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Batch removal of chromium (VI) from aqueous solutions using wheat shell as adsorbent: process optimization using response surface methodology

Papita Das Saha[a,*], Apurba Dey[a], Pritam Marik[b]

[a]*Department of Biotechnology, National Institute of Technology – Durgapur, Mahatma Gandhi Avenue, Durgapur (WB) 713209, India Tel. +913432754036; Fax: +913432547375; email: papitasaha@gmail.com*
[b]*Department of Geology, National Institute of Technology – Durgapur, Mahatma Gandhi Avenue, Durgapur (WB) 713209, India*

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ABSTRACT

The biosorption potential of wheat (*Triticum aestivum*) shells to remove hexavalent Chromium (Cr^{+6}) ions from aqueous solutions was investigated in batch mode experiments. The equilibrium adsorption level was determined and it was observed that equilibrium adsorption of chromium was function of the solution contact time and initial metal concentration. The effect of solution pH on biosorption was also studied. From experimental results it was observed that the biosorptive capacity of the shell was dependent on the pH and initial Cr (VI) ions concentration. The Freundlich and Langmuir constants for biosorption of chromium (VI) on wheat shells were determined and it was observed that the adsorption data fit well with the Langmuir isotherm model. To optimization of this process response surface methodology (RSM) was utilized. The regression equation was obtained using Design Expert 7.0 software. Predicted values thus obtained were closed to experimental value indicating suitability of the model.

Keywords: Chromium; Biosorption; Batch and continuous study; Response surface methodology; Regression analysis; Wheat shell

1. Introduction

Biosorption, a technically feasible and economical process, has gained increased creditability during recent years [1]. Biosorbents are highly porous materials and adsorption primarily takes place on the walls of the pores or at specific sites inside the particles [2–6].

Chromium, a priority metal pollutant is widely used by various modern industries like electroplating, tanning, textile resulting high discharge and accumulation of large quantities into the environment. The interest in chromium is governed by the fact that its toxicity depends critically on its oxidation state. In the environment, chromium, a redox active metal element, usually exists as trivalent (Cr (III)) or hexavalent (Cr (VI)) species. Hexavalent chromium is 500 times more toxic than the trivalent one [7]. The Cr (VI) species may be in the form of dichromate ($Cr_2O_7^{2-}$), hydrochromate ($HCrO_4^-$) or chromate (CrO_4^{2-}) in a solution depending on the pH. Due to repulsive electrostatic interactions, Cr (VI) are poorly adsorbed by the negatively charged soil particles in the environment, and hence they can transfer freely in the aqueous environments. Chromium (VI), which is on the top priority list of the toxic pollutant defined by US EPA, is present in the electroplating wastewater and many other industrial discharges. According to the Indian standards, the permissible limit of Cr (VI) for industrial effluents to be discharged to surface water is 0.1 mg/l. If Cr (VI) is ingested beyond the maximum concentration (0.1 mg/l), it can cause health disorder, such

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*Corresponding author.

as vomiting, skin irritation, lung cancer, hemorrhage well as kidney, liver, and gastric damage [8]. International Agency for Research on Cancer has determined that Cr (VI) is carcinogenic to humans. Hence, its removal from wastewater is of the utmost importance.

The usual methods to remove Cr (VI) from aqueous effluents include chemical reduction, nanofiltration bioaccumulation, ion exchange, adsorption on silica composites and on activated carbon [9–15]. However these approaches are not cost-effective and difficult to implement in developing countries. The search for new and cost effective technologies involving the removal of heavy metals has been oriented to biosorption based on the metal binding capacities of different biological or agricultural materials. Biosorption is a fast and reversible reaction of the heavy metals with biomass.

Wheat husk is an easily available agricultural waste material. From literature survey it was known that the production of wheat husk in India is about 8–12 million tons. Most of these wheat husks were used for cattle feed and as compost in agricultural field. But a large portion of wheat husks were simply dumped as those become spoiled because of unavailability of proper storage system. Wheat husk is the outer covering of wheat and accounts for 5–10% of its weight. The chemical composition of wheat husk is as follows: cellulose (36%), hemicellulose (18%), lignin (16%), starch (9%), protein (6%), fat (5%) and rest of the composition is inorganic and fiber content [16]. Carboxyl, hydroxyl etc. are some functional groups which makes adsorption process possible.

