

Microwave-Assisted in the Preparation of Nitrogen-Doped TiO₂ for the Photogradation of Organic Dyes: Effect of pH and Catalyst Dosage

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ABSTRACT

The unmodified TiO₂ was modified using a microwave technique to produce a visible light active nitrogen (N) doped TiO₂. The modified photocatalyst was prepared by mechanical mixing of unmodified TiO₂ with various amounts of urea and various irradiation power of microwave. It was observed that the N doped TiO₂ at 800 W of microwave power irradiation with urea content 3 g was defined as the optimum condition for a modified photocatalyst. N doped TiO₂ then was characterized using X-ray photoelectron spectroscopy (XPS), photoluminescence (PL) and UV-Vis diffuse reflectance spectra (UV-Vis/DRS) analyses. The XPS and PL proved that the successful nitrogen doped into the TiO₂. XPS results presented with two peaks with binding energy 404.8 and 400.2 eV that indicates the formation of chemical interaction N with titania forming N doped TiO₂. In addition, UV-Vis/DRS confirmed that the introduction of nitrogen into TiO₂ by decreasing the bandgap energy value from 3.02 eV to 2.9 eV. The photocatalytic activity study of N doped TiO₂ was carried out by irradiating 25 mL of 30, 10 and 5 mg L⁻¹ of anionic Reactive Red 4 (RR4), cationic Methyl Violet (MV) and cationic Janus Green dyes (JG) in the presence of fluorescent light and visible light (UV cut-off) with the rate of photodegradation was estimated from aliquot concentration spectrophotometrically. The irradiation of N doped TiO₂ was conducted using two parameters namely the effect of catalyst dosage and the effect of pH. It can be observed that 0.0012 g /mL of catalyst dosages that gives an optimum photocatalytic degradation for both anionic and cationic dyes. Effect of pH was conducted based on the optimum catalyst dosage and conclude that pH 4 and 8 were the optimum pH for anionic and cationic dyes respectively

Keywords: carbon nitride; titanium dioxide; photocatalysis; microwave synthesis.

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1. INTRODUCTION

In many countries, dyes were mostly consumed in the textile industry. This industry has greatly developed because clothes are a necessity for every human being. However, they generate wastewaters with high chemical complexity, low biodegradability and are highly persistent. This will lead to dramatic environmental contamination, and eutrophication and will cause severe harm to all creatures if there is no immediate action performed. In past decades, a more potent approach for the degradation of dye effluents has received great attention because most of the pollutants were not fully treated under the existing effluent treatment methods [1].

One promising technology is heterogeneous photocatalysis in the presence of semiconductors. This method is one of the advanced oxidation processes (AOPs) and has been widely studied by scientists to overcome this wastewater problem. Decomposition and mineralization of organic contaminants in water by the generation of hydroxyl radicals and super peroxide anion under irradiation was the way this method works [2]. The most widely used photocatalyst was titanium dioxide (TiO₂). This is because it has high photocatalytic activity, strong oxidizing power, is non-toxic, is relatively inexpensive and is also durable [3]. It is also a very well-researched material in photocatalysis due to the stability of its chemical structure, biocompatibility, and physical, optical and electrical properties. Pelaez et al. [1] stated that the TiO₂ has received much attention in the photoinduced process since it is

chemically and biologically inert, relatively easy to produce and use, photo-catalytically stable and able to give efficiency in catalyzing the reaction without risks to the environment or human. However, Nawawi and Nawi [2] stated that TiO_2 have its drawback toward photocatalyst that shows its incapability to absorb visible light. TiO_2 is only active in ultraviolet light due to its large bandgap energy which is 3.2 eV that corresponding to a wavelength shorter than 388 nm. Therefore, TiO_2 could only absorb less than 5% of the solar surface that reaches the earth [3].

