

Experimental Study of Influencing Factors and Kinetics in Catalytic Removal of Methylene Blue with TiO₂ Nanopowder

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Abstract In this research, degradation of methylene blue as a dye pollutant was investigated in the presence of TiO₂ nanopowders using photolysis and sonolysis systems separately and simultaneously. Effect of different parameters such as catalyst dosage, initial concentration of dye, UV power, pH and type of catalyst on the removal efficiency was ascertained. The results showed that basic pH is proper for the photocatalytic removal of the dye. Furthermore higher UV power and lower initial concentration of dye leads to higher removal percent. Moreover TiO₂ showed more photocatalytic activity than ZnO in the nanopowder form. The experimental kinetic data followed the pseudo-first order model in both photocatalytic and sonophotocatalytic processes but the rate constant of sonophotocatalysis is higher than it at photocatalysis process. Finally the reaction order of the rate law respect to nanocatalyst dosage in photocatalysis process is obtained 1.45. High activation energy of this process shows its high sensitivity to temperature.

Keywords Methylene Blue, TiO₂ Nanopowder, Photocatalysis, Sonophotolysis, Kinetic Study

1. Introduction

Dyestuffs are the materials which extensively used in the textile and other printing industries. The color and toxicity which dyes impart to water bodies are very undesirable and harmful to the water users for aesthetic and environmental reasons[1,2]. From an environmental point of view, as some synthetic dyes have toxic and carcinogenic properties, they are of great concern. Approximately about 1-20% of the overall dye production of the world is discharged from various industries such as dyestuff manufacturing, dyeing, printing, and textile finishing[3,4]. Methylene blue (MB) is a cationic dye, used extensively for dyeing cotton, wool and silk. The risk of the existence of this dye in waste water may be arisen from the burns effect of eye, nausea, vomiting and diarrhea[4,5]. MB has a maximum absorption in the 660 nm visible area[6].

In general, several methods have been developed for the removal of dyes from effluents including (1) physical methods employing precipitation, adsorption, and reverse osmosis; (2) chemical methods via oxidation (using air oxygen; ozone, NaOCl, and H₂O₂ as oxidants) and reduction

(e.g., Na₂S₂O₄); and (3) biological methods including aerobic and anaerobic treatment. The disadvantages of these conventional methods are sludge formation, waste disposal and high operation cost, time consuming and ineffectiveness in cases where complicated aromatic compounds are presented [7,8].

Advanced oxidation processes (AOPs) have been defined broadly on the intermediacy of the hydroxyl radicals (OH[•]) in driving the oxidation processes. Since AOPs provide different routes to OH[•] radical production, easier tailoring of the treatment process occurs. Ozone, hydrogen peroxide, ultrasonic, ultraviolet radiation, etc are some methods of AOPs that can be used individually or in different combination forms to generate the hydroxyl radicals[9,10].

It is evident that the conduction band electrons (e⁻) and the valence band holes (h⁺) are formed when the aqueous suspension of TiO₂ irradiates with photon energy higher than the band gap (figure 1).

The process of photodegradation starts when TiO₂ absorbs a UV radiation of energy equal or higher than its band gap (3.2 eV for anatase; 3.0 eV for rutile). This leads to the formation of free electrons in the conduction band and holes in the semiconductor valence band. The energized electrons can either recombine with the holes (and then dissipate the absorbed energy as heat) or the electron-hole pairs can participate in redox reactions. They can react with electron acceptors/donors adsorbed on the surface of the photocata-

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lyst. Alternatively, the solid side at the semiconductor/liquid junction creates an electrical field that separates the electrons-holes pairs that fail to recombine. The electron field allows the holes to migrate to the illuminated part of the TiO₂ and the electrons to migrate to the unlit region of the TiO₂ particle surface. Essentially, it is accepted that the initial steps of photocatalytic degradation of a species is the reaction with extremely reactive but short-lived hydroxyl radicals (OH[•]) or direct hole trapping. The OH[•] is formed either in the highly hydroxylated semiconductor surface or by direct oxidation of the pollutant molecules under UV radiation. There is also a possibility that both methods of forming OH[•] occurs in these situation simultaneously. The reduction of adsorbed oxygen species occurs immediately after this process. Dissolved oxygen molecules (in the aqueous system), or other electron acceptors available in the aqueous system can cause this reduction[11,12].

