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Adsorption of Basic Organic Colorants from an Aqua Binary Mixture by Diatomite

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ABSTRACT

Diatomite is an inexpensive natural mineral. It can be used as an adsorbent to remove organic and inorganic pollutants from the waste waters without further improvement. In this research, the adsorption of two different basic colorants including Basic Yellow 28 (BY28) and Malachite Green (MG) by diatomite has been investigated in an aqua binary mixture and the effects of different parameters has been examined. L_{27} matrix of Taguchi method was used to optimize the number of experiments. five parameters in three levels (low, medium, and high) were selected. These parameters were colorants concentration (two parameters), pH, time, and adsorbent concentration. Mixing speeds and temperature maintained a fixed value. The responses were the removal percentages of each colorant, separately. The results showed that each colorant concentration affects on the adsorption of other colorant and this process is sensitive to pH. In addition, the effects of adsorbent amount and time were as same as pH. Prog. Color Colorants Coat. 3(2010), 41-46. © Institute for Color Science and Technology.

1. Introduction

Dyes and pigments have been applied in many industries to color their products. This is the inevitable reason for existence dyes and pigments in industrial wastewater. Colored wastewaters, especially organic dyes, are by products of different industries, such as textile, food, leather, paper, minerals and plastic [1]. Treatment of water and wastewater, contaminated with colorants, are one of the main concerns of researchers in recent decades.

Various physicochemical decolorization processes comprising electrochemical, biological, membrane

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separation, photo-catalysis, coagulation, and ozonation treatment methods have been developed to remove pollutants from the industrial wastewater in recent years. But most of these methods are expensive and certain economical infrastructure is necessary. Among the physicochemical processes, adsorption technology has been found a wide application range in water and wastewater treatment, as one of the efficient and effective technologies [2,3]. Therefore, natural adsorbents such as orange skin, almond skin, sawdust, zeolite, clay and diatomite have been used to reduce the costs and the environmental effects.

In a real wastewater, there is a complex of different materials, such as colorants, polyacrylates, phosphonates, anti-coagulation factors, and so on. Most of these compounds are poisoning and must be completely removed from the treated wastewater and it is necessary for ecological balances. Hence, the governments and the United Nations have recently established many rules to prevent and standardize these materials in environment [3, 4]. Furthermore, it is very important to identify the effect of different parameters on the removal process.

However, the number of experiments and costs are being increased with increasing the number of parameters and it means more time and cost. These cause that reduction of the experiments are being one of important aims of any researchers. To achieve this aim, an experimental design method should be applied. The experimental design method is a regular, systematic and useful method for analysis and optimization in order to facilitate the manufacturing steps and enhancement of confidential level and system performance. These methods can improve product development and related activities and solve many problems significantly [5].

Basis of the modern statistical methods and design processes were sustained by Fisher in 1920 [6, 7]. Kiefer and Wolfwitz started a mathematical theory about the experimental design methods in 1960, but the first applicable algorithm has been established for optimization design in 1970 [8, 9]. At the same time, Taguchi mixed experimental design methods with products and industrial processes in many Japanese companies [8]. Taguchi method is the result and consequence of industrial condition after World War II period in Japan [9, 10].

In this paper, removal of the colorants has been investigated from the simulated textile wastewaters by diatomite. Binary mixtures of Basic Yellow 28 (BY28) and Malachite Green (MG) dyes have been prepared for these artificial aqueous systems. Taguchi experimental design method has been used to optimize the number of experiments. The L_{27} table was chosen for the optimization experiments. Design Expert 7 software was selected to arrange L_{27} table and analyzed responses of the experiments to find the optimized points.

1.1. Diatomite

Diatomite is a sedimentary rock with a light grey color, light weight and fragile that is formed from gathering of silicon skin of tropical plants, called diatom (Figure 1). Each diatom is a protoplasm particle that has located between two silicon pans. Silicon skins of dead diatom would cause diatomite storage with their gathering. Diatomite storage has been formed from milliards silicon skins. Each 1 cm^3 diatomite segment has been formed from three million diatom skins, for instance.

Figure 2 illustrates the SEM image of surface of tested diatomite. This figure explains why its specific gravity is low and can be used as a suitable adsorbent. It is clear that existence of a large amount of pores inside the skeleton of diatom would reduce specific gravity (600 kg/m^3) and its weight. This porous structure would justify its capacity as an adsorbent [11].