Response surface methodology (RSM) is a collection of mathematical and statistical techniques useful for analyzing the effects of several independent variables on the response [17]. RSM has an important application in the process design and optimization as well as the improvement of existing design. This methodology is more practical compared to the approaches like Box-Behnken design, Surrogate model etc. as it arises from experimental methodology which includes interactive effects among the variables and, eventually, it depicts the overall effects of the parameters on the process [18]. In the last few years, RSM has been applied to optimize and evaluate interactive effects of independent factors in numerous chemical and biochemical processes [19,20].

This study reports the use of wheat husk as a biosorbent to remove toxic Cr (VI) ion from aqueous solutions. This will permit the evaluation of wheat husk for their utilization as an adsorbent in the elimination of Cr (VI) ion from aqueous solution. The effect of time, initial concentration of the metal, solution pH and adsorbent dosage on the biosorption at room temperature is also studied. Optimum conditions for elimination of Cr (VI) were determined by RSM using DESIGN EXPERT 7.0 software. The main aim of this work was to find the biosorption characteristics of wheat husks for the removal of Chromium (VI) ions from aqueous solution.

2. Materials and methods

2.1. Preparation of biosorbents

Wheat husks were collected from a local agro-industry and washed properly with distilled water. After that those husks were spreaded on a glass tray and dried in a hot oven drier at 80°C for overnight [21]. The materials were kept in an air tight plastic bottle in the refrigerator to prevent decomposition. The particle size were maintained in the range of 400–700 μm.

2.2. Chromium (VI) solution preparation (Adsorbates)

Cr (VI) solutions were prepared using Potassium di chromate. Stock solution (500 gm/l) of Cr (VI) was prepared by dissolving required quantity of $K_2Cr_2O_7$ in distilled water. The pH of the solution was adjusted with dilute sulphuric acid and sodium hydroxide solutions. This was used as the synthetic source of waste water [22].

2.3. Chromium (VI) concentration determination

The change in Cr (VI) concentration due to adsorption was determined spectrophotometrically (UV-Vis spectrophotometer) according to Standard Methods [22]. A purple-violet colored complex was developed in the reaction between Cr (VI) and 1, 5-diphenylcarbazide in acidic condition. Absorbance was measured at wavelength 540 nm. The percentage of Chromium removal due to biosorption was calculated as % Chromium removal = $\frac{C_i - C_0}{C_i} \times 100$, where C_i and C_0 are the initial and equilibrium concentration of Cr (VI) solution (g/l), respectively [22].

2.4. Batch biosorption studies

Batch biosorption studies were carried out using a certain amount wheat husk and 200 ml solution of Cr (VI) in a conical flask with constant shaking using a rotary shaker. The following operating conditions such as pH, adsorbent amount, contact time and metal concentration were used. For each of the investigation, the mixture was shaken in a rotary shaker followed by filtration using filter paper. The filtrate containing the residual concentration of Cr (VI) was determined spectrophotometrically at 540 nm using the method mentioned above. All biosorption experiments were performed in triplicate and mean values were reported.

2.5. Influence of pH

Biosorption study for Cr (VI) ions on wheat husk were carried out through a batch method. The pH of the solution was adjusted with dilute H_2SO_4 and NaOH solutions before addition of bioadsorbent. 2 g of treated wheat husk was added to 200 ml of 5 mg/l Chromium (VI) in 250 ml Erlenmeyer flask. The pH values of the solution were 2, 4, 6, 8 and 10 respectively. The flasks were continuously stirred at 35°C and samples were taken from the flasks at particular time interval. Solutions concentration was measured by UV/VIS spectrophotometer.