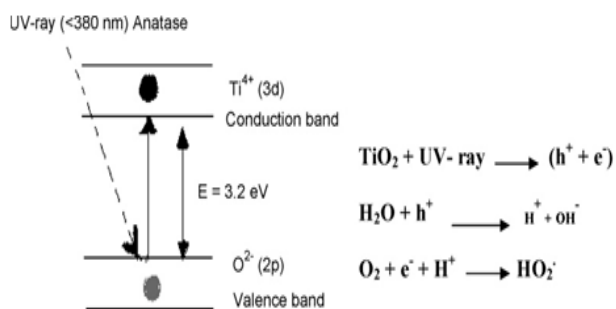


Figure 1. Energy band gap created on TiO₂ surface

After successive free radical attack and fragmentation, most organics are mineralized to water, carbon dioxide and mineral acids[2,13]. González investigated the sonophotocatalytic degradation of methylene blue and found that degradation reaction followed apparent first-order kinetics and was dependent on the pH solution with the highest degradation at pH 7[14].

There is a need to determine the optimal conditions of experimental parameters for effective application of dye wastewater treatment by AOP processes. In this study, a cationic dye basic blue 9 is selected and examined the various parameters in photocatalysis and sonocatalysis treatment using nanopowder TiO₂ in a batch process and then the optimum conditions for removal of color and aromatic part of the dye are reported. Moreover comparison of the two semiconductor photocatalyst, TiO₂ and ZnO, is done at the same conditions. Finally kinetic study of the reactions is considered and kinetic parameters are determined in detail.

2. Experimental

2.1. Materials

Titanium dioxide (Degussa P25) nanopowder was utilized as a degradation catalyst. It is mostly in the anatase form with a surface area of 50 m²/g corresponding to a mean particle size of 20 nm and purity >99%. Zinc oxide

nanopowder as another catalyst of the reaction was used with average particle size of 25 nm, specific surface area 44 m²/g and purity 99.7% that was prepared from Nano Nader-Sama Company.

In this paper, methylene blue was obtained from Merck in the laboratory grade and used without further purification. Adjustment of pH of the dye solutions prior to degradation was carried out with NaOH or H₂SO₄ from Merck. Distilled water was used in all experiments.

2.2. Apparatus

The sonolysis experiments were carried out in an ultrasonic bath with controlling power and temperature. Four UV-A (365 nm) 6W Hitachi black light lamps were applied to irradiate in the photocatalytic experiments. The UV lamps were installed on the top of the ultrasonic bath for alternative photo and/or sono irradiation cases. The reaction region was covered with aluminum foil to create light reflection and to prevent light emission to surroundings. The dye concentration was analyzed with a VinCary 50 UV-vis Spectrophotometer. The solution's pH was detected with a pH meter (Metrohm).

2.3. Methods and Analyses

A solution containing proper concentration of the dye and dosage of TiO₂ nanopowder was prepared and imposed to ultraviolet or ultrasonic depending on the photocatalytic or sonocatalytic cases over a pre-determined period of time. Before analysis, the aqueous samples were filtered through 0.22 μm Biofil syringe filter to remove TiO₂ nanopowders. The absorbance measurements with UV-visible spectrophotometer at 660 nm (which is maximum absorption wavelength of MB) were employed to calculate the dye concentration from the calibration curve (absorbance vs. MB concentration). The removal percent of MB was calculated by using the equation given below:

$$\eta = (C_0 - C_t) / C_0 = (A_0 - A_t) / A_0 \quad (1)$$

Where C₀ and C_t are dye concentration at initial and any time respectively. The parameters A₀ and A_t are the absorbance of the MB solutions in the 660 nm wavelength at initial and any time respectively.

