S.Ü. Müh. Bilim ve Tekn. Derg., c.5, s.3, 2017
Selcuk Univ. J. Eng. Sci. Tech., v.5, n.3, 2017
ISSN: 2147-9364 (Elektronik)

REMOVAL OF REACTIVE BLUE 19 FROM AQUEOUS SOLUTION BY PEANUT SHELL: OPTIMIZATION BY RESPONSE SURFACE METHODOLOGY

[1]Elçin DEMİRHAN

[1]*Yıldız Technical University, Chemical Engineering Department, Davutpasa Campus Esenler Istanbul, Turkey, TR 34220*
[1]demirhan@yildiz.edu.tr

(Geliş/Received: 26.01.2017; Kabul/Accepted in Revised Form: 20.03.2017)

ABSTRACT: In the present study, it was aimed to optimize the removal of reactive blue 19 dye by using peanut shells as a low-cost adsorbent. The influence of various process parameters namely pH (2,3 and 4), temperature (25, 35 and 45°C) and adsorbent amount (0.5, 1 and 1.5 g/100 mL) were studied using Box-Behnken design. According to the ANOVA results, the quadratic model with coefficient of determination (R^2) value of 0.9984 and model F value of 487.80 was showed good fit of the experimental data to. Experimental conditions for optimum dye removal of 93.45% were determined as pH 2, 35°C and 1.5 g/100 mL adsorbent amount. Langmuir fitted better to the obtained equilibrium data for removal of reactive blue 19 than Freundlich and Temkin models. In addition, the adsorption kinetics was also studied for the reactive blue 19 removal onto peanut shell. The kinetic studies showed that the removal of reactive blue 19 fitted to pseudo-second-order model.

Keywords: *Adsorption, Experimental design, Reactive blue 19, Peanut shell*

Sulu Çözeltilerden Yer Fıstığı Kabukları ile Reaktif Mavi 19 Giderimi: Cevap Yüzey Yöntemi ile Optimizasyonu

ÖZ: Bu çalışmada, reaktif mavi 19 boyarmaddesinin düşük maliyetli adsorban olarak yerfıstığı kabukları kullanılarak gideriminin optimizasyonu amaçlanmıştır. Box-Behnken tasarım yöntemi kullanılarak pH, sıcaklık ve adsorban miktarı parametrelerinin etkileri incelenmiştir. ANOVA sonuçlarına göre, regresyon analizi regrasyon katsayısı 0.9984 ve model F değeri 487.80 ile deneysel verilerin quadratik modele uygun olduğunu göstermektedir. Optimum boyarmadde giderimi (%93.45) için deneysel koşullar pH 2, 35°C ve 1.5 g/100 mL adsorban miktarı olarak belirlenmiştir. Reaktif mavi 19 giderimi için denge verilerinden Langmuir izoterminin Freundlich ve Temkin izotermlerinden daha uygun olduğu bulunmuştur. Ayrıca, yerfıstığı kabuğu ile reaktif mavi 19 giderimi için adsorpsiyon kinetiği incelenmiştir. Kinetik çalışmalar yalancı ikinci derece kinetiğe uyduğunu göstermiştir.

Anahtar Kelimeler: *Adsorpsiyon, Deneysel tasarım, Yerfıstığı kabuğu, Reaktif mavi 19*

INTRODUCTION

The dyes in effluents can have serious harm to the aquatic life and also to humans and animals. They can disturb the food chain organisms and lead to ecological disbalance (Cheng *et al*., 2015; Dutta, 2013). Dyes are synthetic, organic, and aromatic compounds and they contain of some heavy metals in their structure. The sources for dye effluents can be the industries such as textile, leather, paper, plastics, etc.

DOI: 10.15317/Scitech.2017.91

Dyes can accumulate into the soil and water. Due to this accumulation and environmental regulations, colour removal from textile effluent has become an imprtant research area. Nowadays, different methods are available for the treatment of dye wastewaters such as an reverse osmosis, ion exchange, chemical precipitation, ozonation and solvent extraction. However, high capital cost and operational costs or secondary sludge disposal problem are the disadvantages of the mentioned techniques (Daneshvara *et al.*, 2015; Etorki and Massoudi, 2011; Ravikumara *et al*., 2005). The adsorption technique has significant adantages and it can be accepted as the best way to treat effluents. The highcost of activated carbon and its regeneration is limited the application of this process (Zaidi and Mohd Zulkhairi, 2014; Koushaa *et al*., 2012).