2.6. Adsorption isotherm

The sorption of chromium ions was carried out at different initial chromium ion concentrations ranging from 0.2–10 g/l; at pH 2 with a fixed amount (2 g in 200 ml chromium solution) of wheat husk used. The washed and dried wheat husk was added in Erlenmeyer flasks and agitated at 35°C. The initial and final concentrations were measured using UV/VIS spectrophotometer. After a period of time, the chromium uptake capacity was calculated according to mass balance on the metal by using Eq. (1):

$$q_e = \frac{(C_i - C_e)\,V}{m} \tag{1}$$

where, C_i is the initial chromium concentration (g/l), C_e is the equilibrium chromium concentration (g/l), V is the volume of the solution (ml) and m is the mass of the wheat husk. The extent of sorption percentage was calculated using Eq. (2):

$$\text{Sorption}(\%) = \frac{C_i - C_e}{C_i} \times 100 \tag{2}$$

The Langmuir and Freundlich adsorption isotherm models were used to analyze the experimental data.

For the Langmuir model the following equation was used [23,24]

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{3}$$

where q_e (mg/g) and C_e (mg/l) are the solid phase concentration and the liquid phase concentration of adsorbate at equilibrium respectively, q_m (mg/g) is the maximum biosorption capacity, and K_L (l/mg) is the biosorption equilibrium constant. The constants K_L and q_m can be determined from the slope and intercept of the plot between C_e/q_e and C_e.

The Freundlich isotherm constants were calculated using Eq. (4):

$$\ln q_e = \ln K_F + (1/n) \ln C_e \tag{4}$$

where q_e is the equilibrium dye concentration on biosorbent (mg/g), C_e is the equilibrium dye concentration in solution (mg/l), K_F (mg/g) $(l/g)^{1/n}$ is the Freundlich constant related to sorption capacity and n is the heterogeneity factor. K_F and $1/n$ are calculated from the intercept and slope of the straight line of the plot log q_e versus log C_e.

2.7. Experimental and optimization of biosorption using response surface methodology

Optimum condition for the biosorption of Cr (VI) by wheat husks was determined by means of response surface methodology (RSM). The RSM consists of a group of empirical techniques devoted to the evaluation of relationship existing between a cluster of controlled experimental factors and measured responses according to one or more selected criteria. Thirty batch adsorption experiments designed by RSM were conducted [Table 1].

The chosen independent variables used in this study were coded according to Eq. (5):

$$x_i = \frac{x_i - x_0}{\Delta x} \tag{5}$$

where x_i is the dimensionless coded value of the i th independent variable, X_0 is the value of X_i at the center point and ΔX is the step change value. The behavior of

Table 1
Factors for response surface methodology

Factors	Name	Unit	Type	Low actual	High actual	Low coded	High coded	Mean	Std. deviation
A	pH	–	Numeric	2.00	9.00	–1.000	1.000	5.500	3.130
B	Conc.	g/l	Numeric	1.00	40.00	–1.000	1.000	20.500	17.441
C	Dose	g	Numeric	0.50	3.00	–1.000	1.000	1.750	1.118
D	Time	g	Numeric	10.00	180.0	–1.000	1.000	95.000	76.026

system is explained by the following empirical second-order polynomial model Eq. (6):

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1} \sum_{j=1+1} \beta_{ij} x_i x_j + \varepsilon \tag{6}$$

where Y is the predicted response, x_i, x_j, . . ., x_k are the input variables, which affect the response Y, x_i^2 , x_j^2 , . . ., x_k^2 are the square effects, $x_i x_j$, $x_i x_k$ and $x_j x_k$ are the interaction effects, β_0 is the intercept term, β_i (i=1, 2, . . ., k) is the linear effect, β_{ii} (i=1, 2, . . ., k) is the squared effect, β_{ij} (i=1, 2, . . ., k; j=1, 2, . . ., k) is the interaction effect and ε is a random error.

The DESIGN EXPERT 7.0 (Stat-Ease Inc., Minneapolis, MN, USA) software was used for regression and graphical analysis of the obtained data. The central composite design (CCD) is the most frequently used under RSM design. The study carried out involving the employment of central composite design to optimize the biosorption process due to it's suitability to fit quadratic surface which usually works well for process optimization. A design of few experiments was formulated. The optimum values of the selected variables were obtained by solving the regression equation at desired values of the process responses as the optimization criteria.

