Modification and characterization of microwave assisted N doped TiO₂ – a photodegradation study under suspension and immobilized system

W. I. Nawawi, M. S. Azami, L. S. Ang, M. A. M. Ishak and K. Ismail

ABSTRACT

A commercially available TiO₂ (P25) was modified to produce nitrogen (N) doped TiO₂ prepared by mixing TiO₂ powder with various amounts of urea as N precursor using a microwave irradiation heating technique. X-ray photoelectron spectroscopy analysis showed that N chemically bonded with TiO₂ produces Ti-N. The measured band gap energy ($E_g$) of the modified sample was ca. 2.9 eV as detected by UV-Vis/DRS. The optimum modified N doped TiO₂ denoted as U3-800 prepared at 230 °C showed an active visible light photoactivity. This observation shows that microwave irradiation is able to form Ti-N at low temperature whereas this previously could not be achieved under conventional heating using a muffle furnace at the same temperature. U3-800 showed visible light active photodegradation for 30, 10 and 5 mg L⁻¹ of reactive red 4, crystal violet and Janus green dyes, respectively, in less than 105 min to complete decolorization under suspension mode while no photocatalytic activity was observed under pristine TiO₂ under the same conditions. Immobilization of a U3-800 sample was carried out using DSAT as a thin layer binder and the photoactivity of Immobilize/U3-800/DSAT is comparable with the suspension mode. Surprisingly, immobilized/U3-800 has a strong coating with glass support material and can be continuously used for 30 cycles without affecting photoactivity performance.

Key words | immobilization, microwave irradiation, suspension, titanium dioxide, visible light

INTRODUCTION

Mostly dyes or pigments are widely used in industries such as textile, paper, cosmetic and plastic for coloring of their products. Excessive usage of dyes will turn it into dye product waste which is difficult to decolorize since most dyes contain highly carcinogenic aromatic amines (Cristina Fernandez et al. 2010). Ogugbue & Sawidis (2011) reported that the textile industries were estimated to discharge over 200,000 tons every year in dyeing and finishing operations. The draft ecological exposure assessment indicates that among textile mills located in 21 Canadian municipalities, textile mills in 16 of these municipalities result in predicted environmental concentrations of azo disperse dyes that may cause adverse effects on aquatic organisms (Canada 2015). Most of these dyes escape from conventional wastewater treatment processes and persist in the environment (Couto 2009). In textile manufacturing, anti-microbial agents resistant to biological degradation using natural fiber such as cotton are used. However, the complex aromatic structures of these agents make them more intractable to biodegradation.

Advanced oxidation processes (AOPs) have been considered as an effective technique in order to treat organic chemical dyes. AOPs are based on generating the hydroxyl radical which is a highly oxidizing agent. This hydroxyl radical is able to oxidize the organic pollutants with complete degradation or mineralization into CO₂ and H₂O.
Photocatalysis is a process employed by AOPs that has emerged as a destructive method which leads to the mineralization of the organic pollutants. This process is the combination of semiconductor photocatalyst such as TiO₂, ZnO, or Al₂O₃ with light as a source of energy. Titanium dioxide (TiO₂), mostly in anatase form, is the most widely used photocatalyst among all of the semiconductors as it is inexpensive, chemically stable, non-toxic, reusable and photostable (Nawi & Shielatina 2012). However, TiO₂ anatase limits the photoactivity due to its wide bandgap energy (E_g = 3.2 eV), thus making TiO₂ incapable of absorbing visible light.

Modification of TiO₂ has been focused towards narrowing the band gaps and thus allowing visible light to degrade the wastewater pollutant since it is a major wavelength for solar. Doping with non-metal and metal is a promising technique in order to narrow the band gaps of TiO₂. Recently, non-metal doping (C, N, S, and F) has gained much attention towards modified TiO₂ in comparison to metal doping (Yuan et al. 2006; Li et al. 2012; Nawawi & Nawi 2013). Wodka et al. (2010) reported that the silver doping in P25 did not reduce the bandgap even though it degrades the oxalic acid better by comparison to P25 under sunlight. Among all the non-metal doped TiO₂ materials, nitrogen doped TiO₂ has been discerned to exhibit superior photocatalytic activity under visible light irradiation (Miguel et al. 2012).