RSM is the combination of mathematical and statistical techniques for optimizing processes and can be used to investigate both the relative and complex interactions of several factors even (Ravikumara *et al*., 2005). The application of experimental design in adsorption process can improve product yields, reduce development time and overall costs and reduce process variability (Arunachalam and Annadurai, 2011; Liu *et al.*, 2010).

In recent years, research on the production of low cost adsorbents alternative to commercially available activated carbon has increased. Therefore, in the present study, peanut shells was used as low cost adsorbent. It was aimed to optimize the adsorption of RB19 dye onto peanut shells. The effects of process parameters (pH, adsorbent amount and temperature) were investigated by applying Box–Behnken design. Moreover, modelling studies were performed to represent the adsorption isotherms and kinetics.

MATERIALS and METHODS

Materials

Reactive Blue 19 used in this work was obtained from Gülerçin Kimya A.Ş., Istanbul, Turkey. It was dissolved in the distilled water to form solutions of 300 mg/L. The pH of the solution was adjusted by diluted HCl or NaOH solution. The peanut shell samples were purchased from a local supplier in Istanbul. For experimental studies, the peanut shells were rinsed with tap water, then washed with distilled water dried at 80°C in a hot air oven for 24 h, ground and then sieved to uniform sizes of 100 mesh. The powder was preserved in airtight bottles for experimental use. Other chemicals of analytical grade were purchased from Sigma Aldrich.

Experimental Design

A three level Box-Behnken design was used to obtain the optimum process variables for the reactive blue 19 removal by using the individual and complex effects of these variables. The independent variables are temperature, pH and adsorbent amount and the dependent variable is the efficiency of adsorption. The range of independent variables and their levels were presented in Table 1. A second order polynomial model (Eq. 1) was fitted to the experimental data obtained from the Box–Behnken design:

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

Where Y is the process response (dependent variable); x_i and x_j are the variables; β_0 is the intercept coefficient; β_i, β_{ii}, β_{ij} are the interaction coefficients of linear, quadratic and the second order terms, respectively; k is the number of independent parameters; ε is the random error. The data were subjected to analysis of variance to show the fitness of the model.

Table 1. Independent process variables, ranges and levels

Independent variable	Coded Levels		
	-1	**0**	**+1**
pH, x_1	2	3	4
Temperature, x_2	25	35	45
Adsorbent amount, x_3	0.5	1	1.5

Batch Experiments

Adsorption experiments were conducted by varying the process parameters obtained from Box–Behnken design. The experiment was initiated by the addition of adsorbent to 100 mL of RB19 solution at desired pH and adsorbent dose value. The mixture was shaken at 175 rpm agitation speed at room temperature on a translatory shaker for the obtained contact time. During the experiments, the samples were taken from the mixture at timed intervals and centrifuged to remove the adsorbent particles. After centrifuging, the concentration of RB19 was measured by using UV/vis spectrophotometer at a wavelength of 592 nm. The assay was carried out in triplicate for each sample and their averages were taken. In the study, all experiments were carried out at least in duplicate and the reproducibility between trials was within ±5%.

Adsorption capacities were calculated from Eq. 2:

$$q_e = \frac{(C_0 - C_e)\cdot V}{m} \tag{2}$$

where q_e is equilibrium adsorbed concentration (mg/g), C_0 and C_e are the initial and equilibrium dye concentrations (mg/L), respectively. V is the volume of the solutions and m is the weight of adsorbent (g).

