Low temperature prepared N doped TiO$_2$ photodegradation of janus green B

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Abstract. N doped titanium dioxide (TiO$_2$) was prepared under low temperature calcination of TiO$_2$ Degussa P25 powder and urea at various mixing ratios. Muffle furnace was used as heating media with the temperature used in the range of 300 to 500 °C. The prepared N doped TiO$_2$ was characterized by using UV-Vis diffuse reflectance spectroscopy (DRS), Fourier transform infrared (FT-IR) and scanning electron microscopy (SEM). It was observed that N doped TiO$_2$ prepared at 0.5 g urea under the 400 °C calcination process (named as U2-400) is the optimum photocatalyst sample with the highest rate removal of Janus green B (JG) dye. The U2-400 had goes the photodegradation rate removal at 0.1071 min$^{-1}$ which is 3.5 times faster compared to unmodified TiO$_2$ sample. The high photodegradation rate removal for U2-400 was due to the N incorporated with TiO$_2$ in U2-400 photocatalyst which narrowed the bandgap energy from 3.2 to 3.0 eV as observed by UV-Vis DRS spectra. This shows the U2-400 sample has increased its photocatalytic activity since it has become more active under wider an optical response compared to the unmodified TiO$_2$

1 Introduction

Janus green B (JG) dye is one of the major contributors of the organic pollutants. This organic pollutant if discharged into the water will cause a dark blue to pink color and unpleasant taste of drinking water [1]. The JG dye is mostly used in industries as pigment agent in coloring the material compounds like textile and polymer materials. The contamination of water caused by JG dye has attracted the vast attention by many researchers due to its toxicity to organisms and degrading difficulties [2]. Physical, biological or chemical treatment process is normally used in conventional wastewater technologies remediation [3].

Advanced oxidation process (AOPs) is a chemical treatment method to remove organic pollutants and break down all organic structures in water or wastewater by oxidation through reaction with hydroxyl radical (·OH). AOPs involves two steps which are hydroxyl

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radicals foundation and the reaction of these radicals with organic contaminants in wastewater. Among many AOPs, titanium dioxide (TiO$_2$) photocatalysis has gained more attention as one of the most environment friendly cleanup technologies, and the cost is lower than the conventional treatment process [4,5].

However, TiO$_2$ is less efficient under visible light region due to its wide bandgap energy. A pure TiO$_2$ has a large bandgap which means it can only be activated under ultraviolet (UV) region. Doped TiO$_2$ with non-metal elements such as boron (B), sulphur (S), carbon (C), flourine (F), and nitrogen (N) is an effective way to narrow the bandgap energy [6]. One of the promising non-metal dopant material is N due to its comparable atomic size with oxygen, small ionization energy, eco-friendly, higher stability and simple synthesis methods that can induce visible absorption [6]. N doped TiO$_2$ has becoming one of the most dynamic modifications of TiO$_2$ for photodegradation of organic pollutants. Several approaches have been employed for the preparation of N doped TiO$_2$ material which are the wet chemical and dry powder methods. However, most of the preparation of N doped TiO$_2$ are focus on wet chemical methods such as hydrothermal treatment, sol-gel processes, spray pyrolysis, and supercritical methods.

In this study, N doped TiO$_2$ photocatalyst sample was prepared by using dry powder method using urea as N source under simple calcination process at low temperature level. The prepared sample was studied for their photocatalytic activity by measuring the effectiveness in removing the Janus Green B dye.

2 Experimental

2.1 Preparation of N doped TiO$_2$.

N doped TiO$_2$ was prepared by mixing TiO$_2$ (P25) with 0.2, 0.5, 1.0, 2.0 and 5.0 g of urea. The mixed powder was placed into a special glass tube reactor. The reactor was placed into a muffle furnace at temperatures ranging from 300 to 500 °C under normal atmospheric condition. The sample is cooled down to room temperature and the products was cleaned by sonicating the sample with 0.1N HCl then centrifuged to isolate the contamination. The modified sample was finally rinsed thoroughly using distilled water using 0.45 μm cellulose nitrate membrane filter. The product is named N doped TiO$_2$.