To improve the photocatalyst of TiO_2 , some modifications have been discovered by shifting its optical response to the visible light regions such as TiO_2 doping with metal and non-metal compounds [4]. The modification of TiO_2 will improve the photocatalyst by narrowing its bandgap allowing the utilization of a wider fraction of the visible light for the production of charge carriers. [5], [6], [7]. Even though its optical response could be shifted to the visible light region, the preparations for samples were complicated. Most current studies stated that the modification of N doped TiO_2 is produce by using the calculations technique. However, the procedure shows deficiency which consumed much energy and took more than 2 hours to prepare modified TiO_2 that can achieve optimum value [2]. In our research, the microwave irradiation technique was successfully applied in the preparation of N doped TiO_2 . It was observed that the N doped TiO_2 at 800 W of microwave power irradiation at 3:7 (urea: TiO_2) ratios were defined as the optimum condition for a modified photocatalyst. The N doped TiO_2 could effectively degrade both anionic and cationic dyes under fluorescent light irradiation.

2. EXPERIMENTS

2.1 Preparation of N doped TiO_2

The preparation of N doped TiO_2 was prepared by using the microwave irradiation technique. N doped TiO_2 was prepared by mixing the TiO_2 with various amounts of urea in the mechanical mixing process. The mixed powder was then placed into a conical flask in the semi-closed reactor and heated by using a microwave at various irradiation power. After the irradiation process, the treated sample was cooled to room temperature and named N doped TiO_2 .

2.2 Characterization and parameter studies

N doped TiO_2 sample and unmodified TiO_2 photocatalyst were characterized by using UV-Vis diffuse reflectance spectra (UV-Vis/DRS), X-ray photoelectron spectroscopy (XPS) and Photoluminescence (PL) analyses. The photocatalytic activity for photodegradation of RR4, MV and JG dyes was applied to affect the pH of pollutant and catalyst dosage.

2.3 Photocatalysis

For the photocatalytic degradation study, 0.03g of photocatalyst sample was added to the 25ml of 30, 10 and 5 mg L^{-1} of anionic RR4, cationic Methyl Violet and cationic Janus Green dyes respectively to form a suspension. These suspensions were then poured into a custom-made glass cell with dimensions 50mm \times 10mm \times 80mm (L \times B \times H). The suspension was then irradiated under 55 W fluorescence lamps with UV cut off the filter and the sampling of treated pollutant was collected for every 15 minutes interval until 60 minutes. The treated RR4, Methyl Violet and Janus Green dye every 15 minutes intervals were then collected and filtered using a syringe filter prior measured the absorbance value by using a Spectrophotometer at $\lambda_{\text{max}} = 517, 586$ and 661 nm for RR4, Methyl Violet and Janus Green respectively.

3. RESULTS AND DISCUSSION

3.1 Optimization studies

The optimum condition for N doped TiO_2 was observed at 800 W in 3 g of urea content with 0.104 min^{-1} of photodegradation rate.

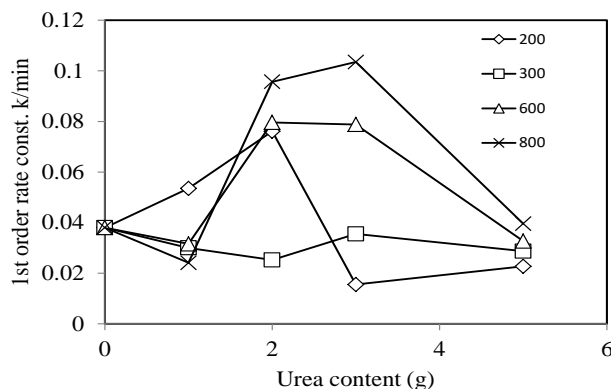


Figure 1: Plots of the pseudo-first-order rate constants (K) for the degradation of 30 mg L^{-1} RR4 under 55 W fluorescent lamp for N doped TiO_2 samples prepared at different irradiation power and different amount of urea.

