



Dye Removing from Industrial Wastewater by Advanced Oxidation Process

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ABSTRACT: The use of TiO₂ and Zeolite-Y as photo catalytic systems was investigated for adsorption and removal of methylene blue from aqueous solutions. As first step, the effect of pH, time and initial concentrations of methylene blue were studied in absence of ultra violet irradiation. Langmuir and freundlich isotherms, first and second order kinetics were used to describe the adsorption process which occurred in absence of UV irradiation. Langmuir isotherm and second order kinetics found to best describe the process. Adsorption was best done at pH=8 for both catalysts and the process were completed in first 30 minutes to reach the equilibrium concentration. Maximum amount of methylene blue which can deposit on the surface of catalyst was found to be 294.11 mg/g and 156.25 mg/g for TiO₂ and Zeolite-Y, respectively. Also the results showed that aeration of solutions had reverse effect on adsorption.

Ultraviolet irradiation started just after reaching to equilibrium in adsorption process. This led the photo catalytic process to begin immediately and reach the equilibrium in 60 minutes. All experiments were repeated in presence of aeration. As result for pH investigation, Ph = 3 and pH = 4 were found to be best pHs for TiO₂ and Zeolite-Y, respectively. The removal of methylene blue by TiO₂ was 60% and 76%, in absence and presence of aeration, respectively. These amounts were 41% and 53% for Zeolite.

Keywords: Methylene blue color, Photo catalytic, Titanium dioxide, Zeolite-Y, Adsorption.

INTRODUCTION

After the industrial revolution, a wide range of pollutants, including aromatic pollutants, have entered the environment, some of these compounds, such as halogenated aromatic and nitro-aromatics, are as xenobiotic compounds to the environment, as a foreign agent. Synthetic dyes, especially Reactive Dyes are considered among the substances that enter the environment as a polluter of nature, along with industrial wastewater treatment plants, and cause pollution in natural ecosystems, such as soil and water, and by which organisms live. After that, man discovered the dye industry in the mid-nineteenth century to the end of the twentieth century, 10,000 of synthetic dyes, with a quantity of more than 105 × 7 Ton presented to the market, which are frequently used in various industries, such as leather, paper and textile industries. Approximately 2% of the colors produced in the manufacturing process, are released directly, and 20% said they would remain in the effluent, textile dyeing process, due to incomplete Adsorption, and the failure of the dying process, and finally, they enter the sewage outlet.

Discharge of the material in this volume, the environment, in addition to the toxic effects of mutagenesis and carcinogenesis due to its color, even in low concentrations, reduces the influence of the sun on the water, causing the loss of optical activity of the ecosystem, and low dissolved oxygen, and temperature increases. Therefore, the dye-containing wastewater, must be treated before they enter the environment.

Conventional methods for color removal from textile effluent can range from physical, chemical and biological methods. Technologies related to physical method can be named by filtration, reverse osmosis, using adsorbents, membranes and flocculation. Although these methods have the ability to physically remove the paint, at least, but first, some have the high technology costs and energy consumption, and secondly, they are transferred from one phase to another phase of infection, and the need for secondary treatment are, therefore, they are not considered as an appropriate solution. The use of chemical methods can range from chemical oxidation, electrolysis and advanced oxidation processes (AOP) (based on hydroxyl free radical formation).

Research pensions, which have been conducted on these methods, introduce advanced oxidation processes, as a convenient and efficient method for the partial or total destruction of these pollutants. Ozonation (O_3), hydrogen peroxide (H_2O_2), Fenton and heterogeneous photo catalyst can be referred to as advanced oxidation methods. Based on what is extracted from previous studies, of Fenton, O_3 and H_2O_2 , high efficiency of the bleaching process, but they show low efficiency in removing COD, and the COD of 600, which reduces the efficiency of bleaching increased sharply. The H_2O_2 , in alkaline conditions with NaOH, precipitated out of Na_2O_2 , and it causes a decrease in its concentration, and the resulting loss of efficiency. Also, in all these cases, the chemicals used in the reaction are used, and in addition to costs, the amount in excess of consumption can be raised at the end of the process, a problem.

