

PRINCIPAL DETERMINANTS OF TOXICITY REDUCTION BY DE-OILED SOYA USING MULTIVARIATE STATISTICS: PRINCIPAL COMPONENT ANALYSIS AND MULTIPLE LINEAR REGRESSION ANALYSIS

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Abstract. De-oiled soya, a commercial-waste release, from the soya oil production industry, is transformed into activated carbon. Characterization study has been conducted on the activated carbon by X-ray analytical microscope, Scanning Electron Microscope, and Fourier Transform Infrared Spectroscopy. Batch adsorption experiments have been executed to assess the efficacy of activated carbon in the removal of chromium from aqueous solution. The optimum conditions of adsorption process are determined by exhausting the regression equation. There is a conspicuous indication of strong association of chromium adsorption with Langmuir and Freundlich isotherm models. The pseudo- second-order adsorption kinetic model perfectly fits into the considered study.

Keywords: *adsorption kinetics, batch adsorption studies, commercial waste, factor analysis, isotherms*

Introduction

Heavy metal contamination of potable water by industrial discharges and exploitative nature of modern technologies have emerged as serious and paramount issues in countries like the USA, UK, Germany, and India. As a result of the intense degree of toxicity, chromium metal is of prodigious concern and has to be monitored for human survivals as well as for maintaining the quality of life. Especially the carcinogenic and mutagenic natures, which are associated to chromium exposure, pose environmental damage and health issues to (Myres et al., 2000; Nosreth, 1981). Environmental pollution owing to chromium is most noticeable in leather manufacturing, electroplating, electronic manufacturing, and other metal-based operations (Tariq et al., 2006; Mughal et al., 2008). Several methods like electrocoagulation (Dermentzis et al., 2011), ion exchange (Rafati et al., 2010), chemical precipitation (Ramakrishnaiah and Prathima, 2012), reverse osmosis (Mousavi et al., 2009) and adsorption are accessible to reduce the chromium concentration that is found in contaminated water. Among the acknowledged methods, adsorption sounds more feasible and economical as it is most viable in adsorbing the pollutant without producing any by-products. Adsorbents such as acid-activated carbon (Attia et al., 2010), chitosan-coated perlite (Hasan et al., 2003), cross-linked chitosan beads (Modrzejewska et al., 2006), agricultural wastes

(Talokar, 2011), bentonite (Wanees et al., 2012), custard apple peel (Krishna and Padma, 2013), Derris indicia (Ulaganathan and Govindan, 2013), magnetic nanoparticles (El-Sherif et al., 2013), Ulthrix zonata (Malkoc and Nuhoglu, 2003) and activated carbon (Ogbaje et al., 2015) prepared from raffia palm seed are being exploited for the removal of chromium. The authors have tried the use of activated-carbon fabricated from de-oiled soya, a flaky, yellow material that is released as a waste product from the soya oil industry in reducing the toxicity of chromium ion. So far, it has been employed in the elimination of hazardous dyes from wastewater (Mittal et al., 2006; Mittal et al., 2013).

Materials and methods

Activated carbon preparation

De-oiled soya has been sponsored by a private company in Tamilnadu, India. Initially it is ground into small pieces and washed with distilled water. It is then dried in an oven till it is dehydrated. To oxidize the impurities the dried de-oiled soya is treated with hydrogen peroxide solution (30 % w/v) at room temperature for about 24 h (Mittal et al., 2013). The resultant material is washed with distilled water. The hydrogen-peroxide-treated adsorbent is placed in an oven at 100°C by which the moisture is removed. Furthermore, it is kept in a muffle furnace at 350°C temperature for a time period of 4 h. Thus, the obtained carbon is reduced in size by crushing the same. Yet again it is set aside in a muffle furnace at 200°C for 1 h. The carbon thus prepared is stored in an airtight container. The carbon is subsequently sieved using IS 150- μ and 90- μ sieves. Carbon that is retained in the 90- μ sieve and passing through the 150- μ sieve is employed for all adsorption experiments.

Preparation of synthetic effluent

Chromium stock solution is prepared by dissolving 2.89 g of $K_2Cr_2O_7$ in one litre of distilled water to make it into 1000 mg/L concentration of chromium (Wanees et al., 2012; Khatoun et al., 2013). All other solutions are prepared by diluting the stock using distilled water.

Statistical analysis methods

The present study is carried out in two parts:

Part I – Identifying determinants of removal of chromium by activated carbon derived from de-oiled soya using factor analysis and multiple regression analysis by SPSS software 16 version.

Part II – Adsorption isotherms and kinetics

The data for the statistical analysis have been fetched from the batch adsorption experiment. Under batch studies, vital parameters such as agitation speed, contact time, initial concentration of chromium solution, and pH are investigated against a known dosage of adsorbent. At random, 39 sets of batch experiments are conducted in a series of conical flasks, consisting 100 ml volume of chromium aqueous solution with a known quantity of activated de-oiled soya at different ranges of levels of parameters described in *Table 1*. Remi made orbital electrical shaker is used to agitate the flasks. Once equilibrium has attained, the solution is filtered with a Whatman filter paper No.

41. The filtrate then undergoes a spectrophotometric analysis of the amount of chromium being removed using UV/Vis spectrophotometer, Lab India UV 3092.

Table 1. Range of levels of variables in batch studies

Parameters (Variables)	Range of levels of variables		
Agitation speed (<i>r/min</i>)	100	150	200
Contact time (<i>h</i>)	1	1.5	2
Initial concentration of chromium solution (<i>mg/L</i>)	30	40	50
Ph	2	6	10

The percentage removal of chromium is calculated from Eq.1:

$$\text{Removal of chromium (\%)} = \frac{(C_o - C_e)}{C_o} 100 \quad (\text{Eq. 1})$$

where, C_o is the initial concentration of chromium (mg/L) and C_e is the equilibrium concentration of chromium (mg/L) (El-Wakil et al. 2014). The adsorption capacity of the adsorbent is calculated from Eq.2:

$$q_e = \frac{(C_o - C_e)}{W} V \quad (\text{Eq. 2})$$

where q_e is the amount of chromium being adsorbed (mg/g), V is volume of the solution (L), and W is the weight of the adsorbent (g) (Ackacha and Elsherif, 2012).

