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Using of Taguchi Robust Design Method to Optimize Effective Parameters of Methylene Blue Adsorption on ZSM-5 Zeolite

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Adsorption of methylene blue from aqueous solution by synthesized zeolite as adsorbent was studied by using Taguchi methods. To understand and optimize the adsorption condition, three factors were selected *i.e.*, methylene blue concentration, contact time and the adsorbent dose, as the main affecting parameters. A Taguchi's $L_{16}4^3$ design was used to optimize the effect of the chosen parameters, Four initial concentrations of 30, 40, 50 and 60 mg/L and four adsorbent doses of 0.005, 0.01, 0.015 and 0.02 g were selected. The experiments were conducted for 50, 150, 250 and 350 min. The maximum adsorption of methylene blue achieved with 0.02 g of zeolite, solution concentration of 30 mg/L and contact time of 180 min. The theoretical calculation was in good agreement with the experimental results.

Key Words: Methylene blue, Adsorption, Taguchi Robust method, Experimental design, ZSM-5 zeolite.

INTRODUCTION

The removal of synthetic dyestuff from aqueous solution is an essential point in the waste water treatment processes due to the frequent appearance of dyestuff in effluents of various industries such as textiles, paper, rubber, plastics and cosmetics wastewaters. The presences of dyes in water streams are condesirable since even a very small amount of these colouring agents is highly visible. Nevertheless, much of them are considered as toxic materials in environmental point of view[1-5]. Therefore, removal of dyes is an important aspect of waste-water treatment before discharging to the ecosystem.

Adsorption is known as one of the effective separation processes for a wide variety of applications, especially for removal of non-biodegrable pollutants (*e.g.* dyes) from waste-water. Moreover, adsorption process is simple and easy to combine with other treatment technologies[1,6]. So far, wide variety of adsorbents including peat, palm fruit, zeolite, fly ash, activated carbon, *etc*. have been studied for different applications[7-10].

Zeolite molecular sieves are renowned category of hydrated crystalline and porous aluminosilicates. Size and shape, of zeolite pores and channels control the reactivity of these materials[11,12]. These inorganic compounds can be found as natural and artificial materials are known because of their chemical, mechanical, radiation and hydrothermal stabilities[12]. These outstanding characteristics of zeolites and zeotype materials made them as the most attractive adsorbents for removal of molecules (*e.g.* molecular dyes), cations (*e.g.* heavy metals) and anions (*e.g.* chromate) from liquids[13-19]. In the present work, adsorption of methylene blue (MB) ($C_{16}H_{18}N_3SCl\cdot 3H_2O$) on the as-synthesized ZSM-5 zeolite was investigated in a batch mode. Adsorption of aqueous solutions of methylene blue has been also used to determine the specific surface area of the zeolite[20].

Furthermore, zeolites modified by methylene blue can be used as optical sensor. In a research, diffuse reflectance spectroscopy has been applied to evaluate the response of an optical humidity sensor made of new methylene blue (NMB) loaded mordenite zeolites by exposing to water vapour. The system has been displayed a novel colour change in the visible region with increasing humidity from blue-violet to dark blue as a result of protonation/deprotonation of NMB-doped zeolite. They have claimed that NMB-doped HMOR can be used as a candidate for optical humidity sensing in the range of 6-95 %, with a forward and reverse response time of 1 and 2 min, respectively[21].

The performance of this type of the zeolite based sensors is based on the change in colour upon protonation/deprotonation of dye molecules incorporated into the zeolite. These processes are associated with the dehydration/hydration of the zeolite[22].

To the best of our knowledge, in the previous studies conducted on the adsorption of the methylene blue, single factor optimization (*e.g.* one factor at a time) approach has been used to understand and optimize the effective parameters on the sorption phenomena[23-25]. Due to possible interactions of the factors, an optimized process *via* this traditional method, in which the interactions can not be taken into account, is not a real optimization. The statistical based optimization methodologies are more effective in order to attain to a more real optimum condition.

