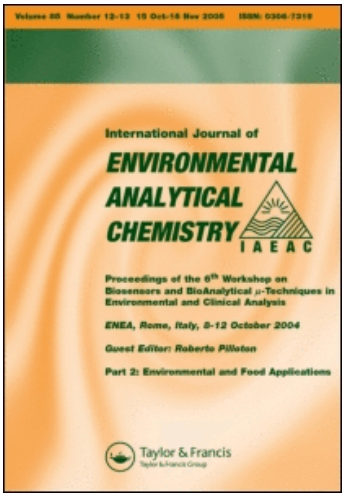

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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Online publication date: 10 March 2010

To cite this Article Azharul Islam, Md. , Nikoloutsou, Zacharoula , Sakkas, Vasilios , Papatheodorou, Michalis and Albanis, Triantafyllos(2010) 'Statistical optimisation by combination of response surface methodology and desirability function for removal of azo dye from aqueous solution', International Journal of Environmental Analytical Chemistry, 90: 3, 497 — 509

To link to this Article: DOI: 10.1080/03067310903094503

URL: http://dx.doi.org/10.1080/03067310903094503

Intern. J. Environ. Anal. Chem.
Vol. 90, Nos. 3–6, 15 March–15 May 2010, 497–509

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(*Received 25 November 2008; final version received 1 June 2009*)

Traditional one by one factor analysis has some drawbacks related to time, cost, feasibility and optimisation. To overcome of these process parameters, response surface methodology (RSM) with Central Composite Design (CCD) was used in this study to evaluate the effects of main factors and their interaction for congo red (CR) removal and to derive the model optimisation by composition of all parameters in order to reduce excessive experiments. The 'profiling and desirability function' was also employed for the specific values of controlled parameters for optimisation and highest desirability. The use of analysis of variance (ANOVA) and '*t*' test showed that the interactions of all studied parameters (pH, dose and concentration) on congo red (CR) dye for adsorbent (used tea leaves) have significant impact of removal %. The lack of fit test (LOF) and residual analysis were also performed for adequacy of the model. Applying desirability function, the optimal conditions of pH, adsorbent dose and initial concentration were found to be 4.32, 0.47 g, and 92.05 mg L^{-1} corresponding to 93.46% removal for used tea leaves. Batch equilibration method was followed for the removal of CR dye for adsorbent. Langmuir adsorption isotherm was conformed well to removal data for used tea leaves.

Keywords: response surface methodology; desirability function; congo red; used tea leaves

1. Introduction

Dyes are used in the process of coloration of various textile manufacturing products, the paper industry and other dye based industries. But the effluents from these industries are very harmful and have contaminated the adjacent river water as well as ground water systems, resulting in serious environmental problems. Congo red (CR) [Dinatirum-3, 3′-[[1,1′-biphenyl]-4, 4′-diylbis(azo)]bis(4-aminonaphthalin-1-sulfonat) is one of the most frequently used secondary diazo dyes. Due to its benzidine based origin, it is expected to metabolise to benzidine, which is known as a human carcinogen and mutagen [1]. Congo red effluents are highly coloured, have low biological oxygen demand (BOD) and high chemical oxygen demand (COD) while they contain high amounts of dissolved solids [2]. Moreover, due to its structural stability, congo red is particularly durable to biodegradation and is a potential threat to the environment [1].

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ISSN 0306–7319 print/ISSN 1029–0397 online

DOI: 10.1080/03067310903094503
http://www.informaworld.com

Activated carbon is widely used as an adsorbent for the removal of hazardous dyes because of the extensive region of surface, microporous structure, high possibility of adsorption and higher degree of surface direct reaction [3]. Nevertheless, the available commercial activated carbons are very expensive. Recently, several studies have reported the efficiency of low cost materials of diverse origin for the removal of CR. These include rice husk [4], N,O-carboxymethyl-chitosans [5], anilinepropylsilica xerogel [6], N,O-carboxymethyl-chitosan/montmorillonite [7], Ca-bentonite [8], surfactant-modified montmorillonite [9], β-cyclodextrin and starch [10], bentonite [11], chitosan hydrobeads [12], *Araucaria angustifolia* wastes [13], fly ash [14], bagasse fly ash [1], Neem leaf powder [15], etc.