Asahi et al. (2001) discovered formation of N doped TiO₂ sample prepared by using ammonia as N precursor. Recently, Yuan et al. (2006) reported that N doped TiO₂ can be prepared directly by heating the mixture of urea and TiO₂. A simple preparation of N doped and S,N doped P25 was carried out by Rengifo et al. (2009) using a simple technique by mixing P25 with thiourea (S,N precursor) and urea (N precursor) annealed at 400 °C for the duration of 1 hour. Simple preparation of C coated and N doped P25 was prepared by Nawawi & Nawi (2014) where the preparation involves mixing P25 with urea under a muffle furnace at 350 °C. It was found that C coated and N doped P25 showed significant enhancement of photodegradation by degrading reactive red 4 (RR4), methylene blue and phenol under visible light, while no photocatalytic activity was observed for pristine P25 under the same conditions.

Modification of N doped TiO₂ under a microwave/sol-gel method by using ethyl titanate (C₈H₂₀O₄Ti) and urea as titania and N precursors, respectively have been reported by Wu et al. (2013), where they discovered the substitution of crystal lattice O to N species in N doped TiO₂, forming Ti-O-N and N-Ti-O. Wang et al. (2013) have studied microwave-assisted synthesis to prepare N doped TiO₂/g-C₃N₄ composites using H₂TiO₃ as the reactant and NH₃·H₂O as the N precursor. In this way, the N doped TiO₂/g-C₃N₄ composite catalysts have a porous structure and large surface area, which increases the contact area of pollutants. Kadam et al. (2014) reported N doped TiO₂ nano structure synthesized by a simple microwave assisted method, where ammonia was used as a hydrolyzing agent for the degradation of Malathion.

In a photocatalytic study, suspension of TiO₂ in aqueous solution is commonly used as it provides high surface to volume ratio (Razak et al. 2014). However, the suspension TiO₂ powder caused treated wastewater in slurry form and required a filtration process. The small particles of TiO₂ remained suspended in water and would clog the filter membranes and penetrate through porous filter materials (Dzinun et al. 2015). Realizing these issues, the immobilization system has been implemented to overcome these problems.

Recently, various organic polymer additives have been used by researchers to promote proper adhesion to immobilized TiO₂ substrate. Polyvinyl alcohol, polyethylene glycol, polyvinyl chloride and polyvinylpyrrolidone are a few examples of polymers that have been employed by previous researchers in their studies (Wang et al. 2003; Kim et al. 2006; Yang et al. 2015; Zhang et al. 2015). In immobilization study, binder and TiO₂ mixing ratio is critical. Adding polymer as a binder in TiO₂ composite makes TiO₂ immobilization become more intact and strong after multiple usages. However, too much polymer causes TiO₂ to be embedded in the polymer matrix which reduces the TiO₂-pollutant surface contact and eventually reduces the photocatalysis process. The lower amount of polymer mixing ratio, the better performance of the photocatalysis process will be observed, however this makes TiO₂ leach out easily. Thus, a new technique of TiO₂ immobilization with good photoactivity and strong coating with support material is required for commercialization.

From the best of our knowledge, there are no studies focused on the modification of N-TiO₂ by using
commercially available P25 and urea as a precursor under a microwave treatment method since all studies on microwave treatments producing N-TiO2 used titanium precursor as the starting material. Moreover, there is no detailed discussion on the effect of microwave irradiation towards the formation of N doped TiO2 process at low temperature and no utilization of immobilization technique at a low mixing ratio of polymer with TiO2 to produce strong TiO2 immobilized with excellent photocatalytic activity performance as good as TiO2 in suspended mode.

The aim of this study is to produce N doped TiO2 by mixing TiO2 with urea as an N precursor under microwave irradiation and to identify the significant effect of irradiation from a microwave by comparing with a conventional heating method using a muffle furnace at a specific low temperature. N doped TiO2 was immobilized on a glass plate support material by using a new technique without using any organic polymer as a binder. This new immobilized TiO2 technique is named as double sided adhesive tape (DSAT) and was successfully carried out in our previous publication (Ismail et al. 2015). DSAT can be used as a thin layer binder to provide good coating of TiO2 onto the glass plate since commercial DSAT is waterproof, durable and has a strongly adhesive thin layer which can be applied to almost all surface materials and is made from non-hazardous substances (Wang et al. 2005). Hence, it has high potential to be used as a thin layer binder for N doped TiO2 immobilized system. The photocatalytic activity of the immobilized photocatalyst was investigated by monitoring the degradation of RR4, crystal violet (CV) and Janus Green (JG) dyes under normal (55 W fluorescent lamp; 530–550 nm) and visible light sources as well as the durability and reusability studies of the new immobilized/N-TiO2/DSAT.