2.2 Photocatalytic degradation of janus green (JG)

In this study, for photocatalytic degradation of JG dye, a 0.024 g sample of N doped TiO$_2$ photocatalyst was placed inside a glass cell that contains 20 mL solution of 10 mg L$^{-1}$ of JG solutions. The mixed photocatalyst sample powder and dye was sonicated for 30s to agitate the particle in the sample. The modified TiO$_2$ was transfered into a custom made glass cell with dimensions 50 mm×10 mm× 80 mm (L×B×H). An aquarium pump model NS 750 was used as the aeration source. A direct reading air flow meter was used to determine the aeration rate supply to the reactor. The TiO$_2$ suspended with 10 mg L$^{-1}$ JG will then be irradiated with 55 Watt fluorescent lamps for every 5 minutes interval until 20 minutes. The degradation degree of JG is determined by spectrophotometer at 660 nm.

2.3 Characterization study

The immobilized N doped TiO$_2$ sample was characterized by using scanning electron microscope model JSM-6700F with an accelerating voltage of 30 kV. The sample was coated with platinum utilizing a GIKO IB-3 ion coater before observation. FTIR spectrometer brand
PerkinElmer with model Frontier was used for determination of compound presented in the samples. UV-Vis DRS was used to determine N present in the sample and estimate the bandgap energy of modified N doped TiO2. About 0.2 g powder sample is placed in UV-Vis DRS with absorption mode ranging from 250-500 nm wavelengths.

3 Results and discussion

3.1 Optimization Study

Fig. 1a shows the photodegradation rate of the prepared N doped TiO2 under different amounts of urea at three calcination temperatures (300, 400 and 500 °C). It was observed that N doped TiO2 prepared under 400 °C has the optimum temperature condition as compared with other temperatures (300 and 400 °C) with the pseudo rate constant was 0.051, 0.107, 0.055, 0.049 and 0.024 min-1 for 0.2, 0.5, 1.0, 2.0 and 5.0 g of urea respectively (Table 1). The photodegradation rate was increased by increasing amount of urea with the highest photodegradation rate was observed at 0.5 g. However, the photodegradation rate is become decreased beyond 0.5 g of urea in prepared N doped TiO2 sample.

Fig. 1. Photodegradation rate of a) unmodified TiO2 and various modified TiO2 samples under different calcination temperatures, b) percent JB dye remaining in 400 °C at different urea loading and c) N doped TiO2 samples at different calcination time under different temperatures.

The same observation was also seen for the samples calcined at 500°C where the photodegradation rate was increased up to 0.5 g urea and it becomes decreased beyond 0.5 g. However, photodegradation rate for samples at 300°C calcination process have increased up to 1.0 g urea and it starts decreased beyond 1.0 g. The low photodegradation rate beyond the optimum amount of urea in modified samples is due to the increasing amount of N in prepared N doped TiO2 where it becomes saturated and thus covered the TiO2 surface and makes less penetration of light to reach on surface of TiO2 photocatalyst.
### Table 1. The photodegradation rate values of unmodified and modified TiO<sub>2</sub> samples under different calcination temperatures.

| Sample name  | Urea (g) | Temperature (°C) | Rate const., K (min<sup>-1</sup>) |
|--------------|----------|------------------|----------------------------------|
| Unmodified TiO<sub>2</sub> | 0        | 0                | 0.030                            |
| U1-300       | 0.2      | 300              | 0.040                            |
| U1-400       | 0.2      | 400              | 0.051                            |
| U1-500       | 0.2      | 500              | 0.033                            |
| U2-300       | 0.5      | 300              | 0.042                            |
| U2-400       | 0.5      | 400              | 0.107                            |
| U2-500       | 0.5      | 500              | 0.055                            |
| U3-300       | 1.0      | 300              | 0.061                            |
| U3-400       | 1.0      | 400              | 0.055                            |
| U3-500       | 1.0      | 500              | 0.048                            |
| U4-300       | 2.0      | 300              | 0.055                            |
| U4-400       | 2.0      | 400              | 0.049                            |
| U4-500       | 2.0      | 500              | 0.039                            |
| U5-300       | 5.0      | 300              | 0.045                            |
| U5-400       | 5.0      | 400              | 0.024                            |
| U5-500       | 5.0      | 500              | 0.027                            |

