Research Journal of Chemical Sciences _____ ISSN 2231-606X
Vol. **3(7),** 31-37, July **(2013)** *Res. J. Chem. Sci.*

Optimization of Process Parameters using Response Surface Methodology (RSM): Removal of Cr (VI) from Aqueous Solution by Wood Apple Shell Activated Carbon (WASAC)

Suantak Kamsonlian and Bipin Shukla
Department of Chemical Engineering, Motilal Nehru National Institute of Technology, Allahabad-211004, UP, INDIA

Available online at: www.isca.in
Received 25th May 2013, revised 17th June 2013, accepted 11th July 2013

Abstract

Industries like tannery, electroplating, textiles etc. have large quantities of heavy metal ions in their effluents which are toxic for human beings. Present paper deals with the study of Cr (VI) removal from aqueous solution by wood apple shell activated carbon (WASAC) using batch experiment. The effect of different process parameters like pH, agitation time, adsorbent dosage and initial concentration were determined. The final filtrate of Cr (VI) solution was analyzed by photo-spectrometer with a wavelength of 540 nm. Initially the process parameter was set at an optimum value of pH 2 and max agitation speed of 140 rpm, further WASAC dosage, Cr (VI) initial concentration and agitation time were optimized for their combined effect using Response Surface Method (RSM). RSM method obtained a correlation between these factors and maximum removal of 98% Cr (VI) was achieved at 500 mg of adsorbent dosage (in 50 ml solution), 176.2 min of agitation time and 95.67 mg/L of Cr (VI) concentration, respectively. This investigation results revealed that WASAC can be used as an alternative adsorbents for removal of Cr (VI) from aqueous solution. Moreover, wood apple shell is abundantly available in nature and hence economical for heavy metal removal.

Keywords: Cr (VI) removal, aqueous solution, response surface methodology, wood apple shell activated carbon, photo spectrometry.

Introduction

An increase in pollution has consequently led to increase in the effluent discharge into the aquatic ecosystem. Ground, surface, and processing waters frequently contain inadequate amount of dissolved heavy metals from sources like mines, factories, and other industries. At least 20 metals are classified as toxic and half of these are emitted into the environment in quantities that pose risks to human health[1]. The most common and harmful heavy metals are chromium, aluminium, lead, copper, nickel, cadmium, mercury, arsenic and zinc. Chromium is considered a hazardous pollutant worldwide because of its mutagen (a substance that causes genetic mutation) and potential carcinogen[2]. Chromium ion exists in solution either in +3 or +6 state out of which +6 (hexavalent Cr) state is toxic (due to its powerful oxidation properties) whereas +3 state causes danger at high concentrations only. Small quantities of Cr(VI) is converted to Cr(V) in human body due to the acidity and action of enzymes. However, the size of these ions is too large to be adopted by a tissue. The only place in human body where the Cr ion is likely to deposit is in the fine capillaries in kidneys, intestines or lungs. The trivalent form of chromium, namely Cr (III), on the other hand, is about 1000 times less toxic than Cr (VI)[3]. Its concentrations in industrial wastewaters range from 0.5 to 270 mg/L[4]. 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 according to Environmental Pollution Act (1990) standards for Cr discharge.

Conventional methods of metal removal from industrial wastewater include chemical precipitation, coagulation, solvent extraction, electrolysis, membrane separation, ion–exchange and adsorption. Most of these methods have disadvantages like high capital and regeneration costs of the materials used, incomplete metal removal and high reagent and energy needs.

