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Process optimization of 2-methylpyridine removal by graphene nanoparticles

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In this study, removal data of 2-methylpyridine (2Mp) using exfoliated graphene oxide nanocomposite (GON) was modelled by response surface methodology using Doehlert design (DD) matrix. DD involves lesser experimental runs than the other statistical designs, while predicting outputs with relatively low error. The individual and combined effects of parameters namely: temperature, GON dosage, pH levels, and initial 2Mp concentration were explored using a 4-Factor DD. The model developed from statistical analysis suggested a strong relation between pH and 2Mp removal efficiency, with a maximum removal observed at a pH 7.0. From the range of values of the factors chosen for analysis, DD predicted pH 7.10, GON dosage = 1.84 g/L, initial 2Mp loading = 12.77 mg/L and temperature = 26.36°C as optimal conditions for a removal percentage of 73.51%. The model showed high coefficient of determination (R^2) = 0.9906 and the predicted error was found to be less than 2% for prediction of 2Mp removal.

Keywords: Doehlert design of experiments, Response surface method (RSM), pyridine derivative, graphene oxide (GO) nanomaterial, parameter optimization.

Introduction

2-Methylpyridine (2Mp) is used extensively in artificial textile and agrochemical industry for the manufacture of vinyl-pyridine and nitrapyrin respectively. It emanates a slight golden yellow colour at higher concentrations, a pungent odour and is neurotoxic to living beings. India, with a populace of a billion people, is a country with a large agrarian and textile demand. This results in generation of large amounts of industrial wastewaters contaminated with methylpyridines as they are used as raw materials or are generated as intermediate products in manufacture processes. 2Mp causes irritation to skin and damage to cornea even when exposure occurs in very small concentrations. Upon consumption it results in multitude of digestive disorders, vomiting and hampering of the central nervous system[1]. 2Mp has a lethal dose (LD_{50}) of 790 mg/kg (oral, rat)[2] and 0.41 mg/kg (skin, rabbit)[3] and a threshold limit value of 15 mg/m^3. It has poor biodegradability and zero net charge[4–6]. Though no discharge limit has been set for 2Mp containing industrial wastewaters, it is imperative to curtail discharge concentration of heterocyclic bases like 2Mp to 0.316 mg/L into subsurface water sources according to the US Environmental Protection Agency's "Clean Water Act'. It is also important to note that even at concentrations lower than 5 mg/L, pyridinic compounds ruin palatability of fishes[16].

Adsorption has been established as a suitable and reliable technique for removal of organic as well as inorganic contaminants from industrial effluents. Compound recovery is also possible by use of adsorption since it captures the pollutant in its original form. Exfoliated graphene oxide nanocomposite (GON) has large potential for removal of such neurotoxins because of large exposed surface area and π-π stacking[7]. It has been shown to have achieved better results than activated carbons and soil-based adsorbents in removal of cyclic organics[8].

While adsorption may be the most suited technique for 2Mp removal, optimal usage of the adsorbent is of utmost importance for conservation, regeneration and disposal of the adsorbent. Factor interactions during adsorption are also to be understood. This is achieved by modelling the process mathematically and optimizing each of the controllable factors affecting the adsorption process. Among design of experiment (DOE) techniques, while full factorial design results

in way too many experimental runs, fractional factorial method fails to capture factor interactions as well[9]. Further drawback of these techniques is the use of only two or three levels per factor in formulation of response models. The DOE by Doehlert design was thus utilized for experimental data modelling. It involves lesser experimental runs required than the other statistical design approaches while predicting outputs with relatively low error[10]. Another advantage is the employability of larger number of levels of operation for each factor in formulation of a non-linear model. In this study, uniform distribution of experimental points was made possible by adoption of a four factor DD matrix[11].

Thus, in this study, 2Mp removal by exfoliated GON was optimized by using Doehlert design matrix formulation. Four factors including pH, GON dosage, initial 2Mp concentration and temperature were investigated for analysis of single, quadratic and factor interaction studies. Response surfaces and contour plots were developed for analysis of multi-factor effects on removal. A mathematical model was developed for the prediction of 2Mp removal and these results were corroborated by experimental results.