Introduced the advanced oxidation methods, heterogeneous photo catalyst method (using nano-titanium (TiO_2)) can be introduced as a method that is having the ability to remove a variety of contaminants [5]. In addition, based on the intrinsic properties of catalysts, the material remains in the reaction without being consumed. The purpose of this study is to bleach and dye degradation in wastewater, using photo catalyst (TiO_2 / UV).

MATERIALS AND METHODS

Since, the actual sampling, continuous textile plant effluent, it was not possible, therefore, experiments were carried out on samples of known concentration, and made of solid methylene blue. Photo catalytic also has been used commercially purchased and used without further treatment.

The reactor used, in principle, is an empty one liter flask, which has been modified to perform experiments.

As can be seen in the figure, the discharge pipe, it is intended, as the samples, which were obtained by sending a flexible tube into the flask, and suction with a syringe. The walls of the flask were protected against light, as well. The mouth of the well is the introduction of the photo catalyst, and the location of the UV light source. On the opposite side of the sampling tube, a drainage tube was implanted again; we blow into the air through the solution. Sampling tube was withdrawn, while blowing air into the solution, to prevent the accumulation of air quickly, and throw out the contents of the flasks. We used a water bath on a magnetic stirrer to maintain the temperature, and mixing samples.

A. Preparation of solutions

First, we have the necessary amount of weight (1g) of methylene blue is a solid, carefully g 0.0001, and we solve it in the least possible amount of ethanol (approximately ml 50). Then, in a 1000ml volumetric flask, 1000 ml with deionized water to bring the volume to produce a concentration ppm1000, achieved. We provide our solution to, the master solution, and using the following equation, which in this case C_1 is equal to ppm1000 and V_1 is the volume of the master solution, which is required to prepare a solution with a volume V_2 and the concentration of C_2 .

$$C_1V_1 = C_2V_2 \quad (1)$$

Since the maximum wavelength (λ_{max}), considered as an indicator to determine the qualitative and quantitative measurements, so the spectrum of dye methylene blue, was scanning the water, the wavelength 200 nm to 800 nm, by a two-beam spectrophotometer. It was determined by analyzing the spectrum, the maximum wavelength of the dye methylene blue is the 660 nm, which can be seen in Fig. 1. It is, therefore, be adopted for all subsequent measurements at wavelengths 660 nm.

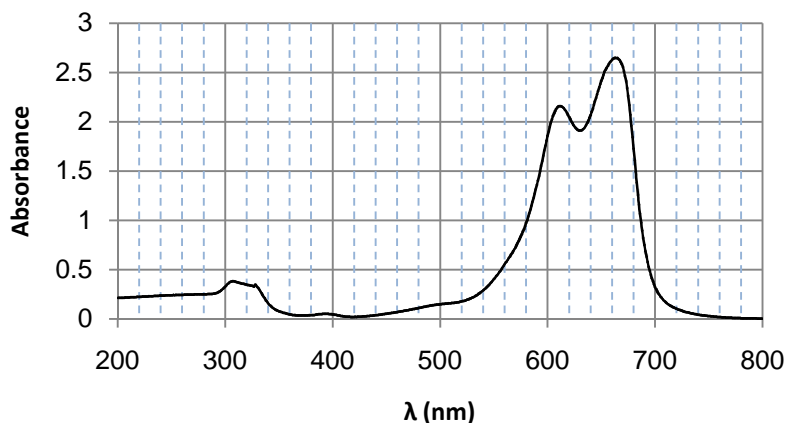


Fig. 1. Methylene blue Shkl2- absorption spectrum of water.

RESULTS AND DISCUSSION

A. Remove studies, the presence of ultraviolet radiation
 After equilibration solution photo catalyst in the dark paint, we've turned on the UV lamp, and samples taken from the solution, at different times. During this work, we must be careful to not change the temperature of the solution, so the processes were carried out in a large volume of water as a coolant. Finally, reaction was initiated with UV radiation; the effect of the presence of oxygen in the environment is studied.

