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Solar Photocatalysis of Methyl Orange Using Multi-Ion Doped TiO_2 Catalysts

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Abstract**—**Solar-light activated titanium dioxide photocatalysts were prepared by hydrolysis of titanium (IV) isopropoxide with thiourea, followed by calcinations at 450 °C. The experiments demonstrated that methyl orange in aqueous solutions were successfully degraded under solar light using doped TiO_2. The photocatalytic oxidation of a mono azo methyl-orange dye has been investigated in multi ion doped TiO_2 and solar light. Solutions were irradiated by solar-light until high removal was achieved. It was found that there was no degradation of methyl orange in the dark and in the absence of TiO_2. Varieties of laboratory prepared TiO_2 catalysts both un-doped and doped using titanium (IV) isopropoxide and thiourea as a dopant were tested in order to compare their photoreactivity. As a result, it was found that the efficiency of the process strongly depends on the working conditions. The highest degradation rate of methyl orange was obtained at optimum dosage using commercially produced TiO_2. Our work focused on laboratory synthesized catalyst and the maximum methyl orange removal was achieved at 81% with catalyst loading of 0.04 g/L, initial pH of 3 and methyl orange concentration of 0.005 g/L using multi-ion doped catalyst. The kinetics of photocatalytic methyl orange dye stuff degradation was found to follow a pseudo-first-order rate law. The presence of the multi-ion dopant (thiourea) enhanced the photoefficiency of the titanium dioxide catalyst.

Keywords**—**Degradation, kinetics, methyl orange, photocatalysis.

I. INTRODUCTION

MAJOR sources of the contamination of surface and ground water are run off from urban areas, return flows from agricultural fields, leaching and textile industries [1]. In the textile industry, it is estimated that 10–15% of the dye is lost during the dyeing process and released as effluent [2]. The release of those colored waste waters in the environment is a considerable source of non-aesthetic pollution since the presence of small amounts of dyes (below 1 ppm) is clearly visible [3]. Dye wastes can also generate eutrophication and dangerous by-products through oxidation, hydrolysis or other chemical reactions taking place in the wastewater phase [4]. Decolouration of dye effluents has therefore received increasing attention. Traditional physical-chemical techniques (adsorption on activated carbon, ultra-filtration, reverse osmosis, oxidation by chemical agents, etc.) can generally be used efficiently [3]. Nevertheless, they are non-destructive since they just transfer organic compounds from water to another phase, causing a secondary pollution [3]. Due to the large degree of aromatics present in dye molecules and the stability of modern dyes, biological treatment is ineffective for degradation [5]. Azo compounds are resistant to aerobic degradation and under anaerobic conditions, the azo linkage is reduced to generate aromatic amines that are colorless but can also be toxic and potentially carcinogenic [6]. For all these reasons, the development of new technologies of wastewater purification leading to complete destruction of the contaminants becomes now essential as the most suitable solution of the problem.

Advanced Oxidation Processes (AOPs) have been proposed as the alternative methods for water purification [7]. These methods were based on the generation of very reactive species such as hydroxyl radicals ($^{\bullet}OH$) that oxidize a broad range of pollutants quickly and non-selectively [3]. Hermann, states that among AOPs, heterogeneous photocatalysis using TiO_2 as photo-catalyst appears as the most emerging destructive technology [8]. More effort is required to meet the regulatory wastewater discharge standards. TiO_2 (titanium dioxide) photocatalysis has emerged as a promising wastewater treatment technology.

The aim of this work was to investigate the possibility of using solar radiation and multi-ion doped TiO_2 for the degradation of different pollutants. Methyl Orange (MO) was used as a model compound because it was possible to use UV–visible spectroscopy to monitor the degradation under different conditions such as MO concentration, pH, TiO_2 concentration and solar intensity.

II. EXPERIMENTAL

A. Materials

Titanium (IV) isopropoxide with 97% purity and thiourea were bought from Aldrich-Sigma and used without further purification. MO was of pure grade powder dye and was used without purification. Double distilled water was used in this work. The other chemicals that were used include ethanol, hydrochloric acid and sodium hydroxide.

