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# Application of Taguchi L16 design method for comparative study of ability of 3A zeolite in removal of Rhodamine B and Malachite green from environmental water samples

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This study aimed to investigate the efficiency of 3A zeolite as a novel adsorbent for removal of Rhodamine B and Malachite green dyes from water samples. To increase the removal efficiency, effecting parameters on adsorption process were investigated and optimized by adopting Taguchi design of experiments approach. The percentage contribution of each parameter on the removal of Rhodamine B and Malachite green dyes determined using ANOVA and showed that the most effective parameters in removal of RhB and MG by 3A zeolite are initial concentration of dye and pH, respectively. Under optimized condition, the amount predicted by Taguchi design method and the value obtained experimentally, showed good closeness (more than 94.86%). Good adsorption efficiency obtained for proposed methods indicates that, the 3A zeolite is capable to remove the significant amounts of Rhodamine B and Malachite green from environmental water samples.



## 1. Introduction

Industrialization in recent decades has left its negative effects on the environment [1]. Dyes are important because of their broad applications in different industries like textile, leather, paper, and food [2]. The total dye consumption in textile industries is upper than 10,000 ton per year [3]. As a result, dye effluents of such industries contain many toxic, carcinogenic, and mutagenic compounds. Therefore, industrial wastewater poses a serious environmental problem [4]. Malachite green (MG) is a cationic dye which is highly soluble in water and can have impact on the human body [5]. The ingestion and inhalation of MG can cause irritation to the gastrointestinal and respiratory systems, respectively [6]. Rhodamine B (RhB) is another industrial dye which due to its low cost and high effectiveness has found a lot of applications in textile industries [7,8]. Like MG, RhB is toxic for humans and animals [9] and its release to environmental can have dire effects [10]. Therefore, wastewater colored contaminants of such industries should be refined using an appropriate method before discharging to the environment [11]. There are many methods for removal of harmful dyes from colored wastewater [12–15]. Adsorption seems simplest and most cost effective technique to remove the water pollutant [16]. As a result, many researchers attempted to use the cost-effective adsorbents for removal of dyes from waste effluents and consequently many absorbents have been evaluated for their ability to remove organic dyes [17–19]. In this study, 3A zeolite was evaluated as a potent adsorbent for removal of RhB and MG from water samples. To find out the optimum removal conditions, Taguchi design of experiment was utilized. Taguchi model (developed by Dr. Genichi Taguchi [20]) is a multivariate optimization method that is applied for optimization of effective parameters [21]. This method is very powerful and has some advantages in comparison with traditional uni-variant optimization techniques such as keeping the experimental cost at a minimum level, reducing the time of experimental investigation, and being able to study the influence of individual factors to determine the most effective parameter [22]. In this study, the analysis of variance (ANOVA) technique was used for identification of the most effective parameters on the removal efficiency of RhB and MG dyes from water samples using 3A zeolite adsorbent.

## 2. Experimental

### 2.1. Instruments and Materials

The 3A zeolite was obtained from Aldrich Chemical Company. Malachite green and Rhodamin B used in this study were purchased from Merck. Other reagents and solvents were purchased from Fluka and were of analytical grade. The test solutions of RhB and MG were prepared freshly every day by sequentially diluting stock solution of each dye containing 100 mg L RhB or MG in deionized water. For pH measurement of sample solutions a pH meter (Easy Seven, Metrohm) was used. Determination of the residual concentration of dyes was done

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using a UV–Vis spectrophotometer (UV 160, Shimadzu). The 3A zeolite was characterized by Fourier transform infrared spectroscopy (Spectrum Two FTIR, Perkin Elmer) and scanning electron microscopy (EM3900M, KyKy). Structure of Rhodamine B, Malachite green and 3A zeolite are shown in supplementary data in Figs. S1, S2 and S3 respectively.

### *2.2. Analytical Procedure*

In order to investigate the efficiency of 3A zeolite adsorbent for removal of RhB and MG dyes from water samples, optimization studies were carried out according to the following procedure: (1) 25 mL aqueous solution of each dye (5 mg/L) was prepared in a 50 mL glass flasks, (2) appropriate amount of sorbent was added to the dyes solution; (3) pH of sample solution was adjusted using 0.1 mol/L HCl and NaOH solutions in the range of 3 to 9, (4) the flasks were subjected to agitation in shaker at 200 rpm for a few minutes to reach equilibrium state, (5) supernatant liquid was taken from the solutions, (6) determination of the residual concentration of RhB and MG were done spectrophotometrically against the blank in 554 and 617.5 nm. The dye removal percentage was calculated as follows:

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

$C_e$ and $C_0$ are equilibrium and initial dyes concentration (mg/L) respectively.

### *2.3. Taguchi Design of Experiments*

The Taguchi design is usually utilized as an experimental design technique which provides the reduction of experimental number using orthogonal array design (OAD) [23]. This technique includes data transformation to a signal to noise (S/N) ratio, which is a measure of presented variations, i.e. the S/N ratio is used to verify the deviation of the output characterization from the desired values [24]. In the case that bigger characteristics are better, the S/N ratio is defined as [25]:

$$\frac{S}{N} = \frac{-10\ \text{Log}\left(\frac{1}{y_1^2} + \frac{1}{y_2^2} + \ldots + \frac{1}{y_n^2}\right)}{n} \quad (2)$$

where n is the replication number of the experiment and $y_i$ is the characteristic property. The unit of S/N ratio is decibel (dB), which is frequently used in communication engineering. In order to estimate the best condition for removal of RhB and MG with Taguchi design, four factors (A–D) in four levels were chosen to design the experiment as shown in Table 1. In total, 16 experiments were defined for each dye. Optimum conditions for adsorption of RhB and MG by 3A zeolite are shown in Table 2. The L16 orthogonal array and obtained results (removal efficiency and S/N ratio) for RhB and MG are shown in Table S1 and Table S2 in supplementary data. The analysis of Variance (ANOVA) was used to assess the orthogonal array design (OAD) results. The ANOVA results for removal of MG and RhB are reported in Table 3.