Used tea leaves are used in the present work as a low cost novel adsorbent material in order to determine the performance of congo red removal from aqueous solution. But use of low cost materials cannot ensure the desired output of removal efficiency if the processes are not well organised and efficient. Therefore, response surface methodology (RSM) is used as a statistical tool for well-organised process optimisation through a relatively small number of systematic experiments that can reduce time and cost [16]. The traditional one-factor-at-a-time approach to optimisation is time-consuming and not competent for achieving the true optimum condition due to lack of interactions among the factors. In addition, calculating all the effects, RSM can derive a model that represents the whole process. In the present study, RSM with central composite design (CCD) was successfully employed to verify the various interactions of factors responsible for removal of CR dye. Optimisation was performed on the basis of desirability approach in order to find maximum removal percentage of CR by recalculating of all studied parameters within their ranges, and later an isotherm study was carried out by using the optimised factors, in order to determine the removal capacity of used tea leaves.

2. Experimental

2.1 *Adsorbent and adsorbate*

Used tea leaves were obtained from a local cafeteria, and were washed thoroughly with normal water and later with double distilled water in order to removal of pigments and other foreign materials. After drying for 3 days at room temperature, leaves were placed in the oven at 80°C for removing extra moisture. The particle size of used tea leaves was in the range of 0.710–1.00 mm.

CR dye [Color Index = 22,120, chemical formula = $C_{32}H_{22}N_6Na_2O_6S_2$, M = 696.66 g Mol^{-1}] was purchased from Riedel-de Haen (Switzerland). An aqueous stock solution of 2000 mg L^{-1} of CR was prepared. From the stock solution, various concentrations of working solutions were prepared. The analysis of CR concentration was estimated spectrophotometrically by monitoring the absorbance at 496 nm using UV–VIS spectrophotometer (Jasco, V-530, Japan).

2.2 *Characterisation of used tea leaves*

Functional groups present on the surface of adsorbents played a great role for adsorption of any compound. FTIR (Fourier transform infrared spectroscopy) spectrometer (Shimadzu-8400, Japan) was used at room temperature with pellet (pressed-disk)

technique in order to determine the active functional groups. Scanning electron microscopy (SEM) pictures of used tea leaves were taken by Jeol JSM 5600 at 20 kV.

2.3 *Experimental procedures*

Batch adsorption experiments were carried out by agitating 25 mL of aqueous dye solution with different pH, amount of dose and concentrations according to the CCD design matrix (Table 1). The kinetic study showed that a contact time of 360 min were sufficient to achieve equilibrium of CR onto used tea leaves (Figure 1). At the end of the shaking the dye solution was separated from the selected adsorbent by centrifugation at 4200 rpm for 5 min and the separated aqueous phase was collected with a pipette for the determination of CR concentration.

The removal % was calculated as:

$$\text{Removal } \% = 100X\frac{(C_0 - C_e)}{C_0} \tag{1}$$

Table 1. Design matrix and results for CR removal % onto used tea leaves.

				Removal %	
Run	pH (X_1)	Dose (X_2)	Concentration (X_3)	Observed	Predicted
1	+1	+1	+1	92.54	93.05
2	0	0	0	90.00	90.47
3	+1	+1	−1	89.35	86.55
4	−1	+1	−1	67.02	68.10
5	−1	−1	−1	74.66	74.36
6	+α	0	0	92.33	95.99
7	0	0	0	87.41	90.47
8	0	0	0	89.82	90.47
9	0	0	−α	64.57	67.56
10	0	0	+α	90.54	87.23
11	0	+α	0	87.63	86.63
12	+1	−1	+1	82.47	81.61
13	−1	−1	+1	88.22	91.25
14	−α	0	0	92.56	88.58
15	0	−α	0	81.59	82.27
16	+1	−1	−1	87.88	85.04
17	−1	+1	+1	91.87	94.33
18	0	0	0	90.59	90.47
19	0	0	0	92.52	90.47
20	0	0	0	92.45	90.47

Factors	Range and Level				
Coded value	−α	−1 (Low)	0 (Middle)	+1 (High)	+α
pH	2.64	4	6	8	9.36
Dose (g)	0.13	0.2	0.3	0.4	0.47
Concentration (mg L^{-1})	7.96	25	50	75	92.04

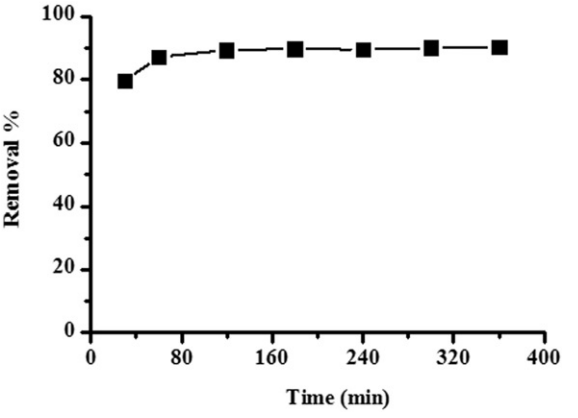

Figure 1. Effect of contact time on CR removal: Adsorbent dose = 0.3 g/25 mL in double distilled water, concentration = 50 mg L^{-1}.

where C_0 and C_e are the initial and equilibrium concentrations of CR dye in the solutions in mg L^{-1}, respectively.