3. Results and Discussion

3.1. Effect of Catalyst Dosage

The effect of the amount of TiO₂ dosage on the MB removal was studied and the results are shown in figure 2 for sonocatalysis (US), photocatalysis (UV) and sonophotocatalysis (US/UV) processes. The experiments were carried out with a 10 ppm dye solution for 60 min.

Basically, the removal efficiency increases with increasing the catalysis dosage and then stays nearly constant in a specific catalyst dosage. The most effective decomposition of MB was observed at 0.2 g/l of TiO₂ for photo and sonophotocatalysis and 1 g/l for sonocatalysis reactions. The

reason of this observation is thought to be the fact that when all dye molecules are adsorbed on TiO_2 , the addition of higher quantities of TiO_2 would have no effect on the degradation efficiency. Another cause for this is supposedly an increased opacity of the suspension, brought about as a result of excess of TiO_2 particles[15,16].

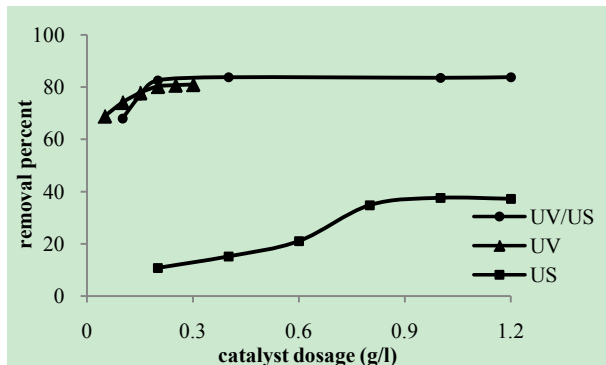


Figure 2. Effect of dosage of TiO_2 on MB removal

In addition the removal percentage of MB in sonocatalytic process increases with an increasing in catalyst dosage and then reaches to the constant amount of 1 g/l. This is due to the fact that ultrasonic irradiation can also be used as an alternative energy source for TiO_2 to generate positive holes without the presence of a UV source[17]. Nanoparticles show a great tendency to aggregate due to high surface energy combined with their high surface area to volume ratio [18] but ultrasonic irradiation can disperse the catalyst particles more efficiently. Despite all these things, when the amount of TiO_2 increases more than 1 g/l the catalyst particles may agglomerate and this results decreasing in removal percentage[19]. As the results show, the optimum amount of catalyst for sonocatalysis is more than the amount for photocatalysis. As can be seen from this figure, the optimum amount of photocatalyst in simultaneous photocatalysis and sonocatalysis is the same as the amount in photocatalysis (0.2 g/l). In sonophotocatalysis both sonolysis and photocatalysis make roles but photocatalysis is the rate limiting ones.

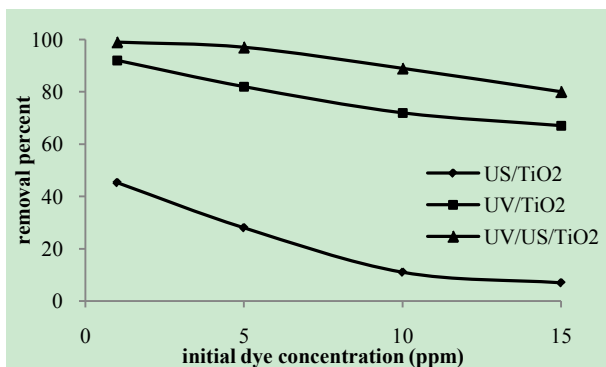


Figure 3. Effect of initial dye concentration on MB removal

3.2. Effect of Initial Dye Concentration

The effect of initial concentration of dye solutions on the removal percentage was investigated at the optimum catalyst dosage determined before (0.2 g/l for photocatalysis and 1

g/l for sonocatalysis) for 90 min during separate and simultaneous photocatalysis and sonocatalysis as were shown in figure 3.

As expected there is a tradeoff between both photo and sonocatalysis degradation conversion of MB and initial concentration of MB. The reason is that when the initial concentration of dye is increased, more and more dye molecules are adsorbed on the surface of TiO_2 .

