Carbon Nitrogen Co-Doped P25: Parameter Study on Photodegradation of Reactive Red 4

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Abstract. Photocatalytic degradation rate of reactive red 4 (RR4) using carbon coated nitrogen doped TiO_2 (C N co-doped TiO_2) in photocatalysis process is main goal on this research. The main operating the parameters such as effect of initial dye concentration, catalyst loading, aeration flow rate and initial pH on degradation of RR4 under 45 W fluorescent lamp was investigated. photocatalytic activity of RR4 dye decreased with increasing RR4 dye concentration. The optimum loading is around 0.04 g and optimum aeration rate is about 25 mL min^{-1} of C N co-doped TiO_2. Effect of pH was conducted based on the optimum loading and conclude that the photocatalytic degradation of RR4 became faster at pH 2 - 7. For the future work, the modification of doping with others element like non-metal or metal with C N co-doped TiO_2 can be enhanced toward the higher efficieny of photodegradation under visible light. Moreover, the immobilized technique can be used in future to overcome the difficulty of filtration on suspension.

1 Introduction

Heterogenous photocatalysis is the process basically based on the oxidation process of photogenerated holes with hydroxide ion or water to form hydroxyl radical. This hydroxyl radical which is highly oxidizing agents will oxidized the organic wastewater pollutants into harmless product. The combination between semiconductor photocatalyst and light sources is the key process of photodegradation. Among of the semiconductor, titanium dioxide (TiO_2) is the most popular and widely used by researchers due to its chemical stability, low cost, atoxic, capability for the reusable and its high photocatalytic activity [1-4]. This material consist a wide band gaps between 3.0 eV to 3.2 eV which require the UV light irradiation which means that only (4-6%) of sunlight has the required energy to activate the photocatalyst [5]. Thus, the doping techniques have been explored to enhance the photocatalysis toward visible light. The non-metal element (N, C, S, F and P) have been discovered as great potential for enhance the visible light in TiO_2 materials [6-8]. Among all the non-metal doped TiO_2 materials, nitrogen doped carbon coated TiO_2 have been discerned to exhibit superior photocatalytic activity under visible light irradiation [9]. Several advantages of carbon coated can be listed such as improved the adsorption of pollutants, improvement of anatase crystalline structure, better rate of sedimentation of the photocatalyst particles and suppression of phase transformation from anatase to rutile at high temperature [10]. Meanwhile, nitrogen doped TiO_2 can

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be supreme potential toward the visible-light absorption due to metastable center formation, small ionization energy and its comparable atomic size in oxygen [11]. In this work, The C, N co-doped P25 sample was already preparad by Nawawi [10]. Subsequent experiments were conducted to investigate the effect of parameter of C N co-doped TiO_2 on the photodegradation of RR4. The effect of initial dye concentration, catalyst loading, aeration flow rate and initial pH on degradation of RR4 was investigated.

2 Experimental

2.1 Materials

C N co-doped TiO_2 preparad by Nawawi [10], Sodium Hydroxide (NaOH), Hydrochloric acid (HCl), Potassium Chloride (KCl), Reactive red (RR4) dye or commonly known as Cibacron Brilliant Red (Colour Index Number: 18105, chemical formula: $C_{32}H_{23}ClN_8Na_4O_{14}S_4$, molecular weight: 995.23 g mol^{-1}, λ max: 517 nm). Ultra-pure water was used to prepare all solutions in this work, 45 Watt fluorescent lamp, aeration pump.

2.2 Methods

2.2.1 Effect of initial dye concentration on the photocatalytic efficiency of the modified photocatalyst

Four sets of RR4 dye with different concentrations (5, 10, 30 and 60 mg L^{-1}) were used as the model pollutant in order to study the effect of concentration of the RR4 dye on the photocatalytic efficiency of the modified photocatalyst. 0.024 g of a selected modified photocatalyst sample was dispersed in 20 ml of RR4 dye solution at different concentrations under ultrasonic sonication for 30 seconds. The respective aqueous suspension of the catalyst within the dye solutions was then irradiated with 45 Watt compact visible light fluorescent lamp for 1 hour. Aliquots were taken at every 15 minutes time interval and the solution was filtered through a 0.45 μm cellulose acetate membrane filter to remove the catalyst particles. The concentration of the remaining RR4 dye was measured spectrophotometrically using HACH DR2000 spectrophotometer.