Results and discussion

Characterization of adsorbent

Table 2 portrays the presence of various elements in the adsorbent that is found by using XGT-2700 X-ray analytical microscope. Figure 1, which is captured using ZEISS, a scanning electron microscopic instrument ascertains the amorphous nature of the adsorbent. A good deal of space is visible from the image which will be more beneficial for the adsorption process to occur on the surface of the carbon. FT-IR analysis is carried out using Perkin Elmer make – model spectrum RX1 (Range 4000 cm^{-1} to 400 cm^{-1}), to identify the functional group present in the activated carbon. The adsorption behavior of the adsorbent can be analyzed by the (Draman et al., 2015) presence of a functional group in it.

Table 2. X-ray analytical microscopic elemental analysis of adsorbent

Element	Si	K	Ca	Ti	Mn	Fe
% by weight	9.77	55.43	27.74	1.11	0.59	5.36

It is observed from *Figure 2* and *3*, that FTIR spectrum consisting of peaks at 3339 cm^{-1} (Draman et al., 2015; Wang et al., 2016), 1603 cm^{-1} (Suresh et al., 2015; Pendekar and Raman, 2013), and $1113\text{--}1161\text{ cm}^{-1}$ (Pendekar and Raman, 2013) could be attributed to OH (hydroxyl) groups, C=O stretch aromatic groups like primary secondary amides, and C-O stretching of alcohols, and carboxylic acid, correspondingly. Further the peak between $700\text{ and }753\text{ cm}^{-1}$ could be assigned to C-H aromatic rings (Pendekar and Raman, 2013). The shifts in the peaks reveal the occupancy of chromium metal onto the carbon.

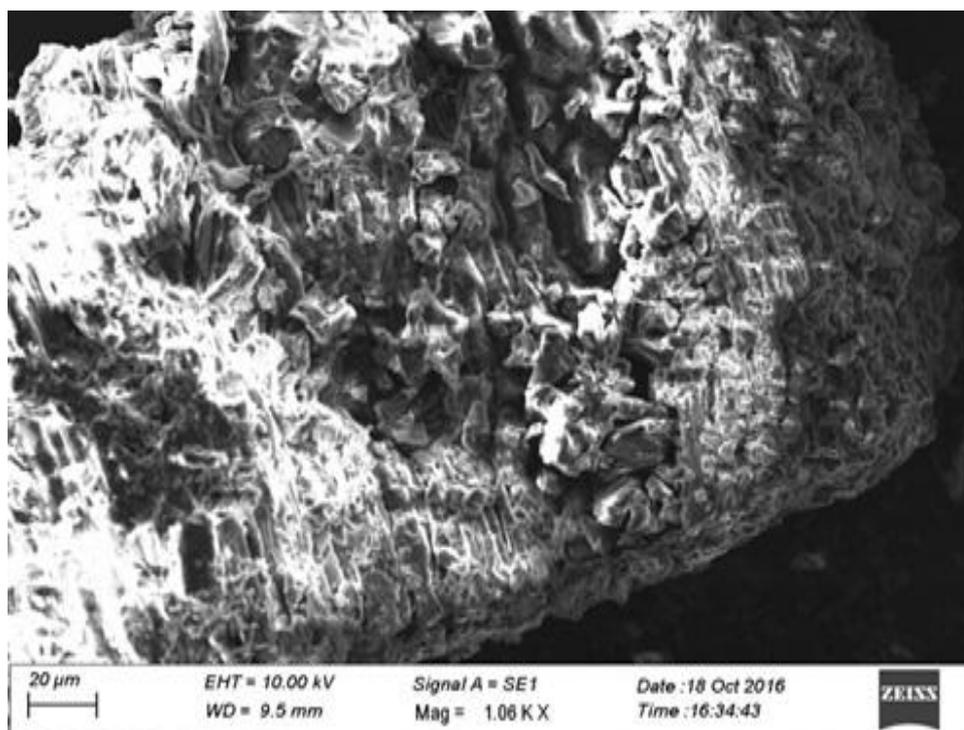


Figure 1. SEM image of the activated carbon de-oiled soya

Part I – Identifying determinants of removal of chromium by activated carbon derived from de-oiled soya using factor analysis and multiple regression analysis

Statistical optimization of adsorption process encompasses two stages for ascertaining determinants accompanying the removal of chromium for reducing water pollution.

Phase I – Factor analysis using principal component analysis for identifying underlying variables,

Phase II – Multiple linear regression analysis for model fit and the Durbin–Watson statistic for detecting the presence of autocorrelation (a relationship between values separated from each other by a given time lag) in the residuals (prediction errors) from a linear regression analysis.

Phase I – Factor analysis using principal component analysis

Factor analysis (through SPSS software version 16) endeavors to identify the underlying variables, or factors, that explicate the pattern of correlations within a set of

observed variables. It is often used in data reduction to identify a small number of factors that explain most of the variance observed in a much larger number of manifest variables and to screen variables for subsequent analysis to identify collinearity prior to performing a linear regression analysis. The author has experimented with the following variables which have been used in previous literature for exploring the effect of variables (Alam et al. 2007) and their significant relationship each other in different combinations during the removal of chromium.