3. Results and discussion

3.1. Effect of pH

pH is an important parameter for adsorption metal ion from aqueous solution as its effects the solubility of metal ions, concentration of the counter ions in the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction. Biomass had active sites which are capable of binding metal ions. Such bond formation could be accompanied by displacement of protons and that was determined by pH of the solution. pH dependence of metal adsorption could be largely related to type and ionic state of the functional group present in the adsorbent and also to the metal chemistry in the solution.

High adsorption of Cr (VI) at low pH can be explained by the species of the Cr and the adsorbent surface. At acidic pH, the predominant species of Cr are $Cr_2O_7^{2-}$, $HCrO_4^-$, $Cr_3O_{10}^{2-}$ and $Cr_4O_{13}^{2-}$, and above pH 8, only CrO_4^{2-} was stable and as the pH decreased into the region 3–6, the equilibrium shifted to dichromate according to the overall equation.

$$2\,CrO_4^{2-} + 2\,H^+ \rightarrow Cr_2O_7^{2-} + 2\,H_2O \tag{7}$$

At lower pH values, $Cr_3O_{10}^{2-}$ and $Cr_4O_{13}^{2-}$ were formed. Under acidic conditions, the surface of the adsorbent became highly protonated and favoured the uptake of Cr (VI) in the anionic form. With increase in pH, the degree of protonation of the surface reduced gradually and hence adsorption decreased. Furthermore, as pH increased there was competition between OH^- and chromate ions (CrO_4^{2-}) and the former was the dominant species at higher pH values. The net positive surface potential of sorbent decreased, resulting in the weakening of electrostatic forces between sorbent and sorbate, which ultimately led to reduce sorption capacity.

The high pH value caused a reduction in the electrostatic attraction between negatively charged Cr ions and positively charged adsorbent surfaces, therefore reduced percent removal was observed at high pH.

In the current study the Fig. 1 showed that adsorption increased with decreasing pH where the maximum metal removal efficiency occurred at pH 3 or lower and then declining at higher pH.

3.2. Effect of amount of biosorbent

The concentrations of biosorbent and metal were important factor for optimal biosorption. It determined the sorbate-sorbent equilibrium in the system. The Fig. 2 showed that the uptake of chromium ions increased upto 2 g of wheat husk and then in case of 4 g of sorbent the uptaking of chromium (VI) was almost equal to 2 g of adsorbent. So it can be concluded that 2 g wheat husk was taken as optimal for biosorption.

3.3. Effect of different initial concentration and contact time

Biosorption studies with 2 g of wheat husk were conducted for 1 mg/l, 2.5 mg/l and 5 mg/l Cr (VI) solutions.

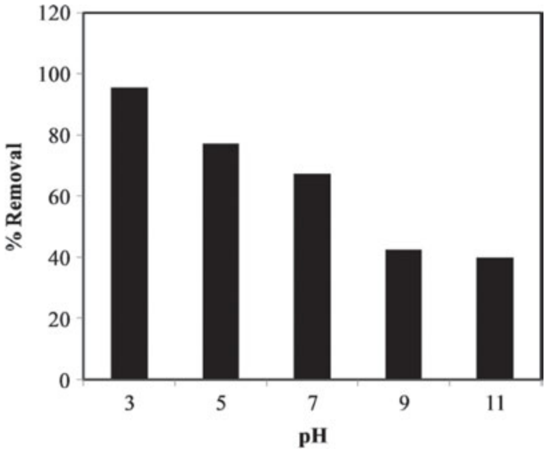

Fig. 1. Amount of chromium removal at different pH by 2 g of wheat husk in 200 ml solution.