Nevertheless, the main purposes of using statistical experimental design is to provide maximum, actual and more reliable information with experimental runs as fewer as possible. Taguchi method is one of the preferable techniques for experimental design. This method differs in several aspects from other experimental design techniques. First, Taguchi methods strongly rely on researcher experience in choosing right parameters and their levels. Second, these methods use orthogonal arrays to investigate the main and interaction effects of parameters in an optimum number of experiments. Third, researcher has to determine a target for their response variables such as "smaller is better", "larger is better" or "nominal is the best". Finally, Taguchi methods suggest the use of a loss function to understand the variation from the desired values. Therefore, depending on the target being smaller, larger or nominal; every response data will be converted to a signal to noise ratio (S/N). Then the maximum values of S/N ratios will be used to select the optimum values for each parameter[26].

In this work, Taguchi method was applied to optimize the effective parameters of methylene blue adsorption on as-synthesized ZSM-5 zeolite. Taking into account the previous literatures on adsorption of methylene blue on different adsorbents, three different parameters of (1) the amount of zeolite, (2) concentration of methylene blue in solution and (3) contact time, were selected as the main effective parameters to be optimized. At the end of each experiment, the measured absorption values of the methylene blue were taken as a response factor according to the "smaller is better" approach.

EXPERIMENTAL

Methylene blue (MB) was purchased from Sigma-Aldrich Co. The maximum wavelength of this dye is 665 nm. The structural formula of methylene blue is shown in Fig. 1. All of the materials (*e.g.* alumina and silicon precursors as well as organic template) for synthesis of ZSM-5 zeolite were analytical grade chemicals purchased from Merck. De-ionized water was used to prepare solutions and for washing purposes.

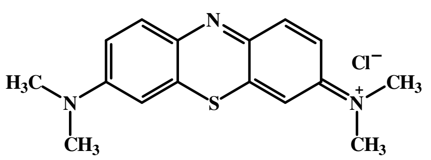

Fig. 1. Chemical structure of methylene blue

ZSM-5 was synthesized under hydrothermal condition at 180 °C for 40 h[27]. The zeolite was calcinated in an electrical furnace at 550 °C for 6 h to remove organic template. No other chemical or physical treatments were applied on the zeolite prior to adsorption experiments. The zeolite was characterized by means of scanning electron microscopy (SEM, JEOL JXA-840), Fourier transform infrared spectroscopy (FT-IR, Vector 22-Bruker) and X-ray diffraction (XRD, GBC MMA Instrument) techniques.

Adsorption test (design of experiments): According to the literature[23,24], the sorption of methylene blue has been minimized at the initial pH of 2 and improved by increasing the pH up to 4 and then remained almost constant at the pH ranges of 4-12. Therefore, fixed pH of 7 was chosen for this study. In all of the experiments, the volumes of methylene blue solution and rotation speeds were kept constant at 10 mL and 600 rpm, respectively. The concentration of methylene blue, the amount of zeolite (dose) and contact time were then selected as the main process parameters. Four levels were applied for each parameter (designated as 1, 2, 3 and 4). The four selected concentrations of methylene blue were 30, 40, 50 and 60 mg/L. Four selected doses of zeolite were 0.005, 0.01, 0.015 and 0.02 g. The experiments were performed in four different contact times of 50, 150, 250 and 350 min. Detailed information is summarized in Table-1. In order to measure the residual methylene blue concentration; Z_i, by completion of each experiment, the solution was immediately centrifuged (DENLEY BS400) and analyzed using a UV-visible spectrophotometer (CECIL, CE 5501).

$L_{16}4^3$ orthogonal array of Taguchi design involves 16 experiments in order to cover the influences of the three parameters in four levels. Experiments were performed randomly. Details of the Taguchi $L_{16}4^3$ array selected for this study are summarized in Table-2.

TABLE-1
PROCESS PARAMETERS AND THEIR LEVELS

Parameter	Level 1	Level 2	Level 3	Level 4
A, Solution concentration of methylene blue (ppm)	30	40	50	60
B, The amount of zeolite (g)	0.005	0.01	0.015	0.02
C, Contact time (min)	0.60	120	180	240