**EXPERIMENTAL**

**Materials**

TiO2 Degussa P25 powder was used as the starting material in the preparation of N doped TiO2. Urea in powder form from Fluka, Switzerland (chemical formula: NH2CONH2, molecular weight: 60.06 gmol\(^{-1}\) ) was used as the nitrogen precursor. Reactive red (RR4) dye, commonly known as Cibacron Brilliant Red (Colour Index Number: 18105, chemical formula: C32H23CIN8Na4O14S4, molecular weight: 995.23 gmol\(^{-1}\), \(\lambda_{\text{max}}\): 517 nm), with a chemical structure as illustrated in Figure 1(a). CV (also known as methyl violet) is a cationic organic compound with the molecular structure C24H28N3Cl. It has six methyl groups that attach to the amine functional group in CV molecular structure, as shown in Figure 1(b).

![Molecular Structures](https://iwaponline.com/wqrj/article-pdf/52/1/51/378589/wqrjc0520051.pdf)
JG or 3-diethylamino-7-(4-di methylaminophenylazo)-5-phenylphenazinium chloride was also used as a model pollutant. The chemical formula for JG is C₃₀H₃₁N₆Cl. The molecular structure of JG is shown in Figure 1(c). Distilled water was used to prepare all solutions in this work.

Preparation of N doped TiO₂ photocatalyst

In this study, N doped TiO₂ was prepared by using mechanical mixing of TiO₂ with various amounts of urea powder for 5 minutes. The mixed powder was placed into a conical flask in the semi-closed reactor. This reactor followed the method described in our previous study (Nawawi & Nawi 2014). The sample in the semi-closed reactor was then heated by using a microwave for various power irradiations under normal atmospheric conditions. The sample was cooled down to room temperature (26°C) and denoted as an N doped TiO₂ sample. All prepared samples were then transferred into screw cap sample bottles and stored in desiccators to minimize the humidity.

Optimization study

N doped TiO₂ photocatalysts at different N precursor loading and power irradiation were optimized by studying the photocatalytic activity for photodegradation of RR4 dye by following the method prepared by Nawawi & Nawi (2014). About 0.030 ± 0.002 g of photocatalyst sample was added in 25 ml of 30 mg L⁻¹ anionic RR4 dye in suspension mode. Suspensions were then poured into a 50 × 10 × 80 mm glass cell (L × B × H) and irradiated with a 55 W fluorescent lamp (530–550 nm wavelengths) at 10 minute intervals until colorless. An aquarium pump model NS 7200 was used as an aeration source to supply oxygen. Figure 2(b) shows the experimental setup for the photocatalysis reactor.

Characterization studies

The optimum N doped TiO₂ and pristine TiO₂ photocatalysts were characterized by using ultraviolet-visible diffuse reflectance spectra (UV-Vis/DRS) for the determination of bandgap energy. The X-ray photoelectron spectroscopy (XPS) measurement was used to detect the presence of surface species on the titania that is responsible for the visible absorption (Rengifo-Herrera et al. 2009). Photoluminescence (PL) spectra have been used extensively in the field of photocatalysis in order to understand the

Preparation of immobilized N doped TiO₂/DSAT and photodegradation study

Typically, N doped TiO₂ solution was prepared by mixing 13 g of N doped TiO₂ with 100 mL of distilled water in a 250 mL reagent bottle. The solution was shaken for 30 minutes using orbital shaker model PSU-20i, obtained from Grant-bio to homogenize the solution mixture. 0.3 g of immobilized N doped TiO₂ on a glass plate was immobilized onto a glass plate by coating with N doped TiO₂ solution using a brush technique (repeatedly brushing and drying until 0.3 ± 0.02 g of immobilized N doped TiO₂ was achieved) onto a 13 × 4.8 cm glass plate, DSAT was stacked on the glass plate prior to coating with the N-TiO₂ solution. The glass cell with immobilized/N doped TiO₂/DSAT was then dried in the oven at 100°C for 20 minutes. Figure 2(a) shows the sample immobilized/TiO₂/DSAT and its cross section. A dried immobilized/N doped TiO₂/DSAT sample was cleaned by using a photo-etching process whereby the sample was placed in a glass cell with 20 ml distilled water under irradiation of an 55 W fluorescent lamp model Qusun E27, 6,400 K in aerated condition for 1 hour prior to photocatalytic degradation.