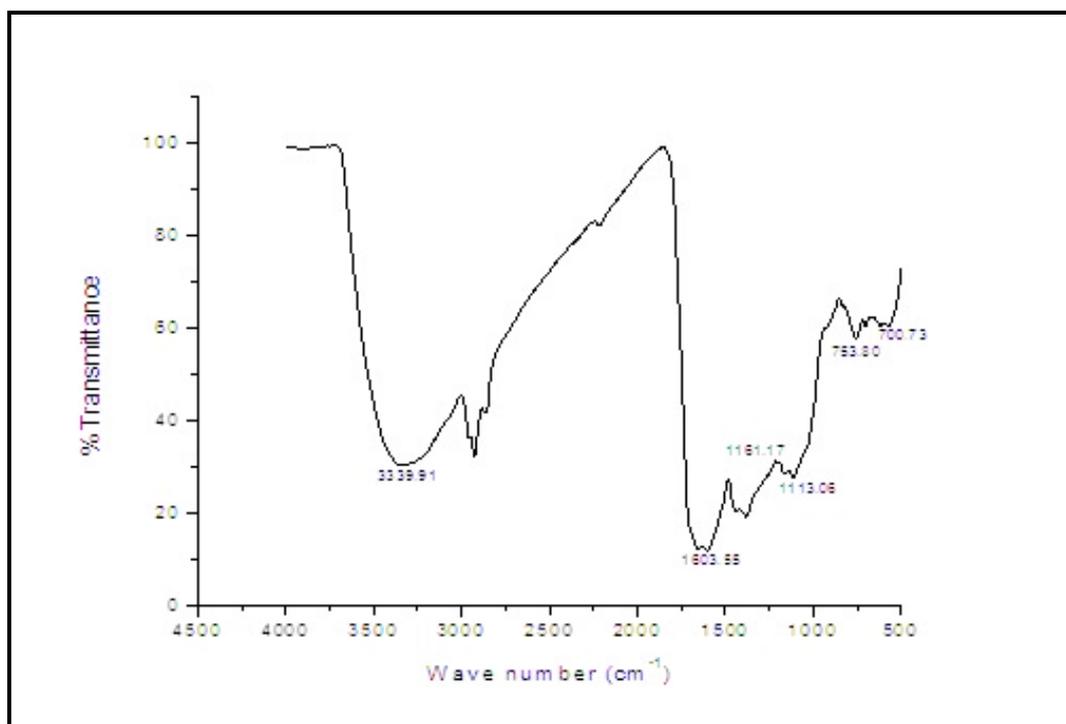


Figure 2. FTIR Spectrum of de-oiled soya before adsorption

Dependent variable: *Y*: experimental adsorption capacity (*mg/g*), where the **independent variables** are: *A*: effect of agitation speed (*r/min*), *B*: effect of contact time (*h*), *C*: effect of initial concentration of chromium solution (*mg/L*), *D*: effect of *pH* of the solution, *AB*: effect of cross product of agitation speed (*r/min*) and Contact time (*h*), *AC*: effect of cross product of agitation speed (*r/min*) and initial conc. (*mg/L*), *AD*: effect of cross product of agitation speed (*r/min*) and *pH*, *BC*: effect of cross product of contact time (*h*) and initial conc. (*mg/L*), *BD*: effect of cross product of contact time (*h*) and *pH*, *CD*: effect of cross product of initial conc. (*mg/L*) and *pH*, *A*²: effect of quadratic component of agitation speed (*r/min*), *B*²: effect of quadratic component of Contact time (*h*), *C*²: effect of quadratic component of initial conc. (*mg/L*), *D*²: effect of quadratic component of *pH*.

Principal component analysis covers four stages (i) Preliminary Analysis (ii) Kaiser-Meyer-Olkin measure of sampling adequacy (KMO) and Bartlett's test of sphericity (iii) Factor Extraction (Total Variance Explained with Initial Eigenvalues, Communalities, and Component Matrix and scree plot) and (iv) Factor Rotation (Rotated Component Matrix and Component Transformation Matrix).

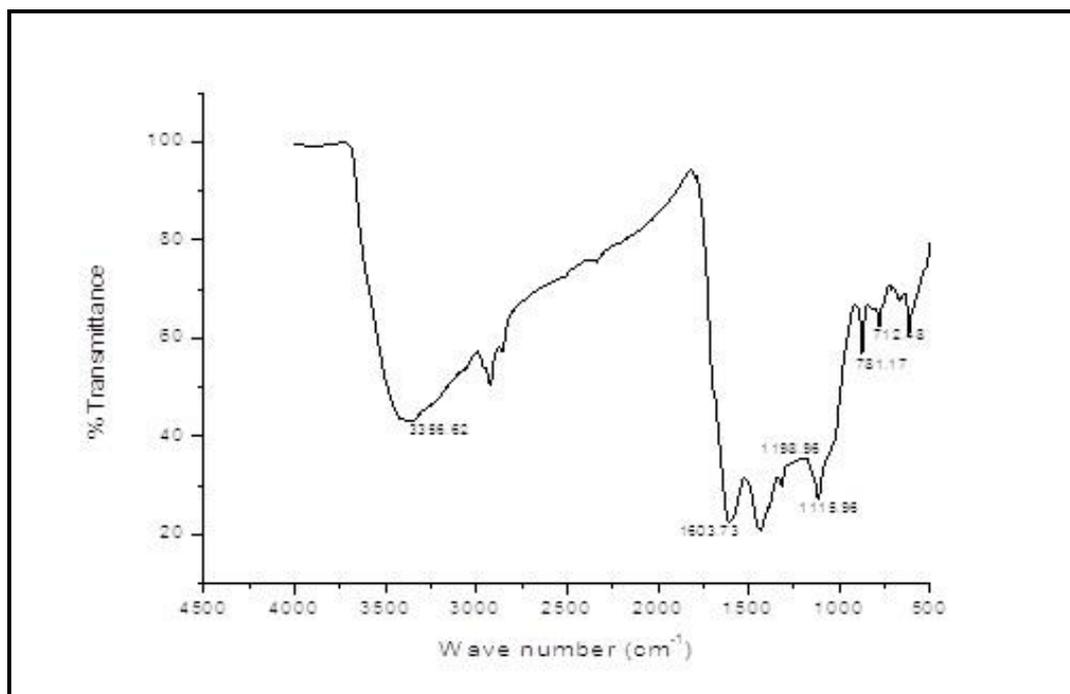


Figure 3. FTIR Spectrum of de-oiled soya after adsorption

Preliminary analysis

SPSS output *Table 3* exhibits an abridged version of the R-matrix to check the pattern of relationships. The top half of this table comprises the Pearson correlation coefficient between all pairs of questions although the bottom half involves the one-tailed significance of these coefficients. It is scanned from the table where a considerable number of the significant values for the corresponding variables are greater than 0.05. The determinant is stated at the bottom of the matrix. If the determinant is 0, then computational problems with the factor analysis will arise. For these data, the corresponding value is 1.47E-018 and therefore the determinant is not 0. Therefore, multicollinearity is not a problem for these data.