TABLE-2
TAGUCHI $L_{16}4^3$ DESIGN AND RESIDUAL CONCENTRATION OBTAINED FROM EXPERIMENTS

Run No.	A	B	C	Y_i*	S/N ratio
1	30	0.005	60	20.608	-26.281
2	30	0.010	120	14.247	-23.075
3	30	0.015	180	6.780	-16.625
4	30	0.020	240	2.735	-8.7391
5	40	0.005	120	34.823	-30.837
6	40	0.010	60	25.807	-28.235
7	40	0.015	240	18.783	-25.475
8	40	0.020	180	10.486	-20.412
9	50	0.005	180	37.754	-31.539
10	50	0.010	240	30.564	-29.704
11	50	0.015	60	27.577	-28.811
12	50	0.020	120	19.336	-25.725
13	60	0.005	240	53.075	-34.498
14	60	0.010	180	37.311	-31.437
15	60	0.015	120	41.183	-32.298
16	60	0.020	60	31.615	-29.998

*Residual concentration of methylene blue in solutions after adsorption test.

RESULTS AND DISCUSSION

XRD pattern of the synthesized sample is presented in Fig. 2. With comparing the main peaks at 2θ = 7.9, 8.9, 23.2 and 24.5 with the reference sample[28-31] crystallization of nearly pure ZSM-5 phase will be ascertained.

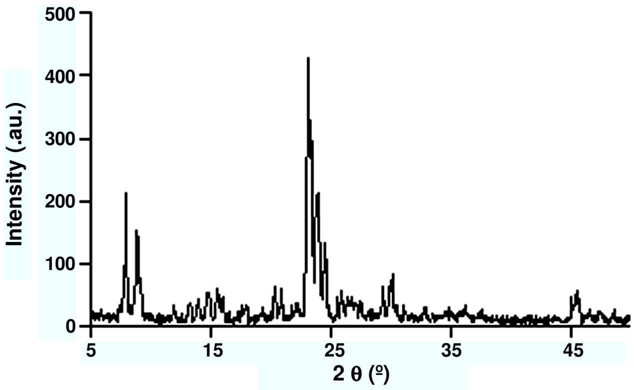

Fig. 2. SEM image of the as-synthesized ZSM-5 crystals

Infrared spectrum of the synthesized sample is shown in Fig. 3. IR band exhibited at wave numbers of 455, 545 and 1222 cm^{-1} are related to MFI structural vibration[32,33]. This can consider as another evidence of successful synthesis of ZSM-5.

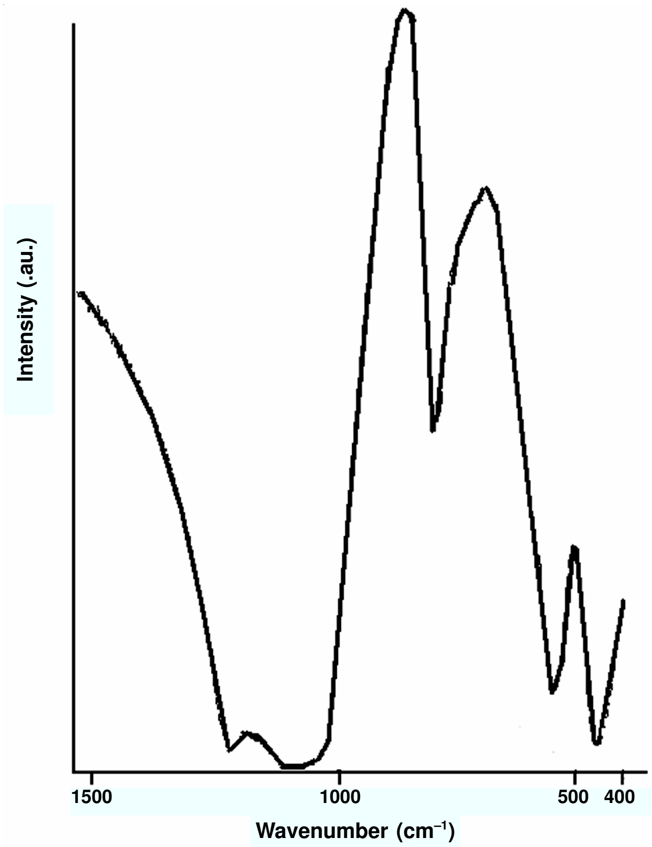

Fig. 3. FTIR spectra of the as-synthesized ZSM-5 zeolite

SEM micrograph of the sample is given in Fig. 4. Formation of MFI typical cubical crystallites with average particle size of ~ 1 micrometer is clearly obvious.

