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SOLAR PHOTOCATALYTIC DEGRADATION OF TARTRAZINE USING TITANIUM DIOXIDE

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Abstract. As wastewater treatments become more important nowadays, photocatalysis, an alternative wastewater treatment method, shows a promising potential. By now, many studies on the photocatalytic destruction of single organic contaminants have been carried out. However, its application to the detoxification of samples of contaminants mixtures with high Total Organic Carbon levels has not been thoroughly investigated. Although presently many treatment methods are being used, most of them do not completely destroy the pollutants but only offer phase transfer or partial degradation of the pollutants. On the other hand, solar photocatalytic process is an exciting clean technology that uses only sunlight, water, and a reusable catalyst to remove toxins or pollutants from water. In a photocatalytic process, a semiconductor photocatalyst is activated with ultraviolet (UV) irradiation from the sun. The activated photocatalyst promotes the formation of hydroxyl radicals, which in turn completely degrade the pollutants. In this study, the photocatalyst used was titanium dioxide (TiO_2) and tartrazine was chosen as the pollutant. Tartrazine is one of the popular water soluble dyes used in food coloring industries but it is carcinogenic at high concentration. The photocatalytic experiments were conducted with varying catalyst loading (0–1.5 g/L), initial concentration (5–35 ppm), and flowrate of tartrazine solution (1.0–1.5 L/min). The dye solution was exposed to sunlight for about two hours. The experimental results showed that a considerable increase in the degradation efficiency of the tartrazine-compound could be obtained by a combination of TiO_2 and solar light. The optimum catalyst weight loading for the degradation of tartrazine dye was found to be 1.0 g/L. The initial concentration of the tartrazine dye and flowrate of tartrazine solution were found to effect the degradation efficiency of the dye. Higher initial concentration resulted in lower degradation efficiencies, while higher tartrazine solution flowrate resulted in higher degradation efficiency.

Keywords: Photocatalytic; solar detoxification; tartrazine; TiO_2 catalyst

Abstrak. Perawatan air sisa semakin mendapat perhatian kebelakangan ini, sehingga menjurus kepada penemuan foto-pemangkinan, satu kaedah alternatif perawatan air sisa yang berpotensi. Sehingga kini, banyak penyelidikan yang berkaitan dengan pemusnahan bahan pencemar organik tunggal telah dijalankan. Walau bagaimanapun, aplikasinya terhadap pendetoksifikasi sampel campuran bahan pencemar dengan tahap Jumlah Karbon Organik yang tinggi tidak dikaji secara menyeluruh. Walaupun terdapat banyak kaedah perawatan pada masa kini, kebanyakannya tidak memusnahkan bahan pencemar secara lengkap, tetapi hanya menyebabkan perubahan fasa atau pemusnahan bahan pencemar secara separa sahaja. Berbeza daripada kaedah perawatan yang lain, proses foto-pemangkinan ialah teknologi bersih yang hanya menggunakan tenaga suria, air dan mangkin yang boleh digunakan semula bagi memusnahkan toksin atau bahan pencemar dalam air. Dalam proses foto-pemangkinan, foto-mangkin semikonduktor boleh diaktifkan hanya dengan menggunakan sinaran ultra lembayung (UV) daripada

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radiasi cahaya matahari. Foto-mangkin yang telah diaktifkan akan menghasilkan radikal hidroksil yang berkebolehan untuk mendegradasikan bahan cemar. Dalam kajian ini, foto-mangkin yang digunakan ialah titanium dioksida (TiO_2) dan tartrazin di pilih sebagai bahan cemar. Tartrazin ialah sejenis pewarna yang banyak digunakan dalam industri makanan dan mudah larut dalam air. Pewarna sintetik ini boleh mengakibatkan kanser pada kepekatan yang tinggi. Uji kaji foto-pemangkinan dijalankan dengan mengubah jumlah mangkin yang digunakan (0–1.5 g/L), kepekatan awal larutan pewarna (5–35 ppm), dan kadar aliran larutan pewarna (1.0–1.5 L/min). Larutan pewarna didedahkan kepada sinaran matahari selama dua jam. Keputusan uji kaji menunjukkan bahawa peratus degradasi pewarna yang tinggi boleh dicapai dengan menggunakan kombinasi sinaran cahaya dan TiO_2. Jumlah mangkin optimum yang digunakan untuk proses degradasi pewarna ini ialah 1.0 g/L. Kepekatan asal pewarna tartrazin dan kadar aliran larutan tartrazin didapati mempengaruhi peratus degradasi pewarna. Kepekatan asal tartrazin yang lebih tinggi mengakibatkan kecekapan proses degradasi menurun, manakala kadar aliran larutan tartrazin yang lebih tinggi mengakibatkan kecekapan proses degradasi meningkat.