Since the existence of the large amounts of adsorbed dye results the lack of any direct contact with the holes or hydroxyl radicals, this might have an inhibitive effect on the dye degradation. Other possible reasons for these results is the effect of UV screening of the own dye. In high dye concentrations a major amount of UV tends to be absorbed by dye molecules. This reduces the efficiency of the catalytic reaction due to the decline in OH^\bullet and OH_2^\bullet concentrations. Another possible reason is the formation of the by-products during the degradation of mother dye molecules. Moreover the percentage removal decreases rapidly at low MB concentrations and then changes slowly as the initial concentration increases[20-22].

As seen, more dye removing is observed in photocatalysis than sonocatalysis in all experiments. It indicates that photocatalytic process has higher efficiency than sonocatalysis. The combined processes of photocatalysis and sonolysis produced synergistic effects and showed the highest efficiency in the all initial concentration of dye.

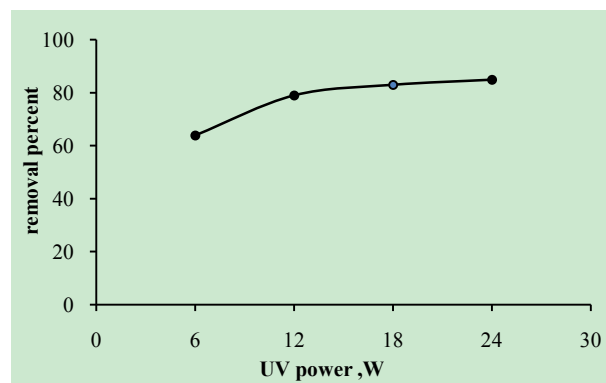


Figure 4. Effect of UV power in the photocatalytic degradation of MB. (0.2 g/l TiO_2 , [MB] = 10 ppm)

3.3. Effect of UV Power

The effect of UV power on the removal of MB was shown in figure 4. The results show that the removal percent increases with increasing the power of radiation. The increasing in UV power from 6W to 12W increases the percentage removal from 64% to 79% and increasing the UV power from 12W to 24W the percentage removal from 79% to 85% for a 10 ppm solution of dye increases after 60 min at ambient temperature. The results show that the UV light intensity plays an important role in degradation of MB. Moreover at the range of UV power that the experiments were done, the percentage removal increases rapidly at low power of UV and then changes slowly as the UV power increases. Increasing the power of UV radiation provides more energy to excite the electron of TiO_2 and creates more

electron-hole pairs, thus improve the photocatalytic process [23,24].

3.4. Effect of PH

Since pH of dye solution is a main parameter on the degradation progress, comparative experiments were performed at different pH values: one acidic pH (3.3), two basic pHs (11.4, 13.3) and one natural pH (7.7). The pH parameter improves the removal percentage and the results are shown in figure 5. The pH influences the characteristics of the photocatalyst surface charge, so pH of the solution is a significant parameter in performing the reaction on the surface of semiconductor particles. Point of zero charge (PZC) for TiO₂ particles is pH PZC = 6.8[3,25]. The surface of TiO₂ has a negative charge in basic media (pH > 6.8), so there is an electrostatic absorption between negative charge surfaces of TiO₂ and cationic dyes. As the pH of the system decreases, the number of surfaces with positive charge increases. The surface sites on TiO₂ do not tend to absorb the cations of dyes made by electrostatic propulsion. H₂SO₄ and NaOH were used to pH adjustment of dye solutions