Figure 1 shows a plot degradation rate of RR4 by using a 55-W compact fluorescent lamp on various N doped TiO_2 samples under different microwave irradiation power at 30 minutes. The lower content of urea shows slightly lower in pseudo-first-order rate constants, K values compared to unmodified TiO_2 . Increasing the ratio of urea content produced a significant photocatalytic activity where K values were higher as compared with unmodified TiO_2 . However, the higher ratio of TiO_2 with urea beyond the optimum sample shows a decrease in K values. The decrease in K value is due to a high amount of N content since the high amount of N may increase the substitution of oxygen

sites by nitrogen. This optimum condition for N doped TiO₂ was conducted in all applications research in this paper.

3.2 Characterization studies

3.2.1 UV-Vis/DRS

Figures 2 (a) and (b) show the UV-Vis diffuse reflectance spectra and plot graph Kubelka-Munk versus energy eV for samples N doped TiO₂ and unmodified TiO₂. Based on Figure 2 a), the absorption edge of unmodified TiO₂ is around 400 nm while for N doped TiO₂ is around 430 nm. A wavelength for UV light is from 200 to 400 nm while the wavelength for visible light is from 401 to 700 nm [8]. At this point, N doped TiO₂ sample shows the shift of its absorption towards the visible light region while the unmodified TiO₂ in the UV region. This observation shows that the N atom in urea was significantly reacted with TiO₂ particles producing a defect structure thus, narrowing the band gap energy of the photocatalyst. Figure 2 (b) shows the graph extrapolate to determine the band gap energy of unmodified and N doped TiO₂. The band gap energy was determined by Tauc's equation.

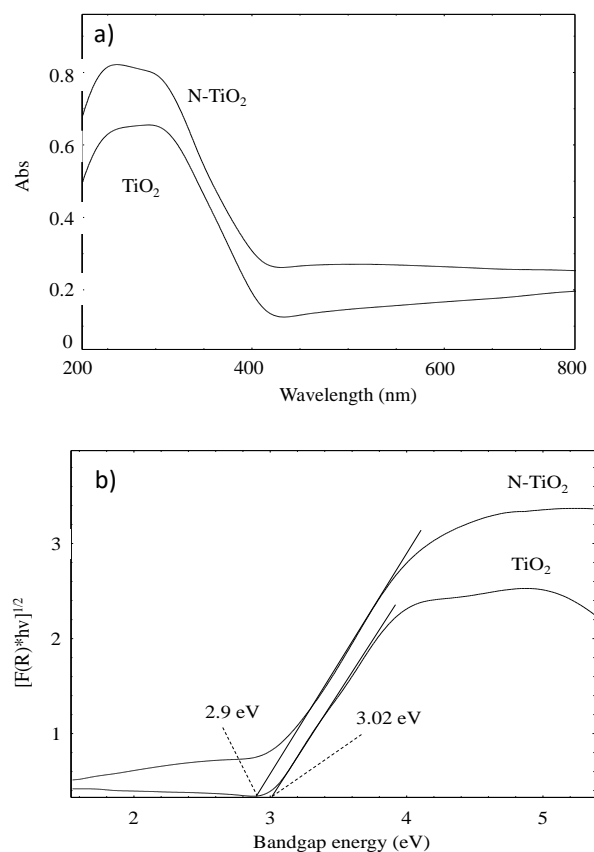


Figure 2: UV-VIS diffuse reflectance spectra of (a) Kubelka-Munk function vs. the energy of the light absorbed and (b) unmodified TiO₂ and N doped P25.

3.2.2 XPS analysis

X-ray photoelectron spectroscopy (XPS) measurement is used to carry out the detection of the surface species on the titania surface responsible for the visible absorption [6]. The N doped TiO₂ shows the presence of N 1s, O 1s and Ti 2p XPS peaks with binding energy at 404.8, 400.2, 532.16 and 457.96 eV respectively as shown in Figure 3. Based on the previous study, binding energy greater than 400eV indicate there was interstitial N doping and formation of N-O-Ti species.