Adsorption Isotherm Models

Langmuir, Freundlich and Temkin isotherm models were used to evaluate the data obtained from the reactive blue 19 adsorption experiments:

Langmuir model:

Langmuir model defines the monolayer adsorption on the surface of the adsorbent, and after that there is not further adsorption takes place (Dada *et al.*, 2012).

$$\frac{1}{q_e} = \frac{1}{Q*b*C_e} + \frac{1}{Q} \tag{3}$$

where q_e is the equilibrium adsorbed concentration (mg g^{-1}), C_e is the equilibrium dye concentration (mg L^{-1}), Q is the maximum sorption capacity (mg g^{-1}) and b is the adsorption equilibrium constant.

Freundlich model:

The Freundlich model describes the multilayer adsorption and generally is used for heterogeneous systems (Piccin *et al.*, 2011).

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \tag{4}$$

where K_F is the Freundlich affinity coefficient, n is the Freundlich exponential coefficient.

Temkin model:

Temkin isotherm can be derived from Langmuir isotherm. In this model, it is assumed that the heat of adsorption is decreased linearly due to sorbate/sorbent interactions. According to Temkin isotherm model, adsorption is a spontaneous process (Sampranpiboon *et al.*, 2014; Khan, 2012).

$$q_e = \frac{RT}{b_T}\ln A_T + \frac{RT}{b_T}\ln C_e \tag{5}$$

where A_T is the Temkin isotherm constant and b_T is a constant related to heat of sorption.

Adsorption Kinetics of Removal of Reactive Blue 19

Several methods are available to study the adsorption mechanism. In this study, in order to determine the adsorption kinetics, the data obtained from the RB19 removal process were analysed with four different kinetic models as follows:

Pseudo first order model:

$$\log\frac{q_e - q_t}{q_e} = \frac{k_1 t}{2.303} \tag{6}$$

where; q_e is the adsorbed amount at equilibrium (mg g^{-1}); q_t is the adsorbed amount at time t (mg/g); k_1 is the pseudo first order adsorption kinetic parameter (min^{-1})

Pseudo second order model:

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \tag{7}$$

where, k_2 is the pseudo second order adsorption kinetic parameter (g mg^{-1} min^{-1}).

Elovich model:

The Elovich equation is valid for chemisorptions kinetics and systems in which the surface is heterogenous.

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \tag{8}$$

where; α is the initial adsorption rate (mg g^{-1} min); β is the constant related to extent of surface coverage and activation energy consumption (g mg^{-1}).

Intra particle diffusion model:

$$q_t = k_i t^{0.5} + C_i \tag{9}$$

where; k_i is the intra particle diffusion kinetic parameter (mg g^{-1} min^{-2}); C_i is the constant related to layer thickness (mg g^{-1}).

RESULTS AND DISCUSSION

Optimization of Reactive Blue 19 Adsorption Process Variables

Box–Behnken design and regression model

In order to obtain the optimum operational variables for the reactive blue 19 removal, a three level Box-Behnken design was employed. According to the Box–Behnken design, a series of experiments was conducted for exploring different combined parameters and for evaluating the combined effects of these factors. The coefficients of the response function (Y) for different dependent variables were determined by using Design Expert 10.0 trial software. Table 2 shows the predicted, and an experimental data related to percentage removals of RB19 obtained. Using the experimental results from Table 2, the full quadratic second order polynomial equation (Eq. 10) was fitted to the data appropriately and the equation was presented as follows:

$$Removal\ (\%) = 45.94 - 18.46X_1 + 1.53X_2 + 13.42X_3 - 0.67X_1X_2 - 4.86X_1X_3 + 0.010\,X_2X_3 + 15.10{X_1}^2 + 1.60{X_2}^2 - 5.43{X_3}^2 \quad (10)$$

On the basis of the coefficients in this equation, it can be said that the removal % of reactive blue 19 increases with decreasing pH and increasing adsorbent amount. The pH and adsorbent amount have a more profound effect on the removal of dye. In order to determine the adequacy of model to represent percentage of removal of reactive blue, the adequacy of the model test were carried out and it was shown that the p-value for the quadratic model was lower than 0.05 and the R^2 for the quadratic model was highest as compared with other model. Therefore, the quadratic model was chosen to illustrate the relationship between independent variable and the response values. Comparison of the observed versus predicted values was shown in Fig.1. This figure showed the correlation between the experimental and predicted values and the cluster points around the diagonal line indicates the good fit of model (Zaidi and Mohd Zulkhairi, 2014).