2.4 *Desirability function*

Desirability function is simply a mathematical method in order to find the optimum values of input parameters and output (response) concurrently by using the optimum input parameters levels. Harrington [17] first developed the desirability function and it was later modified by Derringer and Suich [18].

The desirability function first converts the response (y_n) into an individual desirability function (d_i) that varies from 0 to 1. The desirability 1 is for maximum (Max) and desirability 0 is for non-desirable situations or minimum (Min). Derringer and Suich [18] proposed the equation, which can be expressed as:

$$d_i = \left(\frac{y - A}{B - A}\right)^{wi}, \quad A \le y \le B \tag{2}$$

$$d_i = 1, \quad y > B$$

$$d_i = 0, \quad y < A$$

In Equation (2), A and B are the lowest and the highest values respectively, obtained for the response i, and wi is the weight.

Afterwards the transformations of all individual desirability points for the predicted values are converted into overall desirability function, D, by computing their geometric mean.

$$D = \left[d_1^{v1} \times d_2^{v2} \times \cdots \times d_n^{vn}\right]^{1/n}, \quad 0 \le v_i \le 1 (i = 1, 2, \ldots, n), \quad \sum_{i=1}^{n} v_i = 1 \tag{3}$$

where d_i indicate the desirability of the response y_i ($i = 1, 2, 3, \ldots, n$) and v_i represents the importance of responses.

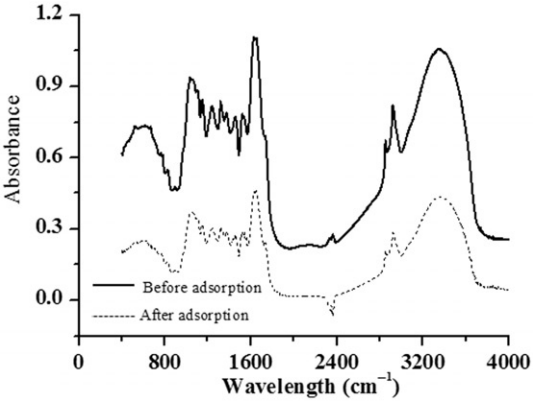

Figure 2. FTIR spectra of uses tea leaves for CR removal.

3. Results and discussion

3.1 *FTIR and SEM analysis*

The FTIR (Fourier transform infrared spectroscopy) analysis showed various functional groups existed in the used tea leaves (Figure 2). A strong sharp peak was observed in the region of 1660–1730 cm^{-1} indicates the presence of C=O (carboxylic acids) group and the peak at 1300–1400 cm^{-1} related to N=O (nitro compounds). The peak at 2850–3000 cm^{-1} corresponds to C-H (alkanes) groups. The broad peak at 3100–3600 cm^{-1} that represents the H-bonded O-H stretch indicates the presence of alcohol and phenol compounds. After the adsorption of congo red onto used tea waste, the IR spectra of peak at 3100–3600 cm^{-1} reduced slightly to wavenumber 2970–3400 cm^{-1} and the peak related to C=O (carboxylic acids) group at wavenumber 1660–1730 cm^{-1} also shifted to 1590–1700 cm^{-1}. These results suggested that the influence of OH and C=O groups were more prominent in the surface of adsorbent.

SEM analysis indicated several small openings on the surface of the used tea leaves which are mainly representation of stomata (Figure 3). These rough perforated structures of used tea leaves were mainly responsible for dye adsorption.

3.2 *Response surface methodology*

In the present study, a 2^3 full factorial CCD with five settings for each of the three factor levels was used to evaluate the quadratic effects and two-way interactions among these factors. To study 3 factors at 5 levels would require 5^3 or 125 runs using conventional experiments, whereas uses of RSM such as CCD require only 20 runs or experiments, consisting of 8 factorial points, 6 axial points and 6 replicates at the centre points ($N = 2^n + 2n + n_c = 2^3 + 2*3 + 6 = 20$, where N is the total number of experiments required, n is the number of factors and n_c is the centre points). The pH (X_1), adsorbent dose (X_2) and initial concentration (X_3) were the input factors in order to get the highest removal % (output) of CR for adsorbent. The centre points are used to determine the experimental error and the replication of the data. The complete design matrix, range and level of factors, together with the results obtained, are shown in Table 1. STATISTICA® statistical

