Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2015.1029003

57 (2016) 6098–6105
March

Taylor & Francis
Taylor & Francis Group

Full factorial experimental design applied to methylene blue adsorption onto Alfa stems

Lamia Hamdi*, Leila Boumehdi Toumi, Zineb Salem, Khedidja Allia

Laboratory of Industrial Engineering Processes Sciences (LSGPI) FGMGP, USTHB, BP 32 El-Alia Bâb – Ezzouar, 16111 Algiers, Algeria, emails: lamiahamdi83@gmail.com (L. Hamdi), leilatoumi@gmail.com (L. Boumehdi Toumi), zsalem141@gmail.com (Z. Salem), khedidja.allia@gmail.com (K. Allia)

Received 12 February 2014; Accepted 6 March 2015

ABSTRACT

Full factorial experimental design technique was used to study the main effects and interactions between operational parameters in batch adsorption of methylene blue (MB) using Alfa stems as adsorbent. The important parameters which affect MB removal efficiency and adsorption amount, such as initial concentration, particle size, solution pH, and contact time, were investigated. One set of full 2^4 factorial designs with two central points (18 experiments) was tested. The effects of individual variables and their interactions were observed on adsorbed MB amount q_t (mg/g). From statistical analysis, the most effective parameters of adsorbed MB amount were initial concentration and solution pH. The interaction between initial concentration and solution pH was the most important factor. The maximum quantity retained was 25.89 mg/g; it was obtained with an initial concentration of 100 mg/L, adsorbent dose of 4 g/L, granulometry of [0.50–0.63 mm], and pH of the solution 12, with a stirring velocity of 500 rpm for 120 min.

Keywords: Alfa; Adsorption; Full factorial design; Methylene blue; Dye; Water treatment

1. Introduction

Dyes are synthetic organic compounds that are increasingly being produced and used as colorants in many industries worldwide, including textile, plastic, paper, etc. The wastewater generated by these industrial processes usually contains up to around 10% of used dyes [1–3]. Furthermore, with the increased demand of textile products, the textile industry and its wastewaters have been increasing proportionally, making it one of the main sources of severe pollution problems worldwide [4]. Therefore, effluent treatment from dyeing and finishing processes in the textile industry is one of the most significant environmental problems [5,6]. Most synthetic dyes have complex aromatic molecular structures which make them inert and difficult to biodegrade when discharged into the environment [7,8].

Dyes present direct toxicity to microbial populations by inhibiting growth, obstructing light penetration, decelerating photosynthetic activity, and causing oxygen deficiency in water bodies. Most of the dyes also affect human health, have carcinogenic effect or cause

*Corresponding author.

Presented at the 3rd Annual International Conference on Water (CI.EAU2013), 18–20 November 2013, Algiers, Algeria

allergies, dermatitis, or skin irritation. In aquatic environments, the adverse effects of dyes arise from their synthetic nature and aromatic structure with relocated electrons and various functional groups which make them considerably resistant to degradation.

Basic dyes are a group of water-soluble cationic dyes which are employed in leather, paper preparing, printing, and textile fiber dyeing. The principl use of basic dyes is the dyeing of acrylics [9].

Methylene blue (MB) is the most commonly used substance for dyeing paper, cotton, wood, and silk but can cause some harmful effects. It can cause eye burns which may be responsible for permanent injury to the eyes of human and animals. On inhalation, it can give rise to short periods of rapid or difficult breathing, while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, diarrhea, and gastritis. Accidental large doses create abdominal and chest pain, severe headache, profuse sweating, mental confusion, painful micturition, and methemoglobinemia [10]. In addition, its chloride salt is listed in the Canadian Workplace Hazardous Materials Information System (WHMIS) ingredient disclosure list [11].

Dye removal techniques such as electrochemical oxidation, photocatalytic oxidation, and electro-Fenton oxidation were found to be inadequate because most textile dyes have complex aromatic molecular structures that resist degradation. The need for more efficient treatment processes has attracted the attention of environmental scientists and engineers. For these reasons, considerable attention has been paid to adsorption technologies as efficient and versatile methods of removing dyes from textile wastewater effluents. Adsorption is a separation process by which certain components of a fluid phase are attracted to the surface of a solid adsorbent and form attachments via physical or chemical bonds, thus removing the components from the fluid phase [12–14].