Materials and methods

(A) Materials:

Analytical reagent grade chemicals were utilized in experimentation. The chemicals used include graphite powder (<20 microgram size, Sigma Aldrich), 2Mp (liquid, Loba Chemicals, India), NaOH pellets (1 *M*, Merck, Germany), H_2SO_4 solution (1 *M*, Merck, Germany), H_3PO_4 (88%, Merck, Germany) and $KMnO_4$ (Merck, Germany). For the analysis of 2-methylpyridine in the aqueous solution, the UV-Vis Double Beam Spectrophotometer (Model 2203, Systronics, India) was used in the present study. The adsorbent, i.e. graphene oxide nanocomposite (GON) was synthesized locally by Tour's method[12], as shown in Fig. 1.

(B) Doehlert design:

A four factor DD was used for the model development, which utilizes uniform shell design. The factors with their selected levels are shown in Table 1. This model was so chosen because it excels in situations that require study of factors that require identification of higher levels. Greater number of levels imply better resolution of an important factor. Geometrically, a 2D and 3D simplex for DD is represented by an isosceles triangle and a tetrahedron respectively. The origin acts as a pivoting centre in both cases with each side

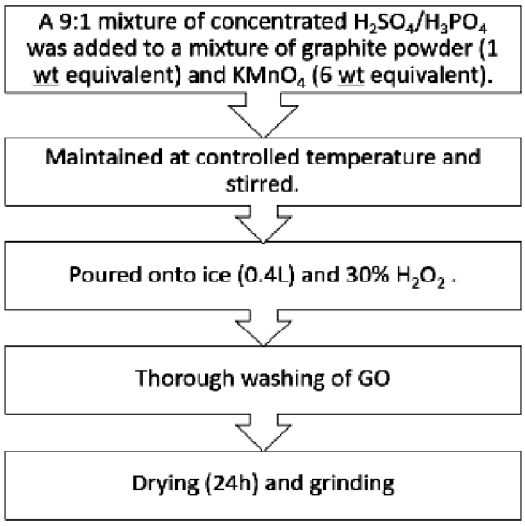

Fig. 1. GON preparation procedure.

Table 1. Range selection for 4-Factor Doehlert design

Factor	pH	GON dosage (g/L)	Initial 2Mp conc. (mg/L)	Temp. (°C)
Lower value	4	1	5	20
Higher value	10	2	20	35

of the figure being of unit length. The full DD can be attained by permutative subtraction of each apex from the centre in accordance with the geometry considered[10]. A 4D and higher order DD simplex is harder to physically visualize, but may be mathematically expressed in relation to a simplex of dimension (D-1) as given in eq. (1)[11],

$$\left(\frac{1}{2}\right),\left(\frac{1}{2\sqrt{3}}\right),\left(\frac{1}{2\sqrt{6}}\right),\ldots\ldots,\left(\frac{1}{\sqrt{2(D-1)(D-2)}}\right),$$
$$\left(\frac{1}{\sqrt{(2D(D-1)}}\right),\left(\frac{\sqrt{D+1}}{\sqrt{2D}}\right) \quad (1)$$

The four factor DD simplex is shown in Table 2. Number of experimental runs (N) and their corresponding factor (F) values are based on this simplex ($N = F^2 + F + 1$, with F = 4, N = 21).

(C) Experimental study:

A 2Mp stock of 1000 mg/L was prepared in DI water and further dilutions were made as required. Spectrophotometer (Model 2203, Systronics, India) was used for absorbance readings at maximum wavelength (λ_{max}, 2Mp) of 262 nm

Table 2. Initial Simplex for Four Factors DD Matrix

Factor / Sr. No.	X_1 pH	X_2 GON dosage (g/L)	X_3 Initial 2Mp conc. (mg/L)	X_4 Temp. (°C)
1.	0	0	0	0
2.	1	0	0	0
3.	0.5	0.866	0	0
4.	0.5	0.289	0.816	0
5.	0.5	0.289	0.204	0.79

for assessment of 2Mp removal percentage. Adsorption experiments were carried out in batch mode in accordance with the DD data given in Table 3. A temperature controlled orbital shaker was used to maintain different temperatures with a shaking rate of 120±2 rpm. Sample pH was modulated by using 0.1 *N* H_2SO_4 or 0.1 *N* NaOH. Contact time was maintained at 90 min as it was observed that the batch system equilibrated at this time[15].

