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Optimization of Adsorption of Textile Dye onto Diatomite

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Authors' contributions

This work was carried out in collaboration between both authors. Author OD designed the study, wrote the protocol and the first draft of the manuscript. Author CY preformed the lab experiments and statistical analysis, managed the literature search. Both authors read and approved the final manuscript.

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ABSTRACT

Various experimental design methods are widely used in various fields including science, social and educational sciences. The use of orthogonal arrays in fractional factorial designs are efficient. For this purpose, in this study, the adsorption performance of diatomite for Maxilon Yellow 4GL as a model basic dye from aqueous solution was optimized using Taguchi experimental design methodology. L_{27} (3^4) orthogonal array was used to optimize the dye adsorption by the diatomite. The selected factors and their levels were dye concentration, dosage of adsorbent, solution pH, and temperature. The predicted dye adsorption capacity for diatomite from Taguchi design was obtained as 0.084 mmol g^{-1} under optimized adsorption conditions. The diatomite (D), Maxilon Yellow 4GL (MY) and Maxilon Yellow 4GL adsorbed diatomite (MY-D) were characterized by SEM, FTIR-ATR, TGA and BET surface area analysis.

Keywords: Optimization; adsorption; dye; diatomite; characterization.

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1. INTRODUCTION

Industrial waste dyestuffs are one of the most hazardous chemical compounds found in waste water. These materials can cause very serious health problems in living organisms [1-3]. Therefore, it is very important to remove dyestuffs from waste water before mixed up with clean water sources [4]. Maxilon Yellow 4GL (MY) is a heterocyclic aromatic chemical compound with the chemical formula $C_{15}H_{19}N_3SO_4$. (MY) is used to some products in textile industries.

A diatomite is a silica sedimentary rock formed in the form of an amorphous silica containing a small amount of microcrystalline material in its structure. Diatomite has its own characteristics in terms of its physical and chemical properties such as high permeability, large surface area, small particle size, low thermal conductivity and high porosity [5,6].

Many methods and processes have been developed to remove color from waste water containing dye. These methods and processes may involve biological [7], physio-chemical [8], membrane filtration [9], ozonation [10] and advanced oxidation [11] and integrated treatment processes [12]. However, industrial applications of these processes are not very economical [13]. Adsorption is an alternative process in terms of simplicity, applicability and economics according to the processes and methods mentioned above [14].

Experimental designs are usually applied to reduce the number of experiments, time and cost of research. Taguchi, one of these is a simple and efficient method used in the optimization of the experiments [15]. The experiments in the Taguchi design are planned according to the orthogonal array technique. The use of orthogonal arrays can predict the effect of multiple process factors on the performance characteristics, while at the same time reducing the number of experiments [16,17].

The purpose of this study was to optimize the adsorption performance of diatomite for Maxilon Yellow 4GL (MY) as a model basic dye from aqueous system using Taguchi design. In addition, the diatomite (D), Maxilon Yellow 4GL (MY) and Maxilon Yellow 4GL adsorbed diatomite (MY-D) were characterized by SEM, FTIR-ATR, TGA and BET surface area analysis.

2. MATERIALS AND METHODS

2.1 Materials

In this research, sample of diatomite was obtained from the Aegean Region of Turkey and some analyses were performed for its characterization. The specific surface area of diatomite was measured by BET N_2 adsorption by Micromeritics FlowSorb II-2300 equipment. The BET surface and pore volumes were calculated from the N_2 adsorption isotherms. The morphologies of diatomite samples were observed in scanning electron microscopy (SEM) of Hitachi. Fourier transform infrared (FT-IR) spectra were recorded on a Perkin Elmer FTIR spectrometer using ATR device. The Thermo-Gravimetric (TG) analysis was obtained simultaneously using a Perkin Elmer instrument. Maxilon Yellow 4GL (MY) was purchased from a textile company in Bursa, Turkey. The molecular structure of the MY is shown in Fig. 1. All the chemicals were of analytical grade and were used without any further purification. The elemental analyses of diatomite and catalase used in this work are shown in Table 1. Results containing some physicochemical properties of diatomite were given in Table 2.