Activated carbon is the most widely used adsorbent for the removal of color and treatment of textile effluents. But due to its high price, it is not used on a large scale [15,16]. This has led many researchers to investigate cheaper and efficient alternative materials such as clays [17–20] and bioadsorbents like fly ash [21], hen feather [22,23], nut shells [24], rejected tea [25], garlic peel [26], plantain peel [27], passion fruit and mandarin peels [28], and granulated waste materials [29].

On the other hand, adsorption is dependent on various factors: pH, adsorbent dose, initial adsorptive concentration, contact time, temperature, particle size, and ionic strength. In conventional methods, to determine the influence of each one of these factors, experiments are carried out by systematically varying the studied factors and keeping the others constant [30,31]. A suitable experimentation technique that will reveal the possible interactions with a minimum number of experiments, as suggested by Bhunia and Ghangrekar [32], should be selected. For this purpose, statistical design of experiments was widely reported [33–35].

The objective of this study is to use Alfa stems as an adsorbent for MB removal. A 2^4 factorial design was applied to investigate the individual effects of the initial dye concentration, solution pH, particle size, contact time, and their interactions.

2. Materials and methods

2.1. Adsorbent

Alfa stems were collected in the highlands of Laghouat in Algeria during the period of March–June 2011. They are mainly composed of cellulose filaments bounded by lignins, pectins, and hemicelluloses [36].

The materials were washed several times with slightly warm water to remove dirt particles and to decrease their hardness. The washed materials were then dried at 105°C for 24 h, cut into small pieces, crushed in a knife mill, and finally sieved to a desired size range [0.50–63 mm].

2.2. Adsorbate

MB was obtained from Biochem chemicals and used without further purification. MB properties are shown in Table 1.

2.3. Instrumentation

Different instruments were used for characterizing the physical and chemical properties of Alfa stems. Its specific surface area was determined using a surface area analyzer (NOVA 2000E) by Brunauer, Emmett, and Teller (BET) methods. Surface aspects of Alfa particles were observed under ZEISS optical microscope equipped with a numerical camera (Nikon 500).

For further characterization of stems, chemical functional groups on the sample surface were elucidated using Fourier transform infrared spectrometer in the range of 4,000–400 cm^{-1}, using KBr pellets. All pH measurements were done on a pH meter equipped with a combined pH electrode, model number HI-8224 (Hanna Instruments).

The pH_{PZC} of Alfa stems was determined using the method described by Barka et al. [37]. This method consists in adding HCl (1 N) or NaOH solution (1 N) to 50 mL of NaCl solution (0.01 M) in a thermostated

Table 1
Properties and characteristics of MB

Generic name	MB
Chemical name (IUPAC)	3,7-Bis(dimethylamino)-phenazathionium chloride tetramethylthionine chloride
Chemical formula	$C_{16}H_{18}ClN_3S$
Molecular weight (g/mol)	319.86
Maximum wavelength (nm)	665
Color index number	52.015

cell maintained at 25°C. When the pH of the NaCl solution is fixed, we added 0.05 g of Alfa stems. Equilibrium pH was measured after 6 h of shaking.

The concentration of dye solutions was estimated by spectrophotometry using a Shimadzu UV/VIS spectrophotometer model 1800 at the wavelength of 665 nm.

2.4. Adsorption studies

The adsorption of MB onto Alfa stems was performed by the batch equilibrium technique. Experiments were carried out by pouring in glass Erlenmeyer flasks 100 mL of MB solution with a known initial concentration, pH, and particle granulometry. The mixtures were then capped and agitated mechanically at 500 rpm using a rotary orbital shaker. The pH of the solution was adjusted to desired values with dilute HCl or NaOH solution. After centrifugation and filtration, the concentration of the MB solution was measured by spectrophotometry at the wavelength of 665 nm.

2.5. Statistical design

Factorial design was employed to reduce the total number of experiments in order to achieve the best overall optimization of operating conditions. For the 2^4 experimental design, the four independent variables were coded as X_1, X_2, X_3 and X_4 at two levels. The higher level was designated as +1 and the lower level as −1.