Sorption by bio-sorbents is an effective method for metal removal and can be easily adopted to remove heavy metals from large quantities of industrial wastewaters at low cost. Lignocellulosic solid wastes such as straw, coconut husks, exhausted coffee[5], waste tea[6], walnut skin, coconut fiber[7], seeds of Ocimum Basilicum[8], defatted rice bran, rice hulls, soybean hulls and cotton seed hulls[9,10], wheat bran, pea pod, cotton and mustard seed cakes[11] has been tested for metal removal and showed good results. Bio-sorbents show good adsorption capacity but major problem about this treatment is that, this method is time consuming and reducing their contact time reduces their capacity largely[12]. Another effective technique for chromium removal from waste water is adsorption by activated carbon because of its high surface area, highly porous characteristics and fast removal rate compared to bio-adsorbent. Traditionally, the activated carbons commercially used for wastewater treatment are generally obtained from coal/lignite, wood or animal bones and hence are costlier than the bio-adsorbents.

Recently, there is a growing interest in the use of alternative and low-cost precursors for the production of activated carbon. Properties of activated carbon are mainly function of the precursor and of the type of thermal and activation process[13-15]. These are available in large quantities and can be disposed of without regeneration due to their lower cost.

A lot of work has been done for Cr (VI) removal from wastewater using different techniques. Some of these works were reviewed to get an insight of the process and following inferences has been made: i. The adsorption of Cr (VI) ions obeyed the pseudo-first-order kinetic equation with removal of 98.05% ions at an initial concentration 90 mg/L with 500 mg (in 50 ml wastewater sample) of WASAC dose after shaking for 180 min at 140 rpm and at constant temperature. It was observed that a pH of 2.0 was found to be an optimum for adsorption of Cr (VI) in nearly all cases by WASAC[12]. ii. The river sand has been used for adsorption of Cr (VI) which had 0.15 mg/g adsorption capacity with 74.3% removal capacity[16]. iii. S.M. Lee et al. (2010) have prepared Manganese-coated sand by wet coating method and reported improvement in adsorption capacity up to 6.27 mg/g[17]. iv. The fly ash from Patratu Thermal Power Station had shown 89.12% removal and 0.266 mg/g adsorption capacity of Cr(VI) at 298 K[18]. v. The adsorption of chromium (VI) from the aqueous phase on dried roots of water hyacinth revealed a very high degree of removal efficiency (almost 100%)[19]. vi. The maximum Cr (VI) ion sorption capacities of walnut (Juglans regia), hazelnut (Corylus avellana) and almond (Prunus dulcis) were 8.01, 8.28 and 3.40 mg/g and percentage removal were 85.32%, 88.46% and 55.00% respectively[20]. vii. The rice husk and saw dust treated with H2SO4 -has shown the 91.75% and 94.33% removal of Cr (VI) respectively[21]. viii. Several materials such as Arkport Sandy Loam Control, Andre Compost, Geneva Municipal Sludge Compost, Mushroom Compost, Milorganite, de-watered Dairy Cow Manure were tested for the removal of Cr oxycations (anion). Efficient absorption occurs at acidic pH & at a solution pH 3.0, chromate ions were relatively effectively removed, with the greatest value being almost 90%[22].

In present study, micro-porous activated carbon was made from Limonia Acidissima (wood apple) fruit shell and was used for adsorption of Cr(VI) from aqueous solution by RSM methodology. The activated carbon developed from wood apple shell was economical and it took less time for adsorption.

Material and Methods

Optimization method: Optimizing any operation means determining the optimum value of different parameter involved that provides maximum desirable output. Traditionally, optimization in analytical chemistry has been carried out by monitoring the influence of one factor at a time on an experimental response[24]. Its major disadvantage is that it does not include the interactive effects among the variables studied. Another disadvantage of the one-factor optimization is the increase in the number of experiments necessary to conduct the research, which leads to an increase of time and expenses[24]. So in our present study we have used a new method of optimization known as response surface method.

Response surface methodology: It is a combined mathematical and statistical technique based on the fit of a polynomial equation (empirical models) to the experimental data. This method generates a polynomial function for response relating it to the variables involved[23]. In doing so it deals with the variables only at specific levels (mostly -1, 0, 1). RSM generates an experimental design for model preparation. An experimental design is a specific set of experiments defined by a matrix composed of the different level combinations of the variables studied[24]. Different methods of determining the response surface require a different experimental design.