Table 1. Elemental composition of diatomite

Constituent	Percentage present (%)
Si	48.40
O	36.80
Al	9.90
Mg	1.40
Fe	2.20
K	0.70
Ca	0.60

Table 2. Some physicochemical properties of diatomite used in this study

Particle size	0 - 105 µm
Colour	White
pH	7.60
Specific surface area (Single point)	170.2 $m^2 g^{-1}$
Total pore volume	0.611 cc g^{-1}

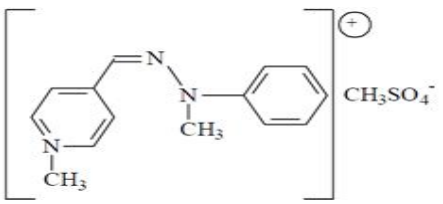

Fig. 1. The molecular structure of MY

2.2 Experimental Procedure

Adsorption and kinetic experiments were carried out using mechanic stirrer. The model kinetic experiment was carried out by agitating 1000 mL of MY solution of initial concentration $1.0x10^{-4}$ M at a constant agitation speed of 150 rpm, pH 9 and 298 K. The adsorption experiments were carried out for 60 minutes with a time sufficient to reach the equilibrium at a fixed agitation speed of 150 rpm. In the optimization experiments of dye adsorption onto diatomite, the initial concentration of MY solution was 1.0, 2.0 and $3.0x10^{-4}$ M, diatomite dosage was selected as 0.1, 0.55, and 1.0 g. The effect of pH on adsorption was analyzed in the pH range from 3.0 to 9.0. The adsorption temperature were carried out at 298, 313, and 328 K in a constant temperature bath. Samples of four milliliter were drawn at suitable time intervals. The samples were then centrifuged for 15 min. at 3.000 rpm and the left out concentration in the supernatant solution was analyzed using UV-Vis spectrophotometer by monitoring the absorbance changes at a wave length of maximum absorbance (about 410 nm). The adsorbed amount of MY at any time t, q_t, was calculated from the mass balance (Eq. (1)) [18].

$$q_t = \frac{(C_0 - C_t)}{m} \mathrm{xV} \quad (1)$$

where C_o and C_t (mol L^{-1}) are the initial and liquid- phase concentrations of MY solution at any time t (min), respectively; q_t (mmol g^{-1}) is the amount of MY adsorbed per unit mass of diatomite at time t (min), V is the volume of the adsorption (L), and m is the mass of the diatomite in the solution (g).

2.3 Experimental Design

Design of Taguchi (L_{27} (3^4) orthogonal array) was used to optimize the dye adsorption onto diatomite. Four factor and their three levels were selected for each of the factors to be low, medium and high. The selected four factors and their three levels were given in Table 3. According to the Taguchi experimental design, Minitab (Minitab Inc., USA) was used to optimize the experimental factors.

3. RESULTS AND DISCUSSION

3.1 Effect of Contact and Equilibrium Times

The adsorption of MY onto diatomite at different initial concentrations and stirring speed of 150 rpm was studied as a function of contact time in order to determine the equilibrium time. Measuring the concentration of MY in solution at different incubation times generated in a time course of the adsorption. Fig. 2. shows the plot of amount of MY adsorbed vs. time. According to Fig. 1, the time required to reach a stationary concentration is about 1 h.