Results and discussion

Majority of the research in 2Mp treatment has been focused on single factor batch studies. In real world scenarios though, multiple factors affect treatment efficiency as a result of interaction effects coming into play. An efficient model developed by Doehlert design of experiments that incorporates single factor, square terms and interaction effects occurring due to variation in factor values was proposed[13]. Uniform distribution of factor data points along with minimum number of experimental runs, at high level of resolution is achieved by use of DD. The experimental design along with experimental 2Mp removal, predicted removal and model error are shown in Table 3. The developed model[14] used for

Table 3. Four factor Doehlert matrix with experimental and predicted outcomes with errors

Run	Coded factor values				Experimental removal	Predicted removal	Error
	X_1	X_2	X_3	X_4	(%)	(%)	(%)
1	0	0	0	0	71.2	71.132	0.07
2	1	0	0	0	50.33	51.929	–1.60
3	0.5	0.866	0	0	67.03	66.932	0.10
4	0.5	0.289	0.816	0	60.54	59.873	0.67
5	0.5	0.289	0.204	0.79	64.04	63.206	0.83
6	–1	0	0	0	50.17	48.571	1.60
7	–0.5	–0.866	0	0	53.5	53.598	–0.10
8	–0.5	–0.289	–0.816	0	62.29	62.957	–0.67
9	–0.5	–0.289	–0.204	–0.79	61.6	62.434	–0.83
10	0.5	–0.866	0	0	56	55.112	0.89
11	0.5	–0.289	–0.816	0	65.19	64.726	0.46
12	0.5	–0.289	–0.204	–0.79	64.11	63.863	0.25
13	–0.5	0.866	0	0	64.2	65.088	–0.89
14	0	0.577	–0.816	0	75.58	74.884	0.70
15	0	0.577	–0.204	–0.79	74.27	74.176	0.09
16	–0.5	0.289	0.816	0	57.82	58.284	–0.46
17	0	–0.577	0.816	0	57.77	58.466	–0.70
18	0	0	0.612	–0.79	70.05	69.557	0.49
19	–0.5	0.289	0.204	0.79	61.03	61.277	–0.25
20	0	–0.577	0.204	0.79	61.52	61.614	–0.09
21	0	0	–0.612	0.79	72.92	73.413	–0.49
22	0	0	0	0	70.93	71.132	–0.20
23	0	0	0	0	70.12	71.132	–1.01
24	0	0	0	0	71.64	71.132	0.51
25	0	0	0	0	72.25	71.132	1.12
26	0	0	0	0	70.65	71.132	–0.48

estimating 2Mp removal by GON can be represented as eq. (2).

$$Y = A_0 + \Sigma_{i=1}^{4} B_i X_i + \Sigma_{i=1}^{4} C_i X_i^2 + \Sigma_{i \neq j=1}^{4} D_{ij} X_i X_j + \varepsilon_{ij} \quad (2)$$

where, A_0, B_i, C_i and D_{ij} are model regression coefficients, μ_{ij} is the error in prediction and Y is the model yield signifying 2Mp removal percentage. MATLAB software was used for variance analysis with up to two factor interactions (beyond which the regression model did not give a good fit). The developed model equation for 2Mp removal by GON can be written in polynomial form as eq. (3),

$$R = 71.1317 + 1.6790\times X_1 + 6.7292\times X_2 - 5.3018\times X_3 - 1.6667\times X_4 - 20.8817\times X_1^2 - 7.6388\times X_2^2 - 4.7452\times X_3^2 - 1.2780\times X_4^2 + 0.1905\times X_1\times X_2 - 0.1778\times X_1\times X_3 + 0.2927\times X_1\times X_4 - 2.6884\times X_2\times X_3 - 2.0607\times X_2\times X_4 - 6.0010\times X_3\times X_4 \quad (3)$$

where, R is the 2Mp removal percentage and X_i are factor values in their coded format. Experimental preset and coded values are related as given in eq. (4),

$$C = \frac{P - (h + l)/2}{(h + l)/(2r)} \quad (4)$$

where, C is the coded form of the factor, P is preset experimental value (or natural value) for the factor, h and l are higher and lower range limits of the factor and r represents the range. The model showed high coefficient of determination (R^2) = 0.9906, implying that 99.06% variability of experimental results was handled well by the model.

