Investigation of TiO₂ doped with nitrogen and vanadium using hydrothermal/Sol-Gel method and its application for dyes photodegradation

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ABSTRACT

The doping process of TiO₂ using a combination method, sol-gel and hydrothermal, has been conducted. The presence of anatase and rutile phase of TiO₂ and doped TiO₂ has been confirmed using UV-DRS, XRD, Raman spectroscopy, and EPR. The Nitrogen-doped TiO₂ (N-TiO₂) showed the highest photoactivity in the powder form than the as-prepared TiO₂ (rutile), anatase and Vanadium-doped TiO₂ (V-TiO₂). The influence of pH during the preparation of N-TiO₂ showed that pH gives a big effect to the morphology and photoactivity of the photocatalyst. The N-TiO₂ at pH 2 showed higher photoactivity than N-TiO₂ at pH 4 and it also showed a fine morphology. The N-TiO₂ also showed the highest photoactivity when it was immobilized in the DPNR matrix. After being immobilized, the photoactivity of the as-prepared photocatalyst was decreased to be 0–30%.

1. Introduction

Titanium oxide (TiO₂) is categorized as semiconductor material that has been widely investigated especially its photoactivity during the degradation of organic compound. In addition, titanium oxide has been applied as membrane for water purification process because of its antibacterial activity (Leon, Monash, Ibrahim, & Pichiah, 2014; Sousa et al., 2013; Velmurugan, Krishnakumar, Subash, & Swaminathan, 2013). In several advanced investigations, TiO₂ has been studied for its properties as a gas sensor (Gao et al., 2018) and solar photovoltaic (Hou et al., 2011) conversion based on its promising application results. Titanium oxide as photocatalyst material has some advantageous properties such as low cost, non-toxicity, high photo-stability and activity under UV light (Guarino, Costa, & Porro, 2008; Wang et al., 2016).

Unfortunately, TiO₂ also has some disadvantages such as low surface area, high recombination, and large band gap, that make it photoactive only in the UV region (Mathews, Cortes Jacome, Angeles-Chavez, & Toledo Antonio, 2015). In order to overcome those limitations, a number of adjustments have been made, such as surface modification, sensitization with plasmonic metal and doping with anion or cation (Ramchiary & Samdarshi, 2015; Serpone, 2006; Stathatos, Lianos, Falaras, & Siokou, 2000; Sudeep, Takechi, & Kamat, 2007). These adjustments were conducted to achieve the new material based on TiO₂ that can be used across a broad spectrum, i.e. visible light and reduction of the band gap value (Ramchiary & Samdarshi, 2015). Such treatment was performed based on the following background: the composition of the exposed sunlight on the earth’s surface only consists of 4% of UV light, 42% of visible light and 54% dominated with infrared. From the data, many studies have been conducted to develop the material based on TiO₂ that can harvest visible light (Ohno, Mitsui, & Matsumura, 2003; Seery, George, Floris, & Pillai, 2007). Numerous studies have been conducted to develop the material based on TiO₂ that can harvest visible light (Choi, Umebayashi, & Yoshikawa, 2004; Di Valentìn, Pacchioni, & Selloni, 2004; Nagalakshmi & Radhika, 2017; Vigissue et al., 2018; Ohno et al., 2003). These materials were prepared by doping one or several atoms of metals and...
The modified TiO$_2$ (Batzill et al., 2006; Nakamura, this process resulted in a reduction of band gap of blue (MB), and reactive black 5 (RB5) solutions azo dye, such as direct blue 71 (DB 71), methylene blue (MB), and reactive black 5 (RB5) solutions is discussed.

In the current research, the doping was processed with the presence of metal and non-metal substances, i.e. vanadium and nitrogen. These two elements were chosen due to the similarity of their atomic radius to the Ti and O atom radius. Further, the doping process of nitrogen into the lattice of TiO$_2$ using various precursors has been performed by many researchers for different applications (Di Valentin et al., 2004; Jagadale et al., 2008; Razali & Othman, 2017). The doping process of nitrogen gives a positive improvement in the photoactivity of TiO$_2$, i.e. the photocatalysis TiO$_2$ can be applied under UV and visible light; it is an impact of the overlapping of the p and 2p orbital of nitrogen and oxygen, and this process resulted in a reduction of band gap of the modified TiO$_2$ (Batzill et al., 2006; Nakamura, Tanaka, & Nakato, 2004; Wang et al., 2009). The other study reported, photocatalyst material with high activity in a visible light region, has been reported based on the doping process of vanadium into the TiO$_2$ and the impact of that process is improvement of photocatalytic ability under the visible range (Bettinelli et al., 2007; Kokorin et al., 2016; Martin, Morrison, & Hoffmann, 1994; Went et al., 1992).