This abundant and inexpensive natural mineral is used as an adsorbent for hazardous chemicals and helps to store and refine strong acids. Large storages of diatomite soil have been found in Middle East [1]. Diatomite has unique physical and chemical properties that made it a special medium as organic pollutants adsorbent and filter [12]. Its high permeability introduces diatomite as an appropriate substitution for expensive and costly adsorbents, such as activated carbon [1].

Figure 1: Photo of diatom [11].

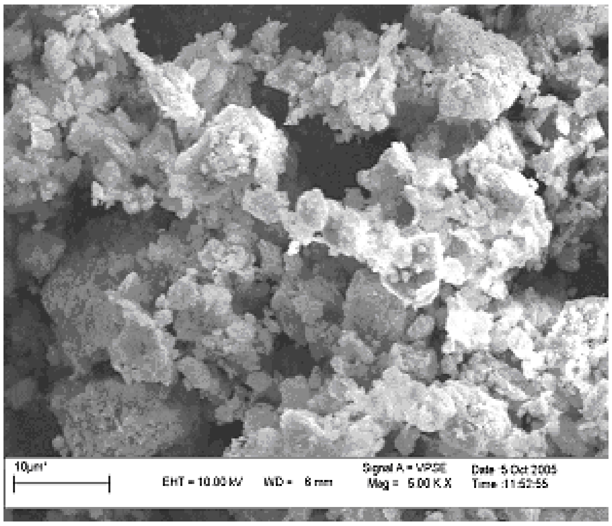

Figure 2: SEM image of diatomite surface.

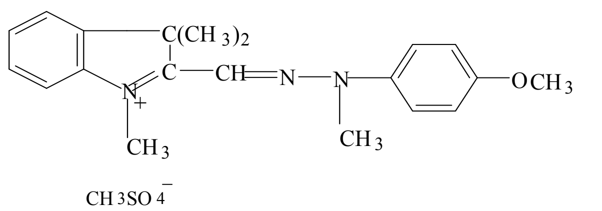

Figure 3: Molecular structure of Basic Yellow 28 colorant [14].

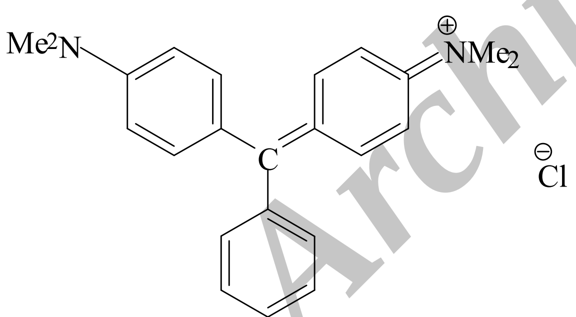

Figure 4: Molecular structure of Malachite Green (Basic Green 4) colorant [14].

2. Experimental

Diatomite was supplied from internal sources (Tabriz, Iran). Raw diatomite was washed to be completely neutralized several times by distilled water. The neutralized sample was then filtered, dried in 40°C and packed for further use. Chemical and physical specifications of diatomite have been presented in the authors earlier paper [13]. Basic Yellow 28 (BY28) and Malachite Green (MG) or Basic Green 4 (BG4) dyes supplied from Ciba company. Figures 3 and 4 show their molecular structures, respectively. Tables 1 and 2 present the specifications of these colorants.

A balance model (Sartorius-d=0.1 mg, max 120g) was used to weight samples. Jar test system (FC6S-VELP) was used to mix 6 samples simultaneously; UV/Visible spectrometer (One beam, Cecil-CE2021-2000 series) was applied to measure the changes of dye concentrations. A Hettich EBA20, 6000 rpm centrifugal system was used to remove colloidal particles, and pH meter (Hach series) was used to measure and adjust solution pH. SEM (Scan Electron Microscope) was applied to increase knowledge and improve insight into diatomite microscopic structure and real nature (Figure 2). Other chemicals, such as sodium hydroxide and chloridric acid, were supplied from Merck Company.

Usually, the number of experiments is high and they need high cost and the experiments take long time. Due to many different factors involved in the project, so performance of the experiments will change to a regular plan by experimental design methods which have been developed to accelerate and adjust the achieved data, reduce necessary tests number and also optimize test sets. Experimental design methods are involved in a number of experiments that their input factors would be changed consciously. These selected experiments can help to find more effective factors from outlet responses [15]. At the first step, all involved factors should be found. Different studies have shown that pH, amount of adsorbent, contact time, dyes concentration, temperature, mixer speed, and specific surface of adsorbent are effective on adsorption process [9, 13].

Table 1: specifications of Basic Yellow 28 [14].

