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Designing a Photo Catalytic Reaction System for Degradation of Organic dyes in Wastewater Using Nanostructured Materials

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Abstract: In this study, degradation of methylene blue (MB) from water was investigated by photocatalysis process in the presence of nanoTiO_2 and nanoTiO_2/AC under solar irradiation process. The parameters studied were amount of catalyst, initial concentration of the organic dye MB and the pH of the MB solution to achieve the best parameters for efficient degradation process. The results showed that pH of solution changed towards basic was found to enhance the photocatalytic efficiency. The amount of the catalyst was found to be 6 mg as optimal. The 10 ppm of MB concentration leads to achieve highest degradation efficiency of MB.
Keywords: photocatalytic, degradation, methylene blue, wastewater, nanostructured materials, nanoTiO_2, nanoTiO_2/activated carbon, adsorption on activated carbon

1 Introduction

The textile dyeing and printing industry consumes large quantities of water and produces consequently large volumes of wastewaters, which are hazardous, and adversely affecting our environment. These effluents contain organic and inorganic chemical species that have a harmful effect on human health and environment. Methylene blue (MB) is one of the undesirable color pollutants, which is present in these effluents. Concentrations of these pollutants in the effluents should be controlled in order to respect environment norms and legislation on water quality, which become more stringent in recent years [1]. Some of the health risks from the dye in wastewater considered for human are nausea, eyes effects and vomiting [2]. Dyes usually have complex aromatic molecular structures, which make them more stable and difficult to biodegrade.

Photocatalysis is the activity occurring when a light source interacts with the surface of semiconductor materials. During this process, there must be at least two simultaneous reactions occurring, oxidation from photogenerated holes, and reduction from photogenerated electrons. The photocatalyst itself should not undergo change and therefore a precise synchronization of the two processes requires taking place. A general view of photocatalysis mechanism and degradation process is given in **Fig. 1.**

Methylene blue (MB) is a colored cationic organic dye and is used as a traditional dye for printing cotton, wool, and silk. Its smell may cause breathe hazards and its direct contact may create local burning, nausea, vomiting, hyperhidrosis, and mental disorders and may damage the human eyes [3]. **Fig. 2** shows the structure of methylene blue molecule.

2 Experimental

2.1 Materials

The materials and chemicals used in this study were nano titanium dioxide (nanoTiO_2), activated carbon, methylene blue (MB) dye, sodium hydroxide and deionized water.

2.2 Experimental Procedure

The nanoTiO_2 was used as received. The nanoTiO_2/AC was prepared by combining equal amount of nanoTiO_2 and activated carbon and homogenized thoroughly through grinding process. Then the mixture was heated in a furnace at 225 °C for 4

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hours under air atmosphere. The nanoTiO_2/AC catalyst was cooled to room temperature and stored. The methylene blue (MB) solutions of 10 ppm concentration was prepared. Eighty (80) ml of this MB solution was taken in a beaker and a known amount of photocatalyst was added to it.

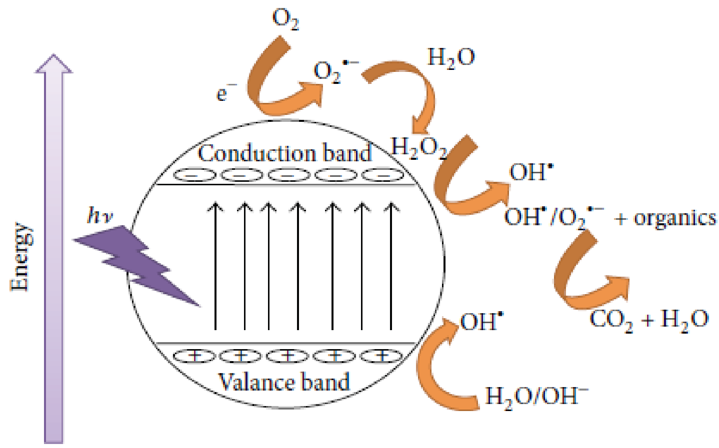

Fig. 1: A general view on photocatalysis mechanism and degradation process [**2**].

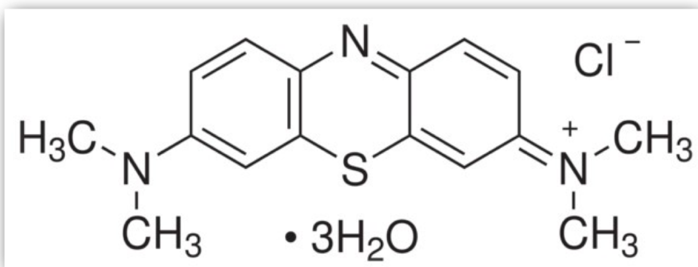

Fig. 2: Chemical Structure of Methylene Blue [2].