Fig. 1b represents the percent remaining of JB for the batch of 400°C calcination temperature. As mentioned earlier, U2-400 has the optimum photodegradation behavior where it takes 20 minutes to remove 85.5% of JG dye followed by U4-400, U3-400 and U5-400 where the photodegradation behavior was 72.9, 66.25 and 34.95% respectively (Table 1). It clearly show that the U2-400 sample is the fastest modified TiO<sub>2</sub> to degrade JG dye compared with other samples and it is used as the optimum condition for N doped TiO<sub>2</sub>. Fig. 1c shows that the prepared N doped TiO<sub>2</sub> using 0.5 g of urea under calcination temperature (U2-300, U2-400 and U2-500) at various calcination time. The N doped TiO<sub>2</sub> prepared samples have significant photocatalytic activity as compared with unmodified TiO<sub>2</sub> sample except for U2-300 at 1 hr calcination time where the photodegradation rate seems slightly lower. The same trend was observed for all calcination times where 400°C is the optimum calcination temperature. The photodegradation rates become decreased beyond 400°C and 500°C at all calcination times except for 4 hrs where photodegradation rate has become slightly increased.

### 3.2 Characterization Studies

The scanning electron microscopy images in Fig. 2 shows the morphology of unmodified TiO<sub>2</sub> and U2-400 photocatalyst samples. The images consist of irregular agglomerated nanoparticles of size ranging from 15 to 20 nm. It can be seen that both samples show the similar morphologies which is spherical shapes with hollow pits and spongy structured surface. The morphology of N doped TiO<sub>2</sub> was not changed by treatment of urea at 400°C due to comparable atomic size of nitrogen atom with oxygen [8]. The UV-Vis diffuse reflectance spectroscopy (UV-vis/DRS) was used to identify the absorption shift and bandgap energy of unmodified and optimum modified TiO<sub>2</sub> samples. The UV-Vis DRS in Fig. 3 shows absorption versus wavelength (nm). The bandgap sample was determined by the equation $E_g = \frac{1239.8}{\lambda}$, where $\lambda$ was determined by the slope extrapolation of the sample spectrum. From the calculation, the bandgap energy of N doped TiO<sub>2</sub> is 3.0 eV compared to
unmodified TiO$_2$ 3.2 eV that according to the literature report. It was proven that modified TiO$_2$ give better photocatalytic activity then unmodified TiO$_2$ due to the narrowed bandgap energy and it is confirmed that nitrogen was successfully doped. This narrowing of bandgap energy on N doped TiO$_2$ may be due to the mixing of N 2p orbitals with O 2p orbitals [9].

![Scanning Electron Microscopy of a) unmodified TiO$_2$ and b) U2-400.](image1)

![UV-Vis DRS spectrum of N doped TiO$_2$ sample.](image2)

4 Conclusion

N doped TiO$_2$ was successfully prepared using calcination process at low temperature with various amounts of urea. The optimum condition for N doped TiO$_2$ was found at U2-400 where it is 3.5 faster as compared with unmodified TiO$_2$ for the photodegradation of JG dye. SEM, FTIR, and UV-Vis DRS studies confirmed that the nitrogen was incorporated in TiO$_2$. SEM image revealsthat no significance changes in terms of the morphology and size of the
particle between U2-400 and unmodified TiO₂ where both samples have spherical shape with hollow pits and spongy structures. UV-Vis DRS shows that the bandgap energy of the N doped TiO₂ was 3.0 eV. This makes the U2-400 sample increased its photocatalytic activity since U2-400 has become more active under wider optical response compared to unmodified TiO₂.

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