A photocatalytic degradation study for immobilization was carried out by using 25 mL of 50 mg L⁻¹ of anionic RR4 dye poured into a glass cell with the dimensions 150 cm × 10 mm × 80 mm. Immobilized TiO₂ was then transferred into a glass cell containing RR4 dye and irradiated with a 55 W fluorescent lamp at specific time intervals until it turned colorless. An aquarium pump model NS 7200 was used as an aerating source to supply oxygen. Figure 2(b) shows the experimental setup for the photocatalysis reactor.
surface process as well as the fate of the electron-hole pairs in TiO$_2$ particles, and scanning electron microscopy (SEM) was used to study the surface morphology of samples.

**Comparison study under different light sources**

A comparison study under different light sources was carried out using two light sources, namely normal and visible lights. Normal light source was obtained from a 55 W fluorescent lamp with visible and UV light irradiations of ca. 461 and 6.7 W m$^{-1}$ respectively. The visible light source was obtained from a filtered 55 W (530–550 nm wavelengths) fluorescent lamp with a HOYA-UV cut-off filter, allowing only a visible light with 450 W m$^{-1}$ light intensity. The light intensity was measured by using a Radiometer brand Solar Light PMA2100. The photodegradation of three different pollutants was carried out under visible light in suspension and immobilized modes.

**Reusability**

The reusability of the photocatalysts was carried out according to the photocatalytic degradation procedure by repeating the same procedure of photodegradation under the immobilization system up to 30 times by using RR4 dye. The photocatalyst sample was alternately cleaned with ultrapure water under a 55 W fluorescent lamp in aerated conditions for 1 hour prior to the next photocatalytic degradation procedure.

**RESULTS AND DISCUSSION**

**Optimization studies**

In this work, anionic RR4 dye was used as the pollutant for optimizing the preparation of N doped TiO$_2$. The Langmuir-Hinshelwood kinetic model was used to determine the pseudo-first order rate constant where the equation is
given as \( \ln \left( \frac{C_0}{C_t} \right) = kt \) where \( C_0 \) is the initial concentration of the RR4 dye while \( C_t \) represents the concentrations at irradiation time \( t \) (min) in \( \text{mg L}^{-1} \). Figure 3 shows a plot of the degradation rate of RR4 under normal irradiation (UV + visible light irradiations) by using a 55 W compact fluorescent lamp on various N doped TiO\(_2\) samples at 30 minutes under different microwave irradiation power.

Figure 3 shows that the optimum preparation condition for N doped TiO\(_2\) was observed at 800 W in 3 g of urea content with a photodegradation rate of 0.104 min\(^{-1}\) and is known as U3-800 with 0.104 min\(^{-1}\) of photodegradation rate. The lower content of urea shows a slightly lower \( k \) value in comparison to TiO\(_2\) control. By increasing the ratio of urea content, significant photocatalytic activity was produced where \( K \) values were higher as compared to the unmodified TiO\(_2\). However, the higher ratio of TiO\(_2\) with urea beyond the optimum sample shows a decrease in \( k \) values. The decreasing of \( k \) values is due to a high amount of N content and may increase the substitution of oxygen sites by nitrogen. According to Yuan et al. (2006), increasing the substitution of oxygen sites by N may cause a massive production of oxygen vacancies, thus promoting the electron-hole recombination process and a lower result of photocatalytic activity may be observed.