Generally, the relationship between the response and the independent variables is unknown. The most common forms are low-order polynomials (first or second-order)[24]. The simplest model which can be used in RSM is based on a linear function:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \varepsilon \quad (1)$$

where k is the number of variables, β_0 is the constant term, β_i represents the coefficients of the linear parameters, x_i represents the variables, and ε is the residual associated to the experiments.

The next level of the polynomial model should contain additional terms, which describe the interaction between the different experimental variables[24]. This way, a model for a second-order interaction presents the following terms:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i<i\leq j}^{k} \beta_{ij} x_i x_j + \varepsilon \quad (2)$$

In order to determine a critical point (maximum, minimum, or saddle), it is necessary for the polynomial function to contain quadratic terms according to the equation presented below [24]:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_i x_i x_i^2 + \sum_{i<i\leq j}^{k} \beta_{ij} x_i x_j + \varepsilon \quad (3)$$

Where, β_{ij} represents the coefficients of the quadratic parameter. A second-order model can significantly improve the optimization process when a first order model suffers lack of fit due to interaction between variables.

The mathematical model found after fitting the function to the data can sometimes not satisfactorily describe the experimental domain studied. So, the quality of the model fitted is evaluated by the application of analysis of variance (ANOVA).

RSM regressively fits the experimental readings of the design to a model (first, second or higher order) and determines the coefficients involved (β). General designs corresponding to these models are[23]: i. First-Order Designs: The most common first-order designs are 2k factorial (k is the number of control variables), Plackett–Burman, etc. ii. Second-Order Designs: The

most frequently used second-order designs are the 3 k factorial, central composite, and the Box–Behnken designs, etc.

The application of three-level factorial designs is not frequent, and the use of this design has been limited to the optimization of two variables because its efficiency is very low for higher numbers of variables. The central composite design is still the symmetrical second order experimental design most utilized for the development of analytical procedures[23]. The Box–Behnken design present more efficient matrices and is more economical and hence has increased number of published works in recent years. That is, Box-Behnken design requires least number of experimental runs and hence is most economical and most suitable in case where less no. of experimental runs is performed.

Box–Behnken design: i. Requires an experiment number according to N=2k(k-1) +cp, where k is the number of factors and (cp) is the number of the central points. ii. All factor levels have to be adjusted only at three levels (-1, 0, +1) with equally spaced intervals between these levels[23].

Preparation of materials: Firstly different stock solution (Cr concentrations of 90mg/L, 110mg/L and 130 mg/L, i.e., -1, 0 and +1 levels of design) for the purpose of experimentation was prepared using potassium dichromate. Then a sample of wood-apple (Limonia acidissima) was collected from local market. Its shell was broken and washed thoroughly with distilled water and kept for sun dry. Then these were crushed in small pieces and again washed with de-ionized water and kept in oven at a temperature of 383 K for 24 h. The crushed pieces were soaked in concentrated H_2SO_4 (used as impregnating agent) at 1:2 ratios (weight of raw material / volume of acid) for 24 h for acid treatment. This material was then washed with deionised water and was kept for activation in muffle furnace at 573 K for 1 h. The excess acid was washed off with distilled water till neutral pH. The dried and powdered activated carbon was then sieved through BSS-25 (screen with mesh size of 0.6mm). The adsorbent prepared was then used for experimentation throughout the study. Batch adsorption experiments were conducted at normal atmospheric conditions. The concentration of free Cr (VI) ions in the effluent was determined using 1, 5-diphenylcarbazide (DPC) in acidic solution by spectro-photometer with a wavelength of 540 nm. In dilute mineral acid solution di-phenylcarbazide produces a soluble violet colour, which is a characteristic test for chromium.

Results and Discussion

Batch experiments using WASAC for Cr (VI) removal has been conducted earlier also using traditional method of optimization[12]. The result obtained by the traditional method yielded the following optimum values of different parameters: i. pH=2, ii. WASAC dose =500mg (in 50 ml of wastewater solution), iii. Time=180 min, iv. Cr conc.=90 mg/L, v. Agitation speed=140 rpm.