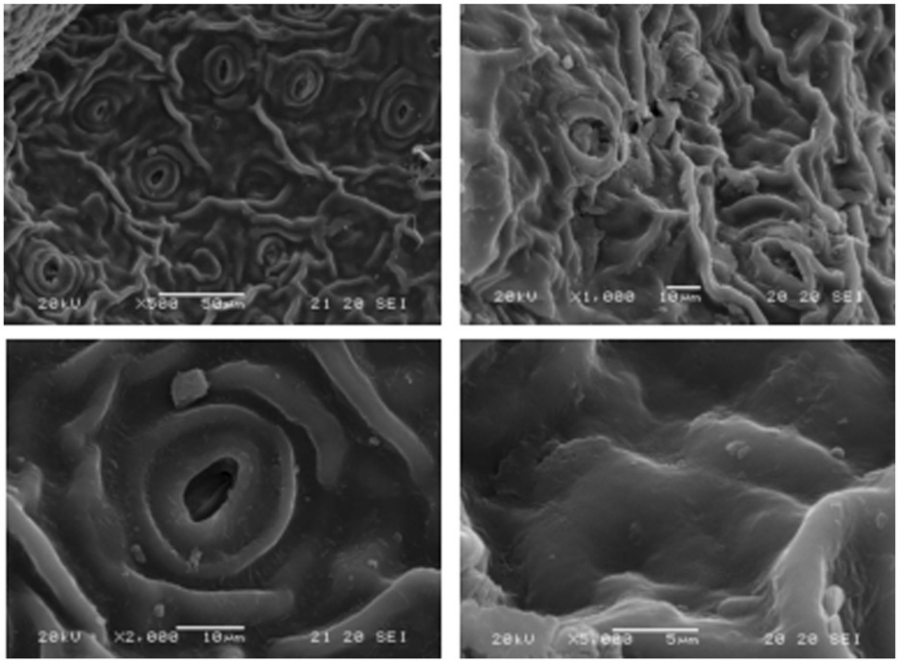

Figure 3. SEM pictures of used tea leaves.

software was used for the design of experiment. A second order polynomial model used to fit the response to the independent variables is shown:

$$y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j \tag{4}$$

where y is the percentage of CR removal, β_0 the intercept and β_i, β_{ii}, β_{ij} are the coefficients of parameters for linear, squared and interaction factor effects, respectively.

The pH, initial concentration and adsorbent dose are the vital parameters which affect adsorption process. In order to evaluate the interactions effects of these factors, experiments were executed with the combinations of different parameters using CCD. The sufficiency of the model was evaluated through analysis of variance (ANOVA). The ANOVA for the response surface quadratic model with two way interactions for CR removal % on used tea leaves is depicted in Table 2. The obtained results through ANOVA, (X_1), (X_3), (X_1X_2), (X_1X_3), (X_2X_3), (X_2^2) and (X_3^2) were found to be statistically significant for used tea leaves. In order to perceive the importance of different actual factors and their interactions Standardized Pareto chart are developed by the software that are represented in Figure 4, according to the rank. The Lack of Fit (LOF) is the variation of the data around the fitted model. LOF is a special investigative test for adequacy of a model fit, because the effects of the additional higher-order terms are removed from the error. In this study, 6 central points is used for calculating the pure error. If the model does not fit the data well, this will be significant. In our present study with regards to CR removal % onto used tea leaves, the LOF is not significant relative to the pure error, indicating good response to the model. The model regression coefficient (R^2) of 0.920 is reasonable agreement with the experimental results, indicating 92.01% of the variability

Table 2. ANOVA and lack of fit test (LOF) for CR onto used tea leaves.

Source	Sum of squares	df	Mean square	F-value	*p*-value Prob > F
$X_1(pH)$	66.27	1	66.27	18.26	0.01
$X_2(dose)$	22.96	1	22.96	6.33	0.05
$X_3(concentration)$	467.06	1	467.06	128.71	0.00
$X_1\ X_2$	30.15	1	30.15	8.31	0.03
$X_1\ X_3$	206.35	1	206.35	56.86	0.00
$X_2\ X_3$	49.45	1	49.45	13.63	0.01
X_1^2	5.92	1	5.92	1.63	0.26
X_2^2	65.32	1	65.32	18.00	0.01
X_3^2	308.04	1	308.04	84.89	0.00
Lack of Fit	87.24	5	17.45	4.81	0.05
Pure Error	18.14	5	3.63		
Correction Total	1319.22	19			

$R^2 = 0.920$; Adjusted $R^2 = 0.848$.