**Characterization studies**

**UV-Vis/DRS**

Figure 4(a) and 4(b) show the UV/Vis diffuse reflectance spectra and plots of Kubelka-Munk versus energy (eV) for U3-800 and pristine TiO\(_2\) samples. With reference to Figure 4(a), the absorption edge of unmodified TiO\(_2\) is around 400 nm while for N doped TiO\(_2\) it is around 430 nm. A wavelength of UV light is 200–400 nm while the wavelength for visible light is 401–700 nm (Orlando & Maurício 2015). At this point, the U3-800 sample shows a shift of its absorption towards the visible light region compared with pristine TiO\(_2\) absorption in the UV region. This observation shows that the N atom in urea has successfully reacted with TiO\(_2\) particles producing a defect structure
thus narrowing the band gap energy of photocatalyst. Figure 4(b) shows the extrapolated graph to determine band gap energy for pristine and U3-800 samples. The band gap energy was determined by Tauc’s equation as stated in Equation (1), where $\alpha$ is the absorption coefficient, $h\nu$ is the photo energy, $n$ is a constant related to the type of optical transition, and $E_g$ is the absorption band gap energy. Since the Kubelka-Munk ratio is a function of reflectance, it is reciprocally used $F(R)$ (Tauc & Menth 1972). Assuming remarkably effective absorption then $\alpha = F(R)$, as stated in Equation (2).

The Tauc band gap can be attained by intercepting the plot of $(F(R)h\nu)^{1/n}$ against $h\nu$ (eV). Band gap energy for samples can be measured by extrapolation of the slope on the graph to $x$-intercept crossing.

\[
(\alpha h\nu) = (h\nu - E_g)^n \quad (1)
\]

\[
(F(R)h\nu)^{1/n} = (h\nu - E_g) \quad (2)
\]

The bandgap energies for pristine TiO$_2$ and U3-800 were measured at 3.02 and 2.9 eV, respectively, based on extrapolation samples on the Tauc bandgap graph as shown in Figure 4(b). It clearly shows that the band gap energy value for U3-800 has slightly reduced compared with pristine TiO$_2$, indicating that the N atom in urea has successfully reacted with the TiO$_2$ particles producing a defect structure as previously explained. This observation is in line with other researchers; according to Feng et al. (2008), they reported the narrowing of band gap energy was due to the introduction of the impurity level between the valence and conduction band of TiO$_2$. Likewise, Nawawi & Nawi (2013) also reported that the narrowing band gap is associated with the nitrogen presence in modified photocatalyst.

### XPS analysis

The XPS peaks of the U3-800 sample show the presence of N 1 s, O 1 s and Ti 2p with binding energies at 404.8, 400.2, 532.16 and 457.96 eV respectively, as shown in Figure 5. Based on previous studies, a binding energy greater than 400 eV indicates that there was interstitial N doping and formation of N-O-Ti species. According to Buzby et al. (2006), the peak at 400.2 eV was assigned to the binding energy of the N atom that chemically bonded to the TiO$_2$ as a Ti-O-N structural feature. A binding energy of 404.8 eV indicates the existence of the N-O bond in the form of nitric oxide,
nitrogen monoxide (NO) or nitrite formations (Ananpattarachai et al. 2009). Based on Figure 5(a), deconvolution of N 1s peak reveals the presence of two peaks with a binding energy of 404.8 and 400.2 eV in the U3-800 sample. This clearly indicates that a chemical interaction has occurred between N and titania forming N doped TiO₂. Figure 5(b) shows the binding energy peak for the O 1s that was located at 532.16 eV. A previous study by Khalid et al. (2012) stated that a binding energy at about 500 eV is attributed to the presence of metallic oxide, i.e. Ti-O. Dong et al. (2009) also reported that the binding energy at approximately 530 eV is attributed to the contribution of Ti-O in TiO₂ crystal lattice. Thus, the binding energy reported in this study is clearly assigned to the Ti-O structure. The binding energy values shown in Figure 5(c) is attributed to Ti 2p. According to Venkatachalam et al. (2006), the Ti 2p region appeared at about 455 eV and above. Thus from this sample analysis, it can be deduced that the value of 457.96 eV observed in Figure 5(c) indicates the presence of a Ti 2p structure. Ti 2p³/₂ and 2p¹/₂ core level peaks appear at 457.96 and 463.71 eV, respectively, which are attributed to Ti 2p peaks of O-Ti-N or N-Ti-N in TiO₂ (Peng et al. 2008; Kusumawardani & Indiana 2010).

