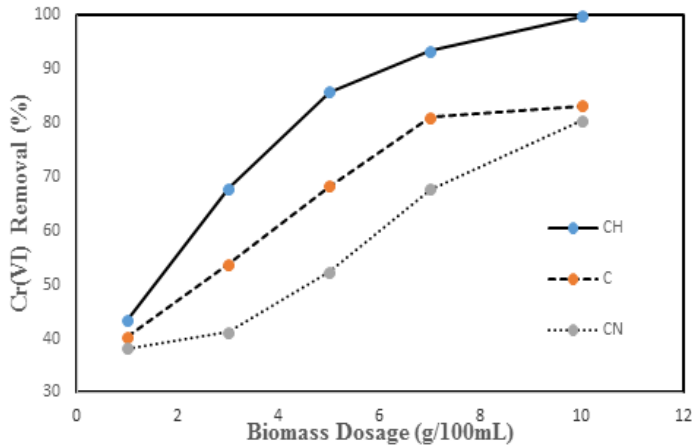
Together, this results in a strong attraction between negatively charged Cr(VI) complex ions and the positively charged biomass surface. Thus, acidic pH favors adsorption of Cr(VI) from aqueous solutions by coconut husk.

**Figure 2.** Graph of % Cr(VI) removal vs. pH

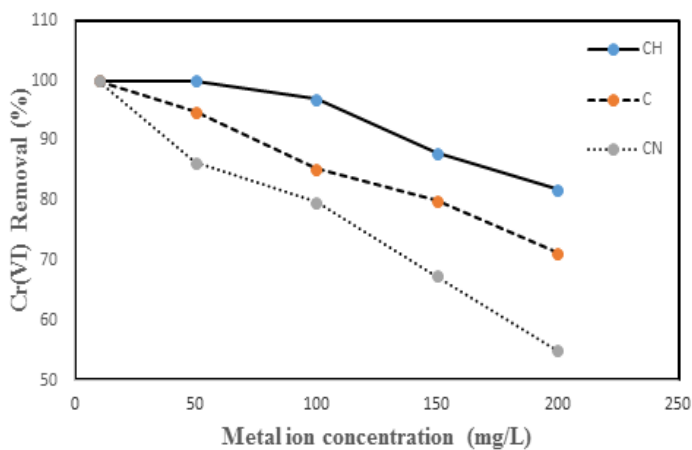
### 3.5.3. Effect of biosorbent dosage

The effect of biosorbent dosage on the adsorption of Cr(VI) was determined by varying biosorbent dosage from 1 to 10 g per 100mL of the solution containing Cr(VI), while other conditions were kept at the optimum values. The observations are displayed

in Figure 3. From Figure 3, it was clear that as the biosorbent dosage was increased, the % removal of Cr(VI) enhanced.



**Figure 3.** Graph of % Cr(VI) removal vs. biosorbent dosage (g/100mL).



**Figure 4.** Graph of % Cr(VI) removal vs. initial metal ion concentration (mg/L).

This pattern may be because of increase in the number of binding sites with increase in the amount of biosorbent. However, beyond a certain adsorbent level (optimum value), the Cr(VI) removal either remained constant or decreased slightly. This may be due to saturation of the sites or the increase in interference between binding sites due to higher biomass availability (Dave et al., 2012). The maximum removal of Cr(VI) observed was 99.9% at a biosorbent dosage of 10 g/100mL by HCl treated coconut husk (i.e. CH).

#### 3.5.4. Effect of initial metal ion concentration

The effect of initial metal ion concentration on the adsorption of Cr(VI) by the biosorbent was studied by varying initial metal ion concentration between 10

and 200 mg/L while other conditions were kept at the optimum values. % Cr(VI) removal was plotted against metal ion concentration (mg/ L) and the observations are displayed in Figure 4. From Figure 4, it was clear that as the initial metal ion concentration increased, the % removal of Cr(VI) decreased. The maximum response observed was 99.9% corresponding to initial metal ion concentration of 10 mg/L for HCl treated coconut husk.

The phenomenon may be explained in the following manner - at low values of metal ion concentration, sufficient binding sites are available for adsorption process resulting in higher removal efficiency whereas, at higher metal ion concentration, the number of binding sites are relatively less compared to the metal ions leading to higher competition for metal complex binding. Similar observations have been reported by Desai et al. (2016).

**Table 4.** Values of Langmuir constants, along with regression co-efficient and separation factor

Biosorbent	Langmuir constants			Separation factor $R_L$
	$Q_0$ (mg/g)	$b$ (L/mg)	$R^2$	
C	15.38	0.32	0.87	0.17
CH	126	0.12	0.99	0.06
CN	62.5	0.01	0.91	0.59

**Table 5.** Values of Freundlich constants, along with regression co-efficient

Biosorbent	Freundlich constants		$R^2$
	$K_F$	$n$	
C	3.31	2.72	0.81
CH	1.4	1.03	0.92
CN	0.72	1.09	0.9

### 3.6. Isotherm Studies

Adsorption equilibrium was studied by varying initial metal ion concentration and recording its effect on the removal of Cr(VI) ions by the different forms of biosorbent under their respective optimum working conditions. The equilibrium data obtained were modeled using the Langmuir and Freundlich isotherm models and the relative suitability of the two models was determined. The results are summarized in Table 4 and 5.