B. Apparatus

T80+ UV/VIS spectrophotometer (PG Instruments Ltd, UK) was used to inspect the degradation process of MO. The solution of MO was irradiated by using solar light and three volumetric flasks were used as reactors. pH meter (Thermo Scientific Orion Star A111 pH Benchtop Meter) was used to measure pH at different time intervals.

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C. Experimental Procedure

1) Catalysts Synthesis and Characterisation

Modified TiO_2 powders were synthesized by mixing 10 mL of titanium (IV) isopropoxide (97%, purity) with appropriate amount (optimum 125 mg) of organic dopant (thiourea) and 10 mL of distilled water. The solution was stirred at room temperature for 45 min, followed by 24-hour thermal treatment at 500 ^{0}C. The resulting powder was separated by filtration, washed with ethanol (10 mL, three times), and calcinated at 450 ^{0}C for 2 h. The reference sample, pure TiO_2, was prepared by hydrolysis of titanium (IV) isopropoxide using pure water and calcinated at 450^{0}C for 2 hours.

2) Photocatalytic Experiments

The model compound chosen for this work was MO. MO was chosen because it is orange in basic and red in acidic medium. When dissolved in water, the UV-visible spectrum shows two maxima. Different concentrations of MO were prepared ranging between 0.01 and 0.03 g/L. The amount of TiO_2 was weighed using Shimadzu AY220 electronic mass balance (Shimadzu Corporation, Japan) and placed in the reactor. MO solution was placed in the reactor together with the catalyst and the mixture was placed at the same position all the time and exposed to solar light. The solution was stirred and the solution was left to exchange oxygen with the environment. The pH variation was measured using Thermo Scientific Orion Star A111 pH Benchtop Meter at definite intervals and at the end of the reaction. During a period of 5 hours, at one hour intervals, a small quantity of solution was collected and placed in the refrigerator for catalyst particles to settle down. The collected solutions were then filtered using syringe filters (Ø= 0.45µm). Afterwards, the concentration of MO was measured using the UV-vis spectrophotometer (PG Instruments) at a λ_{max} of 465 nm. All the measurements were performed for the clear solutions.

D. Experimental Design and Data Analysis

The experiment was performed by exposing the solutions of MO and multi-ion doped TiO_2 and undoped TiO_2 to solar light at the top of the roof for the photocatalysis process to take place. The runs took place on different days to expose the materials to different solar intensity. The parameters that were controlled and varied were as follows:

a) The concentration of the MO was varied three times while catalyst loading and pH were kept constant.
b) The load of the catalyst was varied three times also with the concentration of the MO kept constant as well as the pH.
c) As the solutions were exposed to sunlight, samples were taken to be analyzed at different time intervals, and checked if the length of exposure has an effect on the photocatalysis process.

III. RESULTS AND DISCUSSION

The catalysts obtained in this experimental procedure were in a form of a yellowish powders. The pH of the solutions containing TiO_2 and different concentration of MO were varied. Table I shows that the pH of solutions changed during photodegradation of MO toward a more acidic solution. Only at pH 3 was there no change in pH. The degradation ratios of MO only using doped TiO_2 catalyst were relatively high in acidic and lowest in neutral solution as shown in Figs. 1-5. The best degradation was obtained with pH = 3 (Figs. 1-7). Fig. 1 shows effect of pH on the removal of MO in presence of multi-ion doped and TiO_2.