The coded values of process parameters were determined by Eq. (1):

$$X_{ij} = \frac{(x_{ij} - x_j^0)}{\text{step}} \quad (1)$$

where X_{ij} is the jth coded variable of the ith experimentation, x_{ij} is the jth uncoded variable of the ith test, x_j^0 is the uncoded value of the ith test variable at the center point, and the step is the variation of the uncoded variable j.

3. Results and discussion

3.1. Characterization of the adsorbent

The characterization of the Alfa stems was carried out by conventional chemical methods. It was found that the dry sample contained about 28.2% of lignin, while mineral matter ratio, water absorption ratio, and moisture were 6.26, 65.83, and 8.80%, respectively. Other physicochemical properties like surface area, apparent density, real density, and point of zero charge were obtained as 3.2783 m^2/g, 61.00 kg/m^3, 1,313 kg/m^3, and 6.8, respectively.

The surface morphology of Alfa stems was examined on the basis of optical microscopy analysis and it was found that the stem structure was heterogeneous and their longitudinal section had an irregular form. Furthermore, the presence of fine spines on the surface of the Alfa particles was examined, which indicated a certain degree of roughness. After adsorption, it was observed that the adsorbent surface had been loaded significantly by MB, but it was not fixed in a homogeneous manner. Some parts were more colored than the others due to surface heterogeneity.

FTIR spectra of Alfa stems presented several absorption peaks indicating the complex structure of the adsorbent. This analysis shows a broad band at 3,400 cm^{-1} representing bonded –OH groups and corresponding to alcohols, phenols, and acids carboxylic functions being mainly in lignins, pectins, and cellulose. The peaks observed at 2,900–2,850 cm^{-1} and which correspond to $–CH_2$ and –CH groups appear more marked after adsorption.

A vibration peak was detected at 1,740 cm^{-1} related to the carbonyl group C=O of pectins. The spectra also presented a peak at 1,100 cm^{-1} related to C–O–C stretching groups. The large band located at 700 cm^{-1} was related to the alkene group C=C.

The large band between 1,000 and 1,900 cm^{-1} presents several peaks more clearly marked after adsorption indicating that –OH groups, C–O–C, C=O, C–O, and C–OH stretching groups were particularly involved in MB adsorption.

3.2. Statistical analysis

In order to evaluate the parameters which influence the adsorption process, 16 factorial experimentations were carried out at two levels, and two others at the central point. The high and low levels defined for the 2^4 factorial design are listed in Table 2. The low and high levels for the factors were selected according to some preliminary experiments.

The amount of MB adsorbed (Y) was measured for each of these tests as shown in Table 3.

In the table, Y is the response (mg of adsorbate per g of adsorbent), X_i values ($I = 1, 2, 3, 4$) indicate the corresponding parameters in their coded forms.

A first-order model with all possible interactions was chosen to fit the experimental data:

$$Y = A_0 + A_1X_1 + A_2X_2 + A_3X_3 + A_4X_4 + A_{12}X_1X_2 + A_{13}X_1X_3 + A_{23}X_2X_3 + A_{14}X_1X_4 + A_{24}X_2X_4 + A_{34}X_3X_4 + A_{123}X_1X_2X_3 + A_{124}X_1X_2X_4 + A_{134}X_1X_3X_4 + A_{234}X_2X_3X_{4+}A_{1234}X_1X_2X_3X_4 \quad (2)$$

The statistical calculations and multiple regressions were performed using JMP software.

Factors that influence the adsorbed quantity of dye onto Alfa stems were evaluated using factorial plots: main effect, interaction effect, and the Pareto chart plot. An ANOVA and P-value significant levels were used to check the significance of the effect on the response. The main effect and interactions were also observed in the Pareto chart plot.

Regression analysis was performed to fit the response function (amount of MB adsorbed) with the experimental data. The values of regression coefficient and statistical parameters are given in Table 4.

The central point carried out in duplicate was useful to obtain the standard error of the coefficients. The probability results showed that the central point was significant in the chosen model, $P = 0.013$, at 5% of probability level. It means that a curvature of the factors was detected when the levels were changed from the lower level (−) to the higher level (+), passing through the central point (0). There should be a curvature of the responses.