Traditional way of optimization does not account for the combined effects of different parameter. So, the present study used Response Surface Method (RSM) to optimize different parameter to account for the combined effect of different parameters.

Aiming at maximum removal of Cr (VI) from waste-water by setting pH value at 2 and agitation speed at max value of 140 rpm. Now for optimization of other factors Box-Behnken method was used since it require least number of experimental readings. Experiments were performed according to the design matrix of Box-Behnken design as shown in table-1. The experimental domains for different factors dealt in the present study with their coded values are given in table-2.

Table-1
Readings obtained according to the experimental design for Box-Behnken method

Constant parameters: pH=2; Agitation speed= 140 rpm			
Time (min)	**Cr Conc. (mg/L)**	**WASAC (mg/50ml wastewater)**	**% removal**
150	90	475	95.34
150	130	475	87.90
150	110	450	94.31
150	110	500	94.88
180	90	475	97.50
180	130	475	89.12
180	110	450	96.02
180	110	500	96.60
165	90	450	96.75
165	90	500	97.75
165	130	450	88.68
165	130	500	89.25
165	110	475	96.18

Software "Design-Expert Version 6.0.8" was used for regression and graphical analyses of the readings obtained. Box-Behnken design was used for studying 3 factors affecting percentage removal of Cr (VI). The three factors studied, were agitation time, dosage of the adsorbent and concentration of chromium ions in the solution. The software planned 17 trials to be performed as shown in table-1. Analysis of the measured responses by Design expert software suggested that quadratic model is statistically highly significant for the present system for Cr (VI) removal. The optimum values of the variables were obtained using graphical and numerical analysis. Justification of quadratic model for Cr (VI) removal by WASAC was supported by table-3. It suggested that the quadratic model fitted the present system response very adequately.

Probability> F value indicates the adequacy of any model. Model having prob>F value less than 0.0001 will accurately fit the obtained data. Prob>F value less than 0.0001 means that the experimental data obtained can be experimentally explained with 99% accuracy by the model generated by RSM. In the present investigation quadratic model was the suggested model as shown in Table-3 by RSM since it has prob>F value less than 0.0001 and the model was not aliased.

Analysis of variance (ANOVA): The statistical significance of the quadratic model equation was evaluated by the F-test of ANOVA which revealed that this regression is statistically significant (PB_0=.0001) at 99% of confidence level as shown in table-3.

Table-4 shows significant model terms that is terms with values of "Prob > F" less than 0.0500. In this case A, B, C, A^2, B^2, AB are significant model terms and terms with values greater than 0.1000 indicate the model terms that are not significant and can be omitted.

Table-2
Actual and Coded values for different parameters involved

Factor	Parameter	Units	Low actual(-1)	Mid (0)	High actual(1)
A	Agitation Time	Min	150	165	180
B	Cr Conc.	mg/L	90	110	130
C	WASAC	Mg	450	475	500

Table-3
Sequential Model Sum of Squares with selected highest order polynomial where the additional terms are significant and the model is not aliased

Source	Sum of Squares	Mean Square	F Value	Prob > F	Remarks
Mean	151530.9	151530.9	-	-	-
Linear	137.8608	45.95361	14.12632	0.0002	-
2FI	0.26715	0.08905	0.021191	0.9955	
Quadratic	**41.9298**	**13.9766**	**1055.691**	**< 0.0001**	**Suggested**
Cubic	0.092675	0.030892	63660000	< 0.0001	Aliased
Total	151711	8924.178	-	-	-