Table 3. Correlation matrix

	A	B	C	D	AB	AC	AD	BC	BD	CD	A ²	B ²	C ²	D ²
Correlation	A	1.000												
	B	.038	1.000											
	C	.000	-.054	1.000										
	D	.088	.088	.091	1.000									
	AB	.708	.708	-.020	.114	1.000								
	AC	.850	.018	.507	.149	.597	1.000							
	AD	.500	.081	.122	.879	.393	.513	1.000						
	BC	.047	.852	.459	.143	.619	.288	.153	1.000					
	BD	.081	.500	.078	.879	.393	.134	.770	.494	1.000				
	CD	.109	.080	.376	.943	.126	.318	.858	.282	.833	1.000			

	A ²	.995	.032	.006	.083	.701	.849	.495	.043	.072	.106	1.000				
	B ²	.032	.995	-.056	.083	.701	.009	.072	.846	.495	.072	.025	1.000			
	C ²	.000	-.065	.996	.095	-.025	.505	.131	.444	.077	.380	.007	-.068	1.000		
	D ²	.102	.102	.137	.991	.134	.189	.884	.181	.884	.959	.096	.096	.144	1.000	
Sig. (1-tailed)	A															
	B	.408														
	C	.500	.373													
	D	.297	.297	.291												
	AB	.000	.000	.453	.244											
	AC	.000	.457	.000	.182	.000										
	AD	.001	.313	.229	.000	.007	.000									
	BC	.387	.000	.002	.193	.000	.037	.176								
	BD	.313	.001	.319	.000	.007	.208	.000	.001							
	CD	.255	.314	.009	.000	.222	.024	.000	.041	.000						
	A ²	.000	.424	.486	.308	.000	.000	.001	.396	.331	.261					
	B ²	.424	.000	.367	.308	.000	.478	.331	.000	.001	.332	.440				
	C ²	.500	.348	.000	.283	.440	.001	.213	.002	.320	.008	.483	.341			
D ²	.268	.268	.204	.000	.207	.124	.000	.135	.000	.000	.280	.280	.191			

Determinant =1.47E-18

Kaiser-Meyer-Olkin (KMO) measure of sampling adequacy and Bartlett's test of sphericity

SPSS Output *Table 4* displays the Kaiser-Meyer-Olkin (KMO) measure of sampling adequacy and Bartlett's test of sphericity.

Table 4. KMO and Bartlett's test

Kaiser-Meyer-Olkin (KMO) Measure of Sampling Adequacy.		0.768
Bartlett's Test of Sphericity	Approximate Chi-Square	1.335E3
	Degree of freedom	91
	Significance	0.000

The **KMO statistic** varies between 0 and 1. Kaiser recommends admitting values greater than 0.5 as being acceptable (values below this require the researcher to either collect more data or to rethink about which variables to include). Kaiser-Meyer-Olkin Measure of sampling adequacy value of the present study is 0.768 which is close to 1. Therefore, it is concluded that factor analysis has a better chance to yield distinct and reliable factors.

Bartlett's measure tests the null hypothesis that the original correlation matrix is an identity matrix. For these data, Bartlett's test of the present study is highly significant since $p < 0.001$. It depicts that the R-matrix is not an identity matrix; therefore,

implying that there exist relationships among the variables included in the analysis, and that the factor analysis is appropriate.

Factor extraction

SPSS Output *Table 5* shows the Eigen values associated with each linear component (factor) before extraction, after extraction, and after rotation. Before extraction, SPSS has identified 14 linear components within the data set. It signifies that the first few factors exhibit relatively large amounts of variance (particularly factor 1) whereas subsequent factors elucidate only small amounts of variance. The first four factors together account for 98.8% of the total variance. The eigenvalues associated with these factors are yet again shown (and the percentage of variance explained) in the columns labeled Extraction sums of squared loadings. The values in this part of the table are the same as the values found before extraction. The eigenvalues of the factors after rotation are presented in the final part of the table (labeled rotation sums of squared loadings). Rotation has the effect of optimizing the factor structure and a consequence for these data is that the relative importance of the four factors is equalized. Before rotation, component 1 accounted for considerably more variance than the remaining three components (40.2% compared to 22.1%, 20.3%, and 16.3%), nevertheless after extraction it accounts for only 32.2% of variance (compared to 24.5%, 24.4%, and 17.8%, respectively).

Table 5. Total variance explained

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	Percentage of Variance	Cumulative Percentage	Total	Percentage of Variance	Cumulative Percentage	Total	Percentage of Variance	Cumulative Percentage
1	5.624	40.171	40.171	5.624	40.171	40.171	4.505	32.178	32.178
2	3.095	22.107	62.278	3.095	22.107	62.278	3.432	24.512	56.690
3	2.839	20.276	82.554	2.839	20.276	82.554	3.412	24.369	81.059
4	2.279	16.279	98.833	2.279	16.279	98.833	2.488	17.775	98.833
5	.043	.310	99.143						
6	.038	.269	99.412						
7	.029	.205	99.617						
8	.015	.106	99.723						
9	.013	.092	99.815						
10	.010	.068	99.883						
11	.007	.051	99.934						
12	.004	.031	99.966						
13	.003	.024	99.990						
14	.001	.010	100.000						

Extraction Method: Principal Component Analysis.

Principal component analysis works on the initial assumption that all variance is common; therefore, before extraction the communalities are all 1 which is shown in

SPSS *Table 6*. Extraction column replicates the common variance in the data structure that is, 40.2 % of the variance associated with variable 1. After extraction most of the factors are retained and the amount of variance in each variable that are expounded by the retained factors is represented by the communalities after extraction.

Table 6. Communalities

	A	B	C	D	AB	AC	AD	BC	BD	CD	A2	B2	C2	D2
Initial	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Extraction	0.996	0.996	0.997	.992	.979	.988	.971	.988	.969	.986	.993	.993	.994	.993

SPSS output *Table 7* displays the component matrix before rotation which comprises the loadings of each variable onto each factor. SPSS displays all loadings less than 0.5 by default. The scree plot is used to decide further the number of factors to be extracted.

