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RESEARCH PAPER

Study of Photocatalytic Performance of Doping Titanium Dioxide (TiO_2)

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Abstract

Titanium dioxide is one of the most powerful semiconductor that chemically stable and widely used in the photodegradation of wastewater process. However, titanium dioxide have wide band gap (3.2eV) which only can be activated by using UV light. In order to overcome the weakness of this photocatalyst, the doping technique by using sol-gel method applied to the titanium dioxide. Nitrogen and magnesium were used as dopand. Thus, in this study, nitrogen and magnesium doped TiO_2 will be applied on Reactive Black 5 dye to study the photocatalytic performance and the result will be analysed.

Keywords: photocatalytic, doping, titanium dioxide, reactive black 5

INTRODUCTION

One of the largest sources for water pollution that occur in the world generally and specifically in Malaysia is caused by dye industries. Dye industries including plastic industry, fabric and textile industry, food industry, cosmetic production and also paper and printing industry. Wastewater released from these industries may contain about 15% to 20% dyes (Lucas & Peres, 2005). These dyes have complex chemical structures which cannot be treated easily. These days, the fabric industry is growing fast in our country, as well as cosmetic industry also growing rapidly nowadays which will contribute more pollution each day. If there is no further action taken, it will cause so many implications to our environment especially for the next generation. On top of that, water pollution can give an impact on human health and sustainable development (Shah, 2018).

Besides that, the dye that adsorbs and reflects the sunlight that entering water, will interferes the growing process of aquatic species and hindering photosynthesis to occur. Hence, as the photosynthesis is disturbed the oxygen level will be decreasing. In addition to being toxic, dye also carcinogenic, mutagenic to various organisms (Ratna & Padhi, 2012). As an example, benzidine (BZ) based azo dyes are widely used in dye manufacturing, textile dyeing and color paper printing. The National Institute for Occupational Safety and Health (NIOSH) published a data on 1980 after conducting survey on the experimental animals and epidemiological studies on workers that exposed to the dyes. BZ has been recognized as a human urinary bladder carcinogen and workers could be exposed directly to the carcinogen since they work in dyeing industry (Puvaneswari et al., 2006). This shows that BZ have hazards towards environments but also too health since several years ago.

Some of the wastewater treatment methods such as physical, chemical and biological methods depend on the formation of the secondary pollutants and these methods are not suitable and applicable methods in preserving the environment. In addition, these methods are involving high-cost, difficult to perform and not a sustainable way for wastewater treatment (Shivaraju et al., 2017). Chemical method like ozonation has been extensively applied for remediation of industrial effluent, it has been proved that the ozone cleaves the conjugated double bonds of the chromophere resulting in decolourization however this process will result the formation of toxic by-products (Ratna & Padhi, 2012).

The photocatalytic of TiO_2 is effective in dye removing from aqueous solutions than the conventional techniques. However, the limitations of this technique have been identified and it can affect the photocatalytic effectiveness which are large bandgap, high aggregation tendency and difficult to separate and recover after the treatment process (Houas et al., 2001). Thus, this study is carried out to improve the present photocatalytic process using TiO_2. In order to achieve the objectives of the study, the method that has been chosen is by using sol-gel method. Sol-gel is one of the most exploited methods and it is used mainly to produce thin films and fine powder catalyst. Sol-gel method is easy, low cost and can be conducted at low temperature (Sudha et al., 2018; Lončarević & Čupić, 2019; D'Arienzo et al., 2017). Parameters that involved in the research are including the amount of doping which is varied at 0.5 wt.%, 0.7 wt.% and 0.9 wt.%, type of dopant used (nitrogen and magnesium) and also the calcination temperature varied during the preparation of photocatalyst.

Therefore, doping with another species either metal or non-metal is one of the proposed methods in order to promote the separation of the electron-hole pair, improving the photocatalytic efficiency and at the same time reducing the possibility for the recombination of electron charge carriers to occur (Pelaez et al., 2012). When doping technique is applied, the band gap of titanium dioxide can be narrowed and new energy level will be produced. This is the reason why visible light can be applied to the photocatalytic process despite of using UV light when doping technique is used to modify the semiconductors (Banerjee et al., 2015).