Table-4
Analysis of variance: Partial sum of squares table

Source	Sum of Squares	Mean Square	F Value	Prob > F	Significance
Model	**180.0578**	**20.00642**	**1511.14037**	**< 0.0001**	**Significant**
A	5.797013	5.797013	437.8644456	< 0.0001	Significant
B	131.139	131.139	9905.293634	< 0.0001	Significant
C	0.9248	0.9248	69.85271109	< 0.0001	Significant
A^2	1.975684	1.975684	149.2289126	< 0.0001	Significant
B^2	38.65642	38.65642	2919.826786	< 0.0001	Significant
C^2	0.007605	0.007605	0.574446637	0.4732	No
AB	0.2209	0.2209	16.68519018	0.0047	No
AC	2.5E-05	2.5E-05	0.001888319	0.9666	No
BC	0.046225	0.046225	3.491502563	0.1039	No

Table-5
ANOVA for Response Surface Quadratic Model

Std. Dev.	0.115062	R-Squared	0.999485569
Mean	94.41176	Adj R-Squared	0.998824157
C.V.	0.121873	Pred R-Squared	0.991769102
PRESS	1.4828	Adeq Precision	111.0924159

The ANOVA result given in table-4 shows the F value to be 1511.14037 for the system, which implies that the terms in the model have a significant effect on the response. The value of the predicted R^2 is the measure of the variation in data explained by the model. The model gives R^2 value of 0.9994 and an adjusted R-squared value of 0.9988 as described in table-5. Therefore, it can be assumed that the proposed model does not explain at least .001% of the experimental results. The probability p (~0.0017) is less than 0.05. This indicates that the model terms are significant at 95% of probability level. A value of (predicted R^2–adjusted R^2) >±0.20, indicates a problem with either the data or the model The "Pred R-Squared" of 0.9918 is in reasonable agreement with the "Adj R-Squared" of 0.9988. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Table-5 shows the value of adequate precision, a measure of S/N ratio, as 111.09 which is well above the desirable value of 4 and hence supports the fitness of the model.

The final mathematical model equation in terms of actual factors (confidence level above 95%) as obtained by Design-expert software is given below:

Removal % Cr = +96.18000 + 0.85125**A**- 4.04875**B** +0.34000C - 0.68500$\mathbf{A}^2$ - 3.03000$\mathbf{B}^2$ -0.042500$\mathbf{C}^2$ - 0.23500**AB** + 2.50000E-003**AC** - 0.10750**BC**

In the above model **A**, **B** and **C** denotes agitation time, Cr(VI) concentration and WASAC dosage respectively. Finally, Table-6 gives the comparison of actual data obtained from experimentation with those predicted by the model establishing the validity of the model. The table shows that these two sets of values are in close agreement with each other with negligible residue (difference between predicted and actual).

Figure-1 shows the plot of perturbation for different factors showing the sensitivity of various factors on the response. Range of response change with deviation from the reference point indicates the sensitivity of the response towards that variable. Here in the graph we can see that A and C, which are agitation time and WASAC dosage respectively, will not make significant changes in removal percentage of Cr. However, if Cr concentration (B) is disturbed, the response is affected notably as B has the max range of response change for deviation -1 to 1 from reference point. The 3-D figures show response surface plots for the relationship between dose of WASAC, agitation speed and Cr concentration on the removal of Cr. Figure-2 shows the surface obtained when WASAC is kept constant, here it is 475.00 mg. The WASAC dose can be changed and different surfaces can be observed in the software. Figure-3 shows the surface obtained when Cr concentration is kept constant at 110 mg/dm^{3}and in figure-4, agitation speed is kept constant at 165 rpm.

Table-6
Diagnostics case study- Predicted vs Actual values of Response

Diagnostics Case Statistics			
Standard Order	**Actual Value**	**Predicted Value**	**Residual**
1	95.34	95.4275	-0.0875
2	97.5	97.6	-0.1
3	87.9	87.8	0.1
4	89.12	89.0325	0.0875
5	94.31	94.26375	0.04625
6	96.02	95.96125	0.05875
7	94.88	94.93875	-0.05875
8	96.6	96.64625	-0.04625