Table 7. Component matrix^a

	Component			
	1	2	3	4
AD	.872			
BD	.852			
CD	.822	-.551		
D ²	.792	-.571		
D	.767	-.588		
BC	.591			
AB	.653	.721		
A ²			.696	
A			.690	
AC	.609		.680	
B ²		.588	-.665	
B		.588	-.661	
C				.918
C ²				.913
Extraction Method: Principal Component Analysis.				
^a . 4 components extracted.				

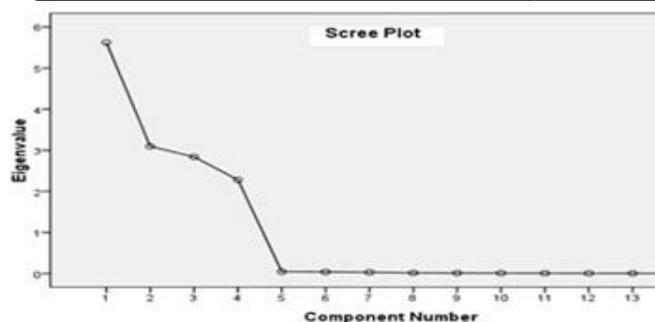


Figure 4. Scree plot

The scree plot is shown in *Figure 4* with a thunderbolt exhibiting the point of inflexion on the curve. It begins to tail off after four factors, but there is another drop after the fifth factor before a stable plateau is reached. Therefore, probably the present study could retain four factors and their relative variables.

Factor rotation

Rotated Component Matrix: SPSS output *Table 8* comprehends the rotated factor loadings (factor pattern matrix), which represent both – how the variables are weighted for each factor and also the correlation between the variables and the factor. Because these are correlations, possible values range from -1 to $+1$. Factor loadings less than 0.5 have not been displayed and the variables are listed in the order of size of their factor loadings. By Kaiser's criterion four factors should be extracted. It is generalized from the principal component analysis that:

1. The variables that load highly on **Factor 1** all contain effect of **pH** of the solution and its compact with **A**: agitation speed in revolution per minute (*r/min*), **B**: Contact time (*h*), **C**: initial concentration of the solution (*mg/L*), and **D**²: quadratic component of **pH**.
2. The variables that load highly on **Factor 2** all cover effect of contact time (**h**) and its closeness with **A**: agitation speed in revolution per minute (*r/min*), **C**: initial concentration of the solution (*mg/L*); and **B**²: quadratic component of contact time (*h*).
3. The variables that load highly on **Factor 3** all comprise of effects of agitation speed in revolution per minute(*r/min*) and its association of **C**: initial concentration of the solution (*mg/L*), **B**: contact time (*h*), and **A**²: quadratic component of agitation speed.
4. The variables that load highly on **Factor 4** all comprise of the effect of initial concentration of the solution (*mg/L*) and its quadratic component (**C**²).

Table 8. Rotated component matrix^a

	Component			
	1	2	3	4
D	.996			
D2	.994			
CD	.946			
AD	.880			
BD	.880			
B		.992		
B2		.991		
BC		.884		
AB		.696	.694	
A			.994	
A2			.993	
AC			.867	
C				.994
C2				.992
Extraction Method: Principal Component Analysis. Rotation Method: Varimax with Kaiser Normalization.				
^a . Rotation converged in 5 iterations.				

In a nutshell, the principal component analysis evidenced that all fourteen variables which are experimented for removal of chromium by activated carbon derived from de-oiled soya are related to one other and can be used for further study.

Phase II – Multiple linear regression analysis for mathematical modeling

We focus on the fourteen predictors, to examine whether they are statistically significant and, if yes, the direction of their mutual relationship. multiple regression analysis is a study focusing on the combined influence of 14 independent variables upon one dependent variable using a linear model. The present research uses multiple liner regression analysis for identifying determinants of experimental adsorption capacity. The process of analysis covers 4 stages.

- Stage I - Model fit and the Durbin–Watson statistic
- Stage II - Statistical significance: (i) F –test for slope (ii) t – Test for intercept
- Stage III - Regression equation for mathematical modeling
- Stage IV - Residues

Stage I - Model fit and the Durbin–Watson statistic

Multiple regression is used to determine the overall fit (variance explained) of the model and the relative contribution of each of the predictors to the total variance explained. The first table of interest is the model summary *Table 9*.

Table 9. Model summary^b

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate	Durbin-Watson
1	0.996 ^a	0.991	0.986	0.17473	2.301
^a Predictors: (Constant), D ² , B ² , A ² , C, AD, BD, AB, BC, AC, CD, D, A, B, C ²					
^b . Dependent Variable: Y					

Table 9 provides the R, R², adjusted R² values, and the standard error of the estimate, which can be used to determine how well a regression- model fits the data. R² is a statistical measure of how close the data are to the fitted regression line. It is also called the coefficient of determination, or the coefficient of multiple determination for multiple regression. Values 0.991 or 99.1% indicates that the model explains all the variability of the response data around its mean. Adjusted R² also specifies how well the terms fit in a curve or in a line, and also adjusts for the number of terms in a model. Adjusted R² will always be less than or equal to R². A value of 0.986 or 98.6% indicates a model that perfectly predicts values in the target field. One of the assumptions of regression is that the observations are independent. If observations are collected over time, it is likely that successive observations are related. If there is no auto correlation where subsequent observations are related, the Durbin–Watson statistic should be between 1.5 and 2.5. The Durbin–Watson statistic of the present study is 2.301 and therefore the data are not auto correlated.

Stage II - Statistical significance

(i) **F – test for slope**

This research endeavors primarily to endorse the F-test for slope to signify and to test the ratios of two variances. The F-Statistics is derived by calculating from (Eq.3) where mean square (MSR) is divided by the mean square error (MSE):

$$F = \frac{MSR}{MSE} \tag{Eq. 3}$$

where $MSR = \frac{SSR}{K}$ and $MSE = \frac{SSE}{n-k-1}$

where k = number of explanatory variables in the regression model. Because there is more than one explanatory variable in the present study, the null and alternative hypotheses are constructed as follows: $H_0 : \beta_1 = \dots \beta_k = 0$ (No linear relationship between experimental adsorption capacity (dependent variable) and explanatory variables), $H_1 : \text{At least one } \beta_j \neq 0$ (linear relationship between experimental adsorption capacity (dependent variable) and at least one explanatory variable). This research attempts to calculate F-Statistics with P value using SPSS package version 16.0. The F-ratio in the ANOVA tests (Table 10) whether the overall regression model is a good fit for the data.