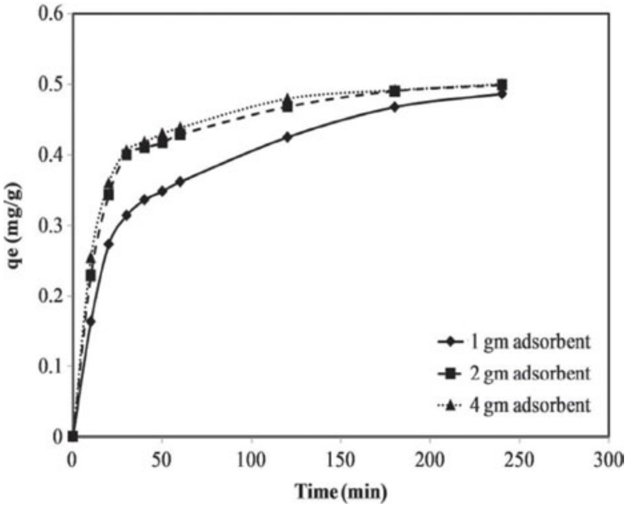

Fig. 2. Adsorption of chromium (VI) by using 1 g, 2 g and 4 g of wheat husk.

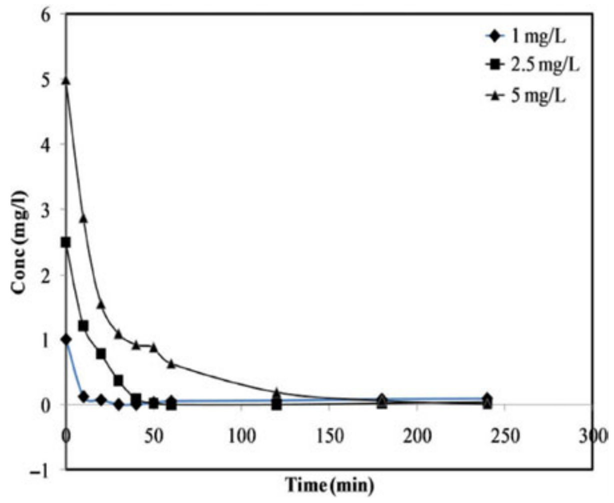

Fig. 3. Adsorption of Cr (VI) at different initial metal concentration at pH 2 using 2 g of wheat husk in 200 ml of sample.

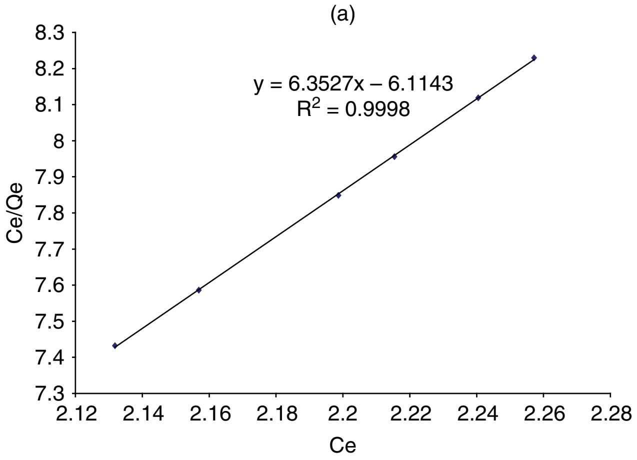

Fig. 4. (a) Langmuir isotherm plots for adsorption of Cr (VI) on wheat husk.

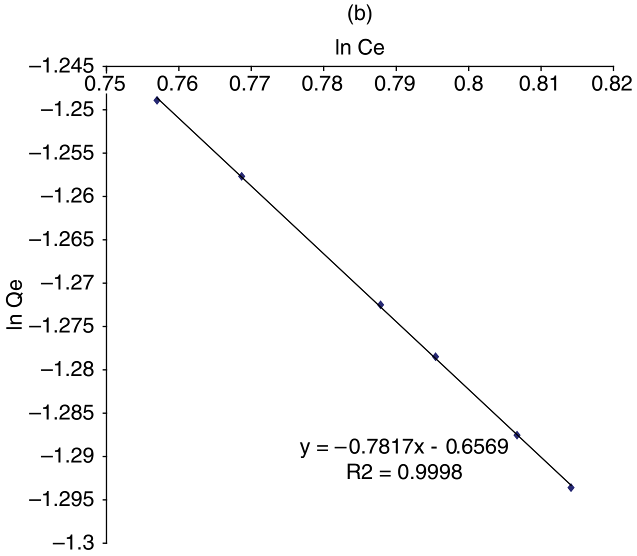

Fig. 4. (b) Freundlich isotherm plots for adsorption of Cr (VI) on wheat husk.