To obtain the optimum condition of 2Mp removal, Lagrange's criterion[10] was established. A negative value of the function was obtained implying a maximizing function. Gradient vectors were developed by finding the derivatives of the yield function with respect to each of the factors. The factors were chosen as X_1 (pH), X_2 (GON dosage in g/L), X_3 (initial 2Mp conc. in mg/L) and X_4 (temperature in °C). Optimum factor settings were achieved by simultaneously solving the gradient vectors. The optimal coded values were X_1 = 0.0344, X_2 = 0.5974, X_3 = 0.0289 and X_4 = –0.5198, which in natural values translated to be pH = 7.10, GON dosage (g/L) = 1.84, initial 2Mp conc. (mg/L) = 12.77 and temperature (°C) = 22.57. The model predicted an optimal removal of 73.51%, which is corroborated by experimental results.

(A) Factor effects:

In eq. (3), the yield or the 2Mp removal performance of GON was affected by the negative/positive sign of the regression coefficient of each factor, which contributed by taking away or adding to the total yield respectively. The effect of a unit change in variable value on total predicted yield is captured by regression coefficients. We found that increase in level of X_1 and X_2 had a positive impact, but X_3 and X_4

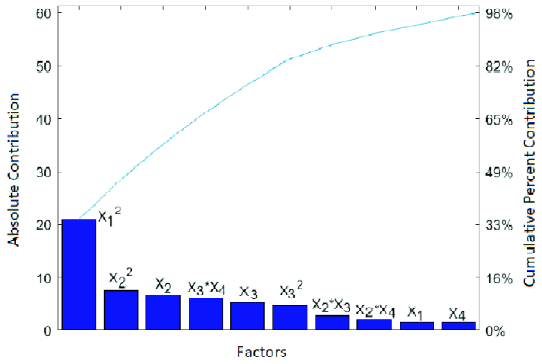

Fig. 2. Pareto plot representing effects of factors on 2Mp removal.

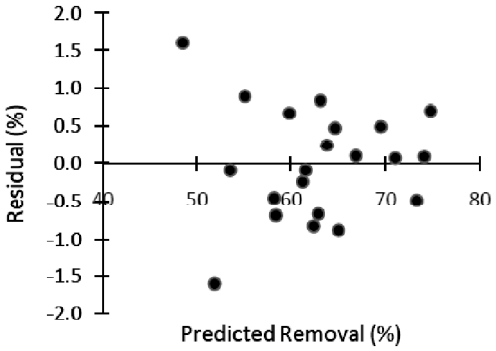

Fig. 3. Plot of predicted removal versus residuals.

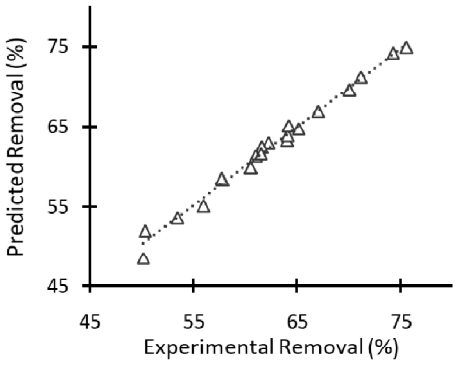

Fig. 4. Checking model correlation with experimental data.

had negative impact on removal. Under batch experimental conditions for 2Mp removal, comparable trends were recorded previously[4,5]. Absolute magnitudes of regression coefficients are used to plot the Pareto chart in Fig. 2. Quadratic effects of solution pH and GON dosage had the most impact on yield variability and prediction, i.e. nearly 21% and 7% re-