Table 2. Box-Behnken design matrix and comparison of observed predicted values of dye removal (%)

Run	X_1	X_2	X_3	% Removal (Experimental)	% Removal (Predicted)
1	0	0	0	45.68	45.94
2	0	-1	+1	53.47	53.90
3	0	0	0	45.11	45.94
4	+1	0	+1	46.22	45.71
5	-1	+1	0	83.38	83.30
6	0	+1	-1	30.55	30.12
7	+1	-1	0	43.23	43.32
8	+1	+1	0	45.71	45.04
9	0	-1	-1	28.44	27.26
10	-1	0	+1	93.45	92.35
11	0	+1	+1	55.98	57.16
12	0	0	0	46.76	45.94
13	-1	0	-1	55.27	55.79
14	+1	0	-1	27.47	28.59
15	-1	-1	0	78.24	78.90
16	0	0	0	46.18	45.94
17	0	0	0	45.98	45.94

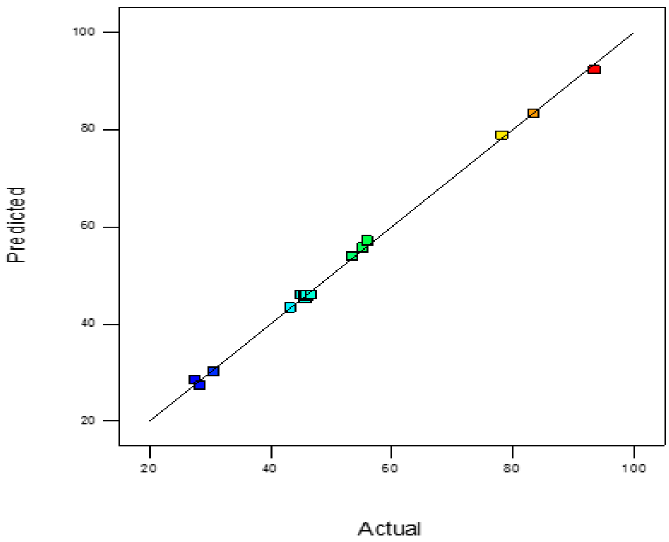

Figure 1. Scatter diagram of predicted response versus actual response of RB19 removal

The results of ANOVA studies for removal of RB19 were given in Table 3. As can be seen from the Table 3, the F value of the model is 487.80 and the p-value is <0.05 and it can be concluded that the model terms are significant. The coefficient of determination (R^2) and adjusted R^2 of this model were 0.9984 and 0.9964, respectively. The differences between these two values are small; therefore, it shows the adequacy of the model to the response. The lack of fit F-value of 6.32 implied that the lack of fit was not significant relative to the pure error. A non-significant lack of fit was considered good and was desired for the model to fit.

Table 3. Analysis of variance (ANOVA) of the fitted quadratic polynomial model

Source	Sum of Squares	df	Mean Square	F-value	P-value	
Model	5353.51	9	594.83	487.80	<0.0001	significant
A-pH	2727.28	1	2727.28	2236.52	<0.0001	
B- Temp.	18.73	1	18.73	15.36	0.0058	
C-Ads. Amount	1441.58	1	441.58	1182.17	<0.0001	
AB	1.77	1	1.77	1.45	0.2676	
AC	94.38	1	94.38	77.40	<0.0001	
BC	0.040	1	0.040	0.033	0.8614	
A^2	959.44	1	959.44	786.79	<0.0001	
B^2	10.82	1	10.82	8.87	0.0206	
C^2	124.36	1	124.36	101.99	<0.0001	
Residual	8.54	7	1.22			
Lack of Fit	7.05	3	2.35	6.32	0.0536	not significant
Pure Error	1.49	4	0.37			
Cor Total	5362.05	16				

Effects of process variables

In order to determine the effects of variables and their interactions, 3D response surface plots for the reactive blue 19 removal were shown in Fig. 2a–c. As can be seen from this figure, the decrease in the pH resulted an enhancement in the adsorption rate of the dye within the experimental range. It can be concluded that adsorption rate increases with increasing adsorbent amount due to the availability of more surface area of the adsorbent for adsorption. The pH and adsorbent amount are considered to be most effective in influencing the dye removal process as mentioned before. Moreoever, in the studied range, the temperature has little effect on the reactive blue 19 removal. A maximum dye removal (93.5 %) was observed at pH 2, adsorbent amount of 1.5 g and 35°C.