2.2.2 The Effect of the photocatalyst loading

A series of 20 mL of 30 mg L^{-1} RR4 dye solution with respective loading of 0.012, 0.024, 0.04, and 0.08 g of the optimum photocatalyst were prepared separately and dispersed under ultrasonic vibration for 30 seconds. Each aqueous suspension was then irradiated with 45 Watt visible light fluorescent lamp for one hour. The remaining RR4 in the sample solution was measured using HACH DR2000 spectrophotometer after every 15 minutes interval of irradiation. The percent degradation of RR4 dye solution was plotted against the dosage of the photocatalyst.

2.2.3 The effect of the aeration flow rate

Various aeration flow rates were applied to the system since air can provide oxygen for the degradation of RR4 dye. For the effect of aeration study, the flow rate of 0, 15, 25, 50 and 100 mL min-1 was respectively supplied into the systems containing the mixture of 0.024 g of the optimum photocatalyst in 20 ml of 30 mg L^{-1} RR4 dye solution. The RR4 solution was irradiated with a 45 Watt fluorescent lamp at each respective aeration rate.

2.2.4 The effect of initial pH values of the RR4 dye solutions

For this experiment, a series of 20 mL, 30 mg L^{-1} RR4 dye solutions at different initial pH values were used. The pH of each solution was adjusted to values of about 2, 4, 7 and 10 respectively before being photocatalytically decolorized using 0.024 g of optimum photocatalyst under a 45 W fluorescent lamp. The pH values of every solution were adjusted using 1 M NaOH and 1 M HCl solutions

2.2.5 Determination of point of the zero charge (pHzpc) for the unmodified and modified photocatalyst

pH of the zero charge (pHzpc) for photocatalysts were determined according to the procedures outlined by Machado and Santana [12]. A series of 50 mL ultra-pure water with different pH ranging from pH 2 to 10 was prepared. The pH of the solution was adjusted using 1 M NaOH and 1 M HCl solutions. 0.01 g of the unmodified and modified catalyst was added into each solution followed by addition of 10 ml of 0.1 M KCl. The solutions were stirred and the final pH values of the solutions were recorded after 24 hours of stirring. The discrepancies of the pH were obtained by subtracting the initial pH with final pH. A plot of pH discrepancies versus the initial pH was constructed and the point of zero charge was obtained from the values which cuts the X-axis.

3 Results and Discussion

3.1 The effect of initial dye concentration on the photocatalytic efficiency of C N co-doped TiO$_2$⁻P25

The effect of initial dye concentration on the photocatalytic efficiency of PU1-350 sample is shown in Figure 1. As expected, the photocatalytic activity of RR4 dye decreased with increasing RR4 dye concentration where the highest photocatalytic activity occurred for 5 mg L^{-1} concentration of RR4 dye solution. Pseudo first order rate constants for the photocatalytic degradation of different concentration of RR4 dye by PU1-350 photocatalyst were 0.290, 0.235, 0.160 and 0.085 min^{-1} for 5, 10, 15, 30 and 60 mg L^{-1} respectively. Accordingly, this is due to the color of the solution that becomes more intense with increasing concentration. Photons from the light irradiation were absorbed by the dye molecules rather than by TiO$_2$ particles which caused the light-screening effect that retarded the penetration of light into the surface of the photocatalyst and this eventually decreased the efficiency of the photocatalyst and thereby reduced the formation of OH• and O$_2$• radicals.
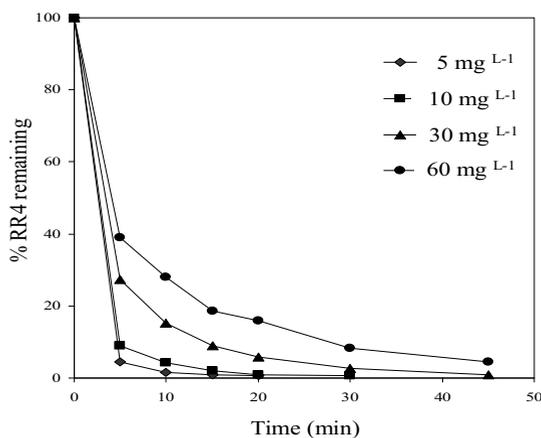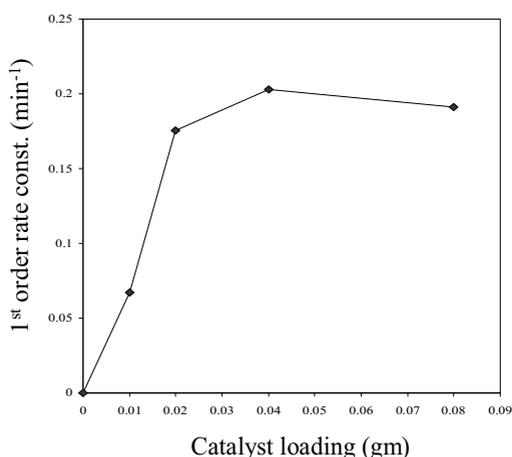