TABLE I
THE EFFECT OF PH ON THE RATE OF DEGRADATION (H^{-1})

pH before radiation	**After 1h**	**After 2h**	**After 3hrs**	**After 4hrs**	**After 5hrs**
pH=3.2	3.3	3.0	3.1	3.2	3.0
pH=5.2	5.8	5.1	5.4	4.8	4.5
pH=6.8	7.2	6.2	5.1	5.9	5.4

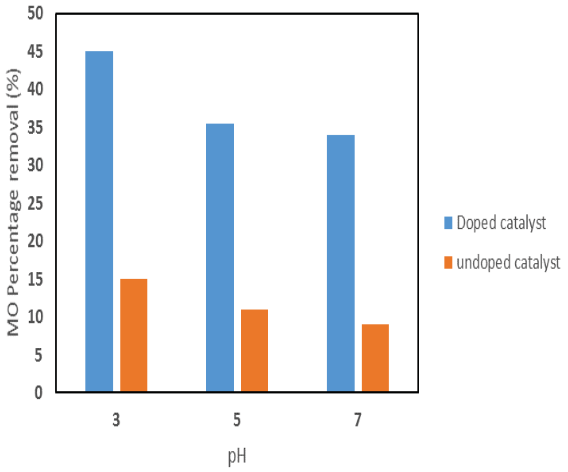

Fig. 1 Effect of pH on the removal of MO in presence of multi-ion doped and TiO_2; Experimental conditions: 0.01g/L MO concentration, catalyst =0.005g /L

Zeleska et al. stated that the most pronounced photoactivity under visible light was exhibited by TiO_2 modified with Thiourea than that which was not modified [9]. The amount of dopant used during catalyst preparation in this work was calculated using optimum amount that was used by Zeleska et al. The assumption made by Zeleska et al. [9] was that the content of nitrogen in the catalyst after hydrolysis should be equal to 0.5, 1, 2 and 5 wt% of the catalyst dry mass, respectively. The authors also claim they did element analysis and found that the dopant contained reasonable amounts of sulphur, nitrogen and carbon.

A. The Effect of pH

The pH of the aqueous solution affects the behaviour of TiO_2 significantly, including the charge on the particles, the size of the aggregates it forms, and the positions of the conductance and valence bands [10]. Often, the pH of industrial wastewater can be very acidic or basic. In this case, the effect of pH on TiO_2 photocatalytic efficiency should be taken into account as the process could be enhanced varying the pH by simple/cheap methods as for example mixing different wastewater streams [11].

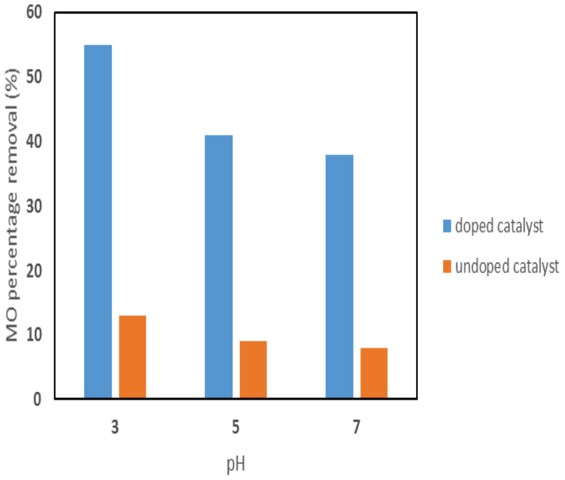

Fig. 2 Effect of pH on the removal of MO in presence of multi-ion doped and TiO_2. Experimental conditions: 0.01g/L MO concentration, catalyst =0.01g /L

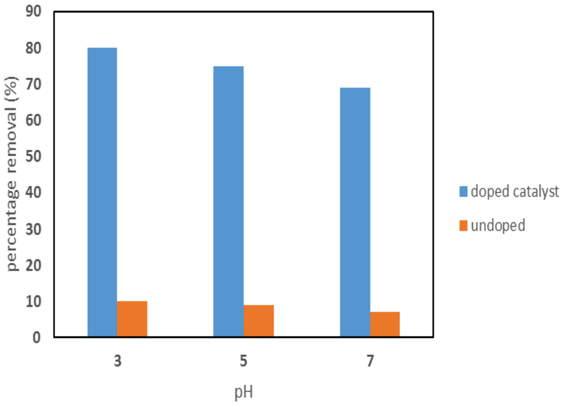

Fig. 3 Effect of pH on the removal of MO in presence of multi-ion doped and TiO_2. Experimental conditions: 0.01g/L MO concentration, catalyst =0.02g /L