The pH of the stock solution measured was 6.5. The mixture was stirred in dark for 20 minutes to bring the system to equilibrium and to check any degradation reaction and/or adsorption of MB with the catalyst in dark. Then, the mixture was exposed to the sunlight under continuous stirring. The external temperature observed during the solar irradiation of the sample was 31 to 35 °C. After an interval of 20 minutes, 5 ml of the solution was withdrawn and centrifuged to separate the catalyst particles from the MB solution. A UV-Vis spectrophotometer was used to measure the absorbance of the MB solutions at a fixed wavelength, 657 nm, which is the λ_{max} for MB. The λ_{max} is the maximum absorbance of a compound at certain wavelength. The absorbance of all MB samples exposed to sunlight for 20 to 120 minutes were measured. The absorbance data was converted to MB concentration in the solution, from which the degradation of MB was calculated. Both catalysts (nanoTiO_2 and nanoTiO_2/AC) were studied at similar conditions and the parameters studied were, amount of catalyst (2, 6 and 10 mg), pH of the MB solution (6.5, 8 and 10) and concentration of MB (5 ppm, 10 ppm, 15 ppm). The absorbance data was evaluated by plotting percent degradation vs. irradiation time (t). In order to determine the rate law for the reaction, three graphs as given below were made using concentration of MB (C_t) and irradiation time (t) and was checked for the order of reaction through getting straight line as given below.

- C_t/C_o versus t (linear for a zero order reaction), rate = k
- ln C_t/C_o versus t (linear for a 1st order reaction), rate = k[C_t]
- 1 / C_t/C_o versus t (linear for a 2nd order reaction), rate = k$[C_t]^2$

Among the three plots, the plot of ln C_t/C_o vs. irradiation time (t) yielded a straight-line equation in which the slope of the equation represented the rate constant (k). This is described as follows:

Percent photocatalytic degradation =100 x $[(C_0 - C_t) / C_0]$

$$C_t = C_0.e^{-kt}$$

$$\ln C_t = -kt + \ln C_0$$

$$\ln C_t/C_o = -kt$$

where C_0 and C_t are the initial concentration of MB and the concentration of MB after exposed to irradiation time t, respectively, and k is the rate constant of the photocatalytic degradation reaction.

3 Results and Discussion

3.1 Effect of Amount of Catalysts (TiO_2/AC and TiO_2)

The effect of amount of nanoTiO_2/AC and nanoTiO_2 catalysts in photocatalytic degradation of methylene blue was observed and presented graphically in **Fig. 3**. It was observed that the degradation of methylene blue was increased using 6 mg of TiO_2/AC at 120 minutes comparing to 10 mg of TiO_2/AC, where the maximum degradation percentage when using 2 mg of TiO_2/AC was approximately 31%, so the optimum amount of catalyst was chosen to be 6 mg.

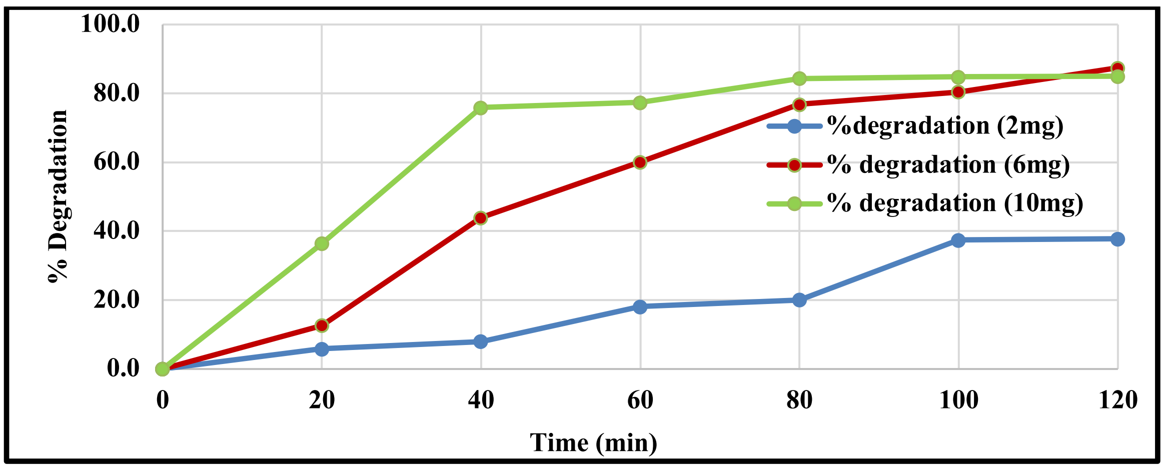

Fig. 3: Effect of amount of catalyst (nanoTiO_2/AC) on the MB degradation efficiency. 0 to 20 min was in dark followed by sunlight irradiation. Catalyst used was nanoTiO_2/AC and showed MB adsorption on activated carbon during 0 to 20 min.