Synonym	Maxilon Golden Yellow GL
Color index number	48054
Molecular formula	$C_{21}H_{27}N_3O_5S$
Molecular weight	433.52
λ_{max}	437 nm

Table 2: specifications of Basic Green 4 [14].

Synonym	Malachite Green
Color index number	42000
Molecular formula	$C_{36}H_{29}Cl_2N_5O_6$
Molecular weight	698.55
λ_{max}	619.5 nm

The temperature was adjusted to lab temperature (20ºC), and the adsorbent was homogeneous and its specific surface was constant. Furthermore, the mixing velocity was too high and bulk mass transfer resistant was negligible. The effective factors and their variation range have been then identified by changing different levels, based on the previous experiences and adsorption process theory [3, 15].

we found that there were five important factors including colorants concentration (two colorants, two factors), pH, amount of adsorbent and time. With respect to these factors and three levels for each factor, the L_{27} orthogonal array of the Taguchi method was chosen (Table 3). This table has 13 columns indeed that the last two columns were used for concentration responses of the colorants to adsorption process; however, seven columns have been presented in Table 1. These columns are important for present research and the others (did not given here) are associated with the interaction between other columns and errors. It means that the number of experiments reduced from 5^3=125 to 27. In addition, this method decreased the time, cost and probability of human and instruments errors. Table 4 shows the levels of each factor. Results were analyzed by Design Expert software, version 7 (DX7).

Table 3: L_{27} orthogonal array of Taguchi method.

No.	Factors					Responses: Removal %	
	MG	BY28	pH	Time	Diatomite	MG	BY28
1	1	1	1	1	1	37.7	36.5
2	1	1	2	2	2	87.0	88.1
3	1	1	3	3	3	78.0	84.3
4	1	2	1	2	3	92.9	93.3
5	1	2	2	3	1	68.2	41.2
6	1	2	3	1	2	83.2	85.5
7	1	3	1	3	2	52.3	58.3
8	1	3	2	1	3	85.8	92.1
9	1	3	3	2	1	50.0	18.4
10	2	1	1	2	3	94.9	89.3
11	2	1	2	3	1	66.7	33.9
12	2	1	3	1	2	81.9	83.8
13	2	2	1	3	2	77.2	34.8
14	2	2	2	1	3	94.2	94.4
15	2	2	3	2	1	20.1	51.4
16	2	3	1	1	1	11.3	11.6
17	2	3	2	2	2	74.7	68.4
18	2	3	3	3	3	91.1	90.6
19	3	1	1	3	2	64.1	70.5
20	3	1	2	1	3	87.0	84.3
21	3	1	3	2	1	57.8	21.6
22	3	2	1	1	1	11.6	17.4
23	3	2	2	2	2	53.4	59.8
24	3	2	3	3	3	96.1	93.4
25	3	3	1	2	3	58.2	68.0
26	3	3	2	3	1	57.0	16.5
27	3	3	3	1	2	54.1	45.9

Table 4: Levels of each factor.

Factor	1	2	3
MG, mg/l	6	12	18
BY28, mg/l	18	24	36
pH	4	6	8
Time, min	30	60	90
Diatomite, g/ (4 ml solution)	0.001	0.004	0.008

Amount of adsorbed colorant was measured from the differences between initial and equilibrium concentrations of solution and reported as percentages (Eq 1). It should be mentioned that the final solution was centrifuged at 4000 rpm for 7 minutes at the first step and 5 minutes at the second step to remove colloidal particles and avoid any error in the spectrometer measurements.

$$\%R = \frac{C_o - C_e}{C_e} \times 100 \qquad (1)$$

where, C_0 and C_e are the initial and equilibrium concentrations of simulated wastewater, respectively, and $\%R$ denotes percentage of dye removal.

3. Results and discussion

Specifications of experiments and their results have been presented in Tables 3 and 4. The responses in Table 3 illustrate that the 24^{th} experiment is the best result without attention to any further test. It means that the best result is for 18 mg/l MG (third level of first dye concentration), 24 mg/l BY28 (second level of second dye concentration), pH equal to 8 (third level of pH), 90 min (third level of adsorption time), and 0.008g diatomite / (4 ml solution) (third level amount of adsorbent).

Furthermore, the effect of MG on adsorption of BY28 is clear, and vice versa, but it is really difficult to discuss and explain the trend of interaction of dyes on adsorption process with this little amount of tests. The experiments are not complete and these data is not enough to establish any formal relation between MG and BY24, so that there are more tests that should be done. It means that discussion about the binary effect of these dyes in mixture needs more experiments, times and expenses without any technical support.