Fig. 1 shows that at lower concentrations and lower modified TiO_2 catalysts loading, pH plays an important role in photodegradation of MO as it is observed that more MO was removed at lower pH that at neutral pH of the solution. At lower pH values (around pH=3) the removal of the dye was more favourable due to the presence of carbonyl and hydroxyl functional groups on the surface on the adsorbent. In acidic condition, these functional groups on the adsorbent surface polarize thereby creating electrostatic interaction, hydrogen bonding and van der walls interaction [12]. The effects of adsorption and desorption can deduce an explanation for degradation ratio at high and low pH values changes. At low pH values, the surface of TiO_2 particles is positively charged and is easily capable of adsorbing the MO ion having a negative charge [12]. At higher pH values, on the surface of TiO_2 particles there are superfluous negative charges which will lead to repulsion to the MO anion in solution, resulting in negligible adsorption [13]. The solution pH also influences the composition of reactive radicals in the solution.

In our work, it was observed that the highest degradation rate was achieved at pH = 3 with the highest being 91%. The best photocatalytic degradation ratios or percentage removal of MO in the presence of TiO_2 powder show that the treatments of some organic pollutants like MO should be performed in highly acidic medium in order to achieve the maximum degradation.

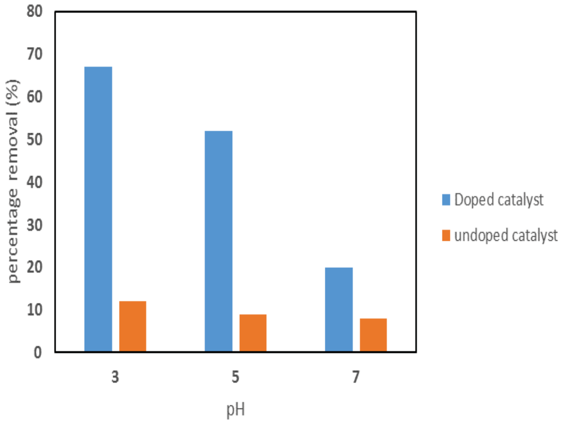

Fig. 4 Effect of pH on the removal of MO in presence of multi-ion doped and TiO_2. Experimental conditions: 0.01g/L MO concentration, catalyst =0.04g /L

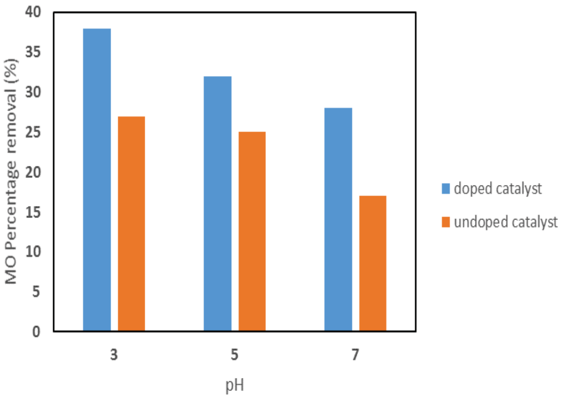

Fig. 5 Effect of concentration of MO in presence of multi-ion doped and TiO_2. Experimental conditions: 0.02g/L MO concentration, catalyst =0.005g /L

A very important feature of photocatalysis is usually not taken into consideration when it is used for decontamination of water. During photocatalysis, a multitude of intermediate products are produced that may behave differently depending on the pH of the solution. To use only the rate of decomposition of the original substrate could yield pH that is for contaminant degradation. Therefore, a detailed analysis of the pH conditions should include not only the initial substrate, but also the rest of the compounds produced during the process. Measurement of an overall parameter as TOC (or

COD, or toxicity, or biodegradability, etc.) should be used for choosing the optimum pH, or at least to determine the effect of pH on the behaviour of the chosen key parameter.