Table 3
Experimental design matrix with the results of 2^4 full factorial design

Run	X_1	X_2	X_3	X_4	Y_{exp} (mg/g)
1	−1	−1	−1	−1	1.08
2	1	−1	−1	−1	3.60
3	−1	1	−1	−1	0.80
4	1	1	−1	−1	6.95
5	−1	−1	1	−1	1.90
6	1	−1	1	−1	19.09
7	−1	1	1	−1	1.39
8	1	1	1	−1	21.70
9	−1	−1	−1	1	1.54
10	1	−1	−1	1	4.98
11	−1	1	−1	1	0.97
12	1	1	−1	1	8.75
13	−1	−1	1	1	2.04
14	1	−1	1	1	19.50
15	−1	1	1	1	2.02
16	1	1	1	1	25.89
17	0	0	0	0	7.77
18	0	0	0	0	8.00

In this way, the amount of MB adsorbed by Alfa stems could be expressed using Eq. (3):

$$Y = 7.64 + 6.17X_1 + 0.92X_2 + 4.05X_3 + 0.57X_4 + 1.09X_1X_2 + 3.68X_1X_3 + 0.14X_2X_3 + 0.40X_1X_4 + 0.27X_2X_4 + 0.1X_3X_4 + 0.097X_1X_2X_3 + 0.249X_1X_2X_4 + 0.258X_2X_3X_4 + 0.08X_1X_3X + 0.16X_1X_2X_3X_4 \quad (3)$$

This function describes how the experimental parameters and their interactions influence MB adsorption.

In Table 5 are presented the values of all effects, interactions, and t values.

In Fig. 1 is presented the Pareto Chart of standardized effects at $P = 0.05$. All the values presenting an absolute value higher than 12.7, which are located to the right of the dashed line, are significant.

Table 2
Factors and levels used in 2^4 factorial design

Parameter	Code	Lower level (−1)	Higher level (+1)
Initial MB concentration (mg/L)	X_1	10	100
Particle size (mm)	X_2	[0.1–0.16]	[0.5–0.63]
Solution pH	X_3	2	12
Contact time (min)	X_4	15	120

Table 4
Values of correlation coefficient and statistical parameters

Parameter	R^2	S	SE coeff.	P
Value	1.00	0.1626	0.0406	0.013

Table 5
Fit model: effect and interaction values, student's t, and P-value

Term	Values	SE coeff.	Ratio t	Prob. > $\|t\|$
A_0	7.640	0.0406	187.857	0.003
A_1	6.170	0.0406	151.751	0.004
A_2	0.921	0.0406	22.652	0.028
A_3	4.054	0.0406	99.708	0.006
A_4	0.574	0.0406	14.117	0.045
A_{12}	1.093	0.0406	26.882	0.024
A_{13}	3.684	0.0406	90.608	0.007
A_{14}	0.138	0.0406	3.394	0.182
A_{23}	0.398	0.0406	9.789	0.065
A_{24}	0.274	0.0406	6.739	0.094
A_{34}	0.098	0.0406	2.410	0.250
A_{123}	0.097	0.0406	2.386	0.253
A_{124}	0.249	0.0406	6.124	0.103
A_{234}	0.258	0.0406	6.345	0.100
A_{134}	0.080	0.0406	1.968	0.299
A_{1234}	0.160	0.0406	3.935	0.158

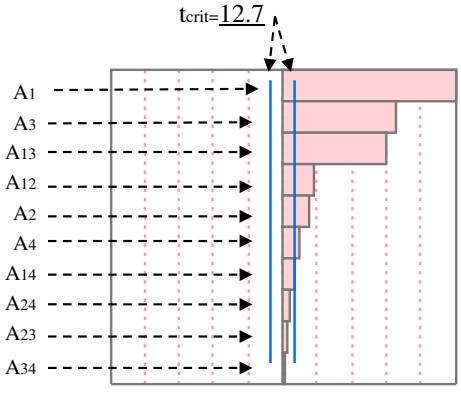

Fig. 1. Pareto chart.

By analyzing the values in Table 5, it can be inferred that the initial concentration (X_1) was the most important parameter of the overall adsorption procedure. The positive value of its coefficient indicates that the amount of MB adsorbed by Alfa grass was favored at high concentrations (100 mg/L).