Table 10. ANOVA^b

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	83.106	14	5.936	194.429	0.000 ^a
	Residual	0.733	24	0.031		
	Total	83.839	38			
^a Predictors: (Constant), D ² , B ² , A ² , C, AD, BD, AB, BC, AC, CD, D, A, B, C ²						
^b Dependent Variable: Y						

The sum squares column, the df column, the MS column, the F column, and the p-value or observed significance of F are shown. From the df column, it is grasped that k = 14 the fourteen predictor variables and that n = 39, sample size of the study. The MSE is 0.031 so this means that $s^2 = 0.031$. The F ratio given under column F is 194.429, and p-value is 0.000^a which is given under the sig. column. Since p-Value is less than 0.05, it implies that the calculated regression coefficient is significant and the variance in the independent variable contributes to the change in the dependent variable. Therefore it is inferred that the experimental adsorption capacity for removal of chromium by activated carbon produced from de-oiled soya depends on any one of the explanatory variables. Further, variance in one of the explanatory variables really contributes to change in adsorption capacity which results in the removal of chromium.

(ii) t – Test for intercept

Further examining the existence of significant relationship between individual variables t-Test (to the intercept) is employed. The null and alternative hypotheses are stated as follows:

$H_0 : \beta_i = 0$ (there is no linear relationship) and

$H_1 : \beta_i \neq 0$ (there is a linear relationship).

If the null hypothesis is rejected, it can be concluded that there is an evidence of the linear relationship between individual variables stated in the regression equation. SPSS output *Table 11* incorporates t-statistic and the p-value.

Table 11. Coefficients^a

Model	Unstandardized Coefficients		Standardized Coefficients	t-test	Significance (p-value)	Collinearity Statistics	
	B	Standard Error	Beta			Tolerance	Variance Inflation Factors (VIF)
(Constant term - α)	-7.713	1.889		-4.084	0.000		
A	0.025	0.009	0.697	2.767	0.011	0.006	174.403
B	5.420	0.938	1.509	5.777	0.000	0.005	187.428
C	0.407	0.086	1.629	4.758	0.000	0.003	321.795
D	1.526	0.143	2.231	10.649	0.000	0.008	120.487
AB	-0.001	0.002	-0.071	-.671	0.509	0.033	30.413
AC	0.000	0.000	-0.337	-2.250	0.034	0.016	61.752
AD	-3.126E-5	0.000	-0.008	-.088	0.931	0.041	24.533
BC	-0.003	0.014	-0.034	-.211	0.835	0.014	69.877
BD	0.150	0.035	0.399	4.325	0.000	0.043	23.364
CD	0.016	0.003	0.967	6.269	0.000	0.015	65.394
A ²	-7.089E-5	0.000	-0.595	-2.880	0.008	0.009	117.151
B ²	-1.757	0.243	-1.474	-7.225	0.000	0.009	114.353
C ²	-0.002	0.001	-0.693	-2.332	0.028	0.004	242.256
D ²	-0.280	0.018	-3.516	-15.786	0.000	0.007	136.230
^a Dependent Variable: Y							

Looking at the p-value of the t-test for each predictor, it is seen that p value of A, B, C, D, AC, BD, CD, A², B², C², and D² have approximately zero value or closer to 0.05 (5% level of significance). The effect of these explanatory variables is significant and its coefficient is positive indicating that except for AD, AB, and BC experimental adsorption capacity for removal of chromium is individually related to all the explanatory variables and are chief determinants. Finally, the effect of AD, AB, and BC seems to be unrelated to foreseeing experimental adsorption capacity and are not key factors in predicting experimental adsorption capacity. This result is however unexpected.

Stage III - Regression equation for mathematical modeling

The researcher postulates the linear model in the standard form as follows (Eq.4):

$$Y = \alpha + \beta_1 A + \beta_2 B + \beta_3 C + \beta_4 D + \beta_5 AB + \beta_6 AC + \beta_7 AD + \beta_8 BC + \beta_9 BD + \beta_{10} CD + \beta_{11} A^2 + \beta_{12} B^2 + \beta_{13} C^2 + \beta_{14} D^2 + \mu \quad (\text{Eq. 4})$$

where α = constant term, $\beta_1, \beta_2, \dots, \beta_{14}$ are regression co-efficients for the respective variable and μ = error term. The values in SPSS output *Table 11* are such that coefficients are fitted in (Eq. 4) to formulate regression (Eq.5) of the present study. The value under column B against the constant is the α value (Y intercept) in the regression equation and the value against explanatory variables defining the slope of the regression lines are the values given by $\beta_1, \beta_2, \beta_3, \dots, \beta_{14}$ in the multiple regression equation. Hence, the multiple regression equation is formulated given by (Eq.5):

$$Y = -7.71295633980286 + 0.0250404873313611A + 5.42028756169779B + 0.406874268673784 + 1.52634152407601D - 0.00116744521224136AB - 0.000284755248436949AC - 0.0000312591312933422AD - 0.00297406383677842BC + 0.150094406054611BD + 0.0163945738729832CD - 0.0000708873971701283A^2 - 1.75685205659759B^2 - 0.00232386116595225C^2 - 0.280097456674347 D^2 + \mu \quad (\text{Eq.5})$$

From the above regression equation, trial and error method is employed to obtain the optimum condition for the adsorption of chromium. The optimum condition for the adsorption process is as follows: agitation speed 150 *r/min*, contact time 1.5 *h*, initial concentration of chromium solution 40 *mg/L*, and pH 2. The optimum adsorption capacity is 20.43 *mg/g*.

Stage IV - Residues

The difference between the experimented (*Table 12*) response (Y_{exp}) and the calculated response (from the multiple regression equation) (Y_{calc}) is very less which depicts that the model has good descriptive quality.