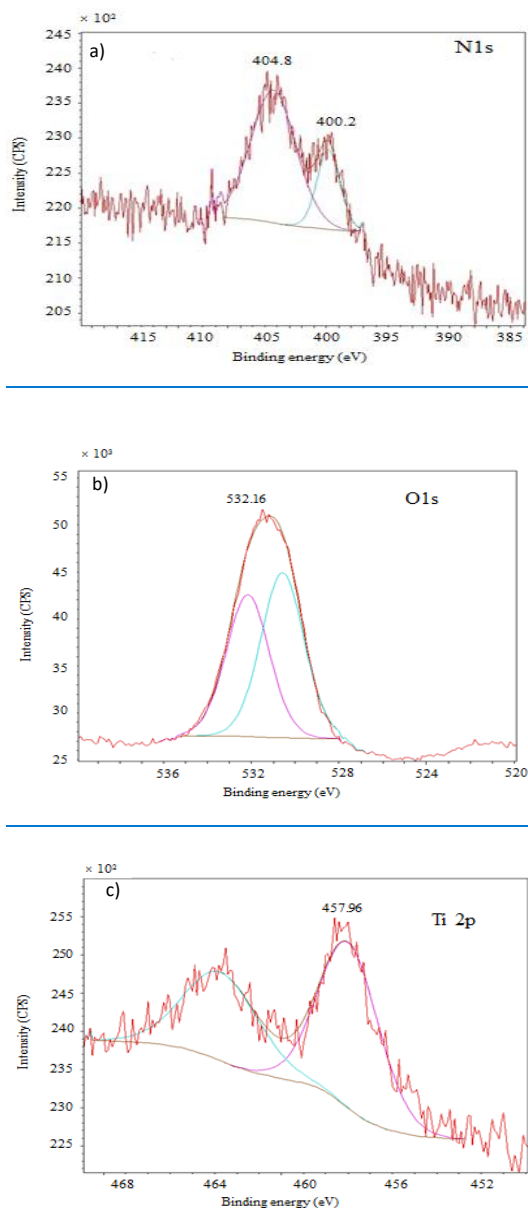


Figure 3: XPS Spectra of N-doped P25. (a) N 1s; (b) O 1s; (c) Ti 2p peaks

Figure 3 a), shows the deconvolution of N 1s peak revealed the presence of two peaks with binding energy 404.8 and 400.2eV in N doped TiO₂ sample. It is shown that a chemical interaction of N with titania forms N doped TiO₂ and this interesting finding explains the sample name (N doped TiO₂). Figure 3 (b) shows the binding energy peak for the O 1s located at 532.16 eV. A previous study by Zhanglian et al. [9] stated that binding energy of about 500 eV was attributed to the presence of metallic oxide, Ti-O. Thus, the binding energy in this study is assigned to the Ti-O structure. Value binding energy is shown in Figure 3 c) indicated to Ti 2p. According to Venkatachalam et al. [10], the Ti 2p region appeared at about 455eV and above. Thus for this sample analysis, it can be deduced that the value 457.96 eV observed in Figure 3 c) assign to the Ti 2p structure.

3.2.3 PL analysis

Photoluminescence (PL) analysis is an optical beam used to excite a material and radiation emitted by the material is spectrally analyzed [11]. PL spectra have been used extensively in the field of photocatalysis to understand the surface process as well as the fate of the electron-hole pairs in TiO₂ particles. Figure 4 shows the PL spectra of pristine TiO₂ and N doped TiO₂ using the excitation wavelength of 325 nm. It can be seen that the peak for both unmodified and N doped TiO₂ shows a similarly shaped curve the peak at about 480 nm and 575 nm. It was generally accepted that nitrogen doping can form a new electronic state (N state) just above the valence band, making TiO₂ absorb visible light. The emission at 480 nm is attributed that the emission signal originating from the charge transfer transition from oxygen vacancy trapped electron[12].

