

PHOTO-CATALYST DEGRADATION OF TARTRAZINE COMPOUND IN WASTEWATER USING TiO₂ AND UV LIGHT

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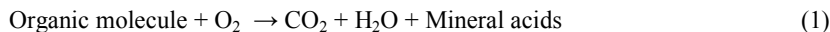
Abstract

Organic contaminants present in industrial wastewater are of major concern with respect to the health of the general public. Photo-catalytic process, one of the Advanced Oxidation Processes, is a promising technology for remediation of organic pollutants at ambient conditions. Photo-catalytic processes in the presence of TiO₂ provide an interesting method to destroy hazardous organic contaminants. The experimental results showed that considerable degradation of Tartrazine organic compound has been achieved by combination of TiO₂ and UV light, the process followed first order kinetics. The results showed that the increased level of TiO₂ concentration does not necessarily increase the rate of degradation of organic compounds. Also, it was found that the higher the TiO₂ concentrations the higher the pH values and more oscillatory behaviors were observed. Not much effect has been noted on the process due to temperature variation.

Keywords: Photo-Catalyst, Tartrazine.

1. Introduction

Organic contaminants present in industrial wastewater are of major concern with respect to the health of the general public. There are several established ways to remove such contaminants. The most widely used method is biological treatment. Other important applied methods include adsorption on activated carbon, hydrogen peroxide/UV-light, Ozone/UV/hydrogen peroxide and γ -radiolysis [1, 2]. Heterogeneous photo-catalytic oxidation, one of the Advanced Oxidation Processes, has proved to be a promising technology for remediation of organic pollutants at ambient conditions, see Eq. (1) below



The main advantage of photo catalytic oxidation is the complete destruction of organic pollutants. In respect to some of the important major destructive methods that are currently used by big wastewater companies to purify water, it has been shown that the photo-catalysis process has the advantage of complete destruction compared with the other more established water purification processes. However, this method is not rapid in action, nor easy to use and maintain, nor cheap to buy [3, 4].

In this regard and in recent years, advanced oxidation processes (AOPs) have been described as efficient procedures for obtaining high oxidation yields from several kinds of organic compounds. These methods are based on the generation of very reactive agents such as hydroxyl radicals (OH) that extremely reactive and strong oxidizing agents ($E_{ox} = 2.8 \text{ V}$), capable of mineralizing organic pollutants [5]. For enhancement in efficiency, the use of TiO_2 catalyst has gradually attracted more interest. This is due to the fact that TiO_2 is the most acceptable and a very cheap catalytic material; also that having the capability of being recovered from treated wastewater [6]. The higher activity of the UV/ TiO_2 process is due to the well-known fact that when TiO_2 is illuminated with UV light, electrons are promoted from the valence band to the conduction band of the semi-conducting oxide to give electron-hole pairs. The valence band hole, h^+ potential is positive enough to generate hydroxyl radicals at the surface. Also, the conduction band electron (e^-) is negative enough to reduce the oxygen molecules, present in the solution, which in-turn leads to the generation of another series of hydroxyl radicals [7].

There are three types of crystal structure in TiO_2 ; anatase, rutile and brookite types. The band gap value for anatase type is 3.2 eV, for rutile is 3.0 eV, and for the brookite is 2.96 eV. The necessary wavelength (λ) for TiO_2 is about 380 nm, which tells us that the light needed to activate TiO_2 is the ultraviolet light. Degussa P25 also can function under the sunlight due to the UV light which is about 5% of solar energy reaching the earth [8]. The estimation of the photo excitation wavelength is considered to be 380 nm.

When photo-catalyst titanium dioxide (TiO_2) absorbs Ultraviolet (UV) radiation from sunlight or illuminated light source (fluorescent lamps), it will produce pairs of electrons and holes. The electron of the valence band of titanium dioxide becomes excited when illuminated by light. The excess energy of this excited electron promotes the electron to the conduction band of titanium dioxide therefore creating the negative-electron (e^-) and positive-hole (h^+) pair. The energy difference between the valence band and the conduction band is known as the 'Band Gap'.

The use of natural solar UV energy (sunlight) instead of artificial UV lamp reduces the cost of photo-catalytic oxidation compared with some alternative technologies. The available solar UV-irradiation for a specific location is the main factor in determining the cost of a solar-based system. It was reported from the literature that lamp-based systems are cheaper than solar powered systems when fewer photons are needed. Solar-based systems with collector apertures of over 100 m^2 are clearly cheaper than lamp-based systems when the average yearly global UV irradiation is over 15 W/m^2 [9, 10].

