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The Photocatalytic Kinetics of the Methyl Orange Degradation in the Aqueous Suspension of Irradiated TiO₂

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A R T I C L E I N F O

A B S T R A C T

Background: In the present study, the photocatalytic (TiO₂/UV) batch process has been used for the methyl orange (MO) degradation.
Methods: In the catalyst range from 0.25 to 1.5 g/L, the optimum concentration of TiO₂ was found to be 0.5 g/L. The kinetic behavior of MO degradation has been evaluated using the non-linear form of pseudo-first order and pseudo-second order models.
Results: The goodness of the fit was evaluated using the correlation coefficient R2 value and the mean square error (MSE) function.
Conclusion: The kinetic studies revealed that the pseudo-first order model ($k_1 = -0.0593$ min^{-1}) is more suitable to fit the experimental data ($R_2 = 0.957$, MSE = 0.00271) of MO degradation.

1. Introduction

The advanced oxidation processes (AOPs) has been used as an alternative for the mineralization of recalcitrant molecules as well as microorganisms. Due to low cost, environmentally friendly nature, and low residuals of TiO₂/UV it has drawn more attentions in water and wastewater treatment studies [1].

The AOP has demonstrated its efficiency in degrading a wide range of ambiguous refractory organics and pathogens [1]. These advanced oxidation processes can be classified as homogeneous or as heterogeneous. Homogeneous:

The photocatalysis refers to those photocatalytic processes where the reactants and the photocatalyst exist in the same phase during the reaction. The term heterogeneous refers to the fact that the contaminants are present in the aqueous phase, while the catalyst is in the solid phase [2].

The usual applications of some features of heterogeneous photocatalysis have been extended such as: 1) ambient operating pressure and temperature, 2) full mineralization of parents and intermediary compounds with no secondary contamination, and 3) small operating costs [1].

Among the semiconductor catalysts, Titanium dioxide (TiO_2), which is one of the most basic materials in our daily life, has received the greatest interest in research for the environmental purification [3].

TiO_2/UV has become a photocatalytic decontamination process for a large variety of organics. Organics can be totally degraded and mineralized to CO_2, H_2O, and harmless inorganic anions. This performance is attributed to hydroxyl radicals (HO•) that are known as indiscriminate oxidizing agents. The oxidizing potential of this radical is 2.80 V which is being exceeded only by fluorine [4].

The light of wavelength about 365 nm (median pressure lamps) is appropriate for the photocatalysis with titanium dioxide that has a threshold energy equal to 413 nm, therefore activation needs smaller wavelengths than these ones. The median pressure lamps give the most energy output that is more than 300 nm, reaching to its highest climax at 365 nm, and slumping above about 600 nm. It has been proven that irradiation with 254 nm light can operate synergic ally with 365 nm light to enhance the photo catalytic kinetics several-fold [5].

It was shown that phenol degradation using anatase TiO_2 as a photocatalyst can be predicted using the first-order kinetics [6]. In a photo catalytic study, dyes are one of the most common model compounds that were used not only to represent a persistent water pollutant, but also when they dissolved in water the bleaching of the dye during the reaction provides a quick and simple qualitative response [7].

A number of investigations have been reported on the photo catalytic degradation of the methyl orange (MO). The degradation of MO was found to be dependent on the initial concentration of nano catalyst, pH and contact time. The methyl orange is clearly visible, even at concentrations as low as 1 ppm, and it can be readily quantified using the UV-Vi spectroscopy. Due to both its stable nature and easy quantification, the methyl orange is frequently used as a model pollutant for the comparative studies of photocatalytic systems [8]. The methyl Orange is an azo dye with the molecular formula of $C_{14}H_{14}N_3NaO_3S$ and its molecular mass is 327.34 (g / mol) [9].

The methyl orange is an organic dye used as a pH indicator in the titration. Many studies revealed the toxicity and carcinogenic nature of this dye. If this colorant is associated with certain drugs in the human body it can induce the allergic and asthmatic reactions in sensitive people. An additional difficulty is that, when it's present, this dye cannot be removed normally by the conventional waste water treatment systems.

Therefore, the effluents must be treated before being released into water bodies [10].