Figure 1. Photocatalytic degradation at different initial concentration of RR4 using C N co-doped TiO$_2$⁻P25 sample (PU1-350).

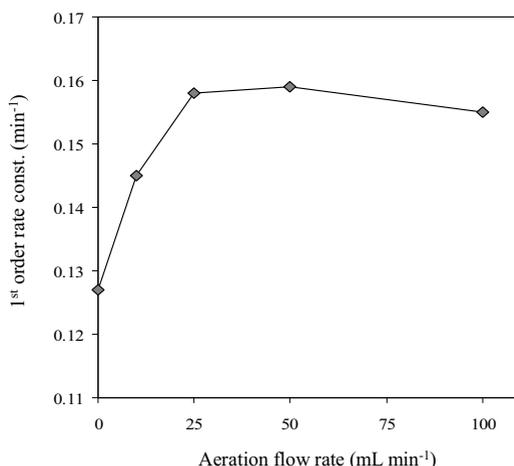## 3.2 Effect of catalyst loading on the photocatalytic efficiency of C N co-doped TiO_2^-P25

Figure 2 shows the rate of the photocatalytic degradation of 30 mgL^{-1} RR4 dye by various amount of C N co-doped TiO_2^-P25 (PU1-350) loading under a 45 W compact fluorescent lamp. As observed with TC1-560 and PP0.6-450, the degradation rate of RR4 dye by PU1-350 increased with increasing catalyst loading until 0.04 g beyond which the rate began to be slightly reduced (Figure 2). The increasing rate of RR4 removal for the loading of 0.012 to 0.04g PU1-350 catalyst was due to increasing amount of PU1-350 particles in the system. By increasing the PU1-350 particles, the number of photon and the dye molecules absorbed on the surface of the active site would also increase which eventually caused the photocatalytic activity of PU1-350 to increase. However, by further increasing the amount of PU1-350 beyond 0.04g, the rate decreased instead of becoming constant. There are two possibilities that influence this phenomenon might be due to the scattering of light and reduction in light penetration through the solution as a result of the excess catalyst particles and the aggregation of TiO_2 particles at high concentration which caused a decrease in the number of surface active sites, thus bringing little stimulation to the catalytic reaction [13].