Kata Kunci: Foto-pemangkinan, mangkin TiO_2, tartrazin, pendetoksifikasi suria

1.0 INTRODUCTION

In recent years, there has been a growing interest in the use of semiconductors as photosentisizers for complete oxidative mineralization of pollutants. As an example, purification of water by semiconductors photocatalyst has been attracting a great deal of interest, not only from researchers but also from manufacturer of water purifier. Other applications of solar photocatalysis may include disinfection of drinking water without the use of chlorine, an increasingly controversial chemical.

Lately, photocatalysis properties of titanium dioxide (TiO_2) are being investigated for the development of oxidation process of organic pollutants in aqueous solutions. The interest in TiO_2 photocatalysis processes is rapidly growing due to its capability of exploiting solar ultraviolet light (UV) for promoting its chemical reactivity. It is believed that photocatalytic reactions occur when charged separations are induced in a large band-gap semiconductor by excitation with ultra band-gap radiation. When TiO_2 is activated by a photon whose energy, $h\eta$, matches or exceeds its band-gap energy, photo-induced electron/hole pair (hydroxyl radicals) are generated within the catalyst particles. The holes in TiO_2 have high oxidation power and therefore, in principle, can mineralize most organic pollutant molecules in an aqueous state to harmless substance that can be released to the environment. The energy needed to activate TiO_2 is 3.2 eV or more, which nearly corresponds to UV radiation wavelength of 380 nm or less. This makes it possible to use the sun as illumination source, since about 4-6% of the solar energy that reaches the earth's surface is less than 400 nm. Field studies have shown that this amount is sufficient to drive the photocatalytic process. This process is referred to as heterogeneous photocatalysis or more specifically, photocatalysis oxidation (PCO). Apart from that, TiO_2 has been shown to be able to inactivate *Escherichia coli*, a form of bacteria associated with fecal contamination. Lately, the use of TiO_2 for the degradation of tartrazine, an organic pollutant, has attracted great interest in researches.

In Malaysia, tartrazine (also known as Yellow Dye No. 5) is widely used in the food industries as coloring agent. A coal tar derivative, tartrazine has been tested for its toxicity, carcinogenicity, and ability to cause mutations in lab animals. It also has a high solubility in water. Some people are extremely sensitive to tartrazine as it can cause breathing difficulties. Thus, it is crucial that tartrazine waste from the food industries to be treated with appropriate yet affordable technology before being released to the environment.

Reeves *et al*. [1] have studied the effects of concentrated sunlight on the destruction rates of dyes by using a 1000-W xenon lamp to simulate solar radiation. The result showed that the light produced by this lamp was comparable to natural solar radiation when the solution is passed through a Schott glass filter. The focused beam produced by this solar simulator has the intensity equivalent to the beam produced by 15 suns (15 times the sun radiation). Stafford et al. [2] reported that titanium dioxide (TiO_2) suspension was mineralized when the suspension was illuminated with long wavelength UV light ($300\ nm<\lambda<400\ nm$). The rate of mineralization relative to initial substrate decay in TiO_2 photocatalysis is also enhanced at lower light intensities. The wavelength of UV light has a great effect on the quantum yield of reaction with significantly faster rates of reaction being caused by 300 nm light than that of longer wavelength.