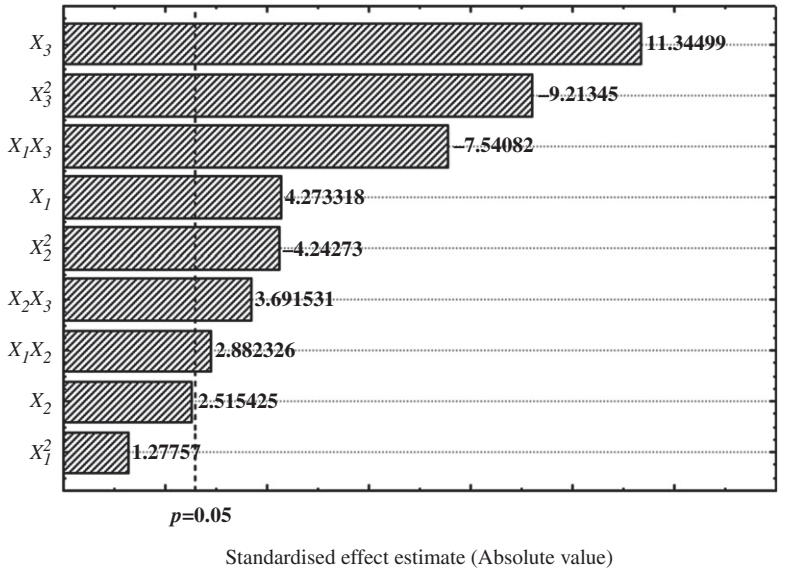

Figure 4. Standardised Pareto chart for main and interaction factors of CR removal by used tea leaves.

can be revealed by the model and are left with 7.99% residual variability for used tea leaves.

In addition to LOF tests, the model was further evaluted by the residual analysis. Residuals are the deviations of the observed values from the predicted values and represent the variance that is not explained by the model. The better the fit of the model, the smaller the values of residuals is; more to the point, residuals should be normally distributed. The histogram of residuals with the *Shapiro-Wilk W* normality test was carried out by the software and depicted in Figure 5. From the plot, residuals look normal and normality

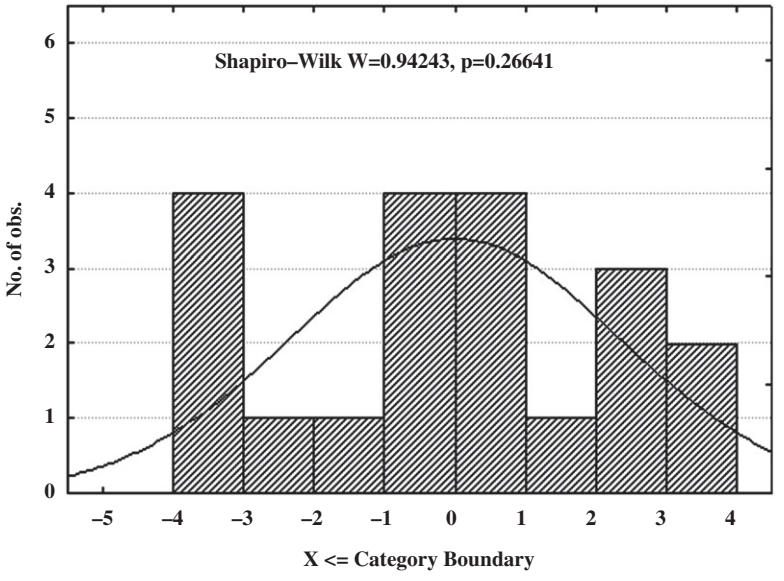

Figure 5. Histogram plot of residuals for CR removal onto used tea leaves.

Table 3. Regression analysis for CR removal % by used tea leaves.

Source	Coefficient	Standard error	*t*-ratio	*p*-value
Mean/Interc.	38.31	10.92	3.51	0.02
$X_1(pH)$	1.35	1.95	0.69	0.52
$X_2(dose)$	32.75	39.02	0.84	0.44
$X_3(concentration)$	1.29	0.14	9.10	0.00
$X_1\ X_2$	9.71	3.37	2.88	0.03
$X_1\ X_3$	–0.10	0.01	–7.54	0.00
$X_2\ X_3$	1.00	0.27	3.69	0.01
X_1^2	0.16	0.13	1.28	0.26
X_2^2	–212.90	50.18	–4.24	0.01
X_3^2	–0.01	0.00	–9.21	0.00

tests gave non-significant value of W statistics, indicating the model may predict very well for CR removal % onto used tea leaves.