Table 12. Set of batch experiments

Run No	Agitation speed in (<i>r/min</i>)	Contact time (<i>h</i>)	Initial Concentration of chromium solution (<i>mg/L</i>)	pH	Experimental Adsorption Capacity (Y_{exp})	Expected Adsorption Capacity (Y_{calc})	Difference ($Y_{\text{exp}} - Y_{\text{calc}}$)
	A	B	C	D			
1	100	1	30	2	9.96	10.01	-0.05
2	100	1	40	2	12.48	12.47	0.01
3	150	2	40	6	13.44	13.30	0.14
4	150	2	40	10	10.56	10.42	0.14
5	200	1	30	2	9.36	9.41	-0.05
6	200	1	40	2	11.68	11.58	0.1
7	150	1.5	30	2	10.32	10.42	-0.1
8	150	1.5	40	2	12.64	12.72	-0.08
9	100	1	30	6	9.84	9.71	0.13

10	100	1	40	6	12.8	12.82	-0.02
11	150	1.5	30	6	10.2	10.41	-0.21
12	150	1.5	40	6	13.6	13.36	0.24
13	200	2	30	2	9.48	9.54	-0.06
14	200	2	40	2	11.52	11.68	-0.16
15	150	2	30	2	10.2	10.07	0.13
16	150	2	40	2	12.32	12.36	-0.04
17	150	2	30	6	10.32	10.36	-0.04
18	100	1.5	40	2	12.96	13.01	-0.05
19	100	1.5	30	6	10.452	10.57	-0.118
20	150	1	30	2	9.84	9.89	-0.05
21	150	1	40	2	12	12.20	-0.2
22	200	1	30	6	9.24	9.10	0.14
23	200	1	40	6	11.68	11.92	-0.24
24	100	1.5	40	6	13.6	13.67	-0.07
25	100	1.5	30	2	10.6116	10.57	0.0416
26	100	2	30	2	10.56	10.25	0.31
27	200	2	30	6	9.72	9.82	-0.1
28	200	2	40	6	12.64	12.62	0.02
29	200	1.5	50	10	12.2	12.34	-0.14
30	100	2	40	2	12.48	12.68	-0.2
31	100	2	30	6	10.4508	10.55	-0.0992
32	200	1.5	30	2	9.96	9.91	0.05
33	200	1.5	40	2	12.32	12.07	0.25
34	150	1	30	6	9.72	9.58	0.14
35	150	1	40	6	12.48	12.55	-0.07
36	100	2	40	6	13.6	13.63	-0.03
37	100	1	50	2	14.6	14.46	0.14
38	200	1.5	30	6	9.84	9.90	-0.06
39	200	1.5	40	6	12.96	12.71	0.25

Part II – Adsorption isotherms and kinetics

Adsorption isotherms

With the optimum condition obtained from the statistical analysis, a series of batch experimentation are performed by equilibrating chromium solution of various concentrations such as, 10, 20, 30, 40, 50, 60 and 70 mg/L, the data thus acquired are applied for the isothermal adsorption study.

Langmuir and Freundlich adsorption isotherm models are employed in the present study to explain the experimental data. The general form of Langmuir equation is given by Eq.6:

$$\frac{C_e}{C_o} = \frac{C_e}{Q_o} + \frac{1}{bQ_o} \quad (\text{Eq. 6})$$

where Q_0 is the maximum adsorption capacity of the adsorbate in mg/g and b is the direct measure of the intensity of sorption in L/mg and they are measured from the slope and intercept of the plot C_e versus C_e/q_e in *Figure 5*. Eq.3 is quoted in the 127th page of the paper published by Jarusiripota (2014). The equilibrium parameter R_L can be determined using Eq.7:

$$R_L = \frac{1}{1+(b C_0)} \quad (\text{Eq. 7})$$

This is referred to in the 587th page of the article by Ackacha and Elsharif, (2012), where R_L is the equilibrium parameter, b is the measure of intensity of sorption in L/mg (Langmuir Constant), and C_0 is the initial concentration of chromium solution in mg/L. The calculated Langmuir isotherm equilibrium parameter $R_L = 0.0816$ lies between 0 and 1 ($0 < R_L < 1$) (Chowdhury et al. 2011). The plot in *Figure 5* is a straight line with R^2 value as 0.989, which is almost nearer to 1, which reveals that the adsorption is favorable and the Langmuir isotherm model is much appropriate for the undertaken adsorption study.

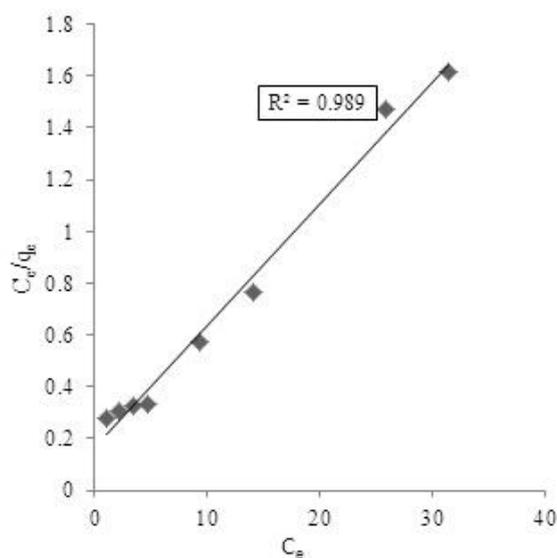


Figure 5. Langmuir adsorption isotherm

Freundlich adsorption model could be well established using the following equation (Eq.8):

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (\text{Eq. 8})$$

which was referred to in the 128th page of an article by Jarusiripota (2014), where n is the Freundlich isotherm constant, K_f is the adsorption co-efficient in mg/g. K_f and n are determined from the intercept and slope of the plot in *Figure 6*. The Plot of $\log C_e$ versus $\log q_e$ in *Fig. 6* is a straight line with $R^2 = 0.842$ and the value of Freundlich constant n is 2.252, which lies between 1 and 10, (Alam et al., 2007; El-Shishtawy and Soltan, 2011) indicates that the Freundlich isotherm perfectly fits the study undertaken.