Treatment for wastewater using TiO_2 as catalyst under an 800 W-UV lamp and solar irradiation were reported by many researchers [3-6]. Matthews [7] have studied the photocatalytic degradation of Methylene Blue, Rhodamine B, and Methyl Orange using solar ultraviolet light in the presence of TiO_2 catalyst. It was reported that for 250 ml of Methylene Blue with an initial concentration of 9.0×10^{-6} M, 87% degradation could be achieved after solar radiation of 50 minutes, while for Rhodamine B with an initial concentration of 8.5×10^{-6} M, 83% degradation was achieved. The same study on Methyl Orange with an initial concentration of 6.0×10^{-6} M gave 82% degradation. Apart from that, it was found that the rate of degradation decreased by about 50% when the source of solar radiation was disrupted (the sun was covered by clouds). It was also reported that the initial concentration of the pollutants had a great effect on the rate of degradation. It was observed that the value of the first order rate constant decreased with increasing initial concentration.

The effect of TiO_2 catalyst loading on the degradation efficiency of various aqueous pollutants was reported by Herrmann [8]. It was reported that when TiO_2 was used as a catalyst in a slurry or immobilized system, the rate of degradation reaction increased linearly with higher catalyst loading. However, after an optimum value, the rate of degradation was no longer dependent on the catalyst loading and in certain cases, the rate of degradation would decrease. Generally, the optimum value of catalyst loading is in the range of 0.5 to 5.0 g/L, depending on the type of pollutants, intensity of solar radiation, and the reactor configuration.

The aim of the present work is to examine the photocatalytic degradation rate of tartrazine solution as a function of catalyst loading, initial concentration, and flowrate of tartrazine solution.

2.0 EXPERIMENTAL

2.1 Experimental Set-up

A recirculating photocatalytic reactor was constructed as shown in Figure 1. The reaction vessel consists of a small cylinder constructed of Pyrex glass. It is connected to a conical flask (800 ml), which is covered by aluminum foil. Masterflex pump was used to circulate the solution. Pyranometer and hybrid recorder are used to record the intensity of the light and temperature of the solution inside the conical flask.

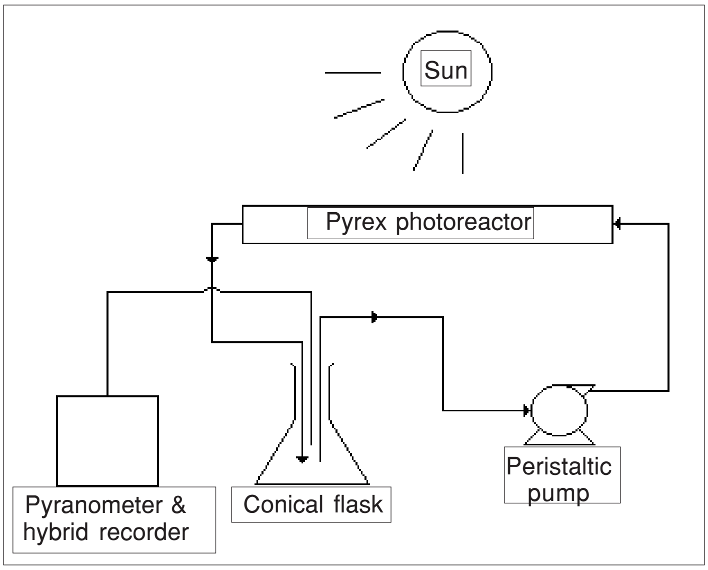

Figure 1 Schematic diagram of the solar photocatalytic reactor system

2.2 Materials

TiO_2 (anatase type) supplied by BDH Laboratory was used in this study. Its specific surface area is 3.8 m^2/g and particle sizes of less than 20 mm. Tartrazine supplied by Nacalai Tesque was used as a source of contaminant. The deionized water used for preparation of all the solutions was obtained from a compact ultrapure water purification unit.