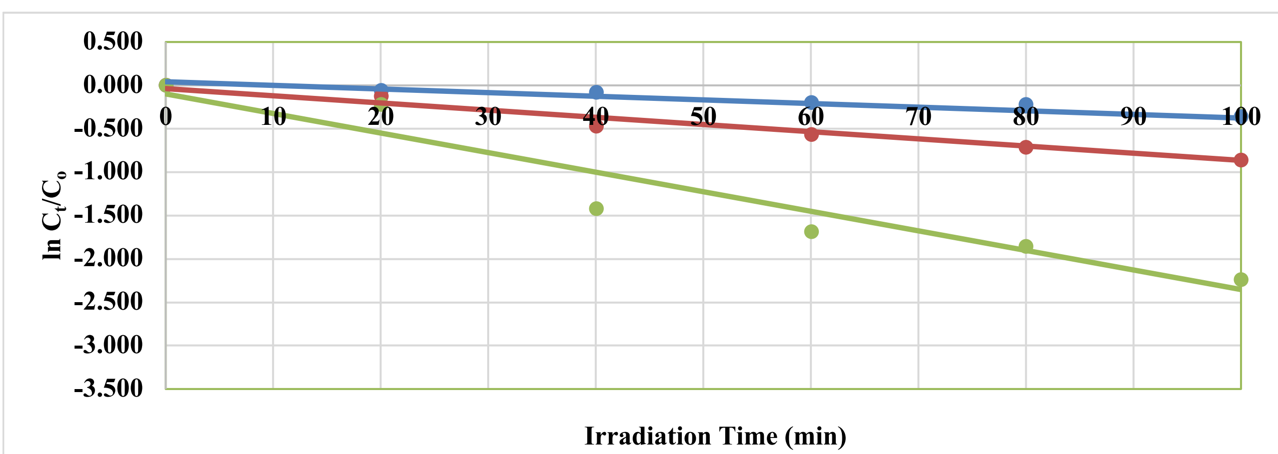

Fig. 4: Plot of ln C_t/C_0 vs. irradiation time for variable amount of nanoTiO_2/AC catalyst.

Fig. 4 shows the plot of ln C_t/C_o vs. irradiation time for variable amount of nanoTiO_2/AC catalyst through which the value of rate constant was obtained. The correlation coefficient indicated that the reaction followed pseudo first order reaction kinetics.

Fig. 5 shows the effect of amount of nanoTiO_2catalyst on the MB degradation efficiency. Catalyst used was nanoTiO_2 and showed no MB degradation during 0 to 20 min. It was observed that the degradation of methylene blue was increases using 6 mg of nanoTiO_2 at 120 minutes comparing to 10mg of nanoTiO_2, where the maximum degradation percentage when using 2 mg of nanoTiO_2 was approximately 13%, so the optimum amount of catalyst was increased using 6 mg of TiO_2/AC at 120 minutes comparing to 10 mg of TiO_2/AC, where the maximum degradation percentage when using 2 mg of TiO_2/AC was approximately 31%, so the optimum amount of catalyst was chosen to be 6 mg. Rate constant (k) was obtained from a plot of ln C_t/C_0 vs. irradiation time as a function of nanoTiO_2 amount added to solution, where 6 mg of catalyst increase rate constant of the reaction ($k = 0.0239\ min^{-1}$). **Fig. 6** shows plot of ln C_t/C_0 vs. irradiation time for variable amount of nanoTiO_2 catalyst. The correlation coefficient indicated that the reaction followed pseudo first order reaction kinetics.