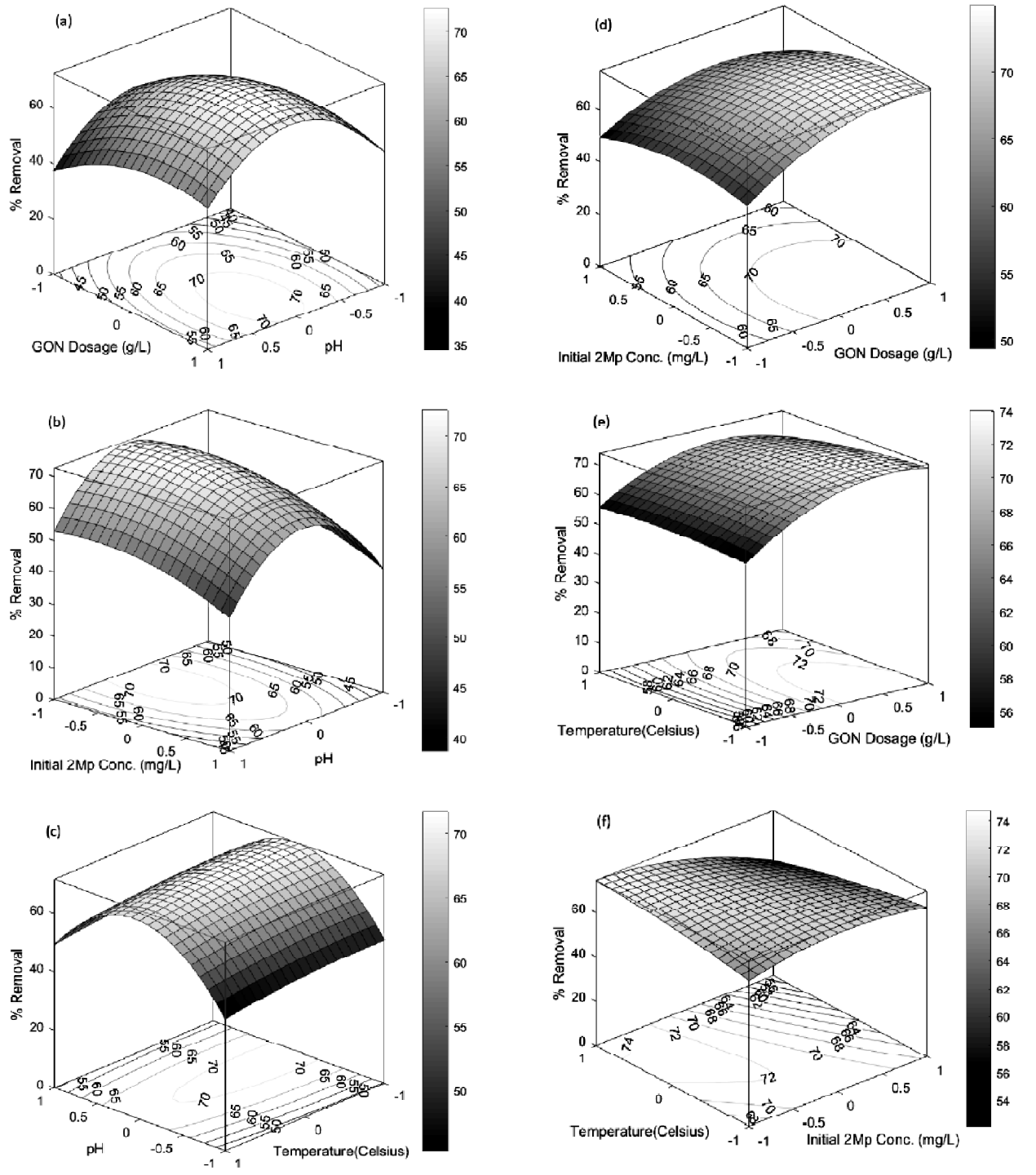

Fig. 5. Interaction between (a) GON dosage and pH; (b) initial 2Mp conc. and pH; (c) pH and temperature; (d) initial 2Mp conc. and GON dosage; (e) temperature and GON dosage and (f) temperature and initial 2Mp conc.

spectively. Around 98% of the 2Mp removal prediction was accounted for by the factor effects shown in the plot.

(B) Model adequacy:

Normal distribution of errors is assumed in model formulation and this was asserted graphically using the normal probability graph of errors. Difference between experimental value and model forecast yield is called error or residual. In Fig. 3, the residual data is randomly distributed and shows no trend, implying normal distribution of predicted data. On plotting experimental removal against the model predicted yield (Fig. 4), we saw a correlation of 0.989 (R^2) that implied an accurate method design.