**Table 1**
Factors and levels in Taguchi design for removal of RhB and MG.

| Dyes | Level | Factors | | | |
|---|---|---|---|---|---|
| | | pH (A) | Amount of adsorbent (g) (B) | Initial dye concentration (mg/L) (C) | Contact time (min) (D) |
| Rhodamine B | 1 | 3 | 0.250 | 5 | 10 |
| | 2 | 5 | 0.500 | 10 | 20 |
| | 3 | 7 | 0.750 | 15 | 30 |
| | 4 | 9 | 1.000 | 20 | 40 |
| Malachite green | 1 | 3 | 0.050 | 5 | 5 |
| | 2 | 5 | 0.075 | 10 | 15 |
| | 3 | 7 | 0.100 | 12 | 30 |
| | 4 | 9 | 0.125 | 15 | 40 |

**Table 2**
Optimum conditions for adsorption of RhB and MG by 3A zeolite.

| Dye | Factor | Optimization level | |
|---|---|---|---|
| | | Based on Mean | Based on S/N |
| Rhodamine B | A | Level 2 (5) | Level 2 (5) |
| | B | Level 2 (0.500 g) | Level 2 (0.500 g) |
| | C | Level 3 (15 mg/L) | Level 3 (15 mgL) |
| | D | Level 2 (20 min) | Level 2 (20 min) |
| Malachite green | A | Level 3 (7) | Level 3 (7) |
| | B | Level 3 (0.100 g) | Level 3 (0.100 g) |
| | C | Level 2 (10 mg/L) | Level 2 (10 mg/L) |
| | D | Level 2 (15 min) | Level 2 (15 min) |

## 3. Results and Discussion

### *3.1. Characterization of Adsorbent*

In the FTIR spectra of 3A zeolite (Fig. S4, supplementary data), the absorption band 400–1200 $cm^{-1}$ is related to the aluminosilicate that associated with Si—O—Al and Si—O—Si stretching and bending. The signals 1500–1700 $cm^{-1}$ and 3000–3800 $cm^{-1}$ could be assigned to OH groups of water molecules adsorbed on the 3A zeolite. The image of SEM (Fig. S5, supplementary data) shows the cubic structure of 3A zeolite. The pores and cavities of surface of this adsorbent indicate that 3A zeolite is capable to trap and remove RhB and MG from water samples. The possible binding of dyes on the surface of 3A Zeolite was shown in Fig. S6.

### *3.2. Effect of Factors in Adsorption of RhB and MG*

#### *3.2.1. Effect of pH*

The initial pH of solution affects the adsorption capacity. To study the effect of initial pH of solution on the removal of dyes, experiments were done at varying of pH ranging from 3 to 9. pH of each solution was adjusted with help of NaOH and HCl solutions (0.1 mol/L). According to the results, the best adsorptions of dyes were obtained in basic pH. At low pH values, due to formation of positive charge on the surface of adsorbent and protonation of dyes little electrostatic interaction occurs between 3A zeolite and dyes. The results based on S/N and Mean are shown in Fig. 1.

#### *3.2.2. Effect of Adsorbent Dosage*

In order to study the effect of adsorbent dose on RhB and MG adsorption, experiments were designed with 4 levels of adsorbent from 0.250 to 1.000 g and 0.050 to 0.125 g, respectively. The results showed that the

**Table 3**
ANOVA results for adsorption of RhB and MG by 3A zeolite.

| Dye | Factor | DOF (f) | Sum of squares (S) | Variance (V) | F. Ratio (F) | Pure sum (S′) | Percent (P%) |
|---|---|---|---|---|---|---|---|
| Rhodamine B | A | 3 | 132.664 | 44.221 | 17.079 | 124.879 | 3.509 |
| | B | 3 | 178.771 | 59.59 | 23.015 | 171.003 | 4.840 |
| | C | 3 | 3194.009 | 1016.669 | 411.2 | 3186.241 | 89.525 |
| | D | 3 | 45.807 | 15.269 | 5.897 | 38.039 | 1.068 |
| | Error | 3 | 7.766 | 2.588 | – | – | 1.094 |
| | Total | 15 | 3559.019 | – | – | – | 100 |
| Malachite green | A | 3 | 10.987 | 3.662 | 158.999 | 10.918 | 47.715 |
| | B | 3 | 7.129 | 2.376 | 103.169 | 7.06 | 30.584 |
| | C | 3 | 1.553 | 0.517 | 22.476 | 1.484 | 6.485 |
| | D | 3 | 3.143 | 1.047 | 45.483 | 3.073 | 13.433 |
| | Error | 3 | 0.068 | 0.022 | – | – | 1.513 |
| | Total | 15 | 22.881 | – | – | – | 100 |