Therefore, data given in Tables 3 and 4 was loaded in Design Expert 7 software to find necessary technical support. Then, the software was executed to solve this problem. Figures 5 and 6 show the results of data analysis and interaction between colorants and also between colorant and pH by Taguchi part of DX7 software, respectively.

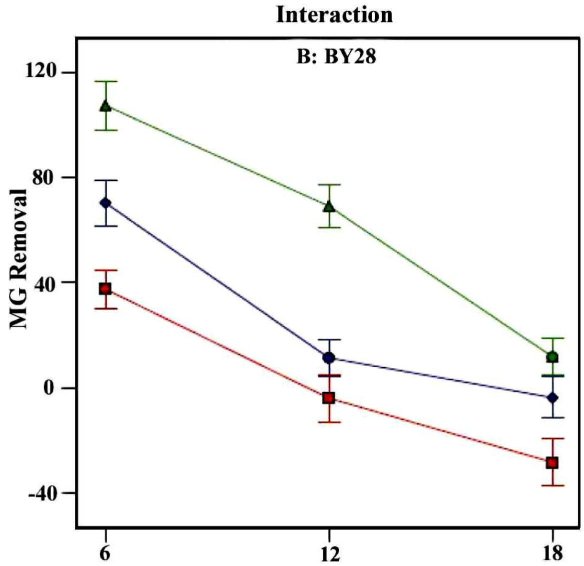

Figure 5: Effect of BY28 colorant concentration on MG removal percentage for pH, time and amount of adsorbent equal to 4, 30 min and 0.001 g/(4 ml of solution), respectively; ■ 18 mg/l, ▲ 24 mg/l, and ◆ 36 mg/l.

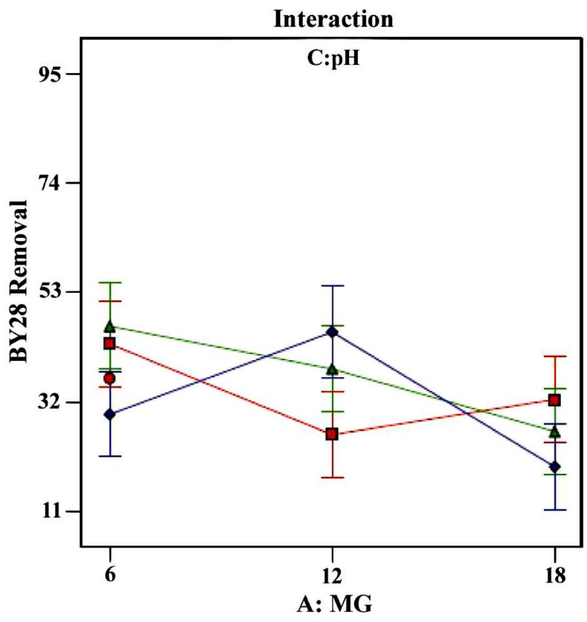

Figure 6: Effect of pH and MG concentration on BY28 removal percentage for BY28 initial concentration, time and amount of adsorbent equal to 18 mg/l, 30 min and 0.001 g/(4 ml of solution), respectively; ■ pH=4, ▲ pH=6, and ◆ pH=8.

Although not presented here, other parameters such as adsorbent amount and time show same effect as that of pH. It is clear that there is an interaction between concentrations of colorants. An increase in the concentration of BY28 increased the removal of MG (from 18 to 24 mg/l). After that, it decreased with growth of concentration (from 24 to 36 mg/l). It means that the mechanism of adsorption was changed by increasing BY28 concentration.

DX7 Software optimized the level of selected factors to maximize the colorants removal percentages. Thus, pH=8 (third level of pH), 0.004 g diatomite / (4 ml of solution) (second level of adsorbent amount) and 60 min (second level of adsorption time) are optimized levels. In this situation, optimized concentration of MG and BY28 were 12 (second level of first dye concentration) and 24 mg/l (second level of second dye concentration), respectively.

Hence, results of this research show that in a binary mixture of colorants, there is an interaction between concentrations of each colorant and this interaction can control the removal process. The results present that mechanism of removal depends upon concentration of each colorant and removal percentage would change with concentration of other colorant. It initially increases by concentration of the second colorant and then decreases.

4. Conclusions

Taguchi Method with technical support of DX7 software is a good tool for analysis of experimental data and distinguishes important and effective parameters. This technique has been applied in this research to investigate the binary interaction of colorants on adsorption process to remove them from simulated waste water. The results illustrated that there is a punctual effect on process in these binary mixture.

In addition, results of Taguchi Method showed that pH, adsorbent amount and time have meaningful effects on the adsorption process in a binary system and there is an optimum situation.

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