3.2 Optimization of Adsorption System

The optimization of dye adsorption for the diatomite was performed using Taguchi experimental design. Taguchi $L_{27}(3^4)$ orthogonal array design containing the selected factors and their levels for this adsorption study is presented in Table 4. Taguchi design employs a generic signal-to-noise (SN) ratio as a quantitative measure for determining the optimum adsorption conditions. There are primarily three categories of SN ratios, namely, “smaller-is-better,” “larger is-better,” and “nominal-is-best.” The selection principle of SN ratio depends on the goal of study. In order to maximize the adsorption of dye, the “larger-is-better” approach was adopted, in which the SN ratio was calculated by the following equation [19]:

$$S/N = -10Log\left[\frac{1}{n}\sum_{i=1}^{n}\frac{1}{y_i^2}\right] \quad (2)$$

where n is the number of experiments and y_i is the value of dye adsorption capacity of each experiment. Based on the approach employed, the level of factor maximizing the SN ratio is optimal condition for the dye removal.

Table 3. The selected factors and their levels for Taguchi experimental design

Factors	Levels		
	-1 (Low)	0 (Medium)	1 (High)
Concentration of MY	$1.0x10^{-5}$ M	$5.5x10^{-5}$ M	$1.0x10^{-4}$ M
Adsorbent dosage	0.1 g	0.55 g	1.0 g
pH	3.0	6.0	9.0
Temperature	298 K	313 K	328 K

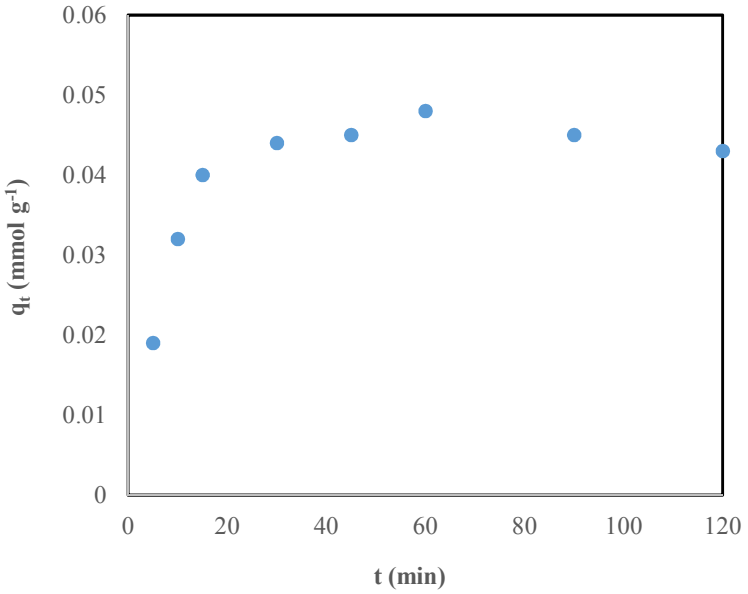

Fig. 2. Effect of time on adsorption of MY by diatomite (Experimental conditions: C_0:1x10^{-4} M, pH 9, 298 K)