METHODOLOGY

Materials

In this research, Titanium (IV) isopropoxide (TTIP) 97% was used as the precursor in the process of photocatalyst preparation. Magnesium chloride 6 hydrate, ammonium nitrate 99 %, ethanol, 95 % and acetic acid glacial, 100 % chemical were used. Reactive Black 5 with dye content ≥ 50 % was for the photodegradation application.

Sample Preparation

The refrigerator centrifuge was used in order to obtain the sol gel from the solution. At 9000 rpm for 10 minutes, the samples were centrifuged, excess liquid was removed and sol gel was collected. Next, for the heat treatment process, a furnace box (model 524120-P) was used. Different calcination temperature of 300 °C, 500 °C, and 700 °C were applied on the sample for 1 hour. Then, during the photodegradation process, samples of aliquot were taken and centrifuged by using low-speed centrifuge (model 406 Gyrozen) in order to separate the samples and photocatalyst.

About 45 ml of deionized water and 5 ml of acetic acid were mixed together and labelled as solution A. Solution B was prepared in another beaker by diluting 15 ml of TTIP with 5 ml of ethanol. Different amount of magnesium chloride and nitrogen nitrate was added into solution B in order to vary the weight percentage of magnesium and nitrogen as the dopants. Next, the solution was centrifuged for 15 minutes at 9000 rpm and the liquid layer was removed and sol gel was obtained. The powder obtained was calcinated in a box furnace at 300°C, 500°C and 700°C to complete the preparation of photocatalyst.

All the photocatalytic activity were carried out using 60 ml Reactive Black 5 with concentration of 70 ppm and 0.1g of each photocatalyst were added into the solution. The irradiation time under visible light using 60 W tungsten bulb is 120 minutes. Aliquots of the solution were collected at every 15 minutes interval. Before undergo UV-vis analysis, the aliquots will be centrifuged in order to separate any catalyst that presence in the sample. The readings were taken for three times to ensure the accuracy. Decolourization of RB5 dye was tracked by its absorption peak at 600nm. The percentage of the decolourization of RB5 was calculated based on Equation 1.

$$\% \text{ Decolourization} = \frac{C_o - C_f}{C_o} \times 100\% \qquad (1)$$

Where,
C_o Initial Concentration of RB5
C_f Final Concentration of RB5

RESULTS AND DISCUSSION

Photocatalytic Activity Analysis

In order to obtain the decolourization percentage of RB5 during the irradiation, the percentage of decolourization during the dark condition need to be found first. This can be calculated by using the initial concentration of RB5 and the final concentration of RB5 after 1 hour left in the dark. Then, the decolourization percentage value during irradiation will be found by subtracting the value of decolourization percentage in the dark condition. Table 1 shows the decolourization percentage of Reactive Black 5 during dark condition and table 2 shows decolourization during irradiation of light. Sample calculation were shown as below.

During dark condition for sample 0.5 wt.% Mg-TiO_2 at calcination temperature of 300 °C;
Initial concentration of RB 5 = 70 [ppm]
Final concentration of RB 5 = 25.2 [ppm]

$$\frac{70\ [ppm] - 66.33\ [ppm]}{70\ [ppm]} \times 100\% = 5.24\ \%$$

Percentage decolourization during irradiation sample 0.5 wt.% Mg-TiO_2 at calcination temperature of 300 °C;

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Initial concentration of RB 5 = 70 [ppm]
Final concentration of RB 5 = 19.26[ppm]

$$\frac{70\ [ppm] - 19.26\ [ppm]}{70\ [ppm]} \times 100\% = 72.49\ \%$$

Decolourization efficiency of sample sample 0.5 wt.% Mg-TiO_2 at calcination temperature of 300 °C;

$$72.49\ \% - 5.24\ \% = 67.53\ \%$$

Thus, the efficiency of decolourization of RB 5 under irradiation condition by using sample 0.5 wt.% Mg-TiO_2 at calcination temperature of 300 °C as photocatalyst is 67.53 %.