**PL analysis**

PL analysis uses an optical beam to excite a material and the radiation emitted by the material is spectrally analyzed (Henry et al. 2000). Figure 6 shows the PL spectra of pristine TiO₂ and U3-800 samples using the excitation wavelength of 325 nm. It can be seen that both unmodified and U3-800 samples show the similar shaped curve of peaks at about 480 and 575 nm. It is generally accepted that nitrogen doping can form a new electronic state (N state) just above the valence band, making TiO₂ to absorb visible light. The emission at 480 nm is attributed to the emission signal originating from the charge transfer transition from the oxygen vacancy trapped electron (Feng et al. 2010). According to Henderson et al. (2003), nitrogen doping favored the formation of oxygen vacancies, which was experimentally found to be about 0.8 eV below the bottom of the conduction band. The oxygen vacancy of nanosized semiconductor can be easily captured or bound with the photo-induced electrons (Liqiang et al. 2005). Hence, the larger the oxygen vacancy content, the stronger the PL intensity. Oxygen vacancy becomes the center to capture photo-induced electrons, so that the recombination of photo-induced electrons and holes can be effectively inhibited (Inagaki 2012). Chen et al. (2012) stated that during the PL measurement, photo-induced electrons in the conduction band will fall into the oxygen vacancy through a non-irradiative process, and it will recombine with the photo-induced holes in the valence band. In Figure 6, it can be concluded that oxygen vacancy in N doped TiO₂ sample is in favor of the photocatalytic reactions. Higher content of oxygen vacancy gives stronger excitonic PL intensity and resulted in increasing the photocatalytic activity for the N doped TiO₂ sample.

**Effect of visible light irradiation**

Figure 7(b) shows the photocatalytic degradation of RR4 dye for U3-800 and pristine TiO₂ under visible light. The decolorization of RR4, CV and JC was observed under pristine TiO₂ and was the effect from its adsorption, as can be seen in Figure 7(a). Hence no photodegradation of these dyes was observed under pristine TiO₂ even after prolonged irradiation time (Figure 7(a)). High bandgap energy on pristine TiO₂ (3.02 eV) is the main factor for insignificant RR4 degradation under visible light and it is already explained by other researchers where the energy from visible light is insufficient to activate the excitation of the electron hole pair (Alexei et al. 2008; Rufino et al. 2009; Federico et al.
U3-800, however, significantly degraded the RR4 dye, and required about 75 minutes to complete the decolorization. This observation proves the previous result from diffused reflectance spectra where the narrowing bandgap energy at 2.9 eV for U3-800, due to the formation of defect TiO₂ structural forming Ti-N, activated U3-800 under visible light. Other researchers reported that certain kind of dyes may become a sensitizer during the photodegradation and the process can occur under visible light, even the bandgap energy of involved photocatalyst is higher than 3.0 eV (Xiangzhong et al. 2002; Malka et al. 2015). Hence, photodegradation study using other pollutants is compulsory. CV and JG dyes were used as model pollutants to confirm the photoactivity of U3-800 sample under visible light. Figure 7(c) and 7(d) show the photodegradation of CV and JG using U3-800 and pristine TiO₂ respectively under visible light. Apparently, no photodegradation for those dyes was observed under pristine TiO₂ since the bandgap energy of pristine TiO₂ sample is insufficient for energy from visible light to activate an excitation of electron hole pair. The photodegradation process, however, was observed for CV and JG dyes under U3-800, with complete decolorization being recorded at 90 and 105 minutes respectively, and it clearly proved that U3-800 sample is active under visible light irradiation. However, photocatalytic degradation rate of U3-800 under visible light irradiation is two times lower as compared to under normal light irradiation. This is due to the higher electron hole excitation in TiO₂ under normal light, making it more prone to produce hydroxyl radical as compared with U3-800 under visible light irradiation.

**Microwave versus muffle furnace**

The U3-800 sample was prepared by using 800 W microwave irradiation for a duration of 30 minutes where the temperature at 230°C was recorded using an IR-thermometer. Previous study has shown that the N doped TiO₂ cannot be prepared at low temperature (230°C) using a muffle furnace (Selvaraj et al. 2013; Shie et al. 2014; Tesfaye Teka Hagos 2014). For further confirmation,
preparation of N doped TiO₂ was repeated by using the method of the U3-800 sample, but under a muffle furnace at a heating temperature of 230°C, the sample was cooled at room temperature and denoted as U3-furnace. The comparative study of U3-800, U3-furnace and pristine TiO₂ in the photodegradation of RR4 dye was observed since incomplete formation of N doped TiO₂ can be simply observed by lower photocatalytic activity in comparison with pristine TiO₂. Figure 8 shows the photodegradation of RR4 using U3-800, U3-furnace and pristine TiO₂ under a normal light source (55 W fluorescent lamp). As expected, the photocatalytic activity of the U3-furnace sample shows the lowest rate value in comparison to U3-800 and pristine TiO₂. From the results, it is obvious that microwave irradiation has a significant effect on producing dielectric heating in which a high frequency alternating electromagnetic radiation localized the materials containing dielectric properties to generate heat caused by the rotation of molecular dipole within the dielectric. This process makes the materials undergo uniform heating under microwave irradiation. Thus, the formation of N doped TiO₂ at 230°C can be achieved by using a microwave heating method, which cannot be achieved under normal conduction heating.