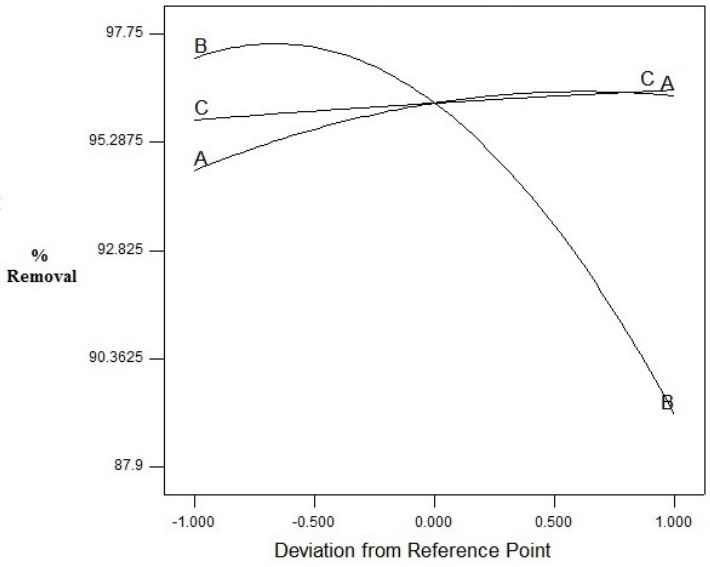

Figure-1
Perturbation curve

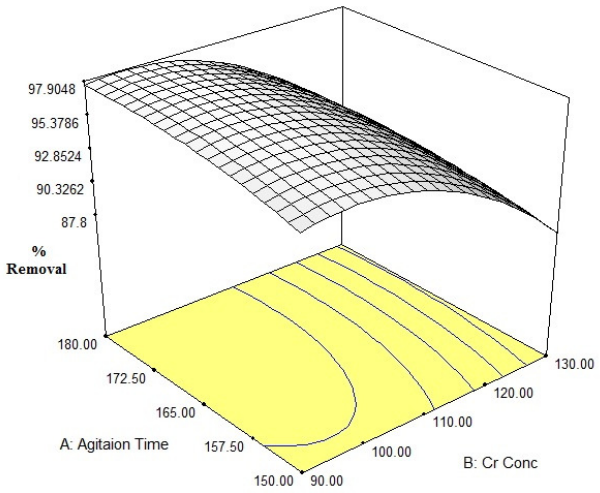

Figure-2
Variation of removal % with agitation time and Cr conc. at constant WASAC dose

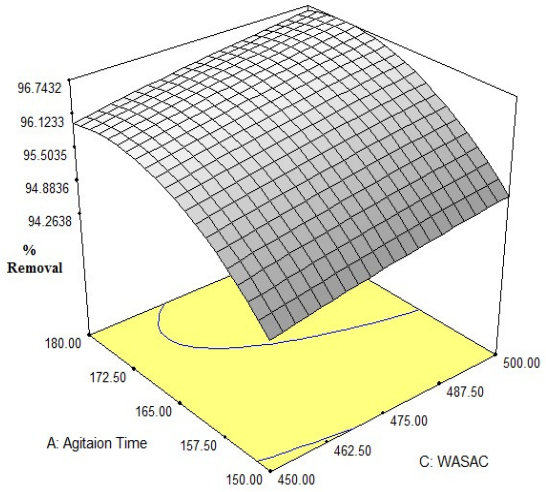

Figure-3
Variation of removal % with agitation time and WASAC dose at const Cr conc

Optimization of the process parameters was done using Numerical Optimization option in the software. Different ranges are selected for each parameter as shown in table-7. The readings obtained from statistical software are listed as table 7.

It can be seen that maximum Cr (VI) removal in percentage is 98.2812% when agitation time is 176.20 min, Cr (VI) concentration 95.67mg/L and WASAC dosage of 500 mg (per 50 ml).