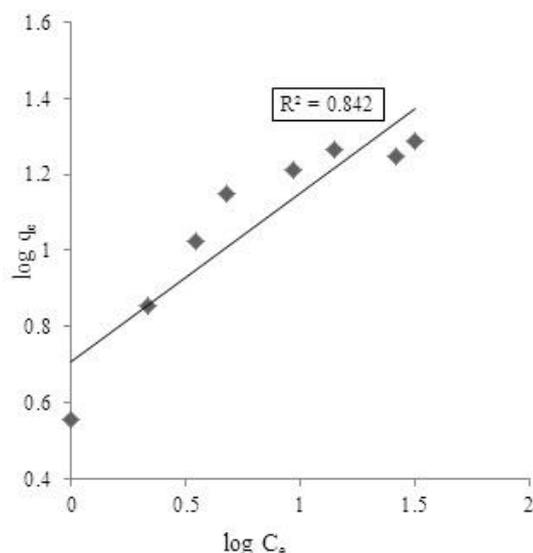


Figure 6. Freundlich adsorption isotherm

Adsorption kinetics

To analyze the trend of chromium adsorption with respect to time, the optimum dosage of DOS has been equilibrated against a known concentration of chromium aqueous solution for different time intervals like 30, 45, 60, 75, 90, 105, and 120 min. The information pertains to the chromium adsorption reaction pathway and the time duration to reach the equilibrium (Krishna and Padma, 2013) could be better explained by the adsorption kinetics models. Pseudo- first-order kinetic model is represented by the following equation (Krishna and Padma, 2013) (Eq.9):

$$\log (q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303} \right) t \quad (\text{Eq. 9})$$

where q_e is the adsorption capacity at equilibrium and q_t is the adsorption capacity at time t , respectively (mg/g) and k_1 is the rate constant of pseudo- first-order adsorption (min^{-1}). In *Figure 7*, a graph is plotted between time t in minutes and $\log (q_e - q_t)$. The co-efficient k_1 is -0.027 which is the slope of the plot in *Figure 7*. The R^2 value of the regression line t versus $\log (q_e - q_t)$ is 0.778. From this value it can be interpreted that the pseudo- first-order adsorption kinetics may not fit to the adsorption process undertaken. Pseudo- second-order kinetic model (Agarwal et al. 2015) can be expressed as given below (Eq.10):

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 \quad (\text{Eq. 10})$$

where k_2 is the rate constant of pseudo- second-order adsorption (min^{-1}). The co-efficient k_2 is 0.068 which is the slope of the plot t versus t/q_t in *Figure 8*. The R^2 value of the regression line t versus t/q_t is 0.999. This value is closer to 1 which indicates that the pseudo- second-order adsorption kinetics model absolutely fits to the adsorption process of chromium by activated carbon.

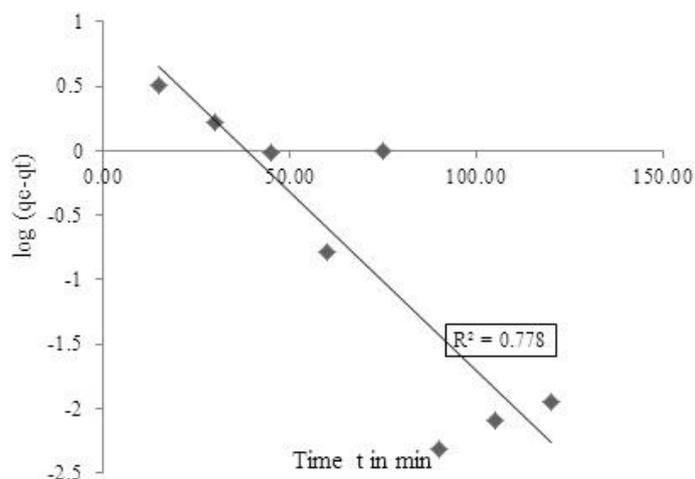


Figure 7. Pseudo- first-kinetic order model

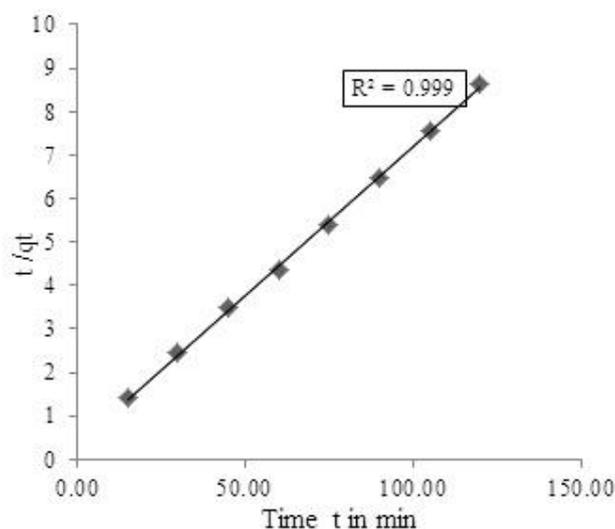


Figure 8. Pseudo- second-order kinetic model

Conclusions

In this study, the factor analysis Bartlett's test with $p < 0.001$ depicts that the R-matrix is not an identity matrix; therefore, there exist relationships between the variables incorporated in the analysis, and that the factor analysis is appropriate. From the principal component analysis it can be better resolved that chosen factors are very well correlated for the enhancement of the adsorption process. The statistical significance analysis is better enlightened through the F-test and t-test where adsorption capacity for the removal of chromium are individually related to all the chosen variables. The optimum conditions found for the concerned study on trial and error basis by regression equation are 150-r/min agitation speed, 1.5 h contact time, 40-mg/L initial concentration of chromium solution, and a pH of 2. The linear regression model perfectly fits with the adsorption that is dealt with for the current study. The calculated R^2 values are 0.989 and 0.842 of Langmuir and Freundlich isotherms, correspondingly.

Thus, it can be concluded that the activated carbon prepared using the de-oiled soya which could not be used even as an animal feed, can be effectively and implicitly employed as a low-cost adsorbent for the removal of toxic chromium ions from an aqueous solution. Additional removal efficiency might be achieved by employing physical or chemical activation methods on the preparation process of activated carbon.

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