2.3 Analysis

Tartrazine dye concentration was measured using the Hitachi U-2000 Spectrophotometer. The calibration curve was prepared using solutions of known concentration with an analytical wavelength of 257 nm. The plot obtained obeyed the Beer-Lambert Law with high precision from 0 to 50 ppm. For higher concentration, samples were first diluted. Degradation of tartrazine is reported in percentage.

2.4 Experimental Procedure

Experiments were carried out using the experimental rig as shown in Figure 1. The system was flushed with water before each run to prevent any error in the reading of the solution concentration. The rig was placed under the sunlight for about 2 hours. Samples were taken for about 30 minutes time interval. The average solar radiation intensity measured was 0.680 kW/m^2 and the parameters studied were catalyst loading, initial dye concentration, and circulation flowrate of tartrazine solution.

3.0 RESULTS AND DISCUSSION

3.1 Effect of TiO_2 Catalyst

The experiment was carried out with an initial tartrazine dye concentration of 25 ppm and circulation flowrate of 1.5 L/min. It was observed that after 2 hours, the percent degradation of tartrazine increased significantly when the catalyst was present in the system. It was found that, the percent degradation of tartrazine was about 20% without any catalyst loading, but with catalyst loading of 1.0 g/L, the degradation increased up to 80% (Figure 2). This is due to the fact that the catalyst provides active sites required for the degradation process of tartrazine. Without the presence of catalyst, the degradation of dye occurs directly by penetration of UV light directly onto the dye

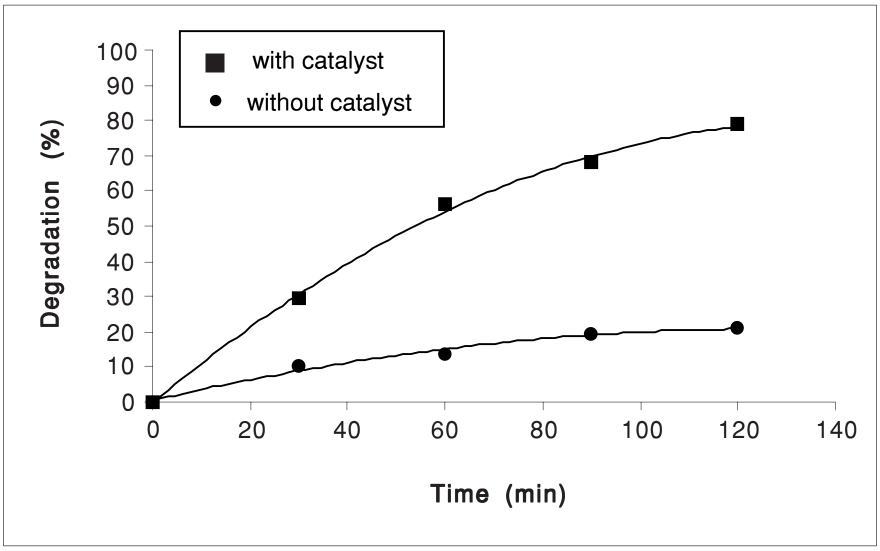

Figure 2 Percent degradation of tartrazine with and without catalyst loading of 1.0 g/L

molecule. This process is shown to be ineffective by the low percent degradation of tartrazine. However, with the presence of catalyst, the UV light will first irradiate the catalyst to produce electron-hole pair or active sites for the degradation of dye. Tartrazine molecules are then adsorbed on the active sites for the degradation process to occur. Thus, it could be observed that, catalyst plays an important role in the degradation process.

3.2 Effect of Initial Concentration

Initial concentration of the pollutant in water is one of the most important parameter, which has to be analyzed as it may affect the efficiency of the treatment process. Therefore, the experiment was carried out by varying the initial concentration of tartrazine from 5 ppm to 35 ppm. It could be observed that the normalized concentration (concentration at time t divided by the initial concentration) of the dye decreased with time (Figure 3). The increase in the initial concentration of the dye reduced the degradation efficiency of the catalyst. This phenomenon is due to the relative ratio of the hydroxyl radicals attacking the dye molecules. When the dye concentration increased, the amount of the dye adsorbed onto the surface of the catalyst also increased. During that process, the amount of the light intensity, radiation time and thus the active site of the catalyst remained constant, resulting in the number of the hydroxyl radicals attacking the dye molecules became limited. As a result, the photocatalytic treatment efficiency decreased.