The ionic state of MO makes this compound essentially non-volatile, therefore MO should exist solely in the particulate phase in the ambient atmosphere. Based on the limited data, this compound is expected to be resistant to aerobic biodegradation in both soil and water; the MO was not degraded over 5 days in an aqueous BOD screening test. Due to its ionic nature the loss of the dye from water surfaces by volatilization should not be important. The potential for t bio concentration in the aquatic organisms is expected to be low based on an estimated bio concentration factor (BCF) of 30 [11].

Therefore this research intends to show the methyl orange degradation and the kinetics by the photocatalytic process.

2. Materials and Methods

TiO_2 nanoparticles (Plasma Chem, 21 nm particle size, 99.5% and 15 _ 50 m^2/ g surface area) was used as a photocatalyst [9]. A UV lamp (6 W UV-C) was used as the UV-light source. Experiments were carried out in a 500 mL photo reactor. All experiments were performed at pH 7.

The MO was purchased from Merck (Germany).

2.1. The Operational parameters

It has been demonstrated that the catalyst dosage, character and the initial concentration of

the target compound, the coexisting compound, the UV light intensity, the oxygen concentration, the presence of supplementary oxidizable substance, the temperature, the circulating flow rate, the pH for aqueous treatments, and the water concentration for gaseous phases photoreactions are the main parameters affecting the degradation rate [4].

The methyl Orange Was used as the model pollutants. The MO degradation experiment by TiO₂/UV system was performed in the batch photocatalytic reactor containing 2 sets of lamps (6 W) and the magnetic Stirrer. The MO was dissolved in the distilled water. The change in concentration of MO during time intervals was recorded with respect to parameters such as the catalyst value and the reaction time. In order to evaluate the optimum concentration of TiO₂ nanoparticles, the catalyst in the range of 0.25 – 1.5 g/l was used. A volume of 200 ml of MO solution with a 19.77 mg/l initial dye concentration was agitated with a known value of catalyst. The samples were taken after a 20 minute reaction. The experiments were carried out in triplicate. Then they were centrifuged by a centrifuge (CE-148) at 4000 rpm for 20 minutes. In order to remove the catalyst particles completely; the amount of dye was measured by spectrophotometer (HACH D$_r$, 5000) at λ_{max} = 465 nm.

The percentage of degradation was calculated using the equation given below:

$$Degradation(\%) = \frac{C_0 - C_E}{C_0} \times 100$$

After selecting the optimum catalyst concentration, the optimum reaction time was investigated. The optimum weight of catalyst for maximum degradation was added to 200 ml MO solution in a reactor and the contents were shaken at the room temperature. The samples were withdrawn at 5 minute intervals. The efficiency of optimum concentration was calculated via the above equation.

2.2. The kinetic studies

In the present study, the experimental kinetic data for MO degradation using TiO₂/UV were fitted to the Lagergren`s pseudo first-order and Ho`s pseudo second-order model. The summary of the kinetic model expressions were given in Table 1.

Table 1: The summary of Kinetic Models Used in the Present Study.

Kinetic models	Parameters	Reference
Pseudo first-order $$q_t = q_e(1 - e^{-K_1 t})$$	K₁: The pseudo first-order rate constant (min⁻¹) q$_e$: Degradation at equilibrium (g g⁻¹) q$_t$: Degradation at time t (g g⁻¹)	[12]
Pseudo second- order $$q_t = \frac{K_2 q_e^2 t}{1 + K_2 q_e t}$$	K₂: The pseudo-second order rate constant[g (g min)⁻¹] q$_e$: Degradation at equilibrium (g g⁻¹) q$_t$: Degradation at time t (g g⁻¹)	[13]

The goodness of fit between the model and the experimental kinetic data was assessed using the presented error functions in Table 2. The determination coefficient was also applied to confirm the agreement between the experimental data and kinetic equations.

It has been shown that the non-linear method is more appropriate than the linear method for fitting the kinetic models [15]. Therefore, a trial and error nonlinear procedure was used to determine the kinetic parameters by minimizing the MSE between the experimental data and the predicted values using the Solver Add-on with Microsoft Microsoft Excel Spreadsheet.

3. Results and Discussion

The determination of optimum TiO₂ nanoparticle concentration is one of the most important, fundamental and economical parameters in the degradation of dyes. In order to avoid the use of extra catalyst, determining the optimum concentration of catalyst is essential to maximize the dye removal efficiency [16].

(Fig. 1) shows that, the maximum MO degradation (initial concentration of 19.77mg/l) reached at TiO₂ equal to 0.5 g/l.