3.3 *Models and effects of different factors on removal of CR*

Table 3 represents the predicted model regression coefficient values of different parameters. Student '*t*' test was used to verify the significance of the regression coefficients. The '*p*' values were used to determine the significance of the variables. Generally, a larger '*t*' value gives the smaller '*p*' value. From the t test, it may be said that the linear effect of pH(X_1) and adsorbent dose (X_2) did not have a significant effect on removal of CR dye. But on the other hand, the main effect of initial dye concentration (X_3) showed a positive significant impact

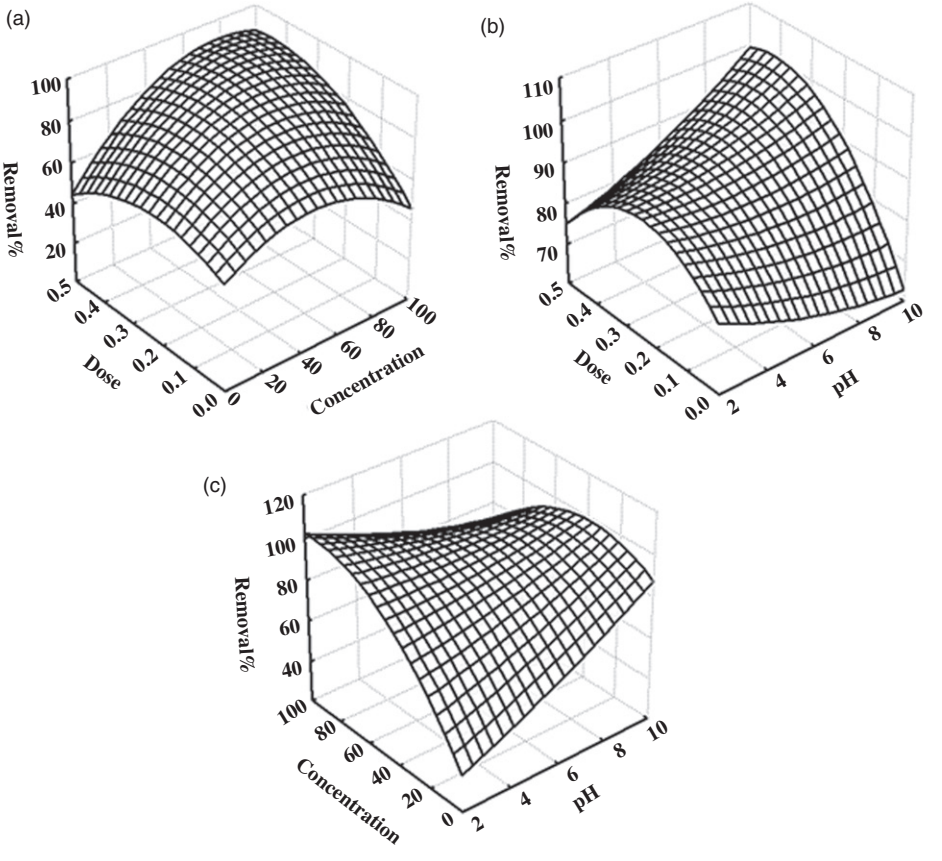

Figure 6. 3D response surface graph for CR removal % by used tea leaves.

on removal percentage. It is evident that if initial concentration increases, the removal percentage of dye increases. According to the Aksu and Tezer [19], a higher initial concentration gives an important driving force to overwhelm all mass transfer resistances of the dye between the aqueous and solid phases, and hence increases the removal percentage. Then again, the quadratic effect of adsorbent dose (X_2^2) and concentration (X_3^2) were a significant effect on removal % of CR.

Interactions effect of all factors have significant role for removal of CR onto used tea leaves. Figure 6(a) represents the interaction effect of adsorbent dose and concentration. The removal % of CR increases with increasing concentration and adsorbent dose but removal % was decreased after certain point of adsorbent dose, indicating that vacant sites of used tea leaves were filled by the CR molecules with increasing concentration.

The synergistic effect between adsorbent dose and pH in Figure 6(b) were also significant for CR removal onto used tea leaves and indicating, at high pH with high adsorbent dose gave the highest removal % of CR dye. It may be surmised by this fact that the adsorbent can be used in wider range of pH if higher adsorbent dose is used.

In Figure 6(c), it can be stated that the interaction effect of pH and concentration has negative effect on removal of CR, and this indicates simultaneous increases of pH and concentration will give reduced removal percentage. The highest removal % is obtained

with pH and concentration in ranges of low pH and high concentrations; nevertheless, the pH effect becomes less important when the concentration level increases.

The final mathematical model in terms of significant actual factors for CR removal % by used tea leaves is given below:

$$\begin{aligned}\text{CR removal \% (Used tea leaves)} = {} & +38.31 + 1.29X_3 + 9.71X_1X_2 - 0.10X_1X_3 \\ & + 1.00X_2X_3 - 212.90X_2^2 - 0.01X_3^2\end{aligned} \quad (5)$$

3.4 *Optimisation by desirability function*

The optimisation process was done by selecting software profile and desirability option. A prediction profile for a dependent variable consists of a series of graphs, one for each independent variable, of the predicted values for the dependent variable at different levels of one independent variable, holding the levels of the other independent variables constant at specified values, called current values. If appropriate current values for the independent variables have been selected, inspecting the prediction profile can show which levels of the predictor variables produce the most desirable predicted response on the dependent variable [20].