To the best of our knowledge, few reports are published on the preparation of N- and V-doped TiO$_2$ using a hydrothermal method assisted with the sol-gel method. This method has many advantages, such as 1) various forms of TiO$_2$ that are different in mixture phase composition, crystalline structure and morphology could be obtained by changing the condition during a hydrothermal process that includes temperature, time, concentration and additive; 2) a low energy consumption and eco-friendly process. In the present study, the aim of this research was 1) to characterize the as-prepared photocatalyst TiO$_2$ and doped TiO$_2$ that were prepared using a combination of hydrothermal and sol-gel methods in the dyes degradation; 3) to evaluate its photocatalytic properties in powder form and immobilized form; and 4) to determine the influence of pH during the synthesis using the most active photocatalyst. The as-prepared photocatalysts were characterized using several instruments such as XRD, UV-Vis reflectance, Raman spectroscopy, and SEM. The effect of metal and non-metal doping on the photocatalytic decomposition rate of cationic and anionic azo dye, such as direct blue 71 (DB 71), methylene blue (MB), and reactive black 5 (RB5) solutions is discussed.

2. Materials and methods

2.1. Materials

Titanium isopropoxide (TTIP, 97%) and TiO$_2$ (anatase) were obtained from Sigma-Aldrich. Urea and ammonium metavanadate were purchased from Merck. Absolute ethanol was purchased from Guangdong Guanghua Sci-Tech Co. Ltd. Dyes in this research were obtained from Sigma-Aldrich. All chemicals were used without further purification.

2.2. Preparation of TiO$_2$ and doped TiO$_2$

TTIP, (NH$_2$)$_2$CO and NH$_4$VO$_3$, were used as starting materials for N and V-doped TiO$_2$. In a typical synthesis, 5 wt.% solution of N and V precursor was added dropwise into a mixture of absolute ethanol (1.5 mol) and TTIP (0.1 mol). The pH was adjusted to 2 and 4 by the addition of HNO$_3$ 0.25 M. During this process, the sol-gel phase was obtained. After 24 h, the mixture was poured into a Teflon-lined stainless autoclave with 100 ml capacity. The autoclave was then sealed and heated up to 180°C, and kept for 24 h, then cooled to room temperature naturally. Finally, the product was separated by centrifugation, and washed with distilled water and ethanol several times, then dried at 60°C. The obtained powder was calcined at 550°C for six hours. The pure TiO$_2$ samples were also prepared by repeating the above procedure without adding N and V precursor.

2.3. Characterization

The crystallography of the as-prepared TiO$_2$ and doped TiO$_2$ was determined using X-ray diffractometer (Bruker D8 Advance X-ray diffractometer). The morphology and nanosize of the as-prepared TiO$_2$ and doped TiO$_2$ were analysed using Scanning Electron Microscopy (Hitachi TM4000). The molecular vibration and phase of the as-prepared TiO$_2$ and doped TiO$_2$ was analysed using Raman Spectroscopy (AvaRaman-785 TEC). The optical data of the as-prepared TiO$_2$ and doped TiO$_2$ was measured using UV-Vis Diffuse Reflectances Spectrophotometry (Shimadzu UV-2600 Series). The magnetic properties of the as-prepared photocatalyst were determined using Electron Paramagnetic Resonance Spectroscopy (EMX micro Bruker Series).

2.4. Photoactivity measurements

The performance of TiO$_2$ and doped TiO$_2$ for dyes degradation was investigated using a 350 mL cylindrical glass reactor with a cooling jacket to control the reaction temperature. An amount of as-prepared photocatalyst, 40 mg/L, was suspended in 10 ppm of
dyes solution (Aldrich, 50% dye content) as the organic pollutant model. For the first 30 min, the suspended system was stirred without the presence of near-UV and visible light source to obtain the equilibrium of desorption-adsorption (Choi et al., 2004; Kokorin et al., 2016). The suspended system was then irradiated with a 125 W high-pressure Hg lamp (Osram) equipped with a cylindrical pyrex tub to ensure that the reaction was only irradiating by near-UV and visible light source (Razali & Othman, 2017). All the system was surrounded by a circulating water jacket to cool and stabilise the temperatures of the lamp and dye solution. To measure the photoactivity of the as-prepared TiO₂ and doped TiO₂, 10 ml aliquots was taken every five minutes. The obtained aliquots were centrifuged to separate the as-prepared TiO₂ and doped TiO₂ with the solution. The discoloration performance was determined at the maximum wavelength of DB71, MB and RB5 by UV-Vis spectrophotometer (Hitachi UH5300). In order to study the effect of light irradiation on dyes degradation, the photolysis experiment was conducted by irradiation of the dyes without the addition of as-prepared TiO₂ and doped TiO₂.