A great deal of research has been conducted on the use of titanium dioxide (TiO_2) as a photo-catalyst for the decomposition of organic compounds, because

of its photochemical stability, non-toxicity and low-cost. Titanium is also reusable and simple to produce. TiO_2 offers great potential as an industrial technology for detoxification or remediation of wastewater due to several factors: Shorter process occurs under ambient condition: Direct UV light exposure increases the rate of reaction, oxidation of the substrates to CO_2 is complete and inexpensive, etc. [11-14].

The aim of the present work was to investigate the degradation of toxic organic and de-colorization mechanisms of colored wastewater under UV light. The selected organic pollutant is Tartrazine dye, which has a wide application in food and drugs industries. The toxic concentration of Tartrazine on humans has been reported to be 7.5 mg/kg [15]. Tartrazine appears to cause more allergic and intolerance reactions than other azo dyes. In the presence of a photo-catalyst such as TiO_2 in a freely suspended solution in a 1 liter glass beaker and circulated into the photo-catalytic reactor, different conditions such as TiO_2 concentration, pollutant (dye) concentration were applied.

2. Materials and Methods

2.1. Materials

In this project, the photo-catalysis that is considered for use was TiO_2 (P25, Degussa AG, Germany) with a surface area of $50 \text{ m}^2 \cdot \text{g}^{-1}$ and a primary particle size of 20 nm. Degussa P25 is a commercially produced form of titanium dioxide and this reference catalyst is composed of both phases; 80 % anatase and 20% rutile.

The organic pollutant, Tartrazine dye was used due to its wide application in food and drugs industries. The chemical structure of the Tartrazine dye is shown in Fig. 1.

As a source for the UV light, UV lamps (2×6 W) were considered for supplying wavelength $\lambda = 384 \text{ nm}$.

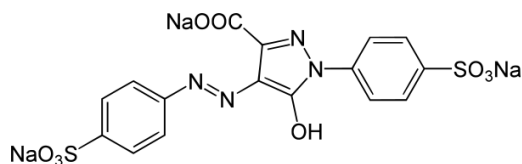


Fig. 1. Tartrazine Chemical Structure.

2.2. Experimental set-up

Experiments were performed in a (26.7 cm × 13.5 cm × 6.5 cm) transparent glass flat vessel as a photo-reactor, the liquid height in the reactor is 1.25 cm. The two UV lamps were placed 10 cm above the liquid surface of the vessel and both the vessel and the lamps were covered with aluminum foil to reflect light onto the liquid as shown in Fig. 2. The experimental tests were started by preparing contaminated solutions at different concentrations of dye (Tartrazine) in 1 liter beakers containing 25, 50 and 75 mg/L separately.

For solution set, different concentrations of titanium dioxide were added separately at 200, 500 and 700 mg/L. Then, the solution was mixed thoroughly. The photo-reactor was connected by a set of tubes in series with a pump to a beaker. The solution was circulated at a flow rate of 0.8 L/min. The reactor was then exposed to the UV light during the experimental time. Samples were taken every 30 minutes from the circulated solution in the beaker. The degradation of toxic organic material was measured using a UV-vis spectrophotometer in the chemistry lab at the University of Nizwa.

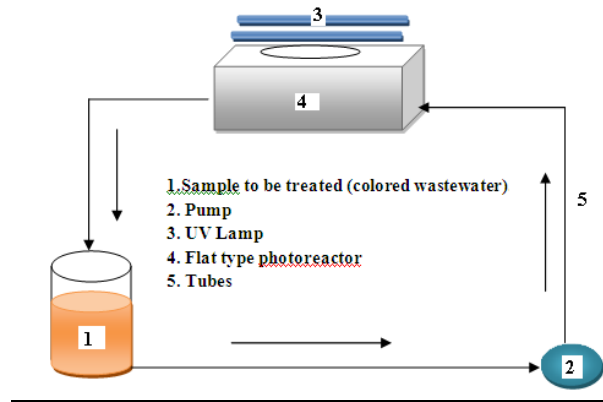


Fig. 2. Experimental Set-up.

3. Results and Discussion

To begin, a calibration curve was drawn for measuring concentration of dye during the experiment based on standard prepared mixtures and the equivalent wave absorption readings on the UV-vis spectrophotometer. The results were plotted as shown in Fig. 3. All data results were obtained at wave length of 421 nm.