Adsorption Isotherms for Reactive Blue 19

In order to determine the adsorption isotherm of the RB19 onto peanut shells, three classic adsorption models (Langmuir, Freundlich and Temkin) were used. The estimated parameters of these models and statistical values were presented in Table 4. Among these isotherm models, Langmuir isotherm model was determined as the most appropriate one for the RB19 adsorption data with the high values of correlation coefficient (R^2). This result indicates that RB19 adsorption occurs as monolayer onto the homogenous adsorbent surface.

Table 4. The estimated parameters and statistical values of isotherm models for RB19 adsorption onto peanut shells

Langmuir İzotermi			
Q_{max}	**b**	R^2	σ
39.53	0.037	0.9827	0.2881
Freundlich İzotermi			
K_F	**n**	R^2	σ
5.165	2.597	0.8791	0.2647
Temkin İzotermi			
A_T	b_T	R^2	σ
0.4694	323.85	0.9436	3.5171

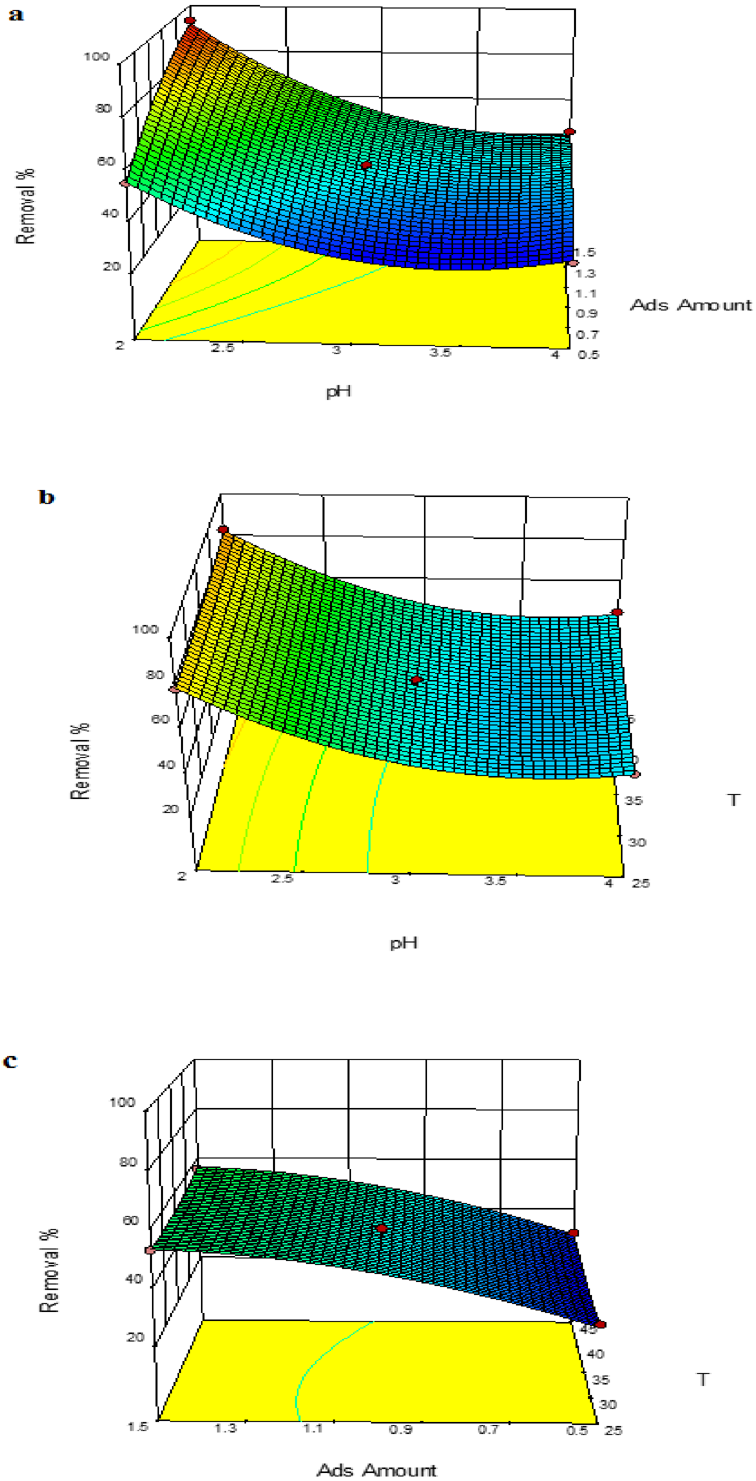

Figure 2. Response surface plots for the combined effects on the reactive blue 19 removal (a) Adsorbent amount and pH (b) T and pH (c) Adsorbent amount and T

Adsorption Kinetics of Reactive Blue 19

Evaluation of the adsorption kinetic as well as adsorption equilibrium is very important to plan and control the adsorption process. In order to describe the adsorption kinetic of RB19 onto peanut shell, the four different kinetic pseudo first order, the pseudo second order, Elovich and the intra particle diffusion models were used. The estimated parameters and statistical data of these models were presented in Table 5. As can be seen from this table, among these models, pseudo second order kinetic model was observed as the most appropriate one for all the experimental data with the high values for the coefficient of determination and low the standard error values. The result obtained was in agreement with the studies for RB19 removal onto rice straw fly ash (El-Bindary et al., 2016), citrus waste biomass (Asgher and Bhatti, 2012) and jujube stems powder (Ghaneian et al., 2014).

Table 5. The estimated parameters and statistical values of kinetic models for RB19 adsorption onto peanut shells