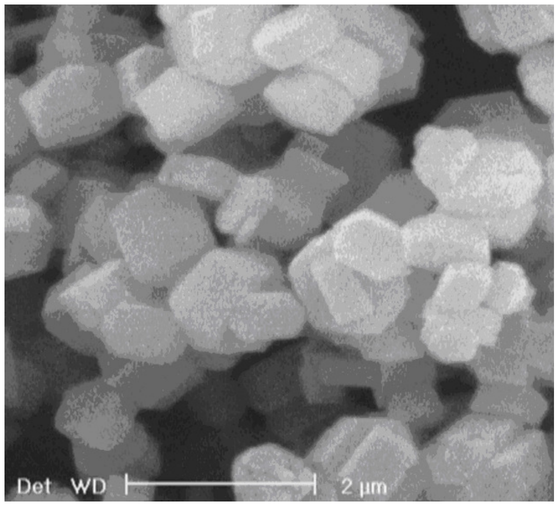

Fig. 4. X-ray diffractogram of the as-synthesized ZSM-5 zeolite

In the Taguchi method, the term 'signal' represents the desirable value (mean) for the output characteristic and the term 'noise' represents the undesirable value (standard deviation, SD) for the output characteristic. Therefore, the S/N ratio is the ratio of the mean to the SD. Taguchi uses the S/N ratio to measure the quality characteristic deviating from the desired value. There are several S/N ratios available, depending on the type of characteristic; lower is better (LB), nominal is best (NB), or higher is better (HB)[34].

ANOVA (Analysis of Variance) and signal/noise ratio analyses were conducted on the residual concentration of methylene blue in the solutions. Minitab software was utilized for this analysis. Table-2 shows the data (Y_i) and corresponding S/N ratios calculated considering Taguchi's "smaller is better" approach using eqn. 1:

$$S/N(\eta) = -10\log[\sum_{i=1}^{n}(Y_i)^2/n] \quad (1)$$

where n is the number of measurements in a trial/row and Y_i is the ith measured value in a run/row.

ANOVA helps in formally testing the significance of all main factors and their interactions by comparing the mean square against an estimate of the experimental errors at specific confidence levels. This is accomplished by separating the total variability of the S/N ratios, which is measured by the sum of the squared deviations from the total mean S/N ratio, into contributions by each of the design parameters and the error. First, the total sum of squared deviations SST for a set of results, Y_1, Y_2, …, Y_n, was obtained by following equation:

$$SS_T = \sum_{i=1}^{n}(Y_i)^2 - \frac{TT^2}{n} \quad (2)$$

where n is the number of experiments in the orthogonal array and TT is total of results. The value of SST is shown at tired column in Table-3.

The sums of squares for mentioned factor were calculated by eqn. 3:

$$SS_A = \sum_{i=1}^{L_A}(\frac{A_i}{n_{A_{ii}}})^2 - \frac{TT^2}{N} \quad (3)$$

where L_A is the number of levels of factor A, n_{Ai} is the total number of experiments in which the level I of factor A is present and A_i is the total of results (Y_i) that include factor A_i. Other quantities calculated as part of the ANOVA table information are derived from the sums of squares. For factor A, they calculated by following equations:

Mean squares (or variance): $$V_A = \frac{SS_A}{f_A} \quad (4)$$

Pure sum of squares: $$SS'_A = SS_A - V_e \times f_A \quad (5)$$

Per cent influence: $$P_A = \frac{SS'_A}{SS_T} \times 100 \quad (6)$$

where f_A is the degree of freedom (DOF) of factor A[35] (DOF of factor = number of levels of factor-1) and V_e is the variance for the error term which obtained by calculating the error sum of squares and dividing by error degrees of freedom.

The effects of parameters are calculated by averaging the S/N ratio for each level. Fig. 5, show that the methylene blue concentration and adsorbent dose greatly influence the S/N ratio. This influence is found to be smaller regarding the contact time. According to the analysis, while solution concentration is the most effective parameter, the contact time is the least effective factor in the sorption reaction of methylene blue over ZSM-5.

Results of ANOVA are summarized in Table-3. As in S/N ratio analysis, ANOVA analysis also reveals that the contact time is less effective than methylene blue concentration and the adsorbent dose.