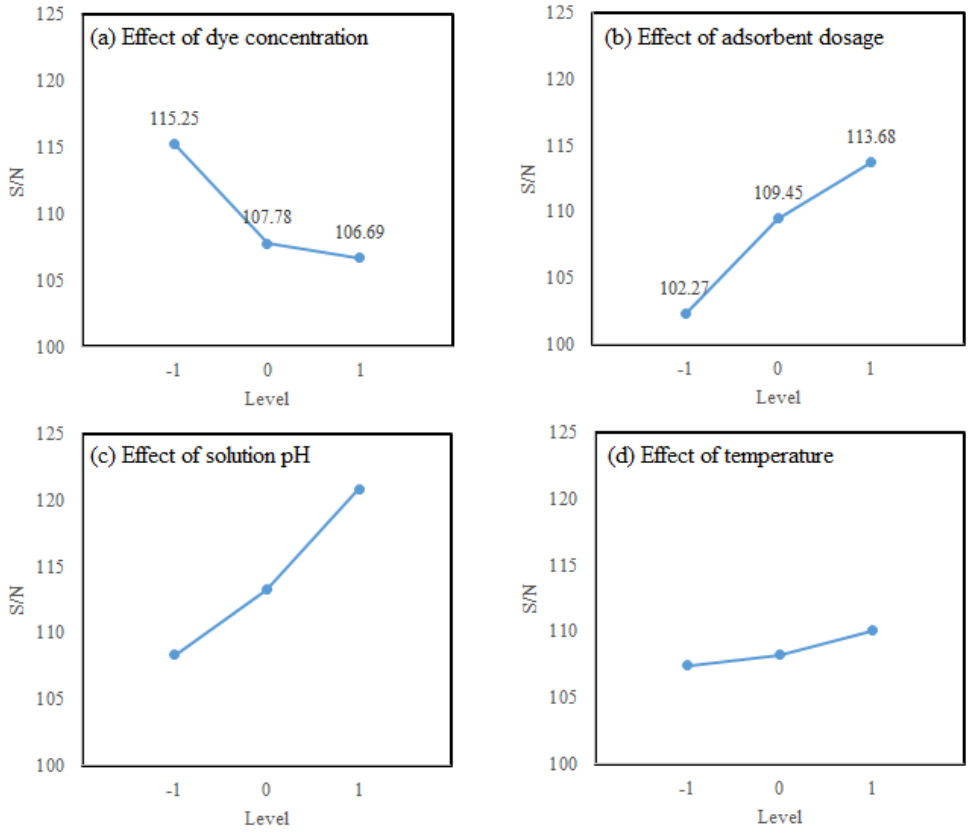

Fig. 3. Effect of each factor studied on adsorption of dye

Table 4. Taguchi L_{27} orthogonal array design

Exp. no:	Concentration of MY	Adsorbent dosage	pH	Temperature	q_t (mol/g)	S/N
1	-1	-1	-1	-1	$4.3x10^{-6}$	107.33
2	-1	-1	-1	-1	$3.55x10^{-6}$	108.99
3	-1	-1	-1	-1	$3.75x10^{-6}$	108.52
4	-1	0	0	0	$1.57x10^{-6}$	116.08
5	-1	0	0	0	$1.63x10^{-6}$	115.76
6	-1	0	0	0	$1.6x10^{-6}$	115.92
7	**-1**	**+1**	**+1**	**+1**	$8.4x10^{-5}$	**121.51**
8	-1	+1	+1	+1	$8.65x10^{-5}$	**121.26**
9	-1	+1	+1	+1	$8.3x10^{-5}$	**121.62**
10	0	-1	0	+1	$5.1x10^{-6}$	105.85
11	0	-1	0	+1	$9.3x10^{-6}$	100.63
12	0	-1	0	+1	$8.25x10^{-6}$	101.67
13	0	0	+1	-1	$4.72x10^{-6}$	106.52
14	0	0	+1	-1	$4.68x10^{-6}$	106.59
15	0	0	+1	-1	$4.74x10^{-6}$	106.48
16	0	+1	-1	0	$2.33x10^{-6}$	112.65
17	0	+1	-1	0	$2.42x10^{-6}$	112.32
18	0	+1	-1	0	$4.19x10^{-6}$	107.56
19	+1	-1	+1	0	$1.26x10^{-5}$	97.99
20	+1	-1	+1	0	$1.23x10^{-5}$	98.20
21	+1	-1	+1	0	$1.31x10^{-5}$	97.65
22	+1	0	-1	+1	$5.16x10^{-6}$	105.75
23	+1	0	-1	+1	$5.24x10^{-6}$	105.61
24	+1	0	-1	+1	$4.81x10^{-6}$	106.36
25	+1	+1	0	-1	$4.51x10^{-6}$	106.92
26	+1	+1	0	-1	$4.56x10^{-6}$	108.82
27	+1	+1	0	-1	$4.56x10^{-6}$	106.82

The dye adsorption capacity as mean response and the value of SN ratio obtained for each experiment are given in Table 4. According to the data presented in Table 3, the optimum dye adsorption conditions based on the approach adopted were obtained as the dye concentration of $1.0x10^{-5}$ M, adsorbent dosage of 1.0 g, pH 9.0, and temperature of 328 K for 120 min. The test of confirmation is a crucial final step of Taguchi experimental design. As can be seen in Table 4, the predicted dye adsorption capacity for diatomite from Taguchi design was obtained as about 0.084 mmol g^{-1} under optimized adsorption conditions. Its purpose is to verify that the optimum adsorption conditions are suggested by the experimental design. Thus, Taguchi experimental design provided reasonable predictive performance of dye adsorption [20].