The effect of ultraviolet radiation, the removal of Methylene blue, by TiO₂ and zeolite. Starting with

ultraviolet radiation, Saturation Methylene blue will start to decrease, due to the photo catalytic cycle, by TiO₂, which at the beginning of this change is rapid, and with time, it is a fixed limit. Contrary to what was observed in the surface phase Adsorption here, acidic pHs, created better conditions for the removal of Methylene blue, and remove the slope, the more the higher pHs. The results of this experiment are shown in Fig. 2 and 3. The first (left) of the graph is related to the adsorption equilibrium, and the second (right), is related to the process, from the moment of turning on the UV lamp.

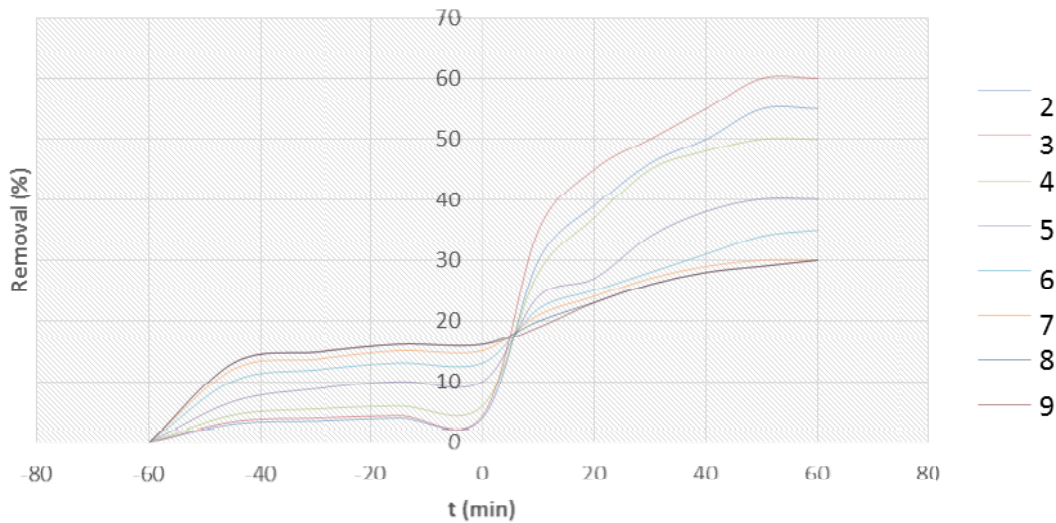


Fig. 2. Effect of ultraviolet radiation on the Elimination of Methylene blue color at different pHs by TiO₂.

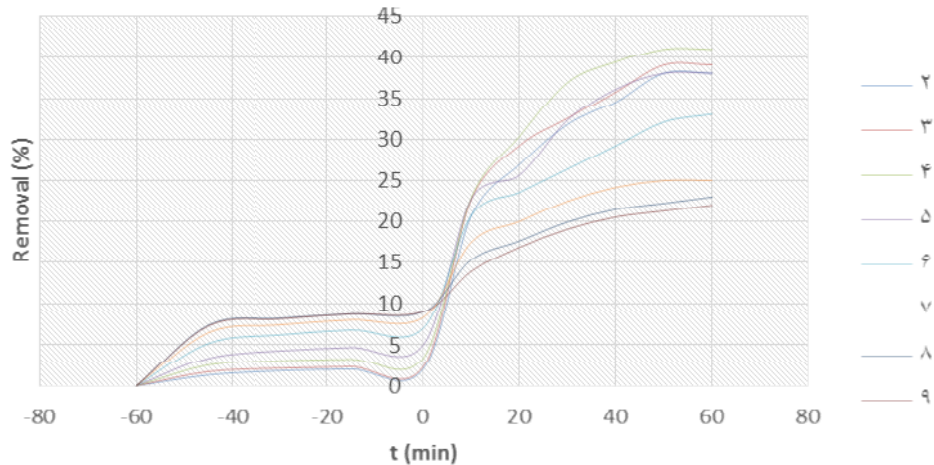


Fig. 3. The effect of ultraviolet radiation on the Elimination of Methylene blue color at different pHs by Zeolite-Y.

As seen in the figure, most have been removed the titanium dioxide at pH 3, and the zeolite at pH 4, but this has not been completely eliminated, and other conditions, such as providing oxygen species to

increase photo catalyst action will be required. All processes, the equilibrium reached within an hour, and there was elimination.