It has been observed that the maximum decolonization efficiency in this optimum concentration was 81.08% and decreased as nanoparticle concentrations increases. The possible reason for this behavior may be raising the turbidity value of the solution and consequently, increasing the opacity and light scattering and decreasing the degradation efficiency [17].

Table 2: The explanation of error functions in the statistical analysis.

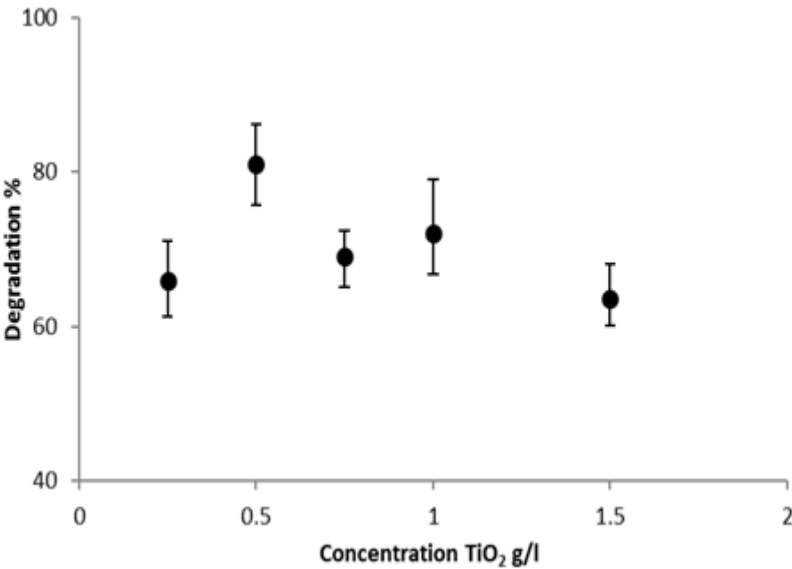| Error Function	Equation	Parameters	Reference
Mean Square Error	$MSE = \dfrac{1}{N}\sum\limits_{i=1}^{N}(q_{cal} - q_{exp})^2$	N: Number of experimental points	
The coefficient of determination	$R^2 = 1 - \left[\dfrac{\sum(q_{exp} - q_{cal})^2}{\sum(q_{exp} - q_{mean})^2}\right]$	q_{exp}: The experimental sorption capacity at equilibrium	[14]
		q_{cal}: Theoretically calculated sorption capacity at equilibrium	
		q_{mean}: Average of experimental values	

Fig. 1: The Effect of TiO₂ concentration (0.25- 1.5 g/l) on the Methyl Orange degradation (19.77 mg/l).
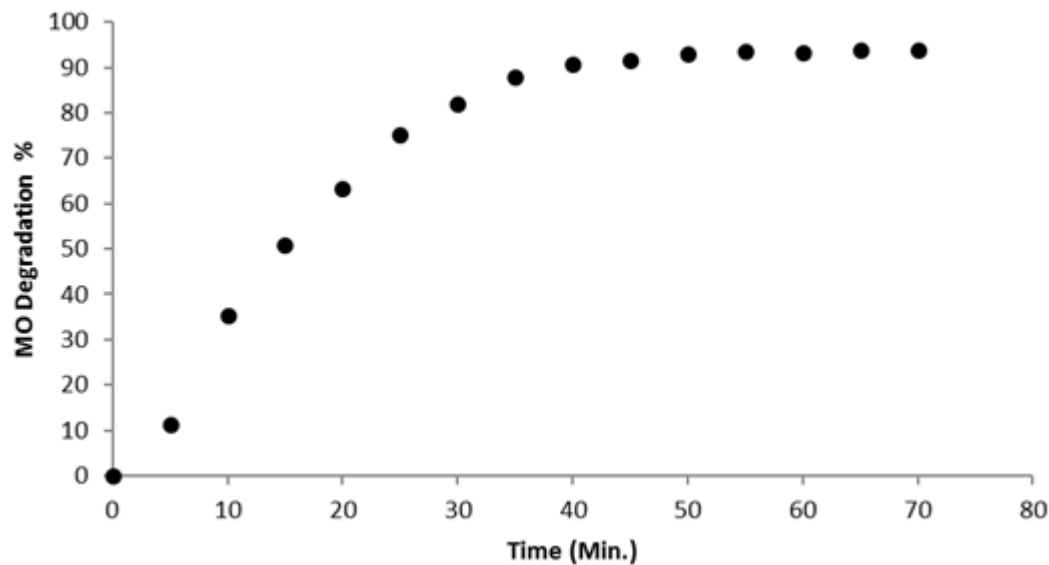
Fig. 2: The Effect of photocatalytic reaction time on Degradation efficiency of Methyl Orange (MO).