The CCD design matrix results from Table 1, represented maximum removal % (92.56%) was assigned as desirability 1.0, minimum (64.57%) as desirability 0.0 and middle (78.57%) as desirability 0.5 (Figure 7). Afterwards, the predicted responses at each level of each factor, holding all other factors constant at their current setting are calculated (Table 4), and the individual desirability scores for the predicted values for each dependent variable are then combined by computing their geometric mean according to Equation (3). By this way, software executes the calculation and finally gives the predicted responses at the current level of each factor in the model. On the basis of the above calculations and choosing a desirability score of 1, the best optimised conditions were found to be pH 4.32, dose 0.47 g and concentration 92.05 mg L^{-1} that also optimised 93.46% removal of CR by utilising used tea leaves.

The individual desirability scores of each parameter are illustrated in Figure 7 (bottom). Since our target is to obtain desirability 1, therefore, the factor levels (4.32, 0.47 and 92.05) were chosen only when they meet our target as well as desirability 1 and finally produce maximum response (93.46%) in the same level that is presented at the top (left) of Figure 7. For example, if pH 2.64 was selected as optimised factor value (although this point showed individual desirability 1 with the highest removal %) while other factors are constant at the same levels (dose 0.13 and concentration 7.96), this pH value optimised more than 93.46 removal % and this is not in the same removal % levels of other selected overall desirability values for specific factors. Similarly, for adsorbent dose 0.47 g was selected instead of 0.30 g or 0.38 g.

After optimisation of each factors level and with their corresponding removal %, a confirmation study was performed using the optimised parameters. The removal % of CR obatined from confirmation study is closely related with the data obtained from desirabilty optimisation by using CCD.

3.5 *Adsorption isotherm*

Freundlich and Langmuir isotherms at room temperature (25°C) were derived on the basis of batch analysis with constant dose and pH obtained from the statistical optimisation in

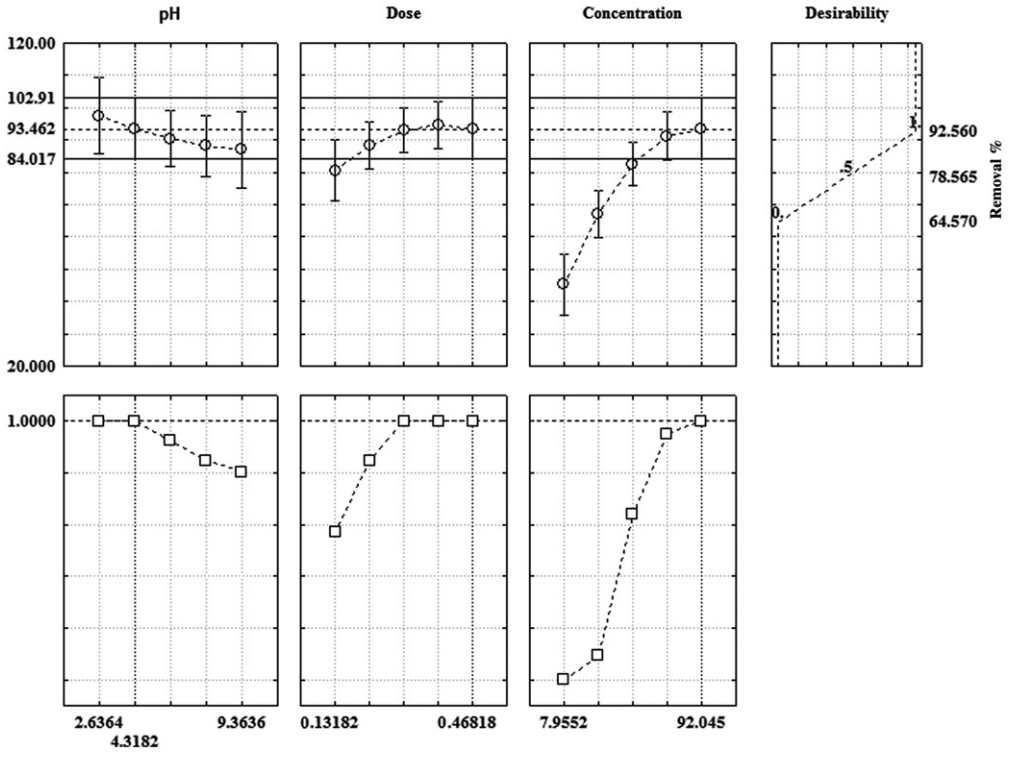

Figure 7. Profiles for predicated values and desirability function for CR removal % by used tea leaves. Dashed line indicates current values after optimisation.