Methylene blue by TiO₂ and elimination kinetics of zeolite in the presence of ultraviolet radiation.

Initially, the change Adsorption increases with time, and after a while, change is very slow, the reaction to reach equilibrium, and the Adsorption constant. Kinetic studies were conducted to both of mechanisms, pseudo-first order and pseudo-second order.

Pseudo-differential equation of the first mechanism, as shown below:

$$(dq_t/dt) = k_1(q_e - q_t) \quad (2)$$

The linear equation is obtained by solving the above equation, as follows:

$$\log(q_{e \text{ exp}} - q_t) = \log q_{e \text{ cal}} - (k_1/2.303)t \quad (3)$$

In this equation, $q_{e \text{ exp}}$, the experimental value of Adsorption at equilibrium (mg / g), and $q_{e \text{ cal}}$, the calculation amount Adsorption at equilibrium (mg / g), and q_t is the amount of Adsorption at time t (mg/g), and k_1 is the pseudo first order rate (1/min) where k_1 and $q_{e \text{ cal}}$, were obtained from the slope of the extrapolation of the plot of $\ln(q_e - q_t)$ versus t (min).

The pseudo-second order mechanism, the rate-limiting step, can be resulted in the formation of bonds, or

through the sharing of electrons between the absorber and Adsorption. Pseudo-differential equation of the second mechanism, as shown below:

$$(dq_t/dt) = k_2(q_e - q_t)^2 \quad (4)$$

Solving the above differential equation, linear equation is obtained as follows:

$$(t/q_t) = (1/k_2 q_e \text{ exp}^2) + (t/q_e \text{ cal}) \quad (5)$$

In this equation, $q_{e \text{ cal}}$, the calculation amount Adsorption, at equilibrium (mg/g), q_t Adsorption amount at time t (mg / g), and k_2 , is a pseudo-second rate (g / mg min). Plot of t/q_t , according t (min), respectively $q_{e \text{ cal}}$ values and k_2 , obtained from the slope of the extrapolation.

Pseudo-first order and pseudo-second-order diagrams are drawn based on the results (Fig. 4, 5, 6 and 7). The results of these charts have been brought together in Table 3 and 4 for comparison. As shown in Tables 3 and 4, the correlation coefficient (R²), the pseudo-second mechanism is much better, and this mechanism can explain the process better. Also, the difference between the values of $q_{e \text{ cal}}$ $q_{e \text{ exp}}$, pseudo-second-order model, is less.

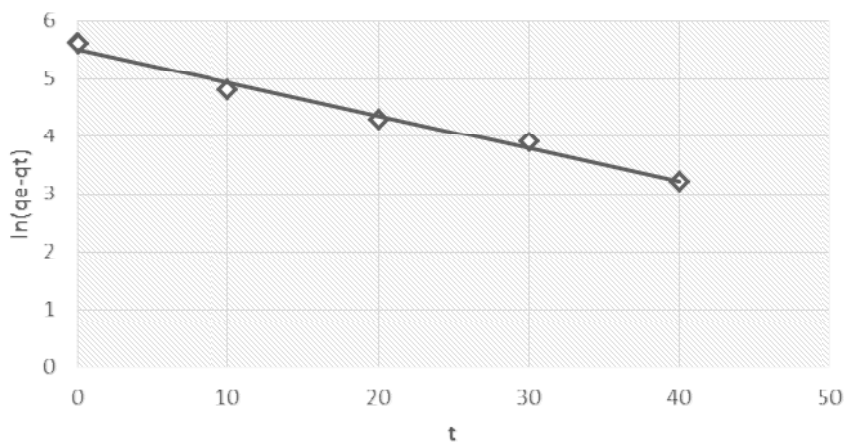


Fig. 4. Graphs pseudo first order kinetics for removal of Methylene blue color by TiO₂, in the presence of ultraviolet radiation.