The second important factor for overall optimization of the adsorption process was pH (X_3). The decrease in the pH led to a remarkable decrease in the MB amount. This behavior can be explained by examining the pH at the point of zero load of the adsorbent which is 6.8. Thus, for a higher pH, the surface is negatively charged which increases the electrostatic attraction of the positively charged cationic dye, whereas, for a pH lower than 6.8, the surface is positively charged which causes a repulsion between the molecules of the adsorbate and the adsorbent.

The interaction of two factors (X_1 and X_3) was more significant than the main factor (X_2 and X_4) alone. The positive value of the coefficient of this interaction meant that an increase in the pH associated with an increase in the initial concentration led to an increase in the response (Y). Only the achievement of this result justifies the use of the statistical design of experiments over the conventional univariate adsorption process. This information would not be acquired in a univariate optimization of the adsorption system.

Fig. 2 illustrates the possible positive and negative effects of two-variable interactions, respectively, among the four variables on the amount of MB adsorbed. These results support the previous findings related to the effect of each factor on the adsorption process. It has been found that the higher the initial concentration, the higher the amount of MB adsorbed and higher the pH of the solution, higher the amount of MB adsorbed.

From the interaction profiles, it can be seen that the interaction between the initial concentration and pH of the solution was the most important interaction because the amount of MB adsorbed increased significantly from 5.1 to 25.05 mg/g with an increase in the initial concentration from 10 to 100 mg/L and an increase in the pH of the medium from 2 to 12. The interaction between the particle size and the duration of the adsorption process was the least influencing factor because the amount of MB adsorbed did not change significantly.

The maximum amount of MB adsorbed obtained in this study was found to be 25.89 mg/g, corresponding to the operating conditions of 500 rpm, 100 mg/L, 4 g/L, pH = 12, and $d_p \in [0.5–0.63\ \text{mm}]$, respectively, of the stirring velocity, initial concentration, Alfa dose, solution pH, and particle size.

So, it would be necessary to retain another model by holding all effects and interactions judged significant. After simplification, the general model is reduced to

$$Y = 7.64 + 6.17X_1 + 0.92X_2 + 4.05X_3 + 0.57X_4 + 1.09X_1X_2 + 3.68X_1X_3 \quad (4)$$

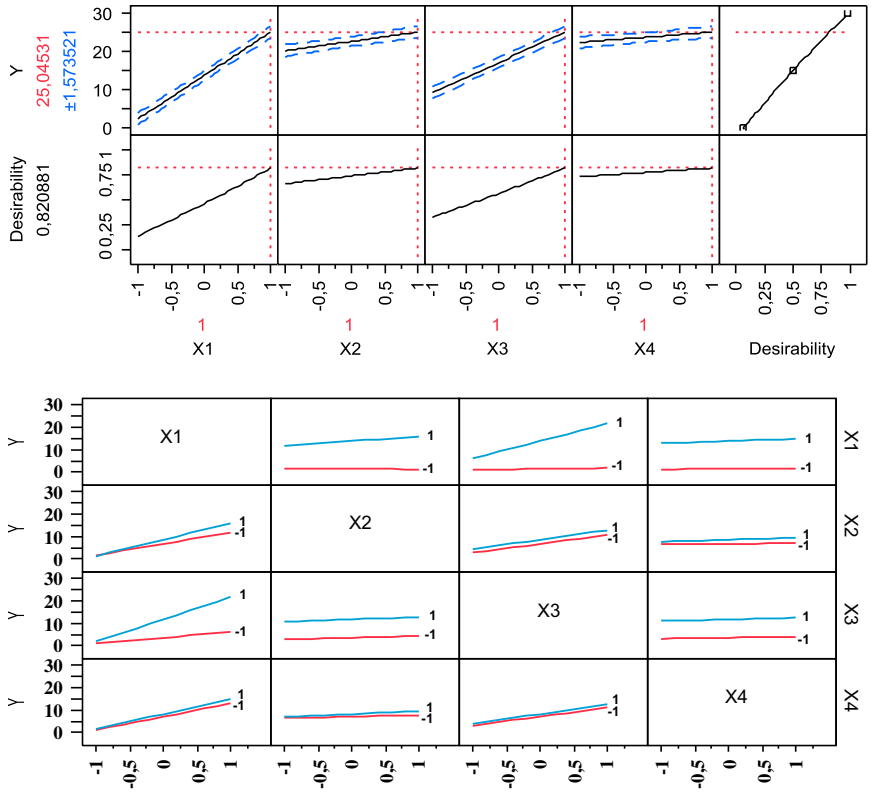

Fig. 2. Prediction profiler and interaction profiles.