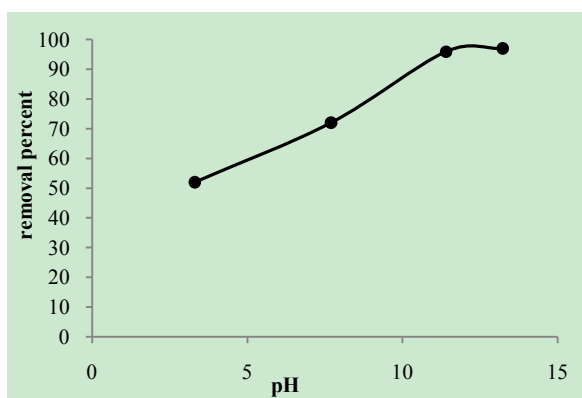


Figure 5. Effect of pH, [MB] = 10 ppm, 1 hr reaction

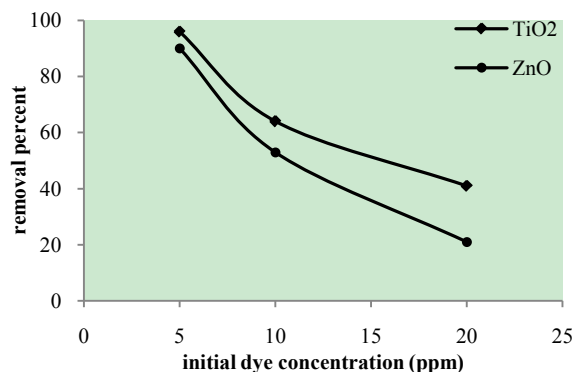


Figure 6. Comparison of TiO₂ and ZnO sonophotoreactivity

3.5. Comparison of the Sonophotocatalytic Removal Using TiO₂ and ZnO Nanopowders

The photocatalytic reactivity results of TiO₂ and ZnO nanopowders in methylene blue removal are presented in figure 6. Particle size of both photocatalysts is almost the same. TiO₂ nanopowders show higher efficiency and higher percentage of dye removal than ZnO nanoparticles in all

initial concentrations of methylene blue. As the initial concentration of dye increases, the differences in removal percent increase.

The photocatalytic activity of semiconductors is dependent on the band gap energy, crystallinity, particle size, surface area, pore structure and concentration of the impurities in the catalysts[26,27]. ZnO has higher band gap energy and this causes lower sonophotoreactivity than TiO₂. In addition, this may be due to lower surface area and higher density of ZnO than TiO₂.

3.6. Removal Kinetics

3.6.1. Investigation of the Order of Reaction in Photo and Sonophotocatalytic Reaction

To estimate the kinetic rate of the removal reaction, an equation form of power law is used:

$$-r_{\text{dye}} = k C_{\text{cat}}^m C_A^n \quad (2)$$

Where k is removal rate constant, C_A is dye concentration, n is reaction order respect to the dye concentration, C_{cat} is photocatalyst concentration and m is reaction order respect to the photocatalyst concentration. As the catalyst concentration is constant, the rate equation can be stated with observed rate constant (k_{obs}) as follows:

$$-r_{\text{dye}} = -\frac{dC_{\text{dye}}}{dt} = k_{\text{obs}} \cdot C_{\text{dye}}^n \quad (3)$$

$$k_{\text{obs}} = k \cdot C_{\text{cat}}^m \quad (4)$$

The pseudo-first order kinetic model ($n=1$) provide equation 3 to following form:

$$-\ln C_{\text{dye}}/C_{\text{dye}0} = k_{\text{obs}}t \quad (5)$$

Figures 7 and 8 show plot of $-\ln C_{\text{dye}}/C_{\text{dye}0}$ of MB versus irradiation time for photocatalytic and sonophotocatalytic reactions respectively. As it is clear from these figures, removal of the dye concentration obeys a linear pattern in this coordinate with good precision in the both cases. This means that the pseudo-first order kinetic of dye removal kinetic is acceptable for both photocatalytic and sonophotocatalytic processes, but comparison of the lines slope show that $k_{\text{sonophotocatalysis}} > k_{\text{photocatalysis}}$ and this shows that the sonophotocatalytic reaction is faster than photocatalytic at the same conditions.