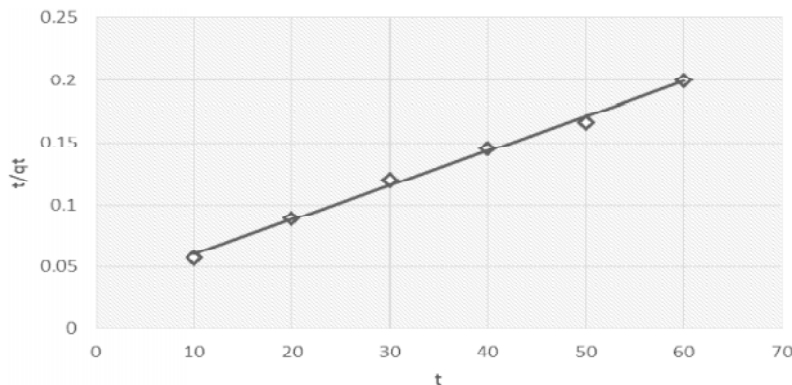


Fig. 5. The pseudo-second order kinetic plot for the removal of Methylene blue color in the presence of UV radiation by TiO₂.

Table 1: Results kinetics for removal of Methylene blue color, the TiO₂ in the presence of ultraviolet radiation.

q_e (mg/g)	Experimental results	
300		
Pseudo-first model		
q_{e cal} (mg/g)	k₁ (l/min)	R²
251.5	0.057	0.9877
Pseudoquadratic model		
q_{e cal} (mg/g)	k₂ (g/mg min)	R²
357.1	0.0028	0.9960

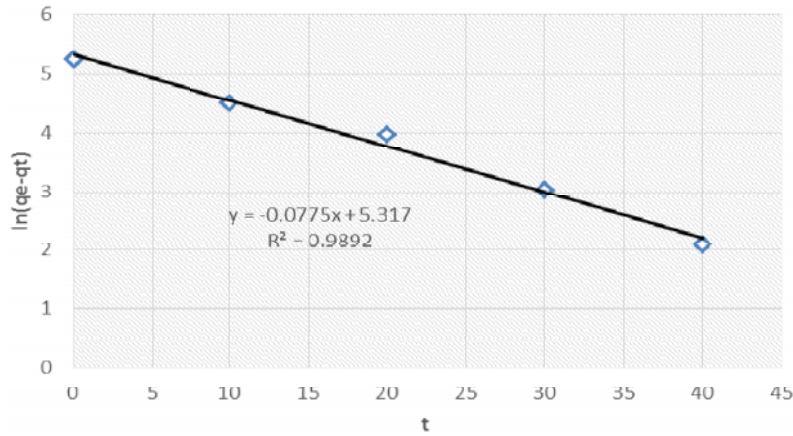


Fig. 6. Pseudo first order kinetics for removal of Methylene blue color, by Zeolite-Y, in the presence of ultraviolet radiation

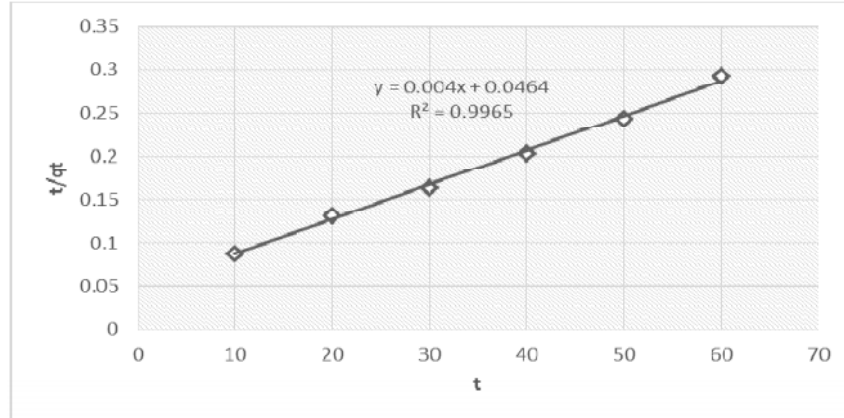


Fig. 7. Kinetics pseudo second diagram, to remove Methylene blue color by Zeolite-Y, in the presence of ultraviolet radiation

Table 2: The results of kinetics for removal of Methylene blue color by Zeolite-Y, in the presence of ultraviolet radiation.