From Fig. 3, it was observed that biosorption was completed at 30 min, 60 min and 240 min for 1 mg/l, 2.5 mg/l and 5 mg/l respectively. This appeared to be due to increase in the number of ions competeting for available binding sites in the biomass.

3.4. Adsorption isotherm

Analysis of the isotherm data was important in order to develop an equation which accurately represents the results of the column and which could be used for column design purposes. Adsorption isotherm also described how solutes interact with adsorbent and so it was critical in optimizing the use of adsorbent. The Cr (VI) uptake capacity of wheat husk was evaluated using Langmuir and Freundlich adsorption isotherms (Figs. 4a and 4b).

At initial metal concentration 5 g/l, 200 ml solution, 35°C temperature and bioadsorbent dose 20 g/l, the Langmuir constants $Q°$ and b were found to be 0.1574 mg/g and 1.309 l/mg respectively with regression coefficient 0.9998 whereas in Freundlich model K_p is 1.9288 (mg/g) (l/mg), n is 1.279 and the regression coefficient is same as in Langmuir model i.e., 0.9998. The adsorption results indicated that the adsorption of hexavalent chromium ion on wheat husk was monolayer adsorption as the value of Langmuir constant $Q°$ was positive. Here as the Langmuir constant b was greater than 1 i.e., the system was exothermic in nature.

Table 2

Different model fit statistical summary

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	9.513379	0.8953326	0.8785858	0.830158	3671.496	Suggested
2FI	10.31883	0.9064128	0.8571563	0.5617812	9473.032	
Quadratic	11.18782	0.9131471	0.8320843	0.3468062	14120.17	
Cubic	0.151052	0.9999937	0.9999694		+	Aliased

The Freundlich model constant K_p indicated the degree of adsorbent surface heterogeneity or the system was heterogeneous in nature. The other Freundlich constant n was found to be greater than 1 but less than 10 showed that the adsorption process was favorable.

3.5. Optimization of the biosorption process

The adsorption process of hexavalent chromium by wheat husk was optimized by DESIGN EXPERT 7.0 software. Here the software generates 30 sets of experiment considering the four factors within their lowest and highest limit. By performing the wet laboratory experiments the % of adsorption which is termed here as response, in each case was determined.

Responses of adsorption in DESIGN EXPERT generated experimental set are given in Table 2.

The Fig. 5 showed the comparison between the experimental and predicted model value using response surface methodology (rsm) which is generated by the software and it showed that these two values were allied in most of the cases which signified the probable and the experimented results were alike in most of the cases.

For optimization, a minimum and a maximum level must be provided for each parameter included. A weight could be assigned to each goal to adjust the shape of its particular desirability function. The goals were combined into an overall desirability function. Starting from several points in the design space improve the chances for finding the 'best' local maximum [17–18]. A multiple response method was applied for optimization of any combination of five goals, namely initial solution pH, initial dye concentration, biosorbent dosage, time of removal and percentage removal of chromium. Considering all the terms the optimum equations generated in terms of coded factor and actual factor were (8–9):

Final equation in terms of coded factors:

$$R = +\,52.09 - 23.15 * A - 8.99 * B + 3.55 * C + 15.19 * D \tag{8}$$

Final equation in terms of actual factors:

$$R1 = +\,75.96737 - 6.61286 * \mathrm{pH} - 0.46110 * \mathrm{Conc} + 2.83785 * \mathrm{Dose} + 0.17870 * \mathrm{Time} \tag{9}$$