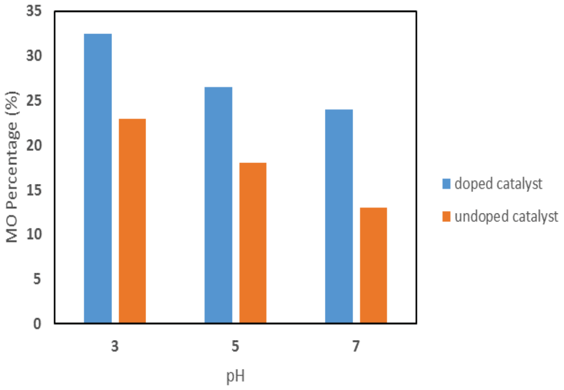

Fig. 6 Effect of concentration of removal of MO in presence of multi-ion doped and TiO_2. Experimental conditions: 0.02g/L MO concentration, catalyst =0.01g /L

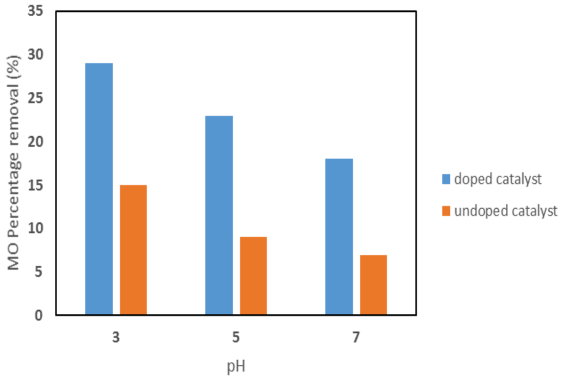

Fig. 7 Effect of concentration of MO in presence of multi-ion doped and TiO_2. Experimental conditions: 0.03g/L MO concentration, catalyst =0.02g /L

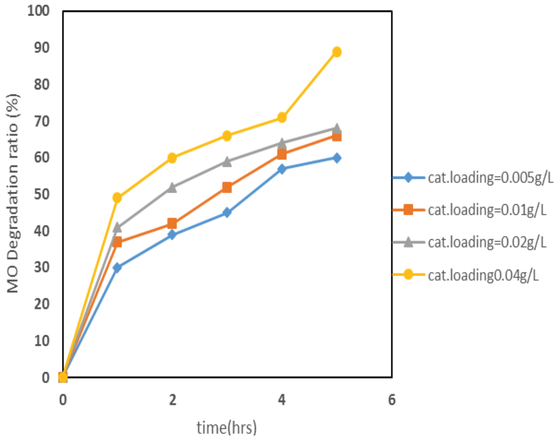

Fig. 8 Effect of catalyst loading on the degradation ratio of MO at pH 3 using doped TiO_2

As explained based on the results on Fig. 1, all the results presented in Figs. 1-5 evidently proved that even with increasing the amount of MO concentration but also increasing the amount of catalyst reasonable in such a way that catalyst particle do not block sun radiation, the best photo degradation will be observed at lower concentrations.

B. The Effect of MO Concentration.

From Figs. 5-7 and it was observed that about 92% degradation of MO was achieved within 5 hours using 0.04 g/L of TiO_2. Fig. 6 shows that MO degradation was well achieved when the solution was left under solar radiation for a longer period of time. It has been reported by [15] and [16] that the photon efficiency of the photocatalytic DCA degradation considerably decreases as the light intensity is increased.

As it can be seen from Fig. 8, adsorption increases more rapidly at the initial time period and the rate of adsorption decreases towards the equilibrium. The equilibrium can be assumed to have been achieved after five hours as the final dye concentration does not seem to increase much after this limit. It was also observed that as radiation time increases, the percentage removal also increases but more removal was observed when catalyst doping increased to 0.04 g/L. The reason might be the saturation of the active sites which does not allow further adsorption to take place.