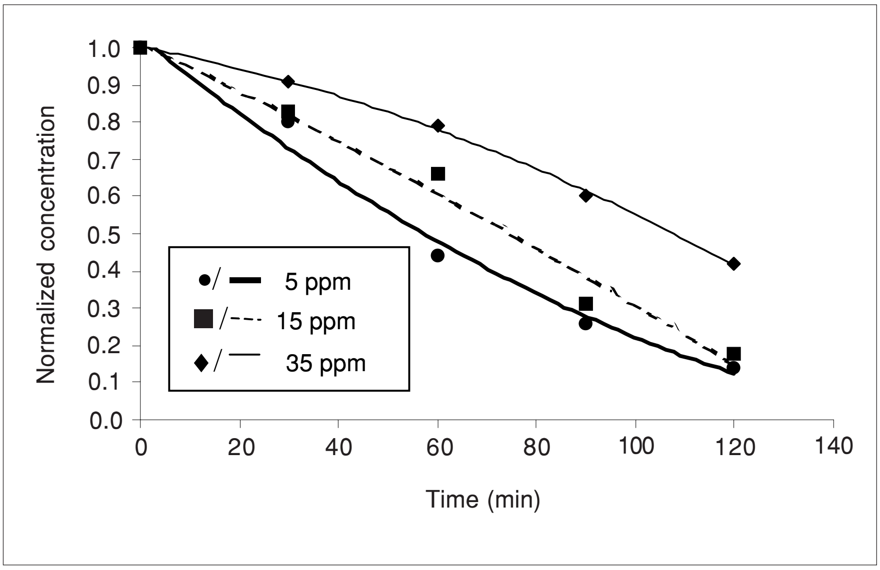

Figure 3 Normalized concentration profile at different initial concentration

3.3 Effect of Various Catalyst Loading

To study the effect of catalyst loading on the photocatalytic system, the experiment was carried out by varying the catalyst loading from 0.5 g/L to 1.5 g/L. In the photocatalytic process, the reaction is taking place on the surface of the catalyst, so the amount of catalyst loaded to the system can effect the efficiency of the reaction. In this study, the amount of degraded tartrazine increased with catalyst loading up to 1.0 g/L but decreased after further loading. This is due to the fact that excess catalysts will block the sunlight from penetrating into the system. Figure 4 shows that after 2 hours, the degradation percentage was at a maximum with 72.0% at 1.0 g/L of catalyst loading. Thus, the optimum amount of catalyst loading was found to be 1.0 g/L.