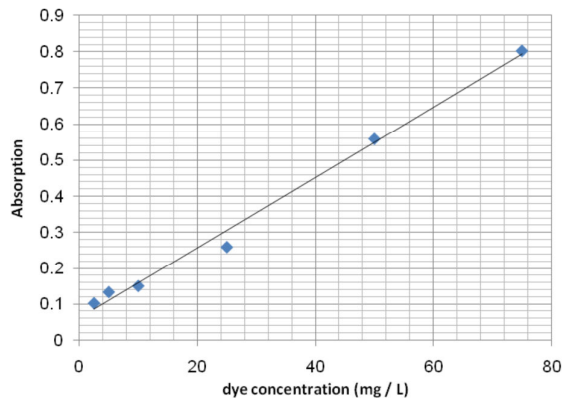


Fig. 3. Calibration Curve for Finding Concentration of Dye in the Solution.

A series of experiments were carried out to find the influence of TiO₂ concentrations on dye solution at different concentrations; 25 mg/L, 50 mg/L and 75 mg/L. The rates of reaction were found to improve as catalyst concentration increased for dye concentration as shown in Figs. 4, 5 and 6. The results were in agreement with those reported in the literature for other types of organic pollutants [5].

Results illustrated in Figs. 4, 5 and 6 show the variation of degradation at two typical times of 60 and 300 min. With catalyst concentrations up to about 500 mg/L, the degradation rate was faster for all dye concentrations compared to those of 200 mg and 700 mg TiO₂ as shown in Figs. 4 and 5. Various reasons for this behavior have been offered without much conviction or quantification. However, the increase of the catalyst concentration up to 700 mg/L, produced a lower degradation rate for all dye concentrations compared to those using concentration of 200 and 500 mg/L of titanium dioxide. A possible explanation is that increased turbidity of the solution reduced the light transmission through the solution; while below this level of concentration; it is assumed that the catalyst surface and the absorption of light by TiO₂ particles was limited. The efficient uses of catalyst concentration are the main key factor in achieving a satisfactory design.

The effect of photo-catalyst concentrations on the degradation kinetics of Tartrazine was investigated for the run using 50 mg/L Tartrazine and employing different concentrations of titanium dioxide. The results are shown in Fig. 7. It is clear that the photo-catalytic process is following a first order kinetics and the decolorization rate constant is then determined by the following equation:

$$\ln(C_t/C_o) = -kt \quad (2)$$

where C_o = dye concentration (mg/L) at time $t=0$

C_t = dye concentration (mg/L) at time $t=t$

k = first order rate constant (min^{-1})

The results in Fig. 7 shows that the slope of the curve for using 500 mg/L of catalyst is greater than the other two concentrations of catalyst. However, for catalyst concentrations below 500 mg/L, it can be seen that the slope increased by increasing catalyst loading, but, at concentrations higher than 500 mg/L, it is not.

The pH value was measured during all sets of experiments. It was found that the higher the TiO₂ concentration, the higher the pH value and more oscillatory behavior were appeared as shown in Figs. 8, 9 and 10. The pH value was increased from 7.4 in a solution of 200 mg TiO₂ and 25 mg dye to just above 8.2 in solution of 700 mg TiO₂ and 25 mg dye during the solution preparation. However, the pH value started to oscillate after dye degradation. It was clear that the higher the concentration of TiO₂ used, the stronger the oscillation is achieved. As less dye degradation was performed in the solution with 700 mg TiO₂, the pH behavior was more oscillatory than that in solution with 200 mg and 500 mg TiO₂. However, the slight change in pH could not be considered to have an impact on the photo-catalyst process, and thus, the solution under treatment was considered to be at neutral level. The pH set at a low level would have a considerable effect on the organic photo-degradation [3].

During all experimental sets, the temperature of the solution was raised only by 3°C from 22°C to 25°C. At this range of temperature, there will be no significant

effect on the process of photo degradation. A very high temperature change would have significant effect on degradation due to solution evaporation and a reduction in O₂ concentration during the experiment. Such an effect was not noticed.

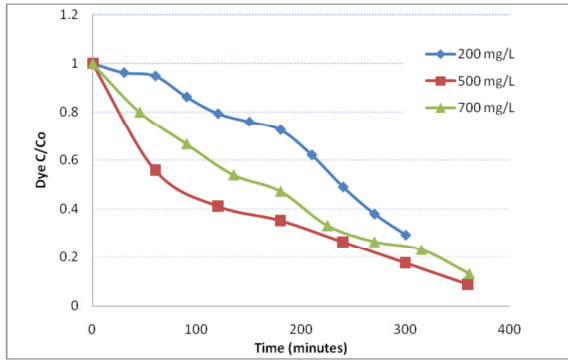


Fig. 4. Effect of TiO₂ Dosage on Dye Degradation (Dye: 25 mg/L).