Pseudo First Order Kinetic Model			
k_1 (1/dak)		**R^2**	**σ**
0.0388		0.8833	0.7892
Pseudo Second Order Kinetic Model			
k_2 (g/mg.dak)		**R^2**	**σ**
0.0565		0.9999	0.0368
Elovich Kinetic Model			
α (mg g^{-1}dak)	**β (g mg^{-1})**	**R^2**	**σ**
4.14E+10	2.0530	0.9668	0.1421
Intra Particle Diffusion Model			
k_i (mg g^{-1} dak^{-2})	**C_i (mg g^{-1})**	**R^2**	**σ**
0.1609	12.925	0.9165	0.2225

CONCLUSION

In the present study, the removal of RB19 from aqueous solution using peanut shell as low-cost adsorbent was investigated. The effect of three parameters as pH, tempearute and adsorbent amount were studied. Results showed that a decrease in the pH resulted an enhancement in the adsorption rate of the dye within the experimental range. The pH and adsorbent amount are considered to be most effective in influencing the dye removal process as mentioned before. Moreoever, in the studied range, the temperature has little effect. A maximum dye removal (93.5 %) was observed at pH 2, adsorbent amount of 1.5 g and 35°C. The isotherm data for RB19 removal using peanut shell fitted well to the Langmuir isotherm model. Furthermore, kinetic data were fitted to the pseudo-second-order kinetic model. As a result, it can be concluded that peanut shell can be employed as an effective adsorbents for removal of RB19.

REFERENCES

Arunachalam, R., Annadurai, G., 2011, "Optimized Response Surface Methodology for Adsorption of Dyestuff from Aqueous Solution", Journal of Environmental Science and Technology, Vol. 4, pp. 65-72.

Asgher, M., Bhatti, H.N., 2012, "Removal of Reactive Blue 19 and Reactive Blue 49 Textile Dyes by Citrus Waste Biomass from Aqueous Solutıon: Equilibrium and Kinetic Study", The Canadian Journal of Chemical Engineering, Vol. 90, p.412-419.

Cheng, Z., Zhang, L., Guo, X., Jiang, X., Li, T., 2015, "Adsorption Behavior of Direct Red 80 and Congo Red onto Activated Carbon/Surfactant: Process Optimization, Kinetics and Equilibrium", Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Vol. 137, pp.1126–1143.