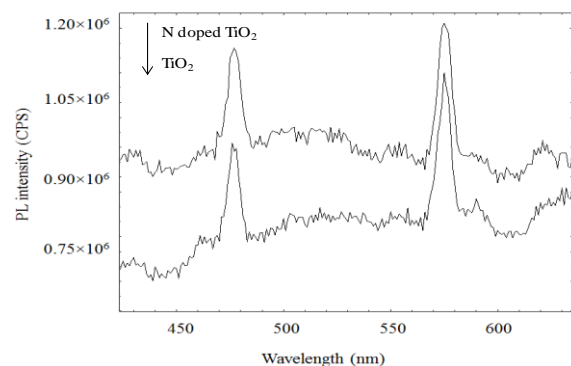


Figure 4: PL analysis of N doped TiO₂

According to Henderson et. al.[13], nitrogen doping favoured the formation of oxygen vacancies, which were experimentally found to be about 0.8 eV below the bottom of the conduction band. The oxygen vacancy of nanosized semiconductors was easily captured or bound with the photo-induced electrons [14]. Hence, the larger the oxygen vacancy content, the stronger the PL intensity. In Figure 4, it can be concluded that oxygen vacancy in N doped TiO₂ sample is in favour of photocatalytic reactions. The larger

the content of oxygen vacancy gives the stronger of excitonic PL spectrum and the higher the photocatalytic activity.

3.3 Parameter studies

3.3.1 Effect of catalyst dosage

At the lower catalyst dosage (0.01g), RR4 dye shows around 50% photodegradation while MV and JG show the photodegradation of dyes at around 60% in 1 hour. This is due to the lack of surface-active site to get absorbed and leads to the reduction in the photodegradation rate.

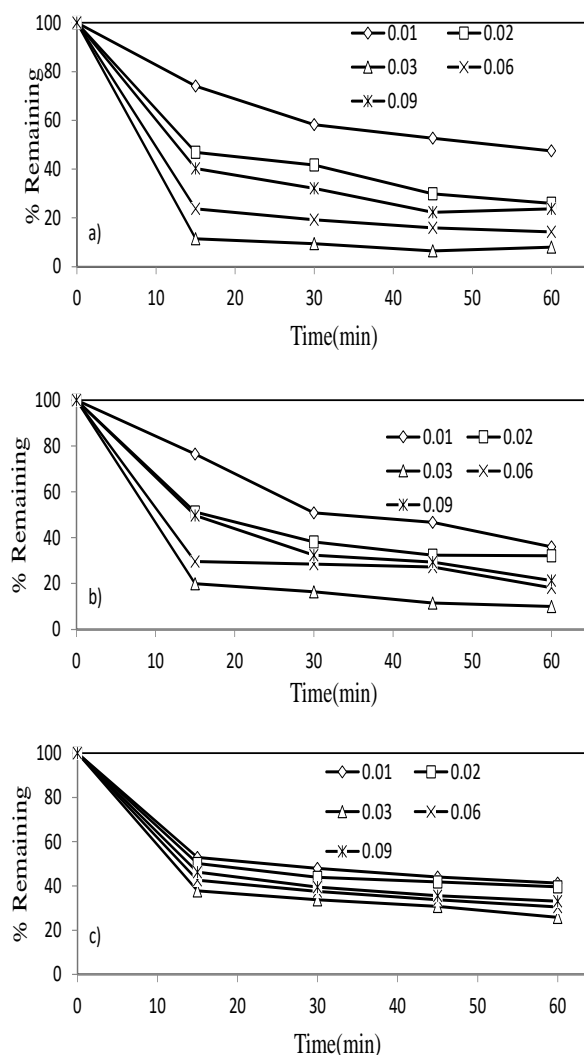


Figure 5: Effect of different catalyst dosage towards photocatalytic degradation based on percent remaining of a) RR4, b) MV and c) JG.

The photodegradation of dyes was gradually increased with optimum dosage achieved at 0.03g whereby RR4, CV and

JG dyes removal were almost 99%. This was due to the increase in the catalyst dosage that lead to the increase in the absorbent surface corresponding to the increasing binding or active site [15]. Thus, more dyes can be removed from the solution due to more molecule dyes can be absorbed onto the adsorbent surface. Therefore, 0.03g is the optimum dosage for N doped TiO₂ sample based on the highest photocatalytic degradation rate under RR4, MV and JG dyes. However, the increment catalyst dosage after the optimum value causes the reduction in the performance of dyes, possibly owing to the excessive particle that can cause turbidity and reduce the light penetration.