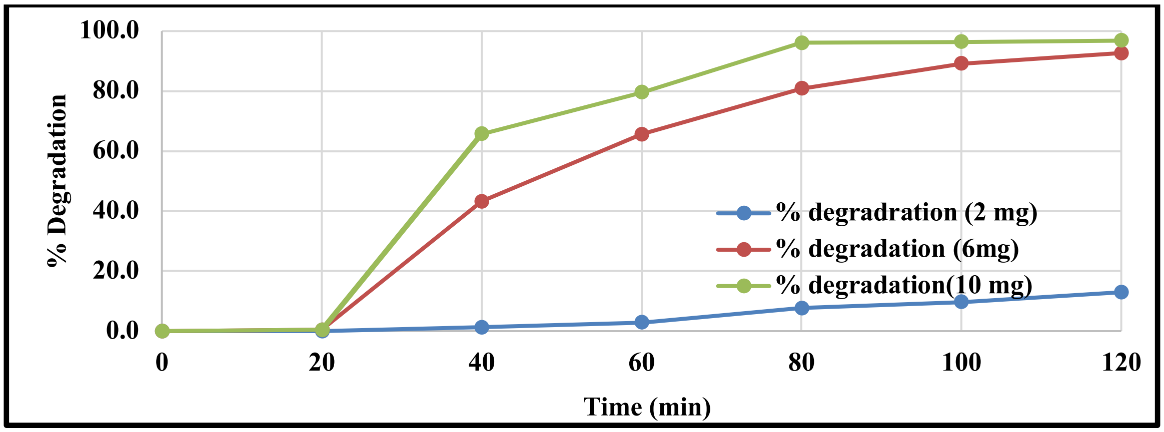

Fig. 5: Effect of amount of catalyst (nanoTiO_2) on the MB degradation efficiency. 0 to 20 min was in dark followed by sunlight irradiation. Catalyst used was nanoTiO_2 and showed no MB degradation during 0 to 20 min.

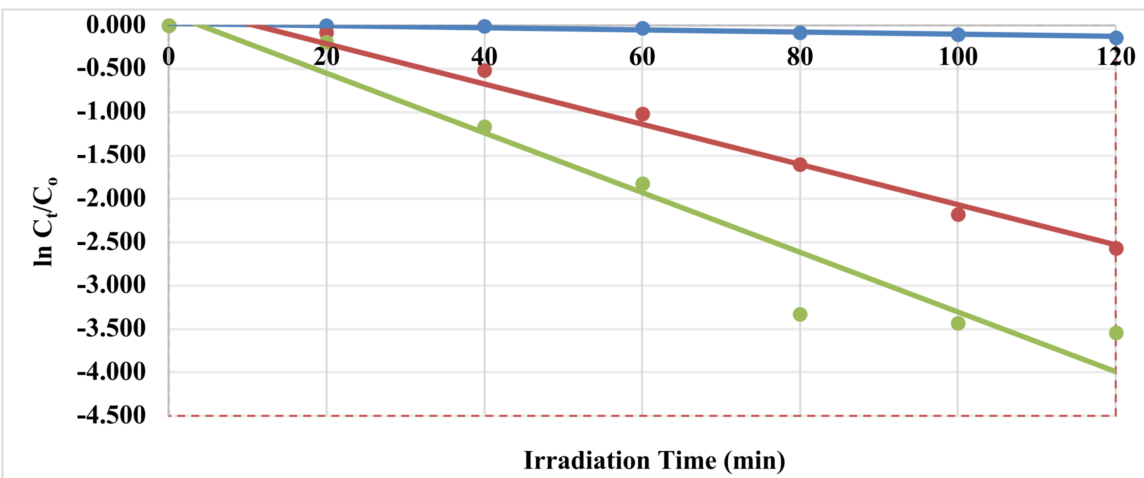

Fig. 6: Plot of ln C_t/C_o vs. irradiation time for variable amount of nanoTiO_2 catalyst.

4.2 Effect of pH of MB Solution

The effect of pH on the photocatalytic degradation of methylene blue using nanoTiO_2/AC was investigated and graphically presented in **Fig. 7**. It is evident from the data that the degradation rates of methylene blue start increasing with increasing pH of solution. The explanations of this behavior in photocatalytic degradation of MB due to when the pH was increased, attraction between cationic dye molecules and hydroxyl ions increases and accordingly the rate of photocatalytic degradation of the dye was increased [2,5]. **Fig. 8** shows the plot of ln C_t/C_0 vs. irradiation time for variable pH of the MB solution obtained for nanoTiO_2/AC catalyst and the value of k was determined. **Fig. 9** shows the effect of pH of the MB solution on the MB degradation efficiency. The catalyst used was nanoTiO_2 and showed no MB degradation during 0 to 20 min. **Fig. 10** shows a plot of ln C_t/C_0 vs. irradiation time for variable pH of the MB solution obtained for nanoTiO_2 catalyst. The correlation coefficient values indicated that the data well fitted and the reaction followed pseudo first order reaction kinetics.