Conclusion

All studies and results obtained indicate that WASAC can be used an economical and effective material for Cr(VI) removal from industrial effluents and wastewater. The Box–Behnken design was successfully used to develop a mathematical model for predicting Cr (VI) removal. The value of $R^2 > 0.99$ for the obtained quadratic model indicates the high correlation between observed or the experimental value of response and response value predicted by the mathematical model. Numerical Optimization using RSM led to the optimum operating condition as agitation time of 176.2 min, Cr conc. of 95.67 mg/L and WASAC dose of 500 mg (per 50 ml wastewater) yielding Cr (VI) removal of 98.28%.

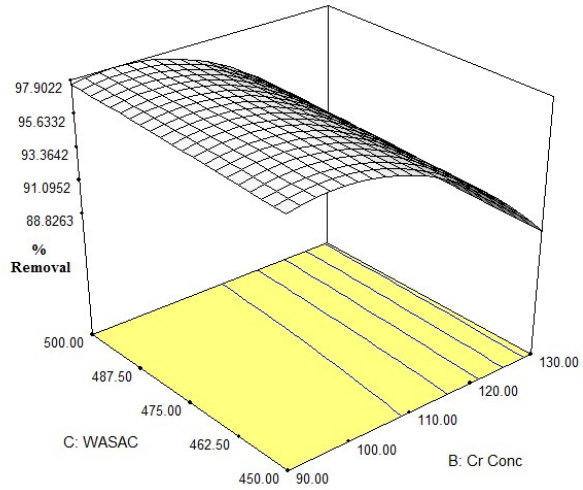

Figure-4
Variation of removal % with Cr conc. and WASAC dose at const agitation time

Acknowledgement

The authors are thankful to the Department of Chemical Engineering, Motilal Nehru National Institute of Technology, Allahabad for providing technical support and facilities.

Table-7
Numerical optimization table

Constraints						
Description	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
Agitation Time	range	150	180	1	1	3
Cr Conc.	range	90	130	1	1	3
WASAC	range	450	500	1	1	3
% removal	range	87.9	100	1	1	3
Solutions						
Number	Agitaion time	Cr (VI) Conc	WASAC	% removal	Desirability	
1	**176.20**	**95.67**	**500.00**	**98.2812**	**0.857952**	**Selected**
2	175.98	95.79	500.00	98.2811	0.857939	-

References

1. Kortenkamp A., Casadevall M., Faux S.P., Jenner A., Shayer R.O.J., Woodbridge N. and O'brien P., A role for molecular oxygen in the formation of DNA damage during the reduction of the carcinogen chromium (VI) by glutathione, *Arch. Biochem. and Biophys.*, **329 (2)**, 199-208 **(1996)**

2. Moreno-Virgen R.M., Tovar-Gómez R., Mendoza-Castillo D.I. and Bonilla A., Applications of activated carbons obtained from lignocellulosic materials for the wastewater treatment. Petriciolet, *Instituto Tecnológico de Aguascalientes*, México **(2012)**

3. Kishore K.K., Parimala V. and Meng X., Detoxification of chromium (VI) in coastal water using lignocellulosic agricultural waste. *Water SA.,* **30(4), (2004)**

4. Patterso J.W., Industrial Wastewater Treatment Technology, *2nd Ed. Butterworth-Heinemann*, London **(1985)**

5. Dakiky M., Khamis M., Manassra A. and Mereb M., Selective adsorption of chromium (VI) in industrial wastewater using low-cost abundantly available adsorbents. *Adv. Environ. Res.,* **6 (4)**, 533-540 **(2002)**

6. Mahvi A.H., Naghipour D., Vaezi F. and Nazmara S., Teawaste as an adsorbent for heavy metal removal from industrial wastewaters, *Am. J. Appl. Sci.,* **2 (1),** 372- 375 **(2005)**

7. Espinola A., Adamian R. and Gomes L.M.B., An innovative technology: natural coconut fibre as adsorptive medium in industrial wastewater cleanup, *Proc. TMS Fall Extract. and Proc. Conf.*, **3,** 2057-2066 **(1999)**

8. Melo M. and Disouza S.F., Removal of chromium by mucilaginous seeds of Ocimum Basilicu. *Bioresour. Technol.*, **92 (2)**, 151-155 **(2004)**