3.3.2 Effect of pH

Based on Figure 6 a), N doped TiO₂ shows the value of pH is inversely proportional to the degradation activity of dye. The higher the pH value, the lower the degradation activity of RR4. As we can see in Figure 6 a), the degradation activity of anionic dye is faster in acidic conditions compared to in alkaline conditions. It can be shown by the value of pH is pH 4. This is because the catalyst surface was positively charged and the surface active sites behave as strong Lewis acid [16].

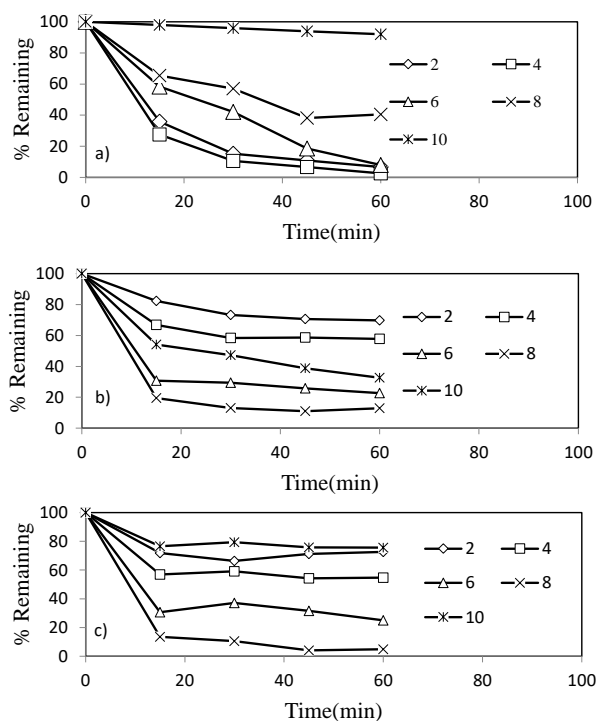


Figure 6: Effect of pH towards per cent remaining of a) Reactive red 4, b) Methyl violet, and c) Janus green dyes

Figures 6 b) and c) illustrates the trend of pH effect on the MV and JG. The MV and JG show the degradation activity was higher in the alkaline condition and lower in the acidic condition. Increasing, pH value indicated the enhancement of absorptivity capacity of cationic dyes, simultaneously

faster the degradation activity [12]. MV and JG show the degradation activity highest at pH 8 as shown in Figures 6 b) and c). The MV and JG have higher degradation at pH 8 compared to the ambient pH of 6. This was because there was N doped at the TiO₂ particle. Increasing the pH value from 6 to 8 will increase the negative charge on the surface N doped TiO₂. When the surface is a highly negative charge, MV dye can be easily absorbed and faster degradation [16].

4.0 Conclusion

The microwave irradiation technique was successfully applied in the preparation of N doped TiO₂. It was observed that the N doped TiO₂ at 800 W of microwave power irradiation at 3:7 (urea: TiO₂) ratios were defined as the optimum condition for a modified photocatalyst. N doped TiO₂ was characterized using X-ray photoelectron spectroscopy (XPS), photoluminescence (PL) and UV-Vis diffuse reflectance spectra (UV-Vis/DRS) analyses. The XPS and PL proved the successful nitrogen doped into the TiO₂. In addition, UV-Vis/DRS confirmed the doped of TiO₂ by decreasing the wavelength value. The irradiation of N doped TiO₂ was conducted using two parameters namely the effect of dosage and the effect of pH. It can be observed that 0.03g of catalyst dosage gives optimum photocatalytic degradation. Effect of pH was conducted based on the optimum dosage and conclude that pH 4 and 8 were the optimum pH for anionic and cationic dyes respectively.

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