**Suspension versus immobilization**

In this study, the same amount of photocatalysts was used in photocatalytic degradation of RR4 for U3-800 under suspension and immobilized modes (immobilized/U3-800/DSAT) under normal light irradiation. As can be seen in Figure 9(a), photodegradation of RR4 under immobilized/U3-800/DSAT system is slightly lower than the suspension mode by 10 minutes. This finding should be considered as a good photo-response under the immobilized system although the suspension mode is slightly higher than the immobilized mode. In fact, the photocatalytic activity of immobilized TiO₂ is always much lower than the suspension mode with the photodegradation rate being more than two times slower with the suspension mode based on reports by other researchers (Mansilla et al. 2006; Silva et al. 2012), with the exception of one pretreatment process called photo-etching applied prior to photocatalysis where this pretreatment gives the immobilized TiO₂ a slightly higher photoactivity compared with the suspension mode (Nawi et al. 2012). However, more time is required for this photo-etching process (8 hours) thus making the system less effective for commercialization. This new immobilization technique is also strong enough to bind U3-800 on glass plate support material using DSAT as a thin layer binder. Hence, immobilized/U3-800/DSAT can be reused without affecting its photocatalytic activity. Figure 9(b) shows the photocatalytic activity of immobilized/U3-800/DSAT upon the number of cycles under the degradation of RR4 dye. The photodegradation rate of immobilized/U3-800/DSAT is around 0.050–0.070 min⁻¹ and it remained almost constant for up to 30 times. It can be deduced that the coated U3-800 is fully intact on the glass plate and this statement is supported by SEM images of immobilized/U3-800/DSAT. Figure 9(c) and 9(d) show the morphology images for immobilized/U3-800/DSAT after the RR4 photodegradation process for the 1st and 30th cycles respectively, where the surface morphology for both images are almost the same with the spherical shape of TiO₂ particles strongly intact with support material on both images. Moreover, no filtration process is required for immobilized/U3-800/DSAT to separate between U3-800 and treated RR4 where it is a main problem for suspension mode for photocatalyst recycling (see Figure 9(b)).

**CONCLUSIONS**

A simple technique of visible light active N doped TiO₂ was successfully applied by mixing urea and TiO₂...
under microwave irradiation. It was observed that the utilization of urea and TiO\textsubscript{2} with ratio 3:7 and 800 W of irradiation power for 30 minutes produced N doped P25 with optimum photocatalytic activity. XPS analysis showed N was incorporated into TiO\textsubscript{2} by replacing the lattice oxygen atom, thus forming Ti-N-O with a binding energy of 400.2 eV. The bandgap energy of U3-800 was ca. 2.9 eV observed by UV-Vis/DRS spectrum. An immobilized/U3-800/DSAT shows a good photocatalytic response under visible light irradiation and is almost comparable with U3-800 under suspension mode. Immobilized/U3-800/DSAT has a strong coating with the glass plate support material. The \( k \) value of the photodegradation rate of immobilized/U3-800/DSAT remains almost constant for every RR4 photodegradation cycle.

ACKNOWLEDGEMENTS

We would like to thank the Malaysian Ministry of education (KPM) for providing generous financial support under RAGS grants (600-RMI/RAGS 5/35/2014) to conduct this study and Universiti Teknologi Mara (UiTM) for providing all the needed facilities.

REFERENCES

Ananpattarachai, J., Kajitvichyanukul, P. & Seraphin, S. 2009 Visible light absorption ability and photocatalytic oxidation


First received 5 January 2016; accepted in revised form 21 December 2016. Available online 13 January 2017.