3.3 Effect of aeration flow rate on the photocatalytic efficiency of C N co-doped TiO_2 P25

Aeration was supplied continuously to the solution throughout the experiment by using an aquarium air pump as the source of aeration. The presence of air bubbles from the aeration in the system promoted a significance agitation of the aqueous suspension for homogeneous distribution of the catalyst in the solution and to provide oxygen for the oxidative photocatalytic degradation. Figure 3 shows the effect of flow rates towards photocatalytic degradation of RR4 dye using C N co-doped TiO_2^-P25 (PU1-350) as photocatalyst. It was found that 25 mL min^{-1} was the optimum aeration rate for a (PU1-350) where the the degradation rate of RR4 was almost two times faster than the system running without aeration (stirring process) with pseudo first order rate constant (k) for 25 mL min^{-1} aeration and stirring process ca. 0.058 and 0.027 min^{-1} respectively. All photocatalytic and adsorption experiments in this work were therefore carried out under this optimum aeration rate.
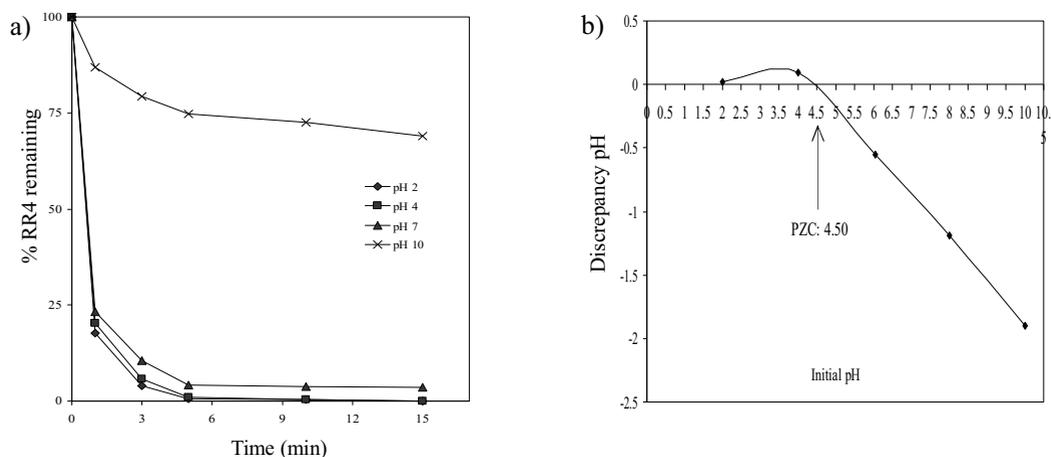

Figure 2. Photocatalytic degradation of RR4 dye by different amount of PU1-350 loading irradiated with a 45 Watt fluorescent lamp.

Figure 3. Effect of aeration flow rate on the photocatalytic degradation of RR4 under a 45 W fluorescent lamp.

3.4 Effect of initial pH of the RR4 dye solution on the photocatalytic efficiency of C N co-doped TiO₂⁻P25

Figure 4a shows the rate of the photodegradation of RR4 under C N co-doped TiO_2^-P25 (PU1-350) at different pH conditions as a function of the irradiation time. The results indicated that the highest rate of photocatalytic degradation of RR4 was within the range of pH 2 - 7 while at pH 10, the rate was significantly slower where less than 30% of RR4 removed after 10 minutes of irradiation. Slower photocatalytic degradation of RR4 at pH 10 was due to the repulsion between the dye molecules and PU1-350 particles which led to decreased adsorption efficiency. The photocatalytic degradation of RR4 became faster at pH 2 - 7 due to the PZC value for PP0.6-450 to be c.a. 4.5 (Figure 4b) thus making it's particles to be positively charged with less agglomeration thus increased adsorption process.

Figure 4. a) Photocatalytic degradation at different pH of RR4 dye under PP0.6-450 sample irradiated with 45 Watt fluorescent lamp, and b) Point of zero charge for C N co- doped TiO_2^-P25, PU1-350.

4 Conclusion

The irradiation of C N co-doped TiO_2 was conduct using four parameters namely initial concentration,effect of loading, effect of aeration flow rate and effect of pH. It can be observed the photocatalytic activity of RR4 dye decreased with increasing RR4 dye concentration where the highest photocatalytic activity occurred for 5 mg L^{-1} meanwhile 0.04g of catalyst loading give optimum photocatalytic degradation. It was found that 25 mL min^{-1} was the optimum aeration rate for a (PU1-350). Effect of pH was conducted based on the optimum loading and conclude that the photocatalytic degradation of RR4 became faster at pH 2 - 7 due to the PZC value for PP0.6-450 to be c.a. 4.5. This research studies will generate towards the green technology that can be destructive the wastewater especially from dyes industries. This parameters study can be proved that C N co-doped TiO_2 can be purify contaminated water in various situation. For the future work, the modification of doping with others element like non-metal or metal with C N co-doped TiO_2 can be increase the efficiency of photodegradation under visible light. Moreover, the immobilized technique can be used in future to overcome the difficulty of filtration on suspension.

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