3.3 Effect of Each Factor Studied on Adsorption of Dye

The dye adsorption capacity as mean response and the value of SN ratio obtained for each experiment are given in Table 4. Besides, Table 4 and Fig. 3 show the adsorption efficiencies and SN ratio values of all the levels of factors studied and the effect of each factor on the adsorption, respectively. Fig. 3(a) displays that the adsorption capacity of diatomite increased with increase in the initial dye concentration. This may be due to the high driving force for mass transfer at a high initial dye concentration. In addition, if the dye concentration in solution is higher, the active sites of adsorbent are surrounded by much more dye molecules and the adsorption occurs more efficiently [21]. The effect of dosage of the adsorbents on the adsorption was shown in Fig. 3(b). From the figure, it was observed that the removal of the dye increases with increasing the adsorbent doses from 0.1 g to 1.0 g. The increase in the dye removal with increase in adsorbent dose is due to the greater availability of the exchangeable sites or surface area at higher concentration of the adsorbent [21]. The adsorption capacity and SN ratio of diatomite increased with increase in solution pH as shown in Fig. 3(c). The amount of dye removed increases as pH increase from 3 – 9 and increased to maximum at pH 9. This can be explained by the electrostatic attraction between the positively charged MY and the negatively charged surface of diatomite. At the same time, the charge neutralization occurs at the surface of diatomite which leads to the increased adsorption of MY dye molecules at elevated pH [22]. In addition, at low pH, the diatomite surface sites are closely linked to the H^+ ions, thereby making these unavailable for other cations. However, with an increase in pH, there is an increase in dyes with negative charges which results in increase binding of cations [22,23]. The amounts of MY adsorbed on the diatomite as function of solution temperature are shown in Fig. 3(d). The figure indicates that the increase in solution temperature increases the adsorbed quantities of MY. Temperature presents a notable effect on the adsorption process because it affects the diffusion of dye molecules at dye-external boundary layer interface, and also inside the adsorbent pores [21-23]. The results show that adsorption is an endothermic process.