- Validity of the reduced model.

Tests of adsorption were carried out to check the validity of the model in the studied experimental field and its extension.

The variations of the experimental results compared to the computed values are given using Eq. (5):

$$Ecart\ (\%) = \frac{q_{\text{theor}} - q_{\text{exp}}}{q_{\max}} \cdot 100 \tag{5}$$

Table 6
Validity of the model reduced in the study field

Run	X_1	X_2	X_3	X_4	q_e measured (mg/g)	q_e calculated (mg/g)	*Ecart* (%)
1	+1	+1	+1	−0.50	23.51	23.06	1.89
2	+1	+1	+1	+0.50	23.43	24.03	2.52
3	−0.94	+1	+1	−0.75	2.38	2.27	4.62
4	+1	+1	+0.5	+0.75	20.68	20.11	2.74

Table 7
Validity of the model reduced except the study field

Run	X_1	X_2	X_3	X_4	q_e measured (mg/g)	q_e calculated (mg/g)	*Ecart* (%)
1	+1	+1	+1.18	+3.28	26.93	25.11	6.77
2	+1	+1	+1	+1.75	21.91	25.25	13.23
3	+1	+1	+1	−1.19	20.89	22.39	6.70
4	−0.93	+1	+1.35	−1	2.64	2.46	6.82

where q_{theo} is the amount of MB adsorbed calculated by the mathematical model, q_{exp} is the amount of MB adsorbed measured experimentally, and q_{max} is the maximal amount of q_{theo} and q_{exp}.

The results obtained in Tables 6 and 7 show that the mathematical model suggested represents in a satisfactory way the experimental results in the studied field since the differences between the two values are lower than 5%. Values of variation being higher than 5%, the extension except the study field of the reduced model cannot be carried out.

4. Conclusion

This study showed that the factorial experimental design approach is an excellent tool and could successfully be used to develop empirical equation for the prediction and understanding of MB adsorption on Alfa stems:

$$q_t = 7.64 + 6.17\left(\frac{C_0 - 55}{45}\right) + 0.92\left(\frac{d_p - 0.3475}{0.2175}\right) + 4.05\left(\frac{\mathrm{pH} - 7}{5}\right) + 0.57\left(\frac{t - 67.5}{52.5}\right) + 1.09\left(\frac{C_0 - 55}{45}\right)\left(\frac{d_p - 0.3475}{0.2175}\right) + 3.68\left(\frac{C_0 - 55}{45}\right)\left(\frac{\mathrm{pH} - 7}{5}\right) \quad (6)$$

A 2^4 factorial design of experiments was successfully employed for optimizing the best conditions to attaining the maximum amount of MB up taken adsorbed by Alfa stems. This statistical design of experiments led to the following conditions: $C_0 = 100$ mg/L, $d_p \in [0.5–0.63$ mm], pH = 12, and $t = 120$ min.

Most of the factors and the interactions considered in the experimental design were statistically significant at the 95% confidence level.

As observed, the most effective parameters in the adsorption process were initial concentration and solution pH. Increasing the pH from 2 to12 and the initial concentration from 10 to 100 mg/L promoted the adsorption capacity, while increasing the particle diameter from [0.1–0.16 mm] to [0.5–0.63 mm] and the contact time from 15 to 120 min did not significantly influence the adsorption process. The interaction between the initial concentration of the dye and the pH of the solution was the most influencing factor.

Lists of symbols

FTIR	—	Fourier transform infrared (FTIR) spectroscopy
P	—	probability
pH_{PZC}	—	point of zero charge
q_{exp}	—	amount of MB adsorbed measured experimentally (mg/g)
q_{max}	—	maximal amount of q_{theo} and q_{exp} (mg/g)
q_{theo}	—	amount of MB adsorbed calculated by the mathematical model (mg/g)
R^2	—	correlation coefficient
S	—	standard error
SE Coeff.	—	standard error of the coefficient
Step	—	the variation of the uncoded variable j
t	—	student value
X_1	—	MB initial concentration (C_0)
X_2	—	particle size (d_p)
X_3	—	solution pH
X_4	—	contact time (t)
X_{ij}	—	the j coded variable of the ith experimentation
x_{ij}	—	the j uncoded variable of the ith test
x_j^0	—	the uncoded value of the ith test variable at center point
Y	—	response (mg/g)