4.3 Effect of Initial MB Concentration

The effect of initial dye concentration on the degradation efficiency was investigated by varying the initial dye concentration. 5 ppm, 10 ppm, and 15 ppm of MB concentrations were used to evaluate the photocatalytic activity and graphically presented in **Fig. 11**. As a result photocatalytic degradation efficiency increased when concentration of dye increase up to 10 ppm after 100 min irradiation time, while photocatalytic degradation efficiency was to decrease with further increase in the concentration of dye. This fact explain as , adsorption capacity will be higher at lower concentration of dye (more active site in nanoTiO_2/AC surface to adsorbed MB molecules), but when dye concentration increase the dye start acting as a filter for the incident light and it does not permit the desired light intensity to reach the photocatalyst surface [2,5].
Fig. 12 shows the plot of ln C_t/C_o vs. irradiation time for variable initial concentration of MB in the solution obtained for nanoTiO_2/AC catalyst and the value of k was obtained.

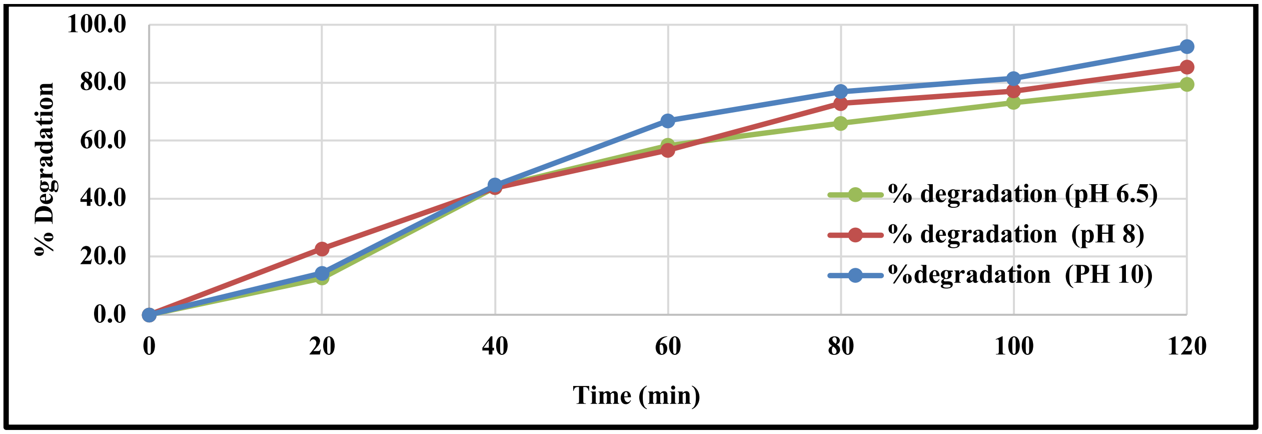

Fig. 7: Effect of pH of the MB solution (6.5, 8 and 10) on the MB degradation efficiency. 0 to 20 min stirred in dark followed by sunlight irradiation. Catalyst used was nanoTiO_2/AC and showed MB adsorption on activated carbon during 0 to 20 min.

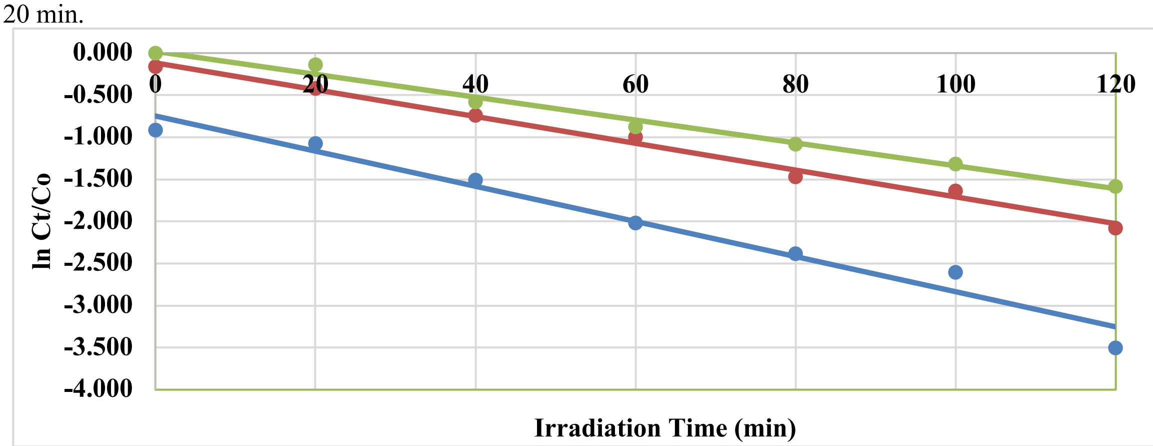

Fig. 8: Plot of ln C_t/C_o vs. irradiation time for variable pH of the MB solution obtained for nanoTiO_2/AC catalyst.