q_e (mg/g)	Experimental results	
205		
pseudo-first model		
q_{e cal} (mg/g)	k₁ (l/min)	R²
203.7	0.077	0.9892
Pseudoquadratic model		
q_{e cal} (mg/g)	k₂ (g/mg min)	R²
250	0.0003	0.9965

Effect of aeration on the removal of Methylene blue by TiO_2 and zeolite, in the presence of ultraviolet radiation. Starting with ultraviolet radiation, Methylene blue dye concentration and aeration process, it starts to decline, in parallel to the solution, because the cycle photo catalytic TiO_2 , which at the beginning of this change is rapid, and with time, it is to a fixed limit. Here, acidic pHs, created better conditions for the removal of Methylene blue, and remove the slope, the more the higher pHs. The test was repeated at different volumetric flow. By increasing the air flow rate is increased bleaching, but there is a maximum value, the amount of aeration, after which the increase in the rate

of bleaching there, and it seems that it has reached a saturated solution of terms of dissolved oxygen, and this also depends on the amount of oxygen consumed by the catalyst particles. The first (left) on the graph corresponds to the adsorption equilibrium, and the second (right), is related to the process, from the moment of turning on the UV lamp and an air pump. With this process, at different pHs, would-be achieved in a three-dimensional graph, the optimum point for airing in January titanium oxide test is equal to 1 / min 1.5 and zeolite, which is equal to 1 / min 1.7. (Figs. 8, 9, 10 and 11)

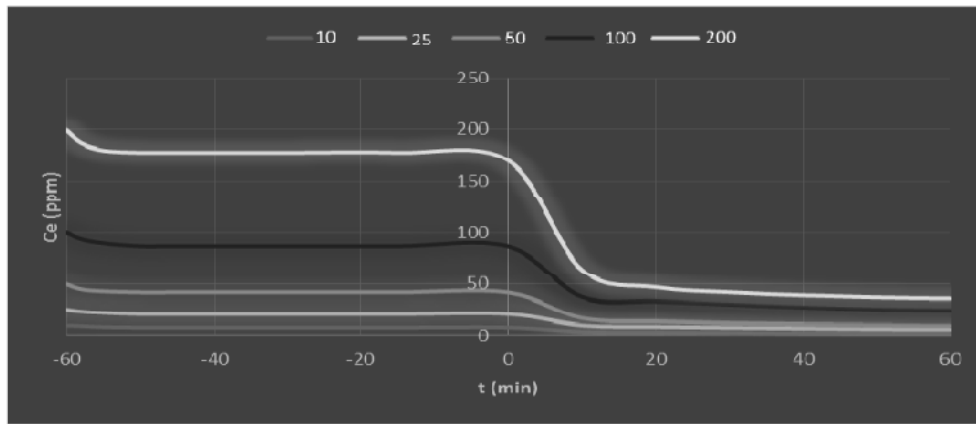


Fig. 8. Effect of aeration on the removal of Methylene blue color formed by the TiO_2 , in the presence of UV radiation at pH = 3.

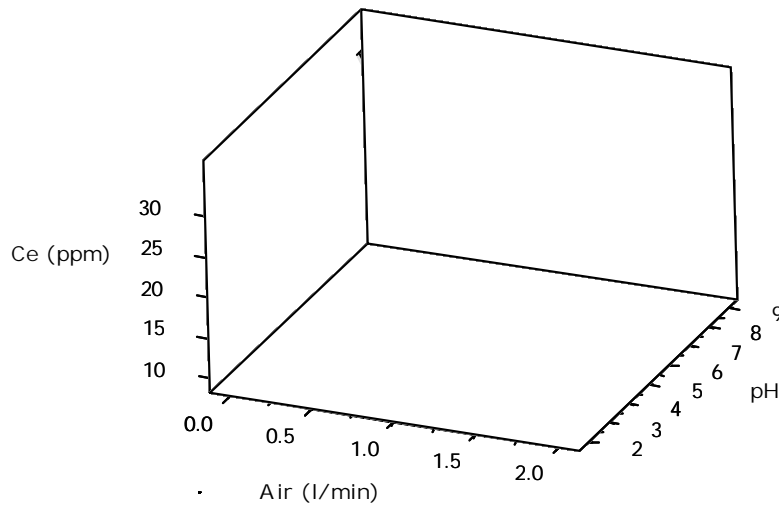


Fig. 9. Three-dimensional diagram of the effect of aeration and pH, the removal of Methylene blue color by TiO_2 .