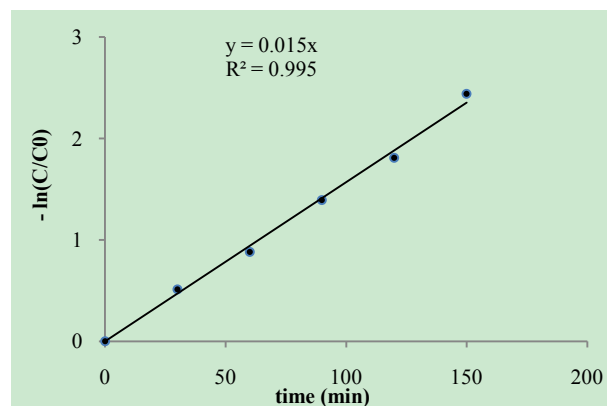


Figure 7. Pseudo-first order of the reaction rate in photocatalytic state, $C_{\text{dye}0} = 10$ ppm, room temperature

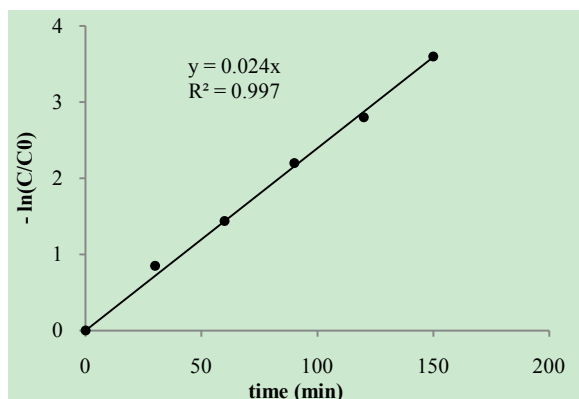


Figure 8. Pseudo first order of the reaction rate in sonophotocatalytic state, $C_{dye,0} = 10$ ppm, room temperature

3.6.2. Calculation of rate constant and order of reaction respect to photocatalyst concentration in sonophotocatalytic reaction.

Logarithmic form of the equation 4 can be used to find out the order of reaction respect to catalyst dosage:

$$\ln k_{obs} = \ln k + m \ln C_{cat} \quad (6)$$

Three k_{obs} are determined in three different catalyst dosages (0.1, 0.15, 0.2 g/l) base on determination route of section 3.6.1 and the curves are plotted in figure 9. The regression results are listed in table 1. The catalyst concentrations were selected lower than its optimum dosage. These results are then used for determination order of reaction rate respect to the concentration of catalyst (parameter m in equation 2).

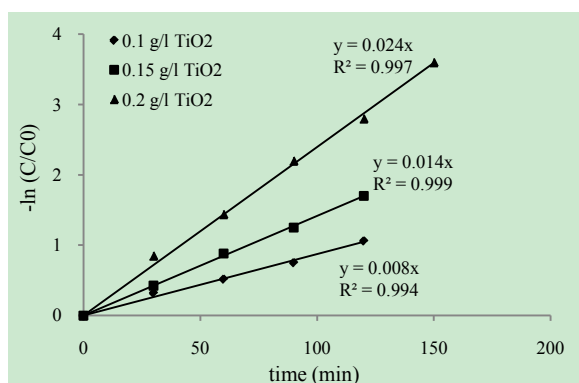


Figure 9. Determination of K_{obs} in three dosages of photocatalyst

Table 1. k_{obs} values in different concentrations of photocatalyst

TiO ₂ dosage (g/l)	k_{obs} (1/min)	R^2
0.1	0.0087	0.993
0.15	0.0142	0.999
0.2	0.0240	0.997

At this step considerations of the order of reaction respect to the concentration of catalyst can be done. Plotting $\ln(k_{obs})$ versus $\ln(C_{cat})$ base on equation 6 is presented in figure 10 and gives m and k (equation 2), according to calculating slope and intercept of the line.

Slope of the line is 1.45 which is the order of reaction rate respect to the concentration of photocatalyst and its intercept is -1.437. Therefore the reaction rate constant (k) is 0.237 (gr/l)^{-1.45}/min for sonophotocatalytic reaction at room tem-

perature. So the rate equation for sonophotocatalytic process at room temperature can be stated as follows:

$$-r_A = -dC_A/dt = 0.237 \cdot C_A \cdot C_{cat}^{1.45} \quad (7)$$

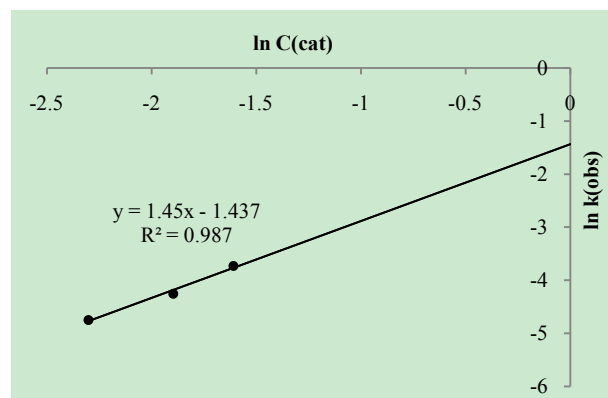


Figure 10. Determinations of m and k in sonophotocatalytic reaction

where dye concentration (C_A) in this equation is based on (ppm) and concentration of catalyst (C_{cat}) is based on (g/l). The value of k in the rate equation depends on temperature and Arrhenius equation shows this dependence as follows:

$$k = k_0 e^{-E/RT} \quad (8)$$

k_0 is pre-exponential factor and E (j/mol) is activation energy of the reaction. The sonophotocatalytic process of dye removal was conducted at three temperatures and the experimental results were analyzed to determine the reaction rate constant at each temperature. Table 2 specifies k_{obs} and k at three temperatures and catalyst dosage of 0.2 g/l. The Arrhenius plot of these data is presented in figure 11.

Table 2. k_{obs} and k value in sonophotocatalytic process at different temperatures, $C_{cat} = 0.2$ g/l

T (°C)	k_{obs} (1/min)	k (gr/l) ^{-1.45} /min
22	0.0158	0.1624
47	0.0240	0.2467
67	0.0288	0.2960

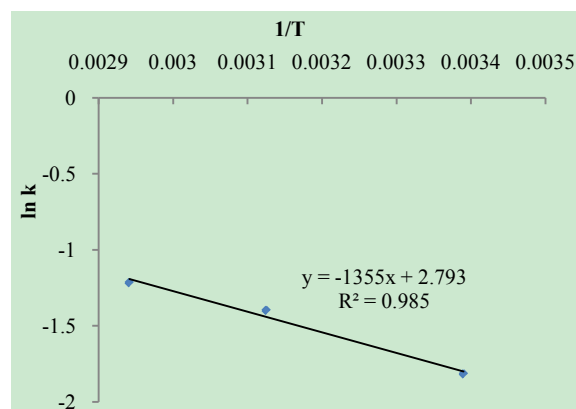


Figure 11. Arrhenius plot of the rate constant in sonophotocatalytic reaction

Regression of the experimental data in figure 11 gives activation energy and pre-exponential factor of the reaction (equation 8) using slope and intercept of the line. Therefore the calculated rate constants are $E = -11265$ j/mol and $k_0 = 0.272$ (g/l)^{-1.45} /min.

$$-r_A = -dC_A/dt = 0.272 e^{-11265/RT} C_A C_{cat}^{1.45} \quad (9)$$

This equation describe degradation rate of MB in the sonophotocatalysis process with dimension g/l.min.

4. Conclusions

In this study the dye MB was appropriately mineralized by separate and simultaneous photocatalytic and sonocatalytic reactions in the presence of nanoparticles titanium dioxide in the form of slurry. The effect of efficiency parameters like dosage of catalyst, concentration of dye, UV power pH and type of nanocatalyst were investigated. It was found that optimum dosage of catalyst was 1, 0.2 and 0.2 for sonocatalytic, photocatalytic and sonophotocatalytic reactions respectively. The results revealed that the dye removal was inversely proportional to the initial methylene blue concentration in all processes. photocatalysis seems to be more efficient than sonocatalysis in the same environmental situations. the removal rate of dye increases with increasing UV power from 6 to 24 W. photocatalytic and sonophotocatalytic removal of methylene blue obey pseudo first order kinetic at low initial concentrations and the sonophotocatalytic kinetic parameters was determined for initial MB concentration of 10 ppm. Also it was observed that TiO₂ was found to be more efficient than ZnO for methylene blue removing via photocatalytic process.

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