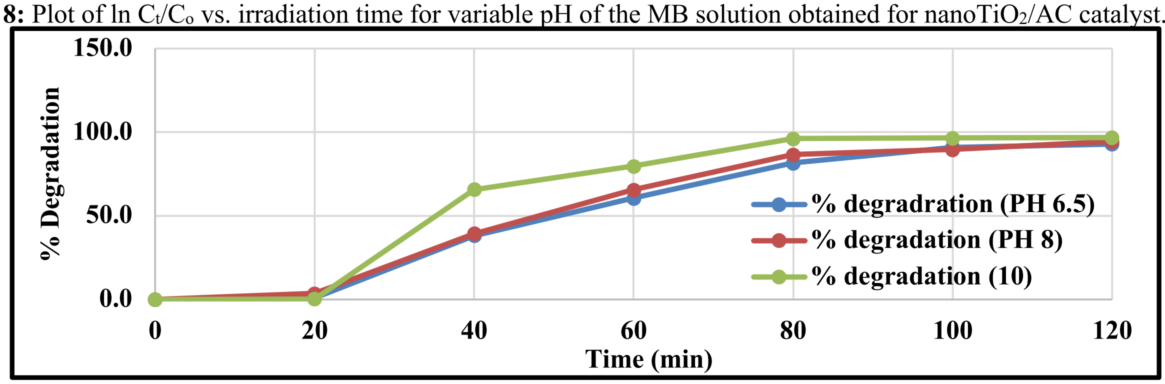

Fig. 9: Effect of pH of the MB solution (6.5, 8 and 10) on the MB degradation efficiency. 0 to 20 min stirred in dark followed by sunlight irradiation. Catalyst used was nanoTiO_2 and showed no MB degradation during 0 to 20 min.

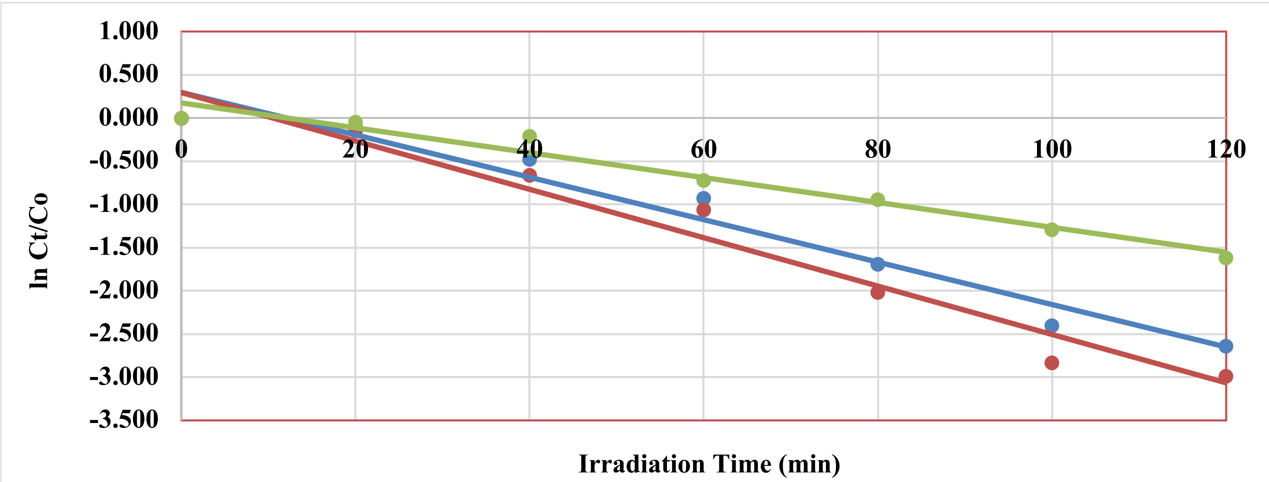

Fig. 10: Plot of ln C_t/C_o vs. irradiation time for variable pH of the MB solution obtained for nanoTiO_2 catalyst.