References

[1] S.T. Ong, S.T. Ong, Y.T. Hung, Y.P. Phung, Application of conventional and statistical experimental methodology to optimize malachite green dye removal from aqueous solutions, Desalin. Water Treat. (2014) 1–13, doi: 10.1080/19443994.2014.925830.
[2] F.C. Wu, R.L. Tseng, High adsorption capacity NaOH-activated carbon for dye removal from aqueous solution, J. Hazard. Mater. 152 (2008) 1256–1267.
[3] E. Forgacs, T. Cserháti, G. Oros, Removal of synthetic dyes from wastewaters: A review, Environ. Int. 30 (2004) 953–971.
[4] J.H. Weisburger, Comments on the history and importance of aromatic and heterocyclic amines in public health, Mutat. Res./Fundam. Mol. Mech. Mutagen. 506–507(507) (2002) 9–20.
[5] S. Şen, G.N. Demirer, Anaerobic treatment of real textile wastewater with a fluidized bed reactor, Water Res. 37 (2003) 1868–1878.
[6] C. Hessel, C. Allegre, M. Maisseu, F. Charbit, P. Moulin, Guidelines and legislation for dye house effluents, J. Environ. Manage. 83(2) (2007) 171–180.
[7] V.A. Shenai, Azo dyes on textiles vs. German ban: An objective assessment, Part III, Another study, Colourage XLIII 8 (1996) 41–46.