Concentrations ranging from 0.01 to 0.03 g/L MO were used. The maximum degradation was observed with commercially produced catalyst as observed from Figs. 6-8. For the synthesized catalyst, it was observed that doped catalyst performed better than the undoped. It was observed that MO is quite stable under solar conditions and the rate constant for the degradation of MO was calculated to be 0.0001 h^{-1}.This shows that the degradation of MO under solar radiation without any catalyst is quite slow.

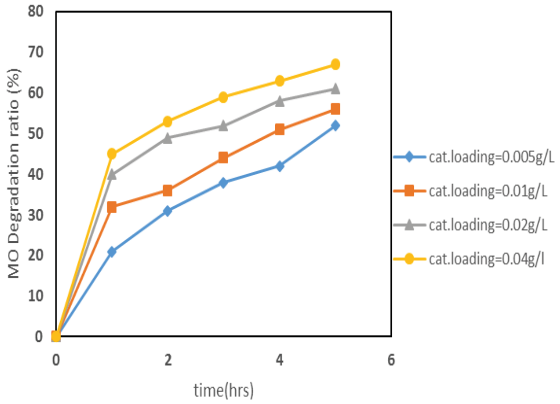

Fig. 9 Effect of catalyst loading on the degradation ratio of MO at pH 3 using undoped TiO_2

The photocatalytic degradation efficiency was observed to be inversely proportional to the concentration of MO as it was observed that the degradation efficiency increased with the decreasing concentration of MO. Al-Qaradawi and Salman stated that this may be attributed to the fact that MO degradation at high concentration of reactant reaches a saturation limit [14].

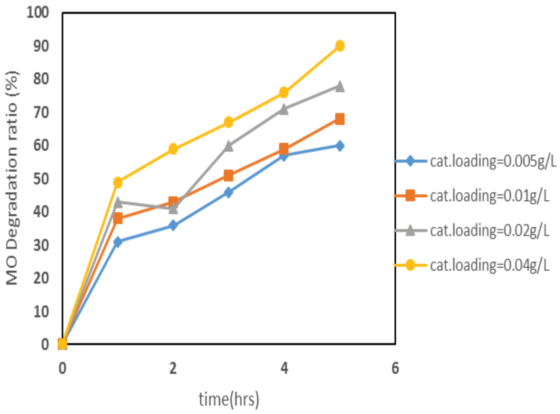

Fig. 10 Effect of irradiation time on the degradation ratio of MO at pH 3 using commercially produced TiO_2

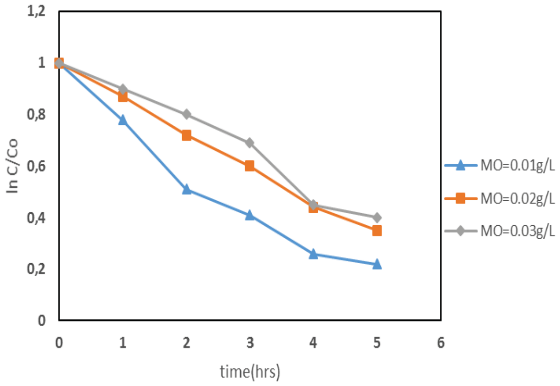

Fig. 11 Reaction kinetics on photocatalytic degradation of MO using doped catalyst

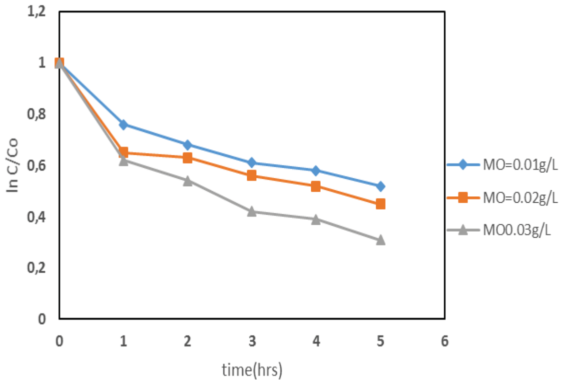

Fig. 12 Reaction kinetics on photocatalytic degradation of MO using doped catalyst

C. The Effect of Catalyst Loading

The amount of catalyst added on the solution was optimized by varying the TiO_2 between 0.005 and 0.04 g/L in order to achieve the highest degradation ratio. It was found that the best results were obtained when the added amount of TiO_2 in the solution was about 0.04 g/L as shown in Figs. 6-8.