The Degradation of methyl orange during the reaction time of 5 to 70 minutes of photocatalytic reaction at 5-minute intervals was investigated.

The findings of this study demonstrate that after 55 minutes of reaction, the degradation reaches its plateau (93%). These results may be explained by large number of binding sites available in the TiO₂ nanoparticle at the initial period of reaction, the decolonization process accomplished slowly due to the saturation of binding sites and consequently was repulsive between the adsorbed molecules on the surface of nanoparticle and MO molecules in solution.

The predicted degradation profile of MO kinetic models is displayed in Fig. 3. The experimental data are also shown for the visual comparison of the fitting. The correlation coefficient (R_2) and (MSE) demonstrated that the pseudo-first order kinetic model fitted the MO degradation experimental data better than the two others.

The calculated kinetic parameters of the studied models as well as predicted q_e values by non-linear analysis are given in Table 3.

From Table 3, it is evident that the first order model is adequate to explain the degradation of MO with higher values of the coefficient of determination appropriately (R_2) which is equal to 0.957 and the lower values of MSE are equal to 0.00271 compared to the second order model.

4. Conclusion

This study confirms that the degradation efficiency of MO is reduced by increasing the amount of nanoparticles. It is proposed that increasing the turbidity of solution as well as light scattering is responsible for this phenomenon. The Photocatalytic degradation of the Methyl-orange is best suited to the quasi-first-order kinetics model.
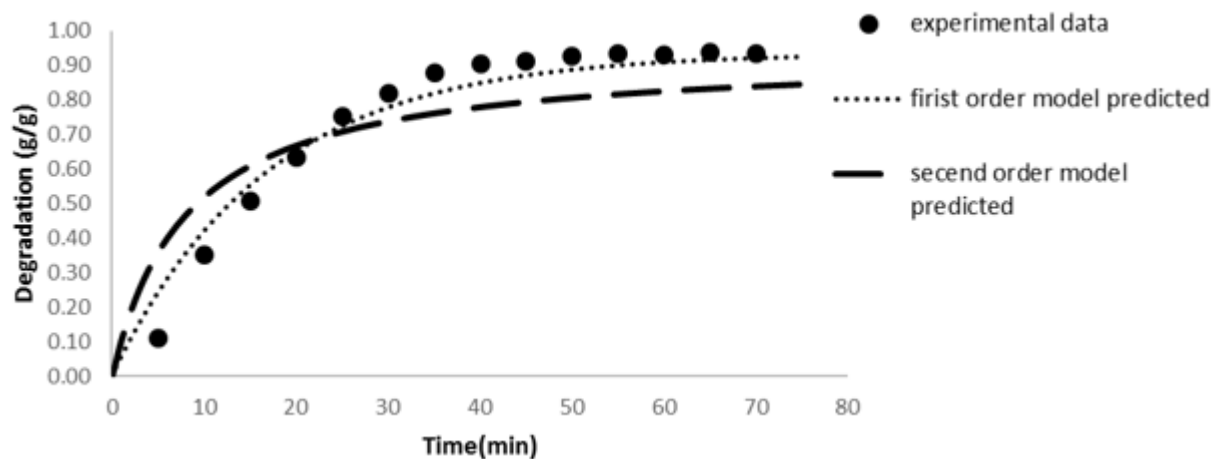
Fig. 3: The non-Linear plots for the pseudo-first and second order kinetic model for the methyl orange degradation.

Table 3: The Kinetic parameters obtained by fitting the experimental data to the pseudo-first and pseudo-second order model for the methyl orange photocatalytic degradation.

Kinetic model	Parameters	Methyl orange Degradation
Pseudo first- order	q_e (g g^{-1})	0.937
	K_1 (min^{-1})	-0.0593
	R_2	0.957
	MSE	0.00271
Pseudo second-order	q_e (g g^{-1})	0.937
	K_2 [g (g min)$^{-1}$]	0.132920888
	R_2	0.758075817
	MSE	0.01519

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