Table 1. Decolourization performance on Reactive Black 5 in dark condition

Temperature		0.5 wt.% Mg	0.5wt.% N	0.7wt.% Mg	0.7wt.% N	0.9wt.% Mg	0.9wt.% N
300°C	Decolourization efficiency (%)	4.96	5.24	5.37	5.12	5.12	5.19
500°C		5.16	5.00	5.04	4.88	4.96	5.07
700°C		5.00	5.30	5.24	4.92	5.32	5.21

Table 2. Decolourization performance on Reactive Black 5 during irradiation of light energy

Temperature		0.5wt.% Mg	0.5wt.% N	0.7wt.% Mg	0.7wt.% N	0.9wt.% Mg	0.9wt.% N
300°C	Decolourization efficiency (%)	67.53	69.79	67.77	64.52	63.38	72.20
500°C		65.84	61.61	66.53	61.73	59.47	66.06
700°C		61.81	73.13	72.66	74.01	57.88	83.46

Table 1 showed the photocatalytic performance on Reactive Black 5 using 0.5wt. %, 0.7wt. % and 0.9wt. % of N-TiO_2 and Mg-TiO_2. The highest efficiency of decolourization of RB 5 showed when 0.7 wt. % Mg-TiO_2 and 0.9 wt. % N-TiO_2 (calcinated at 700°C). There were not much different seen for the degradation efficiency for every each weigh percentage between 0.5 wt. %, 0.7 wt. % and 0.9 wt. %. This is because of the small difference value between the weight percentages. This showed, that the weigh percentage did not give much effect towards the photocatalytic performance compared to the calcination temperature. Basically, as it can be seen in the table, the degradation efficiency was affected by the difference value of calcination temperature. According to Nur 'Aliaa and Siti Amira (2019), this is due to some factors that affect the photocatalytic process including the surface area, particle size, phase of the photocatalyst and the band gap which may affected the efficiency of decolourization of RB 5.

Figures 1 showed the final UV-vis spectra of each photocatalyst after the decolourization process. From the graph on figure 2, it can be observed that most of the photocatalyst prepared at calcination temperature of 700°C showed the highest decolourization of Reactive Black 5 dye as the final reading of the absorbance at the lowest value. This is due to a contribution of the effectiveness of the photocatalytic process of dye. Calcination temperature were found to give significant effect to the size of particle, surface area and phase structure of photocatalyst. According to Mozia (2008), during the heat treatment of TiO_2, the dehydration takes place and as a result the crystals grow to a size larger than those of the original particles. While a study conducted by Kumar et al. (2016), found that at lower temperature (300 °C -500 °C) only anatase phase was observed and at 600 °C the rutile peaks started to appear. Based on the absorbance recorded, photocatalyst prepared at calcination temperature of 700°C, the degradation rate is higher compare to the other photocatalyst that prepared at 300°C and 500°C.