D. Kinetics

All photocatalysis experiments were standardized by using the same concentration of MO with the same type of reaction vessel. The vessel was situated at the same location on the roof or where there was plenty of visible sunlight throughout this work. The UV–visible spectra for MO in distilled water show two absorption maxima as previously reported [14]. Al-Qaradawi and Salman [14] observed that MO has the band at 270 nm and the second band was at 465 nm. The band at 465 nm is normally used to monitor the effect of the photocatalysis on the degradation of MO. Optimum conditions and the effect of different parameters on the degradation of MO under solar radiation were studied at different experiments and from Table III, it can be seen that the degradation followed first order kinetics. The rate constants found in Table III were determined using the slopes of $\ln C/C_o$ vs Time from Figs. 11 and 12.

TABLE II
RATE OF DEGRADATION K(H^{-1}) UNDER DIFFERENT CONDITIONS

pH of reaction mixture	K(h^{-1})	R^2
3	2.33	0.971
5	0.457	0.902
7	0.628	0.940

The initial kinetics of photodegradation of a single general pollutant, P by oxygen sensitized by TiO_2, upon steady state illumination is often described by Langmuir-Hinshelwood kinetic scheme [8], [17]-[19] and represented by (1):

$$R = \frac{[C_o]-[C_t]}{t_o - t_t} = \frac{kK[C_o]}{1+K[C_o]} \qquad (1)$$

where R = Rate of pollutant degradation (mg/L), $[C_o]$ = Initial concentration of pollutant (mg/L), $[C_t]$= Concentration of pollutant (mg/L), t_o = Time at initial concentration (min), t_t = time at concentration (min), K is equilibrium adsorption constant (mg/L), K = pseudo first order reaction rate constant (min^{-1}).

Rate constants for degradation of MO in water were obtained from solutions of the linearized rate equations for all concentrations ranges:

$$\mathrm{In}\left(\frac{C_t}{C_o}\right) = kt \qquad (2)$$

where: C_o is the initial concentration of MO at t=0 and C_t is the residual concentration of MO left in solution at time t.

Plots of $\mathrm{In}\left(\frac{C_t}{C_o}\right)$ as a function of time for solutions of MO with varying catalyst loading on the plot gave linear curves, typical of pseudo first order kinetics of photocatalytic systems. Pseudo first order rate constants were obtained from linear transforms of the plot $\mathrm{In}\left(\frac{C_t}{C_o}\right)$ as a function of time from apparent first order kinetic equation. The results obtained in this work gave good fit of the data to the first order plots at all catalysts loading studied, as indicated by the high R^2 is an indication the degradation of MO can be described with first order kinetics

This result for the degradation of MO indicates that photocatalysis is a promising technology for the removal of dyes and other undetectable limits of other hazardous compounds from polluted water with careful choice of reaction conditions to ensure complete decolorization

IV. CONCLUSION

TiO_2, both doped and undoped, were used as photocatalysts for the degradation of MO which was used as a model compound. TiO_2 was successfully doped with thiourea producing a yellowish catalyst. MO photodegradation in the presence of the catalysts that were doped with thiourea was influenced by various factors such as pollutant concentration, catalyst loading and pH. The highest photodegradation efficiency was observed when pH=3, therefore pH has a large effect on the degradation rate constant and the pH of all solutions changed toward lower value (more acidic) after 5 h. The photocatalytic degradation of MO was fitted well with the first-order model. The optimum concentration of MO was 0.01 g/L for this work and high percentage removal of MO was observed, and increasing the concentration cause the degradation rate to decrease. In general, maximum degradation of MO was achieved after 5 h. It was found that doped TiO_2 is more active or performs better than pure TiO_2.

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