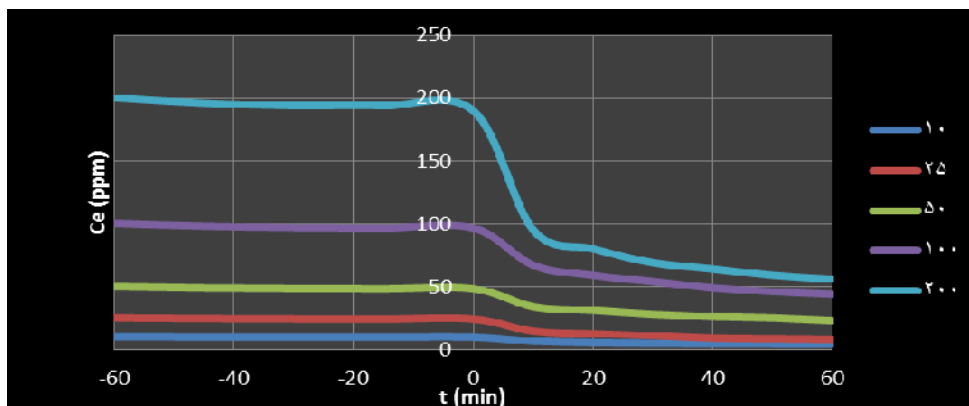


Fig. 10. The effect of aeration on the removal of Methylene blue color, by Zeolite-Y, in the presence of UV radiation at pH = 4.

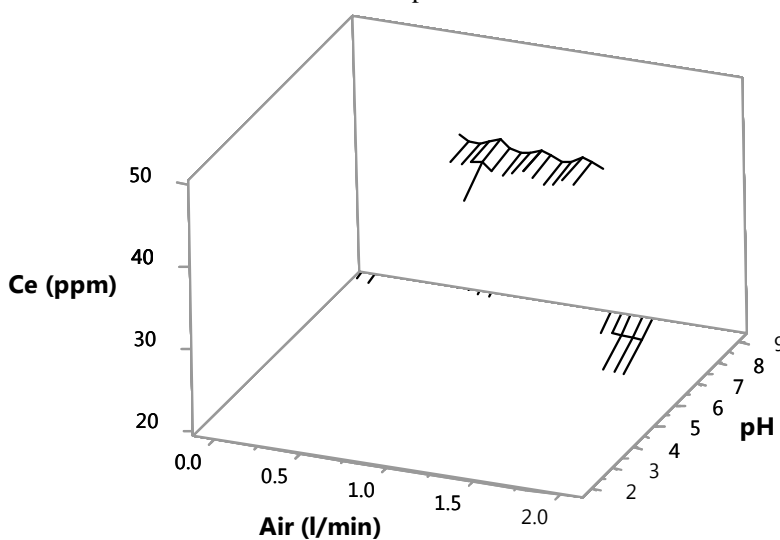


Fig. 11. Three-dimensional diagram of the effect of pH and aeration on the removal of Methylene blue color by Zeolite-Y.

CONCLUSION

In this study, TiO_2 and Zeolite-Y, were used for the removal of dyes from aqueous solution of Methylene blue. Although the quantity of Methylene blue, in different conditions, as surface Adsorption, Adsorption occurs on the matter, but this is not enough for the amount of the concentrated solution, and other factors must be used to improve color removal of contaminants from water. As this study shows, ultraviolet radiation, is able to improve the efficiency of color removal, but increased the efficiency of aeration. To insist on the air, we should remember that, as stated, to prevent the return of photo catalyst conduction band electrons agitated by an external factor such as molecular oxygen, is very important, therefore, the oxygen molecules act is an efficient electron acceptor, and superoxide anion radical as it constitutes a before returning electrons, the radical, the reaction of the

cation produces $\text{H} + \text{radical HO}_2$. This justifies the increased removal of Methylene blue in acidic pHs.

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