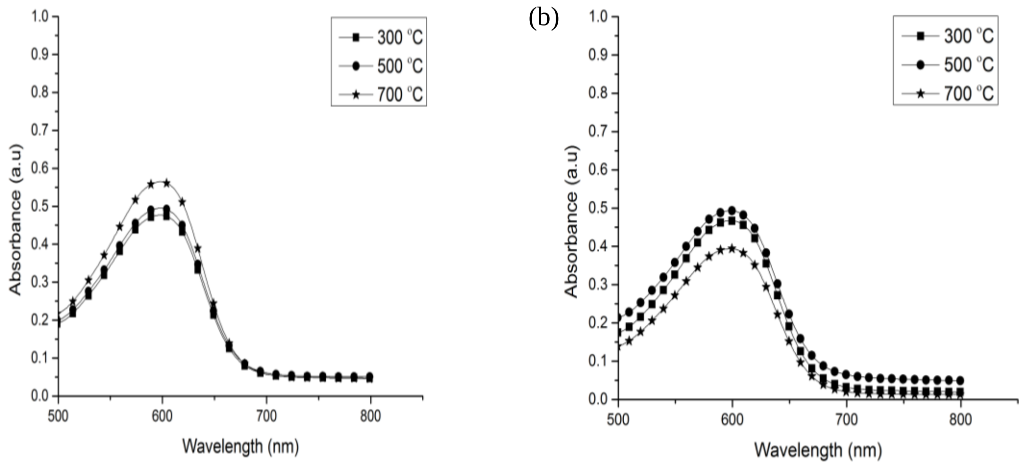
Yu and Wang (2009) reported one of the factors that may affect the decolourization efficiency is the content of anatase (70 % in mass percentage) and rutile (30 % in mass percentage). However, Hanaor and Sorrell (2011) mentioned in their review article that photocatalyst containing 80 wt% anatase and 20 wt% rutile, may exhibited greater photocatalytic performance. It is well known that the composite of two kinds of semiconductors or two phases of the same semiconductor is capable in reducing the combination of photo-generated electrons and holes, thus will improve the photocatalytic activity.

Photocatalyst that calcined at 300°C 0.5 wt. % Mg-TiO_2 and 0.9 wt. % Mg-TiO_2 showed 27.48 % and 50.78 % of efficiency. This is due to the pure anatase phase that presence in the photocatalyst which helps a lot in the photodegradation process. As the size particle is smaller, the surface area is larger, thus increases the efficiency of the photocatalytic process. Besides, with the doping technique that applied, the band gap also showed shifted from UV region to the visible region which also give significant effect on the photodegradation process.

Besides phase composition that might affect the photocatalytic activity, size and distribution of particles also may affect the photocatalyst performance. Samples calcinated at 700 °C also were observed to have better crystallinity compared to other. Thus, this also affect the photocatalytic activity. Other than that, based on band gap analysis have done, it can be seen that all the band gap of all samples have been shifted to the lower band gap. Lower band gap also may improve the photocatalyst efficiency. Behnajady et al. (2011), reported that lower band gap energy and high crystallinity, are important reasons to improve the photocatalytic activity under visible light irradiation.

(a)

(b)



(c)

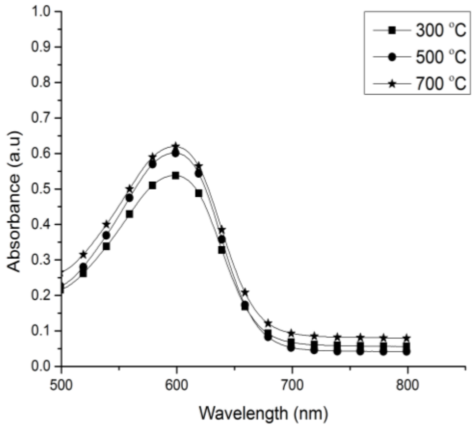


Figure 1. UV-Vis spectra of (a) 0.5wt. % (b) 0.7wt. % (c) 0.9wt. % Mg-TiO_2 at different temperature 300°C, 500°C and 700°C.