Table 4. Factor levels and predicted responses of desirability function for used tea leaves.

Factors	Factor level	Predicted removal %	Desirability value
pH	2.64	97.41	1.00
pH	4.32	93.46	1.00
pH	6.00	90.42	0.92
pH	7.68	88.29	0.85
pH	9.36	87.07	0.80
Dose	0.13	80.53	0.57
Dose	0.22	88.28	0.85
Dose	0.30	93.02	1.00
Dose	0.38	94.74	1.00
Dose	0.47	93.46	1.00
Concentration	7.96	45.36	0.00
Concentration	28.98	67.19	0.09
Concentration	50.00	82.49	0.64
Concentration	71.02	91.24	0.95
Concentration	92.05	93.46	1.00

Table 5. Isotherms parameters for the adsorption of CR onto used tea leaves.

Freundlich				Langmuir			
K_F	1/n	R^2	F_{error}	q_m (mg g^{-1})	K_a (l mg^{-1})	R^2	F_{error}
0.90	0.57	0.997	0.0577	6.41	0.087	0.993	0.0005

order to determine the possible adsorption capacity of the used tea leaves towards the CR. For these, adsorption isotherm studies were carried out in 50 mL polypropylene centrifuge tubes with 25 mL of the different CR initial concentrations (10, 25, 50, 75 and 100 mg L^{-1}). The centrifuge tubes were capped and shaken in a wrist action shaker for 360 min at room temperature. The amount adsorbed by the selected adsorbents was calculated by the following equation (Equation (6)):

$$q_e = \frac{(C_0 - C_e)\cdot V}{m} \tag{6}$$

where C_0 and C_e are the initial and equilibrium concentrations (mg L^{-1}), V is the volume of solution (L) and m is the mass of the used tea leaves (g).

All the adsorption isotherms were constructed for used tea leaves using the linearised Freundlich (Equation (7)) and Langmuir (Equation (8)) isotherm equation by plotting $\log(q_e)$ versus $\log(C_e)$ and $1/q_e$ versus $1/C_e$, respectively.

$$\log q_e = \log(K_F) + \frac{1}{n}\log(C_e) \tag{7}$$

$$\frac{1}{q_e} = \left(\frac{1}{K_a q_m}\right)\frac{1}{C_e} + \frac{1}{q_m} \tag{8}$$

where q_e is the adsorbed amount (mg g^{-1}), C_e is equilibrium concentration (mg L^{-1}), K_F is the Freundlich coefficient that represents the degree or strength of adsorption. Then, $1/n$ is an exponential coefficient that reflects the curvature in the isotherm; q_m (mg g^{-1}) is the maximum adsorption capacity of the adsorbent; K_a is the Langmuir's constant.

Langmuir and Freundlich isotherms parameters for the adsorption of CR onto used tea leaves are presented in Table 5. According to the regression coefficient value (R^2), adsorption data fitted to both Freundlich and Langmuir isotherm models. But only R^2 values cannot reveal the better fitting of the model, and for this, all the models were evaluated by error function [21] in order to find the best fit isotherm model. Error function can be expressed as (Equation (9)):

$$F_{error} = \sqrt{\frac{\sum_i^p ((q_i cal - q_i \exp)/q_i \exp)^2}{p}} \tag{9}$$

where $q_i\ cal$ is each value of q_e predicted by the fitted model and q_i exp is each value of q_e measured experimentally; p is the number of experiments conducted.

By comparing the results of the values of error function presented in Table 5, it can be concluded that the Langmuir isotherm model fits better to the adsorption data for CR removal. Uddin *et al*. [22] recently also found the same trends for the removal of methylene blue onto tea waste.

4. Conclusion

In the present study, the analytical utility of multivariate chemometric techniques in the investigation of CR removal has been demonstrated. RSM was applied successfully in order to establish a relationship among the different removal processing factors (pH, adsorbent dose and concentration) with response removal %; moreover, desirability function was used to identify optimum removal % by calculating specific factors optimisation simultaneously. By using CCD with desirability function, 93.46% removal of CR by used tea leaves is possible within the studied parameters levels. It has been also proved that the used tea leaves are a very effective and low cost agricultural waste for the removal of CR. Therefore, from this study, it may be concluded that the use of statistical methods by RSM with desirability function can be optimised well by avoiding unnecessary experiments, providing a further perspicacity for potential use of other processes.

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