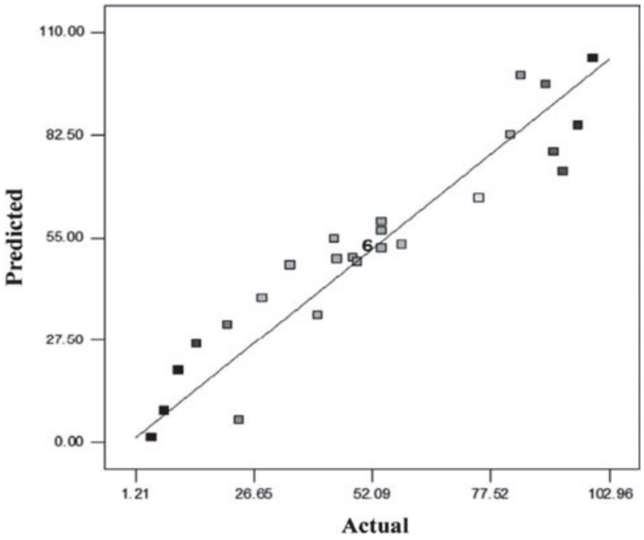

Fig. 5. Predicted value and experimental value of chromium removal.

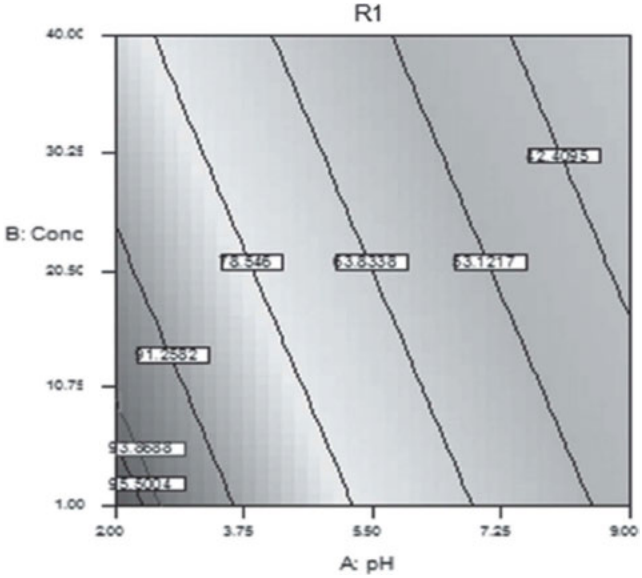

Fig. 6. Response vs. pH, concentration curve.

Table 3
Differences between the estimated values and experimental values

Sl No.	pH	Conc	Dose	Time	Estimated value of reduction	Experimental value of reduction	% of Error
1.	5.5	20.5	1.75	95	52.09	54.32	4.1
2.	9	1	0.5	180	49.57	48.16	–2.92
3.	2	1	3	180	102.96	99.6	–3.37
4.	1.5	20.5	1.75	95	78.53	81.15	3.32
5.	9	40	3	10	8.3	7.98	–4.01
6.	5.5	20.5	1.75	265	82.46	81.95	–0.62

A minimum level of dosage, maximum level of initial dye concentration, maximum percentage removal and the initial solution pH respectively were set for maximum desirability. Fig. 6 showed a ramp desirability that was generated from 30 optimum points via numerical optimization. By seeking from starting points in the response surface changes, the best local maximum was found at initial solution pH 2.00, biosorbent dosage of 2.28 g/l, dye removal of 95.5%. The equilibrium time and temperature were 152 min and 303 K, respectively. The obtained value showed that the estimated function might represent the experimental model and desired conditions.

3.6. Validation of the RSM model

From Table 3, it was observed that the maximum error between the experimental and predicted equation from Design Expert software is approx ± 4% indicating that nearly 96% of the validation could be explained by the model.

4. Conclusions

Wheat husk has the potential to adsorb hexavalent chromium ions from aqueous solution. The adsorbtion process strongly depended on pH of the solution, initial concentration of chromium ions and concentration of wheat husk and 98% adsorbtion can be achieved by making the chromium solution acidic (pH 2). It was also found that the biadsorption of chromium time dependent and the initial concentration of chromium ions determined the optimum time required for adsorption. Optimization conditions for the maximum removal efficiency of chromium were obtained by applying a desirability function in RSM. The corresponding removal efficiency in optimum conditions was found as 95.5%. So it can be concluded that, laboratory trials do show their potential for commertialization at optimum conditions since it is technically feasible, eco friendly with good amount metal binding capacity.

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