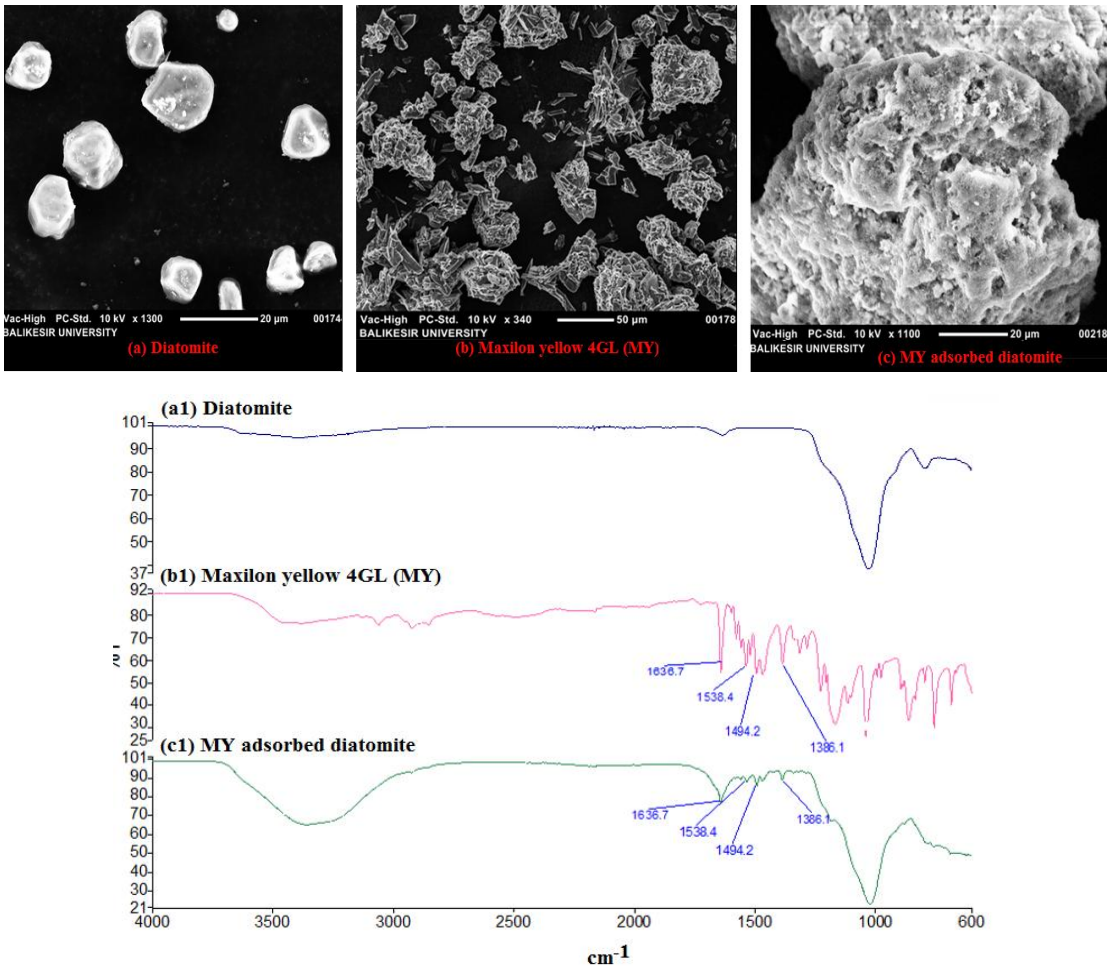

Fig. 4. SEM microphotographs and FTIR spectra of (a, a1) diatomite, (b, b1) MY and (c, c1) MY adsorbed diatomite after 60 min

3.4 Analysis of Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscope (SEM) Images

From the derived FTIR spectra of representative samples (Fig. 4a_1, b_1, and c_1), we inferred the following results:

- As seen in Fig. 4(a_1), spectrum of diatomite, the broad band, near 3450 cm^{-1}, is due to H-O-H vibration of absorbed water. The band at ~1635 cm^{-1} is due to OH bending vibrations of adsorbed water in sheet silicate minerals. The ~ 1038 cm^{-1} band arises from the Si-O-Si vibration. The ~792 cm^{-1} band occurs because of the OH translational vibration [24]
- From Fig. 4(b_1), FTIR spectrum result of Maxilon Yellow 4GL (MY) showed strong peaks at $\nu = 1620–1680$ cm^{-1}, $\nu = 1480–1580$ cm^{-1}, and $\nu = 1225–1300$ cm^{-1} mainly associated with C=O stretching, N–H bending vibration and C–N stretching vibration bands, respectively [25,26].
- As shown in Fig. 4(c_1), FTIR spectrum obtained for MY adsorbed on diatomite show the peaks of the stretching and vibration bands at about 1636, 1538, 1494, and 1386 cm^{-1}, which are typical of MY.
- As can be seen clearly in Figs. 4(a-c), the surface of diatomite, MY and MY adsorbed diatomite show time-dependent morphological changes. According to the figure, surface morphology of the MY adsorbed diatomite changed completely after 120 min. It can be concluded that the images are consistent with experimental data and FTIR spectra.