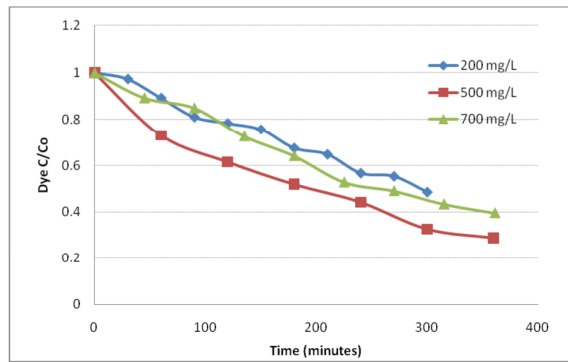


Fig. 5. Effect of TiO₂ Dosage on Dye Degradation (Dye: 50 mg/L).

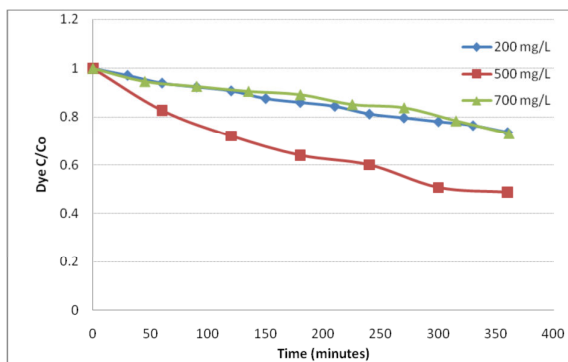


Fig. 6. Effect of TiO₂ Dosage on Dye Degradation (Dye: 75 mg/L).

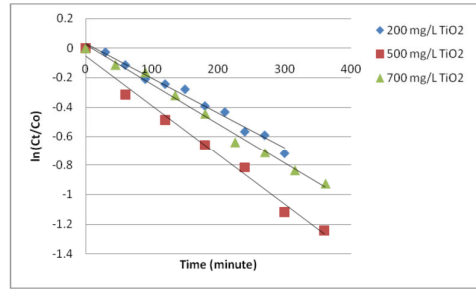


Fig. 7. Effect of TiO₂ on the Degradation Kinetics.

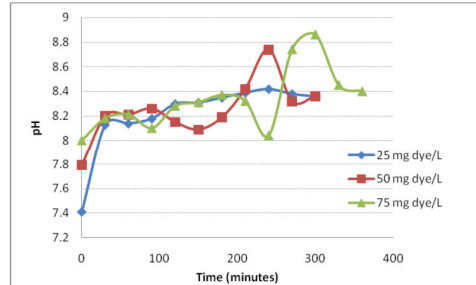


Fig. 8. Behaviour of pH During Experiment Using 200 mg/L TiO₂.

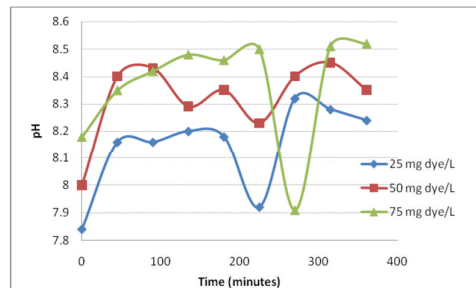


Fig. 9. Behaviour of pH During Experiment Using 500 mg/L TiO₂.

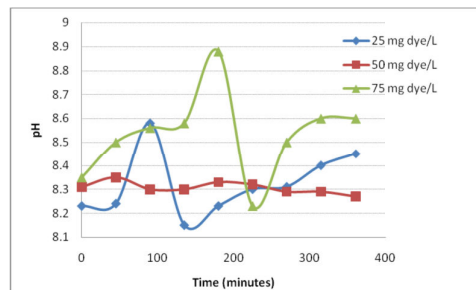


Fig. 10. Behaviour of pH During Experiment Using 700 mg/L TiO₂.

4. Conclusions

This study showed the potentialities of photocatalytic degradation of organic compounds such as Tartrazine in water purification. Out of different processes employed, a significant enhancement of the photo-catalytic activity was observed in the system using the photocatalyst irradiated under UV light. The concentration of photo-catalyst greatly influences the degradation rate. It can be seen that the degradation follows first order kinetics. The result shows that the maximum rate of degradation is $3.4 \times 10^{-3} \text{ min}^{-1}$ in a solution of 500 mg/L titanium dioxide. The analysis of the contained materials showed that the efficiency of the applied degradation system was high for all the identified present organic pollutants. Photodegradation can be a recommended approach for the treatment of other complex organic compounds in wastewaters. Keeping in view all the factors, it can be easily said that the combined system is an efficient one compared to all other processes. As less dye degradation was performed in the solution with 700 mg TiO_2 , the pH behavior was more oscillatory than that in solution with 200 mg and 500 mg TiO_2 . However, the slight change in pH cannot be considered to have an impact on the photo-catalyst process.

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