9. Marshall W.E. and Champange E.T., Agricultural byproducts as adsorbents for metal ions in laboratory prepared solutions and in manufacturing wastewater, *J. Environ. Sci. and Health -Part A Environ. Sci. and Eng.,* **30 (2)**, 241-261 **(1995)**

10. Teixeria T., Cesar R., Zezzi A. and Marco A., Biosorption of heavy metals using rice milling by-products. Characterisation and application for removal of metals from aqueous solutions, *Chemosphere,* **54 (7)**, 905-915 **(2004)**

11. Saeed A., Iqbal M. and Akhtar M. W., Application of biowaste materials for the sorption of heavy metals in contaminated aqueous medium, *Pak. J. of Sci. and Indust. Res.*, **45 (3)**, 206-211 **(2002)**

12. Sartape A.S., Raut P.D. and Kolekar S.S., Efficient adsorption of Cr (VI) from aqueous solution on low cost adsorbent developed from Limonia acidissima (Wood apple) shell, *Adsorp. Sci. and Technol.,* **28 (6)**, 547-560 **(2010)**

13. Altenor S., Carene-Melane B. and Gaspard S. Activated carbons from lignocellulosic waste materials for water treatment: a review, *Int. J. Env. Tech. and Manag.*, **10(3-4)**, 308-326 **(2009)**

14. Elizalde G.M.P., Mattusch J., Peláez-Cid, A.A. and Wennrich R., Characterization of adsorbent materials prepared from avocado kernel seeds: natural, activated and carbonized forms, *J. Analy. and Appl. Pyrol.,* **78 (1)**, 185-193 **(2007)**

15. Mohamed A.R., Mohammadi M. and Darzi G.N., Preparation of carbon molecular sieve from lignocellulosic biomass: A review, *Ren. Sus. Ener. Rev.*, **14(6),** 1591-1599 **(2010)**

16. Sharma Y.C. and Weng C.H., Removal of chromium (VI) from water and wastewater by using riverbed sand: Kinetic and equilibrium studies, *J. Hazard. Mater.* **142**, 449–454 **(2007)**

17. Lee S.M., Kim W.G., Laldawngliana C. and Tiwari D., Removal Behavior of Surface Modified Sand for Cd(II) and Cr(VI) from Aqueous Solutions, *J. Chem. Eng. Data,* **55**, 3089–3094 **(2010)**

18. Sharma Y.C., Uma S.N.U. and Weng C.H., Studies on an economically viable remediation of chromium rich waters and wastewaters by PTPS fly ash Colloids and Surfaces, *Physicochem. Eng. Aspects,* **317,** 222–228 **(2008)**

19. Sarkar D., Das S.K., Mukherjee P. and Bandyopadhyay A., Proposed Adsorption diffusion model for characterizing chromium(VI) removal using dried water hyacinth roots, *Clean – Soil, Air, Water*, **38,** 764–770 **(2010)**

20. Pehlivan E. and Altun T., Biosorption of chromium (VI) ion from aqueous solutions using walnut, hazelnut and almond shell, *J. Hazard. Mater.,* **155 (2008)**

21. M. Bansal, D.Singh, V.K. Garg, A comparative study for the removal of hexavalent chromium from aqueous solution by agriculture wastes' carbons, *J. Hazard. Mater,* **171,** 83–92, **(2009)**

22. Harman G., Patrick R. and Spittler T., Removal of heavy metals from polluted waters using lignocellulosic agricultural waste products, *Indust. Biotechnol.*, **(3)4,** 366-374 **2007**

23. Andre I.K. and Mukhopadhyay S., Response surface methodology, *WIREs Comp. Stat*. **(2)**, 128–149 **(2010)**

24. Bezerraa M.A., Santelli R.E., Oliveira E.P., Villar L.S. and Escale L.A.E., Response surface methodology (RSM) as a tool for optimization in analytical chemistry, *Talanta,* **(76),** 965–977 **(2008)**