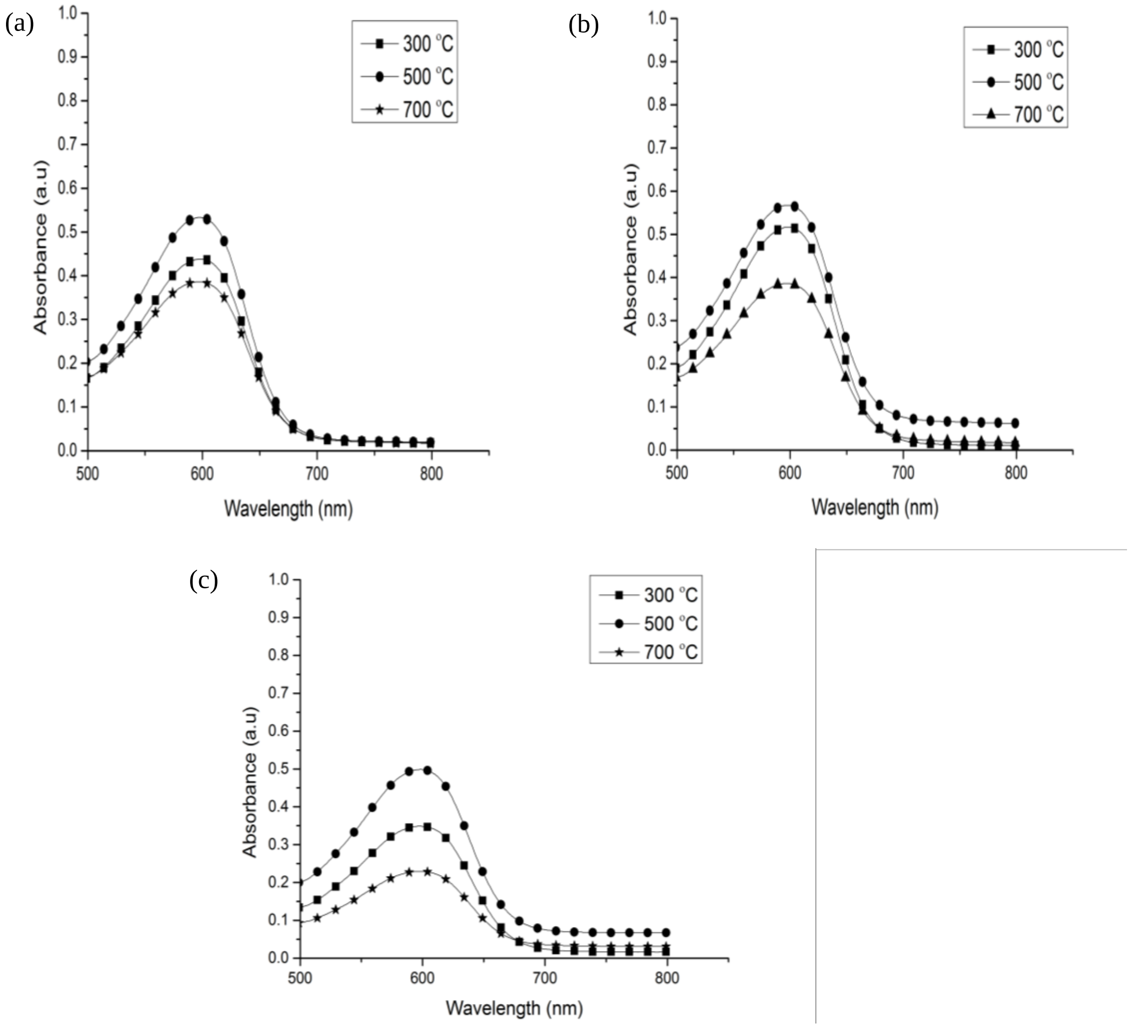


Figure 2. UV-Vis spectra of (a) 0.5 wt. % (b) 0.7 wt. % (c) 0.9 wt. %N-TiO_2 at different temperature 300 °C, 500 °C and 700 °C.

CONCLUSION

Results obtained from this experiment show that titanium doped with magnesium and nitrogen are able to degrade Reactive Black 5 effectively and the maximum percentage of dye degradation occurred at 83.46% and 72.66% respectively for 0.9 wt. % N-TiO_2 and 0.7 wt. % Mg-TiO_2 calcinated at 700 °C respectively. Basically, all photocatalyst that undergo heat treatment of 700°C perform the decolourization of dye efficiently with efficiency of 73.13 % and 74.01 % respectively for 0.5 wt. % N-TiO_2 and 0.7wt. % N-TiO_2. However, the photocatalyst of 0.5 wt. % and 0.9 wt. % Mg-TiO2 reached the highest decolourization efficiency when the samples prepared at 300 °C with efficiency value of 67.53 % and 63.38 % respectively.

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