Dada, A.O., Olalekan, A.P., Olatunya, A.M., Dada, O., 2012, "Langmuir, Freundlich, Temkin and Dubinin–Radushkevich Isotherms Studies of Equilibrium Sorption of Zn2+ Unto Phosphoric Acid Modified Rice Husk", IOSR Journal of Applied Chemistry, Vol. 3, No. 1, pp. 38-45.

Daneshvara, E., Koushaa, M., Sohrabia, M.S., Panahbehaghb, B., Bhatnagarc, A., Younesid, H., Sternberg, S.P.K., 2015, "Application of Response Surface Methodology for The Biosorption of Acid Blue 25 Dye Using Raw and HCl-Treated Macroalgae", Desalination and Water Treatment, Vol. 53, pp.1710–1723.

Dutta, S., 2013, "Optimization of Reactive Black 5 Removal by Adsorption Process Using Box–Behnken Design, Desalination and Water Treatment, Vol. 51, pp.7631–7638.

El-Bindary, A.A., Abd El-Kawi, M.A., Hafez, A.M., Rashed, I.G.A., Aboelnaga, E.E., 2016, Removal of Reactive Blue 19 from Aqueous Solution Using Rice Straw Fly Ash, Journal of Materials and Environmental Sciences, Vol. 7, No. 3, pp.1023-1036.

Etorki, A.M., Massoudi, F.M.N., 2011, "The Use of Peanut Hull for the Adsorption of Colour from Aqueous Dye Solutions and Dye Textile Effluent", Oriental Journal of Chemistry, Vol. 27, No. 3, pp.875-884.

Ghaneian, M.T., Ehrampoush, M.H., Sahlabadi, F., Mootab, M., Rezapour, I., Jasemizad, T., 2014, "Reactive Blue 19 Dye Adsorption Behavior on Jujube Stems Powder from Syntetic Textile Wastewater: Isotherm and Kinetic Adsorption Studies", Journal of Community Health Research, Vol. 3, No. 1, pp.67-78.

Khan, A.S.A., 2012, "Evaluation of Thermodynamic Parameters of Cadmium Adsorption on Sand from Temkin Adsorption Isotherm", Turkish Journal of Chemistry, Vol. 36, pp. 437 – 443

Koushaa, M., Daneshvara, E., Dopeikara, H., Taghavia, D., Bhatnagarb, A., 2012, "Box–Behnken Design Optimization of Acid Black 1 Dye Biosorption by Different Brown Macroalgae", Chemical Engineering Journal, Vol. 179, pp.158– 168.

Liu, Y., Zheng, Y., Wang, A., 2010, "Response Surface Methodology for Optimizing Adsorption Process Parameters for Methylene Blue Removal by a Hydrogel Composite", Adsorption Science & Technology, Vol. 28, No. 10, pp.913-922.

Piccin, J.S., Dotto, G.L., Pinto, L.A.A., 2011, "Adsorption Isotherms and Thermochemical Data of FD&C Red n° 40 Binding by Chitosan", Brazilian Journal of Chemical Engineering, Vol. 28, No. 02, pp. 295 – 304.

Ravikumara, K., Pakshirajanb, K., Swaminathanc, T., Balua, K., 2005, "Optimization of Batch Process Parameters Using Response Surface Methodology for Dye Removal by A Novel Adsorbent", Chemical Engineering Journal, Vol. 105, pp.131–138.

Sampranpiboon, P., Charnkeitkong, P., Feng, X., 2014, "Equilibrium Isotherm Models for Adsorption of Zinc (II) ion from Aqueous Solution on Pulp Waste", Wseas Transactions on Environment and Development, Vol. 10, pp. 35-47.

Zaidi, Y.R., Mohd Zulkhairi, A.R., 2014, "Removal of Methyl Red From Aqueous Solution by Adsorption on Treated Banana Pseudostem Fibers Using Response Surface Method (RSM)", The Malaysian Journal of Analytical Sciences, Vol. 18, No. 3, pp.592 – 603.