[8] J.C. Greene, G.L. Baughman, Effects of 46 dyes on population growth of fresh green algae *Selenastrum capricornutum*, Text. Chem. Color. 28 (1996) 23–30.
[9] A. Hassani, L. Alidokht, A.R. Khataee, S. Karaca, Optimization of comparative removal of two structurally different basic dyes using coal as a low-cost and available adsorbent, J. Taiwan Inst. Chem. Eng. 45 (2014) 1597–1607.
[10] D. Ghosh, K.G. Bhattacharyya, Adsorption of methylene blue on kaolinite, Appl. Clay Sci. 20 (2002) 295–300.
[11] S.A. Kordkandi, M. Forouzesh, Application of full factorial design for methylene blue dye removal using heat-activated persulfate oxidation, J. Taiwan Inst. Chem. Eng. 45 (2014) 2597–2604.
[12] S. Mohanty, N.N. Rao, P. Khare, S.N. Kaul, A coupled photocatalytic-biological process for degradation of 1-amino-8-naphthol-3, 6-disulfonic acid (H-acid), Water Res. 39 (2005) 5064–5070.
[13] N.N. Rao, G. Bose, P. Khare, S.N. Kaul, Fenton and electro-Fenton methods for oxidation of H-acid and reactive black 5, J. Environ. Eng. 132 (2006) 367–376.
[14] O. Marmargne, C. Coste, Colour removal from textile plant effluents, Am. Dye Rep. 85 (1996) 15–21.
[15] F.C. Wu, R.L. Tseng, R.S. Juang, Kinetics of color removal by adsorption from water using activated clay, Environ. Technol. 22 (2001) 721–729.
[16] D. Hank, Z. Azi, S. Ait Hocine, O. Chaalal, A. Hellal, Optimization of phenol adsorption onto bentonite by factorial design methodology, J. Ind. Eng. Chem. 20 (2014) 2256–2263.
[17] K. Zhou, Q. Zhang, B. Wang, J. Liu, P. Wen, Z. Gui, Y. Hu, The integrated utilization of typical clays in removal of organic dyes and polymer nanocomposites, J. Cleaner Prod. 81 (2014) 281–289.
[18] N. Abidi, J. Duplay, F. Ayari, S. Gangloff, M. Trabelsi-Ayadi, Adsorption of anionic dye on natural and organophilic clays: effect of textile dyeing additives, Desalin. Water Treat. (2014) 1–16, doi: 10.1080/19443994.2014.895781.
[19] J.E. Aguiar, B.T.C. Bezerra, A.C.A. Siqueira, D. Barrera, K. Sapag, D.C.S. Azevedo, S.M.P. Lucena, I.J. Silva Jr., Improvement in the adsorption of anionic and cationic dyes from aqueous solutions: A comparative study using aluminium pillared clays and activated carbon, Sep. Sci. Technol. 49 (2014) 741–751.
[20] Q. Ma, F. Shen, X. Lu, W. Bao, H. Ma, Studies on the adsorption behavior of methyl orange from dye wastewater onto activated clay, Desalin. Water Treat. 51 (2013) 3700–3709.
[21] M. Visa, A. Duta, TiO_2/fly ash novel substrate for simultaneous removal of heavy metals and surfactants, Chem. Eng. J. 223 (2013) 860–868.
[22] A. Mittal, V. Thakur, V. Gajbe, Adsorptive removal of toxic azo dye Amido Black 10B by hen feather, Environ. Sci. Pollut. Res. 20 (2013) 260–269.
[23] A. Mittal, J. Mittal, L. Kurup, Utilization of hen feathers for the adsorption of indigo carmine from simulated effluents, J. Environ. Prot. Sci. 1 (2007) 92–100.
[24] B.H. Hameed, J.M. Salman, A.L. Ahmad, Adsorption isotherm and kinetic, modeling of 2,4-D pesticide on activated carbon derived from date stones, J. Hazard. Mater. 163 (2009) 121–126.
[25] N. Nasuha, B.H. Hameed, Adsorption of methylene blue from aqueous solution onto NaOH-modified rejected tea, J. Chem. Eng. 166 (2010) 783–786.
[26] B.H. Hameed, A.A. Ahmad, Batch adsorption of methylene blue from aqueous solution by garlic peel: An agricultural waste biomass, J. Hazard. Mater. 164 (2009) 870–875.
[27] S.E. Agarry, C.N. Owabor, A.O. Ajani, Modified plantain peel as cellulose-based low-cost adsorbent for the removal of 2,6-dichlorophenol from aqueous solution: Adsorption isotherms, kinetic modeling, and thermodynamic studies, Chem. Eng. Commun. 200 (2013) 1121–1147.
[28] F.A. Pavan, Y. Gushikem, A.C. Mazzocato, Silvio L.P. Dias, E.C. Lima, Statistical design of experiments as a tool for optimizing the batch conditions to methylene blue biosorption on yellow passion fruit and mandarin peels, Dyes Pigm. 72 (2007) 256–266.
[29] A. Mittal, D. Jhare, J. Mittal, Adsorption of hazardous dye Eosin Yellow from aqueous solution onto waste material De-oiled Soya: Isotherm, kinetics and bulk removal, J. Mol. Liq. 179 (2013) 133–140.
[30] J. Goupy, L. Creighton, Introduction aux plans d'expériences, third ed., l'usine nouvelle, Dunod, France, 2006.
[31] S.C.R. Santos, R.A.R. Boaventura, Adsorption modelling of textile dyes by sepiolite, Appl. Clay Sci. 42 (2008) 137–145.
[32] P. Bhunia, M.M. Ghangrekar, Statistical modeling and optimization of biomass granulation and COD removal in UASB reactors treating low strength wastewaters, Bioresour. Technol. 99 (2008) 4229–4238.
[33] J.T. Batalon, P.S. Madamba, pH—Postharvest technology, J. Agric. Eng. Res. 78 (2001) 167–175.
[34] M.Y. Can, E. Yildiz, Phosphate removal from water by fly ash: Factorial experimental design, J. Hazard. Mater. 135 (2006) 165–170.
[35] J. Ren, W.T. Lin, Y.J. Shen, J.F. Wang, X.C. Luo, M.Q. Xie, Optimization of fermentation media for nitrite oxidizing bacteria using sequential statistical design, Bioresour. Technol. 99 (2008) 7923–7927.
[36] S. Hattalli, A. Benaboura, F. Ham-Pichavant, A. Nourmamode, A. Castellan, Adding value to Alfa grass (*Stipa tenacissima* L.) soda lignin as phenolic resins 1. Lignin characterization, Polym. Degrad. Stab. 76 (2002) 259–264.
[37] N. Barka, A. Assabbane, A. Nounah, L. Laanab, Y. Ichou, Removal of textile dyes from aqueous solutions by natural phosphate as a new adsorbent, Desalination 235 (2009) 264–275.