From Table 4 and 5, it can be observed that among the two Isotherm models, the Langmuir isotherm model fits the experimental data better compared to the Freundlich isotherm model. This is also indicated by the higher value of regression coefficient  $R^2$  in the case of Langmuir model (0.87 - 0.99) than the Freundlich model (0.81 - 0.92) for all the biosorbent forms examined.

## 4. CONCLUSIONS

In the current study, adsorption of hexavalent chromium was studied using coconut husk as the adsorbent. The study was designed using Central Composite Design to obtain experimental conditions for the independent variables temperature, pH, initial metal ion concentration and adsorbent dosage. Batch adsorption studies were conducted with three pre-treated forms of biomass of coconut husk – untreated coconut husk (C), acid-treated form (CH) and alkali-treated form (CN). Regression analysis of the obtained results was done using Response Surface Methodology and the high value of regression coefficient for all the three forms of biosorbent (between 0.84 and 0.90) indicated that the second degree polynomial equation model fitted the experimental observation to a high extent. Analysis of Variance (ANOVA) showed that the regression model was in good agreement for all the three adsorbents (C, CH and CN). While the Linear and square effect of the variables was significant, the interaction effect was not significant in the case of all the three adsorbents. Optimization of the independent variables indicated that the acid-treated form CH was the best among the adsorbents selected for study with maximum Cr(VI) removal capacity of 84.06% at 2.35 pH and 34.3 °C temperature, with highest initial metal ion concentration of 165.47 mg/L and lowest adsorbent dosage of 4.89 g/100mL. Isotherm studies were conducted which showed that Langmuir Isotherm fitted the experimental data well with correlation coefficient  $R^2$  values  $\geq 0.87$ . From the studies conducted, it was observed that, among the biosorbents tested, coconut husk treated with HCl (CH) displayed the maximum potential for adsorption of the targeted Cr(VI) metal ion.

## REFERENCES

- Ahalya, N., Ramachandra, T.V., Kanamadi, R.D. (2003) Biosorption of heavy metals. Research Journal of Chemistry and Environment, 7, 71-79.
- Aksu, Z., Kutsal, T.A. (1990) Comparative study for biosorption characteristics of heavy metal ions with *C. vulgaris*. Environmental Technology, 11, 979–987.
- Aksu, Z., Ozer, D., Ekiz, H., Kutsal, T., Calar, A. (1996) Investigation of biosorption of chromium(VI) on *C. crispate* in two staged batch reactor. Environmental Technology, 17, 215–220.
- Aleboye, A., Daneshvar, N., Asiri, M.B. (2008) Optimization of C.I. Acid Red 14 azo dye removal by electrocoagulation batch process with response surface methodology. Chemical Engineering and Processing, 47, 827-832.
- Arief, V.O., Trilestari, K., Sunarso, J., Indraswati, N., Ismadji, S. (2008) Recent progress on biosorption of heavy metals from liquids using low cost biosorbents: characterization, biosorption parameters and mechanism studies. Clean, 36, 937–962.
- Bailey, S.E., Olin, T.J., Bricka, R.M., Adrian, D.D. (1999) A review of potentially low cost sorbents for heavy metals. Water Research, 33, 2469–2479.
- Calace, N., Muro, D.A., Nardi, E., Petronio, B.M., Pietroletti, M. (2002) Adsorption isotherms for describing heavy metal retention in paper mill sludges. Industrial and Engineering Chemistry Research, 41, 5491–5497.
- Casarett, L.J., Doull, J. (1980) Toxicology: The Basic Science of Poisons. Macmillan, New York, pp. 323-330.
- Chakravarti, A.K., Chowdhury, S.B., Chakrabarty, S., Chakrabarty, T., Mukherjee, D.C. (1995) Liquid membrane multiple emulsion process of chromium (VI) separation from waste Waters, Colloids and Surfaces A. Physicochemical Engineering Aspects, 103, 59–71.
- Cieslak-Golonka, M. (1995) Toxic and mutagenic effects of chromium (VI). Polyhedron, 15, 3667–3689.
- Cukierman, A.L. (2007) Metal ion biosorption potential of lignocellulosic biomasses and marine algae for wastewater treatment. Adsorption Science and Technology, 25, 227–244.
- Dakiky, M., Khamis, M., Manassra, M., Mer'eb, M. (2002) Selective adsorption of chromium(VI) in industrial waste water using low cost abundantly available adsorbents. Advances in Environmental Research, 6, 533–540.
- Das, D.D., Mahapatra, R., Pradhan, J., Das, S.N., Thakur, R.S. (2000) Removal of Cr(VI) from aqueous solution using activated cow dung carbon. Journal of Colloids and Interface Science, 232, 235–240.
- Dave, P.N., Pandey, N., Hannah, T. (2012) Adsorption of Cr(VI) from aqueous solutions on tea waste and coconut husk. Indian Journal of Chemical Technology, 19, 111 – 117.
- Desai, S.M., Charyulu, N.C.L.N, Behara, D.K., Satyanarayana, S.V. (2016) Statistical optimization of adsorption variables for biosorption of chromium(VI) using carrot based adsorbents equilibrium and kinetic studies. Journal of Environmental Research And Development, 10, 392-406.
- Dupond, L., Guillon, E. (2003) Removal of hexavalent chromium with a lingo cellulosic substrate extracted from wheat bran. Environmental Science and Technology, 37, 4235–4241.
- Hamadi, N.K., Chen, X.D., Farid, M.M., Lu, M.G.Q. (2001) Adsorption kinetics for the removal of chromium(VI) from aqueous solution by adsorbents derived from used tyres and sawdust. Journal of Chemical Engineering, 84, 95–105.
- Israel, U., Eduok, U. M. (2012) Biosorption of zinc from aqueous solution using coconut (*Cocos nucifera* L) coir dust. Archives of Applied Science Research, 4, 809-819.
- Kongsricharoen, N., Polprasert, C. (1996) chromium removal by a bipolar electrochemical Precipitation process. Water Science and Technology, 34, 109–116.