TABLE-3
ANOVA ANALYSIS RESULTS FOR ALL FACTORS

Factor	DOF (F)	Sum of squares (SS)	Variance (V)	F-Ratio (F)	Per cent (P) (%)
A	3	1845.177	615.059	186.187	66.093
B	3	869.626	289.875	87.749	30.961
C	3	42.143	14.047	4.252	1.160
Error	6	19.820	3.303	–	1.786
Total	15	2776768	–	–	100

By taking into account the results obtained from S/N and ANOVA analyses, another analysis was conducted by pooling this parameter to error (Table-4.)

The methylene blue concentration and the adsorbent dose are found to be more effective. However their slopes are opposite to each other. This indicates an interaction between these parameters.

TABLE-4
ANOVA ANALYSIS RESULTS AFTER POOLING

Factor	DOF (F)	Sum of squares (SS)	Variance (V)	F-Ratio (F)	Per cent (P) (%)
A	3	1845.177	615.334	89.334	65.706
B	3	869.625	289.875	42.102	30.575
Error	9	61963	6.884	–	3.720
Total	15	2776768	–	–	100

As shown in Fig. 5, by increasing of methylene blue concentration, adsorption was decreased, whereas the increasing of the zeolite dose increases the methylene blue adsorption.

Less effect of contact time can be considered as a result of fast kinetic of the adsorption reaction. Rotation rates and volume of solutions were kept constant in all experiments then the flow dynamics was the same in solutions during adsorption process. The surface properties of adsorbent, such as surface area and surface charge are major factors for efficient adsorption of methylene blue on zeolite. Zeolites are microporous materials with large surface area. The electrostatic forces that arise of the interaction of negative charges of zeolite surface with positive charge of methylene blue molecules can be considered as one of the responsible phenomena for efficient adsorption of this molecule.

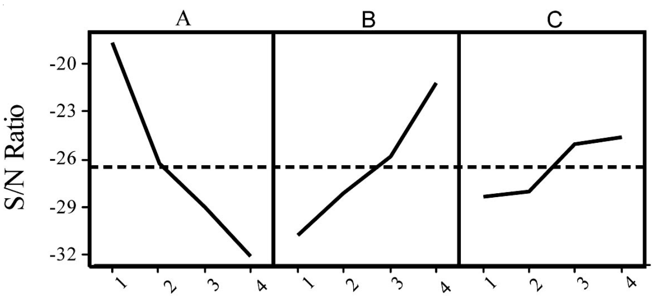

Fig. 5. Main effect plots for S/N ratios of methylene blue concentration in ppm; (A) the concentration of solution, (B) the amount of ZSM-5 and (C) contact time.

According to the analyses, the highest adsorption of methylene blue is achieved when 0.02 g of zeolite was used in the 30 ppm solution of methylene blue for 180 min. In order to obtain the highest adsorption, the optimum methylene blue concentration calculated by eqn. 7:

$$\mu = \frac{T}{n} + \left(\frac{A_1}{r} - \frac{T}{n}\right) + \left(\frac{B_4}{r} - \frac{T}{n}\right) + \left(\frac{C_3}{r} - \frac{T}{n}\right) \quad (7)$$

μ represents the optimum value, T (-423.68) denoted the total level of each parameters in S/N ratios, n the number of experiments (16) and r is the number of replications for each parameter (4) in $L_{16}4^3$. A1, B4 and C3 are selected as the optimum values for the studied parameters. The estimated value is found as -1.396 db corresponds to 3.12 ppm of methylene blue in the solution. An adsorption experiment was carried out with optimum condition. The measured concentration of methylene blue was 3.56 ppm, which was in good agreement with the calculated result.

Conclusion

In this study, a Taguchi's $L_{16}4^3$ orthogonal array was used to optimize the effect of the chosen parameters, on the methylene blue sorption by ZSM-5 zeolite. While solution concentration and the zeolite dose were found to be the most effective parameters, the contact time was shown the least effect on the adsorption. The highest efficiency is achieved when 0.02 g of zeolite used in the methylene blue concentration of 30 mg/L for 180 min. A verification experiment was conducted at the calculated optimum conditions. The result (3.56 ppm) was in good agreement with the calculated value (3.12 ppm). The results obtained in this research revealed that statistic experimental design could be apply in order to optimize influence of parameters on adsorption reaction.

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