(C) Response surface analysis:

Visualization of effects of more than two independent factors is difficult on a 3-D plane, thus the model equation (eq. (3)) was restricted to two factors. The six generated equations ($^4C_2$) consisting of linear, quadratic and interaction terms were used to generate removal data. The remaining factors that were not varied and were kept at a constant mid-level value which corresponds to zero in coded format.

Further combinations are generated accordingly. The 3-D visualization of the interaction results are shown in Fig. 5(a-f), representing the 2Mp removal data with contour diagrams and the response surfaces. As seen from Fig. 5(a-c), the most conducive pH for 2Mp removal is coded 0 value, which is near to the natural pH of 2Mp.

(D) Model validation:

Experimental analysis was carried out at central level values for each of the factors. A set of five runs were performed to confirm repeatability and reproducibility of experimental results. Removal percentages of 2Mp were noted. Serial numbers 22–26 in Table 3 represent these runs. The model succeeded in predicting experimental outcomes for these runs with an average absolute error of 0.66%. It can thus be reasonably accepted that the model has the capability to predict removal percentages for given conditions of factors that play a role in 2Mp removal by GON.

Conclusion

The model developed for simulation of 2-methylpyridine removal by exfoliated graphene oxide nanocomposites was successful in doing so. It suggested that pH followed by GON dose were the most important factors affecting the overall removal. Maximum yields were obtained at a pH 7.1, even when other three factors were varied experimentally. Good correlation was obtained between experimental and modelled data with a R^2 = 0.989 and a significantly low prediction error. Upon utilizing optimal factor values, the optimum removal was predicted as 73.51%. Quadratic factor effects of pH and GON dosage were found to be most substantial. While two-factor interactions were found significant, higher order interactions bore no weight on the removal prediction. Experimental repeatability corroborated by model predicted values implied a good model fit and successful model development. More complex model development with consideration of interfering solutes in effluent is required for large-scale implementations.

References

1. R. Snyder, "Ethel Browning's Toxicity and Metabolism of Industrial Solvents: Nitrogen and phosphorus solvents", Elsevier Science Limited, Vol. 2, 1990, **222**.
2. G. Sanitariya, V/O Mezhdunarodnaya Kniga 113095 Moscow, 1936.
3. AMA Archives of Industrial Hygiene and Occupational Medicine, 1951, **4(119)**.
4. D. Mohan, K. P. Singh, S. Sinha and D. Gosh, *Environ. Sci. Technol.*, 2005, **39(13)**, 5076.
5. Z. Rawajfih, H. A. Mohammad, N. Nsour and K. Ibrahim, *Micropor. Mesopor. Mater.,* 2010, **132(3)**, 401.
6. S. Hashemian and Y. Parsaei, *Orient. J. Chem.,* 2015, **31(1)**, 177.
7. Y. Gao, L. Zhang, H. Huang, J. Hu, S. M. Shah and X. Su, *J. Colloid Interface Sci.*, 2012, **368(1)**, 540.
8. J. Wang, Z. Chen and B. Chen, *Environ. Sci. Technol.*, 2014, **48(9)**, 4817.
9. D. C. Montgomery, "Design and analysis of experiments", 4th ed., Wiley, New York, 1984.
10. C. Majumder, *J. Environ. Eng.,* 2017, **144(3)**, 04017115-1-5.
11. D. H. Doehlert, *Journal of the Royal Statistical Society: Series C (Applied Statistics)*, 1970, **19(3)**, 231.
12. D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu and J. M. Tour, *ACS nano*, 2010, **4(8)**, 4806.
13. D. H. Doehlert and V. L. Klee, *Discrete Mathematics*, 1972, **2(4)**, 309.
14. I. Forsal, M. E. Touhami, B. Mernari, J. E. Hajri and M. F. Baba, *Portugaliae Electrochimica Acta,* 2010, **28(3)**, 203.
15. R. Chatterjee and C. Majumder, *J. Indian Chem. Soc.*, 2019, **96(4)**, 499.
16. R. A. Pandey and S. Sandhya, *Journal of Environmental Science & Health, Part A*, 1997, **32(5)**, 1325.