- Korbathi, B.K. (2007) Response surface optimization of electrochemical treatment of textile dye wastewater. *Journal of Hazardous Materials*, 145, 277-286.
- Kratochvil, D., Pimentel, P., Volesky, B. (1998) Removal of trivalent and hexavalent chromium by seaweed biosorbent. *Environmental Science and Technology*, 32, 2693-2698.
- Lin, C.F., Rou, W., Lo, K.S. (1992) Treatment strategy for Cr(VI) bearing wastes. *Water Science and Technology*, 26, 2301-2304.
- Low, K.S., Lee, C.K., Ng, A.Y. (1999) Column study on the sorption of Cr(VI) using quaternized rice hulls. *Bioresource Technology*, 68, 205-208.
- Nriagu, J.O., Nieboer, E. (1988) *Chromium in the Natural and Human Environments*. Vol. 20, John Wiley & Sons, New York.
- Pagilla, K., Canter, L.W. (1999) Laboratory studies on remediation of chromium contaminated soils. *Journal of Environmental Engineering*, 125, 243-248.
- Periasamy, K., Srinivasan, K., Muruganan, P.R. (1991) Studies on chromium(VI) removal by activated ground nut husk carbon. *Indian Journal of Environmental Health*, 33, 433-439.
- Raji, C., Anirudhan, T.S. (1998) Batch Cr(VI) removal by polyacrylamide-grafted sawdust: kinetics and thermodynamics. *Water Research*, 32, 3772-3780.
- Ravikumar, K., Pakshirajan, K., Swaminathan, T., Balu, K. (2005) Optimization of batch process parameters using response surface methodology for dye removal by a novel adsorbent. *Chemical Engineering Journal*, 105, 131-138.
- Reddad, Z., Gerente, C., Andres, Y., Cloirec, P. (2002) Adsorption of several metal ions onto a low cost biosorbent: kinetic and equilibrium studies. *Environmental Science and Technology*, 36, 2067-2073.
- Rich, G., Cherry, K. (1987). *Hazardous Waste Treatment Technologies*, Pudvan Publishers, pp. 107-110.
- Saner, G. (1980). *Chromium in Nutrition and Disease*. Alan R. Liss Inc., New York.
- Seaman, J.C., Bertsch, P.M., Schwallie, L. (1999) In situ Cr(VI) reduction within coarse-textured, oxide-coated soil and aquifer systems using Fe(II) solutions. *Environmental Science and Technology*, 33, 938-944.
- Sekar, M., Sakhi, V.S., Rengaraj (2004) Kinetics and equilibrium adsorption study of lead(II) onto activated carbon prepared from coconut shell. *Journal of Colloid and Interface Science*, 279, 307-313.
- Selomulya, C., Meeyoo, V., Amal, R. (1994) Mechanisms of Cr(VI) removal from water by various types of activated carbons. *Journal of Chemical Technology and Biotechnology*, 74, 111-122.
- Selvi, K., Pattabhi, S., Kadirvelu, K. (2001) Removal of Cr(VI) from aqueous solution by adsorption onto activated carbon. *Bioresource Technology*, 80, 87-89.
- Tan, W.T., Ooi, S.T., Lee, C.K. (1993) Removal of Cr(VI) from solution by coconut husk and Palm pressed fibres. *Environmental Technology*, 14, 277-282.
- Tiravanti, G., Petruzzelli, D., Passiono, R. (1997) Pretreatment of tannery wastewaters by an ion exchange process for Cr(III) removal and recovery. *Water Science and Technology*, 36, 197-207.
- Zhou, X., Korenaga, T., Takahashi, T., Moriwake, T., Shinoda, S. (1993) A process monitoring/controlling system for the treatment of wastewater containing chromium(VI). *Water Research*, 27, 1049-1054.