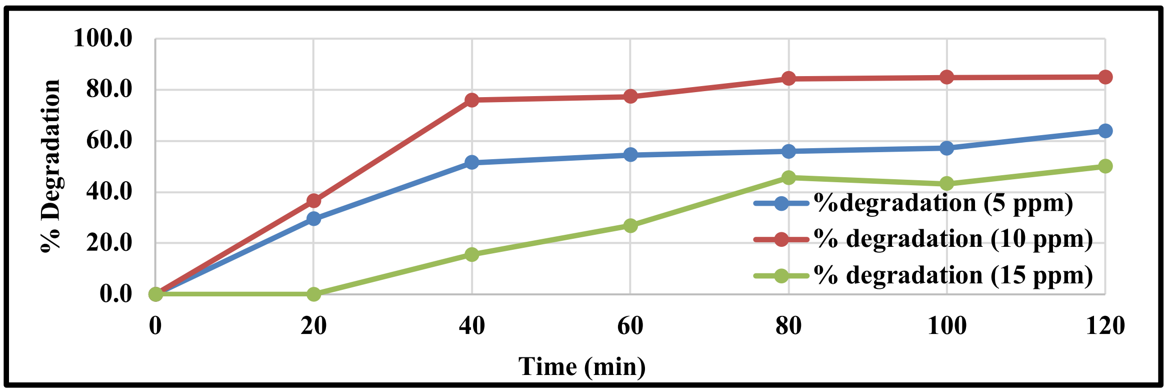

Fig. 11: Effect of initial concentration of MB (5 to 15 ppm) on the photocatalytic degradation efficiency. Catalyst used was nanoTiO_2/AC and showed MB adsorption during 0 to 20 min.

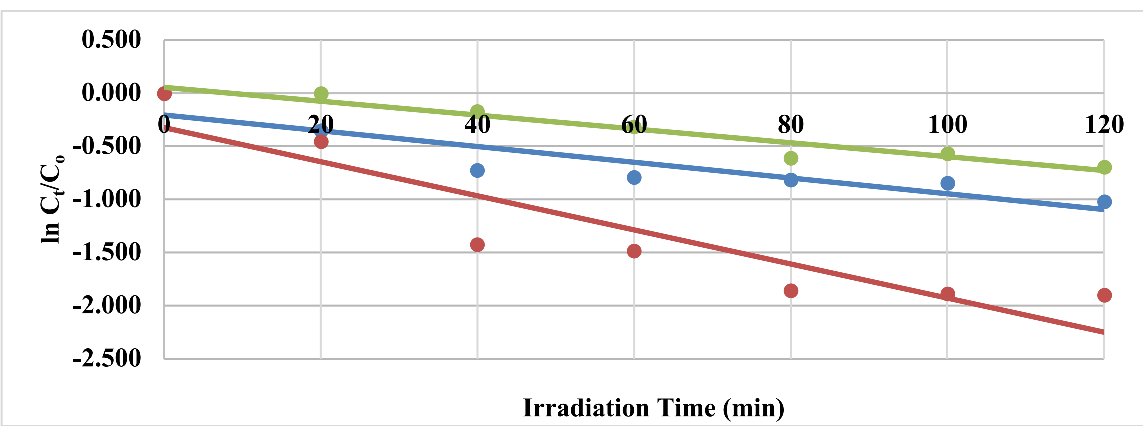

Fig. 12: Plot of ln C_t/C_o vs. irradiation time for variable initial concentration of MB in the solution obtained for nanoTiO_2/AC catalyst.

Fig. 13 shows effect of initial concentration of MB on the photocatalytic degradation efficiency of the nanoTiO_2 catalyst and showed no MB degradation during 0 to 20 min stirring which was done in dark. **Fig. 14** shows plot of ln C_t/C_o vs. irradiation time at initial concentration of MB in the solution using nanoTiO_2 catalyst. The correlation coefficient was 0.9609, 0.9646 and 0.9011 at pH 6.5, 8 and 10 respectively. The correlation coefficient values indicated that the data was well fitted and the reaction followed pseudo first order reaction kinetics.

Table 1 shows correlation coefficient and rate constant values obtained for the degradation of MB under solar irradiation for the three variables as a function of ln C_t/C_o vs. irradiation time using nanoTiO_2/AC and nanoTiO_2 catalysts. The data clearly indicates that the data was well fitted with pseudo first order kinetics.