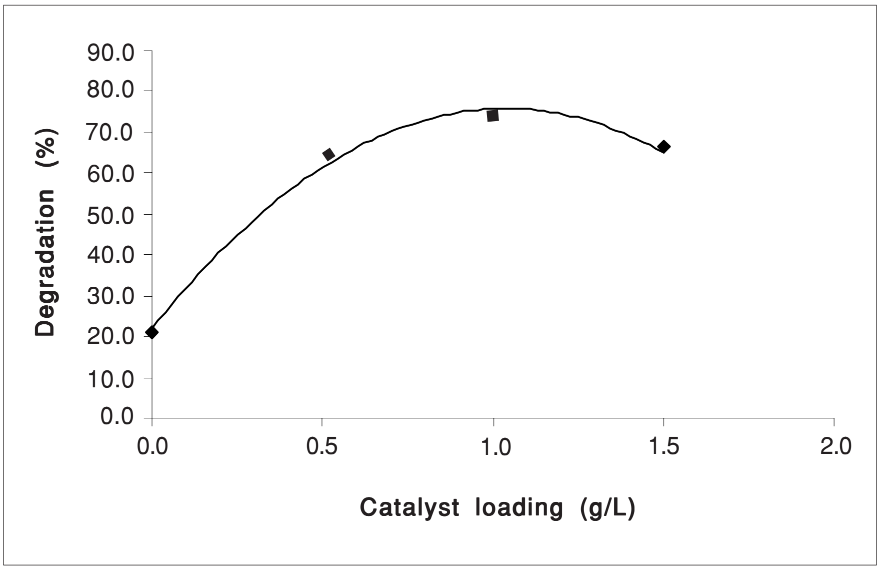

Figure 4 Degradation of tartrazine at different catalyst loading

3.4 Effect of Flowrate

This experiment was carried out to investigate the effect of tartrazine solution flowrate on the percent degradation of tartrazine in water. The effect of tartrazine solution flowrate will give a rough estimation on the amount of tartrazine per unit catalyst that can be treated at one time. The effect of flowrate on the percent degradation of tartrazine is usually associated with the kinetics reaction between tartrazine and TiO_2. Higher rate of reaction will indicate that more tartrazine can be treated at one time while still be able to maintain the percent degradation of tartrazine at a high level. As this is a solid-liquid reaction, the rate of reaction is usually influenced by the external mass transfer from the bulk solution to the catalyst surface. The effect of tartrazine solution flowrate was investigated by varying the flowrate from 0.98 L/min to 1.35 L/min. The amount

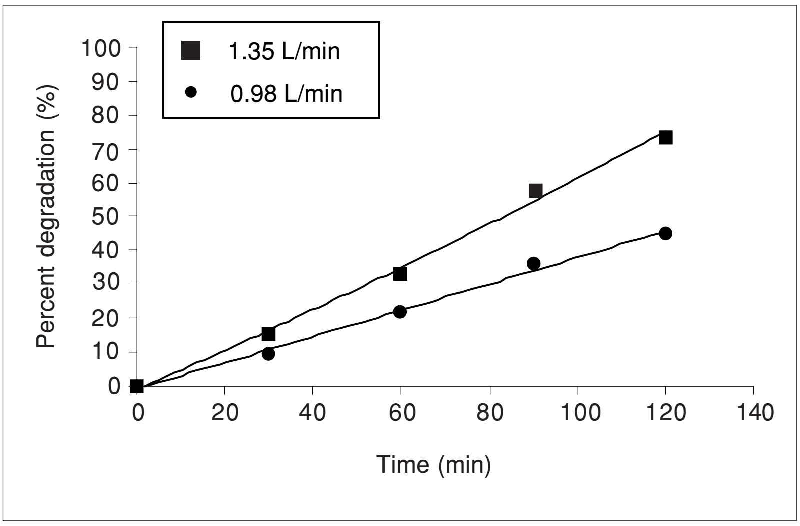

Figure 5 Percent degradation of tartrazine at different circulation flowrate

of catalyst loading was fixed at 1.0 g/L. Figure 5 shows that the percent degradation of tartrazine increases almost linearly with time. After 2 hours, at a flowrate of 0.98 L/min, the percent degradation of tartrazine was low (45%) compared to the percent degradation of tartrazine at a flowrate of 1.35 L/min (75%). The increase in percent degradation of tartrazine at higher flowrate could be due to the formation of turbulence in the solute. With the formation of turbulance in the solute at higher flowrate, the external mass transfer from the bulk solution to the catalyst surface will be reduced. This will indirectly increase the global rate of reaction between the catalyst and tartrazine and in turn will results in higher percent degradation of tartrazine.

4.0 CONCLUSION

In this study, the presence of catalyst (TiO_2) in the solar photodegradation system has increased the degradation rate of tartrazine in water. The presence of catalyst in the degradation of tartrazine dye was found to be much higher compared to without catalyst. The degradation of tartrazine was up to 80% within two hours, which indicates that the system has the potential to be operated in a larger scale. The optimum catalyst weight loading for the degradation of tartrazine dye was found to be 1.0 g/L. Further increase in catalyst weight loading reduced the efficiency of the photocatalytic degradation of the dye. Higher initial concentration of tartrazine resulted in lower degradation efficiencies, while higher flowrate of solution containing tartrazine resulted in higher degradation efficiency.

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