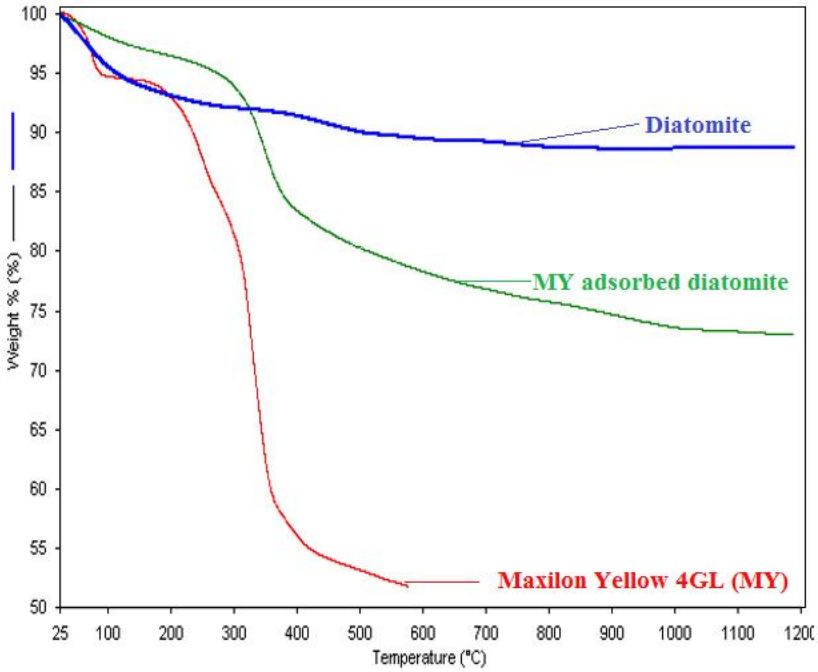

Fig. 5. Thermal gravimetric analyses of samples

3.5 Thermal Gravimetric Analysis (TGA)

As seen in Fig. 5, the thermal gravimetric analysis (TGA) of diatomite, MY and MY adsorbed diatomite were measured by thermal gravimetric analyser. From the TGA curves of a representative sample (Fig. 5), we conclude that:

- In the temperature range from 25°C to 105°C, the weight loss due to absorbed water is 6.7% for diatomite, 7.5% for MY and 4.0% for MY adsorbed diatomite.
- As shown in Fig. 5, the second dehydration step observed in the temperature range 105-300°C, corresponds to the release of water molecules, which were in the interlayer space of sample [19]. In addition, samples loose the crystalline water at the same range of temperatures.
- In the temperature range from 400°C to 500°C, the rapid weight loss is documented by the steep slope of the TGA curve of diatomite. This is attributed to the dehydroxylation of the diatomite, (due to the loss of OH groups, surrounding the Al^{VI} atoms) and the progressive transformation from the octahedral coordinated Al, in diatomite, to a tetrahedral coordinated form through the breaking of OH bonds [19].
- It can be observed from the profiles of the TGA curves, both MY and MY adsorbed diatomite are practically similar. As illustrated in Fig.5 curves, there are two weight loss stages at room temperature −200°C and 200 – 500°C, respectively. For the MY and MY adsorbed diatomite, the first stage is attributed to the structural water; the second stage is assigned to the decomposition of MY.

4. CONCLUSIONS

The present study shows that diatomite can be used as an adsorbent for the MY from its aqueous solutions. The amount of dye uptake was found to increase with increase in contact time, initial dye concentration, pH and temperature. According to the experimental results, the dye adsorption performance for the diatomite was successfully optimized using Taguchi experimental design model. The predicted dye adsorption capacity for diatomite from Taguchi design was obtained as 0.084 mmol g^{-1} under optimized adsorption conditions. Consequently, experimental data obtained from this investigation reveal that physical adsorption is suitable for the attachment of dye into diatomite as support. Diatomite has a high potential to adsorb these dye from aqueous solutions. Therefore, it can be effectively used as an adsorbent for the adsorption of this dye.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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