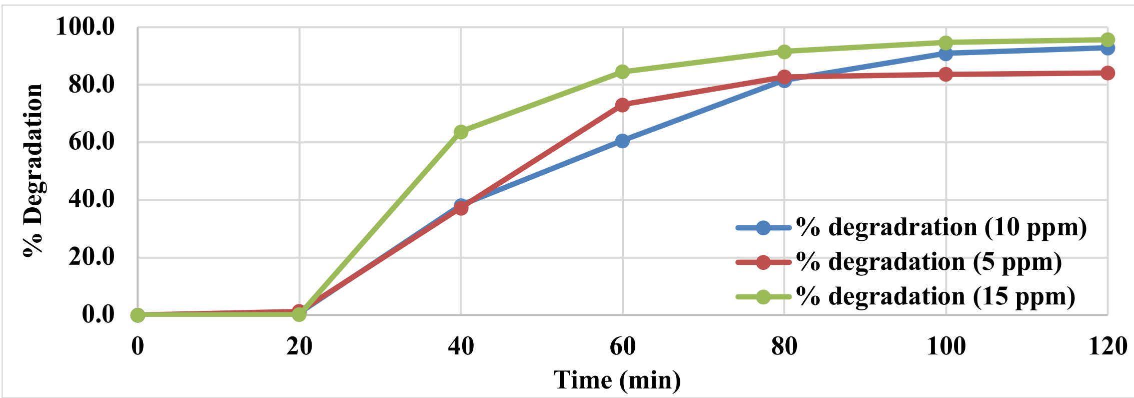

Fig. 13: Effect of initial concentration of MB (5 to 15 ppm) on the photocatalytic degradation efficiency. Catalyst used was nanoTiO_2 and showed no MB degradation during 0 to 20 min. The correlation coefficient were 0.9609, 0.9646 and 0.9011 at pH 6.5, 8 and 10 respectively.

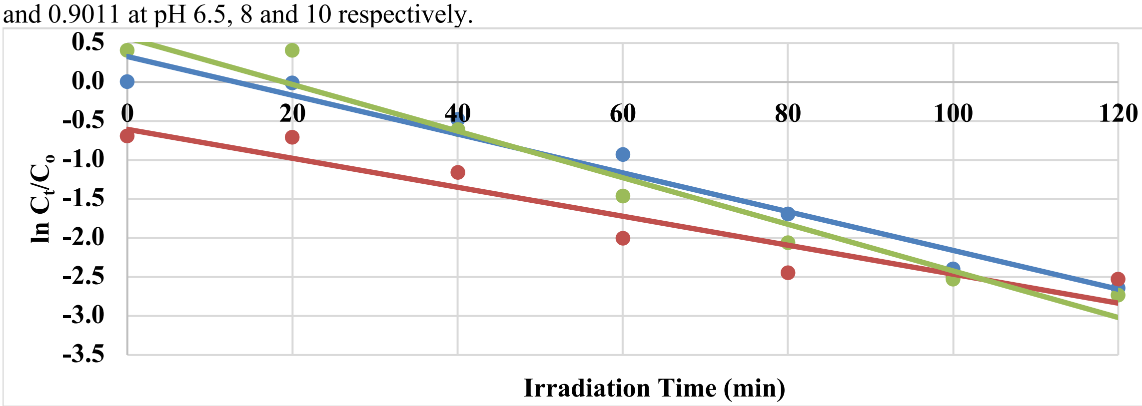

Fig. 14: Plot of ln C_t/C_o vs. irradiation time for variable initial concentration of MB in the solution obtained for nanoTiO_2 catalyst.

Table 1: Correlation coefficient (R^2) and rate constant (k) values for the degradation of MB under solar irradiation using nanoTiO_2/AC and nanoTiO_2 catalysts.

	nanoTiO_2/AC Catalyst		**nanoTiO_2 Catalyst**	
Amount of Catalyst, mg	**R^2**	**k, min^{-1}**	**R^2**	**k, min^{-1}**
2	0.8700	0.0030	0.9219	0.0012
6	0.9860	0.0180	0.9772	0.0239
10	0.8320	0.0160	0.9257	0.0342
pH of the MB Solution	**R^2**	**k, min^{-1}**	**R^2**	**k, min^{-1}**
6.5	0.9880	0.0130	0.9609	0.0249
8	0.9920	0.0150	0.9646	0.0261
10	0.9680	0.0200	0.9011	0.0342
Initial Concentration of MB (ppm)	**R^2**	**k, min^{-1}**	**R^2**	**k, min^{-1}**
5	0.8290	0.0070	0.9019	0.0186
10	0.8320	0.0160	0.9609	0.0249
15	0.9350	0.0060	0.9594	0.0299
R^2 = Correlation coefficient, k = Rate Constant				

5 Conclusions

This study clearly demonstrated efficient photodegradation of methylene blue dye using nanoTiO_2 and nanoTiO_2/AC catalysts. The effect of parameters such as amount of catalyst added to the MB solution, pH of the solution and initial concentration of MB were studied. Following are the main conclusions of this study.

- The study shows efficient photodegradation of methylene blue dye using nanoTiO_2 and nanoTiO_2/AC catalysts.
- Degradation of the MB was found increasing with higher amount of catalyst and towards basic pH.
- Higher reaction rates were achieved using nanoTiO_2 compared to nanoTiO_2/AC catalyst.
- Adsorption of the MB dye was observed in dark over nanoTiO_2/AC catalyst.
- The titania-based heterogeneous catalysts were found quite efficient to degrade pollutants from industrial wastewater.
- The experimental data obtained for both nanoTiO_2 and nanoTiO_2/AC catalysts was well fitted to pseudo first order reaction kinetics.

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