3. Result and discussion

3.1. XRD analysis

The XRD patterns of the as-prepared TiO₂ (rutile) and doped TiO₂ are shown in Figure 1, that reveals the presence of rutile phase on the as-prepared TiO₂ spectrum and anatase phase on the TiO₂ doped with nitrogen and vanadium. The change of crystalline phase from rutile to anatase of undoped to doped-TiO₂ is caused by the introduction of N and V into the lattice of TiO₂, but the mechanism and the clear explanation of this transformation has not been found yet (Batzill et al., 2006; Bettinelli et al., 2007; Breeson, Sankar, Goh, & Palgrave, 2016; Went et al., 1992). The corresponding peaks of rutile phase were shown at 27.44 (110), 36.06 (101), 39.11 (200), 41.2 (111), 44.05 (120), 54.34 (211), 56.65 (220), 62.77 (002), and 64.28 (130) degrees (JCPDS 96-7433). As observed at the XRD data of the doped TiO₂, the main peak of rutile at 27.44 disappeared, whereas the main peak of anatase appeared at 25.27°. The corresponding peaks of anatase phase for those doped TiO₂ were shown at 25.27, 37.91, 48.05, 54.04, 55.10, 62.14, 62.75, 68.66, 70.38, and 75.06 degrees corresponding to (011), (004), (020), (121), (123), (024), (116), (220) and (125) planes, respectively (JCPDS 96-6076). The crystallite size of TiO₂, N-TiO₂ and V-TiO₂ that calculated from the Scherrer formula along (101) and (110) plane for anatase and rutile phase were found to be 5.03, 2.02 and 1.52 nm, respectively. The crystallite size of TiO₂ doped with nitrogen and vanadium is less than the undoped TiO₂, this impact is also discussed in several studies (Cong, Zhang, Chen, & Anpo, 2007; Martin et al., 1994; Yang & Zhou, 2007). The d spacing value of the as-prepared photocatalyst is 3.25, 3.52 and 3.52 Å for TiO₂ (rutile), N-TiO₂ (anatase) and V-TiO₂ (anatase), respectively. In addition, the introduction of N and V into the lattice of TiO₂ has effect to the unit cell dimension, as the impact of the d spacing value for the doped TiO₂ is increased.
3.2. SEM images

Figure 2 shows the SEM images of the as-prepared TiO$_2$ and doped TiO$_2$. The scanning electron microscope images show that the as-prepared TiO$_2$ and doped TiO$_2$ have irregular nanostructure. Those results indicate that the morphology structure of TiO$_2$ cannot be changed by the addition of (NH$_2$)$_2$CO and NH$_4$VO$_3$, the precursor material for the doping process. Based on SEM images, the particle size of the as-prepared TiO$_2$ and doped TiO$_2$ is 6.24–49.89 and 6.00–48.59 nm, respectively. Also, the obtained nanoparticle has an agglomerated structure; the agglomeration of the doped TiO$_2$ is less than 160 nm while the undoped TiO$_2$ has agglomerates over 500 nm. The particle size has a significance effect to the photoactivity of photocatalyst material and the smaller particle size will have a higher surface area that will provide more photocatalytic sites.

3.3. UV-Vis diffuse reflectance spectrometric analysis

The UV-Vis DRS of the anatase, the as-prepared TiO$_2$ (rutile), N-TiO$_2$ and V-TiO$_2$ are shown in Figure 3. The DRS image shows the absorption onset of band gap for anatase, N-TiO$_2$, the as-prepared TiO$_2$ (rutile), and V-TiO$_2$ at 375, 385, 410 and 434 nm. Those absorption onsets are corresponding to the energy band gaps of 3.31, 3.24, 2.99 and 1.95 eV, respectively. After the doping process using nitrogen and vanadium, the optical absorption of the N and V – TiO$_2$ shifts to the wavelengths from 400 to 700 nm. The doping process using nitrogen and vanadium has a big contribution to the reduction of the TiO$_2$ band gap value (Di Valentin et al., 2004; Jagadale et al., 2008; Kokorin et al., 2016; Martin et al., 1994; Razali & Othman, 2017; Sathish, Viswanathan, Viswanath, & Gopinath, 2005; Xing, Zhang, & Chen, 2009; Yang & Zhou, 2007).

The decrease in the band gap value by the effect of the doping process has been reported in previous works by several authors. For the vanadium doping, the decrease of band gap is caused by the overlapping of 3d and 2p orbital of vanadium and oxygen; those overlapping initiated the formation of intermediate bands (Liu et al., 2009; Mathews et al., 2015). In addition, for the nitrogen doping, the decrease is explained as the overlapping of the p and 2p orbital of nitrogen and oxygen (Batzill et al., 2006; Nakamura et al., 2004; Wang et al., 2009).
3.4. Raman analysis

The crystalline structure of the as-prepared TiO$_2$ and doped TiO$_2$ that has been analysed by XRD pattern showed as rutile and anatase phase. Those results are corroborated by Raman spectroscopy (Figure 4); using this technique, the presence of the different phase of TiO$_2$ can be determined. Based on references, the anatase phase has four Raman signals, such as 399 (B$_{1g}$), 513 (A$_{1g}$), 519 (B$_{1g}$) and 639 cm$^{-1}$ (E$_g$). On the other hand, the rutile phase shows two Raman signals at 447 (E$_g$) and 612 (A$_{1g}$) (Ohsaka, Izumi, & Fujiki, 1978). The Raman spectra of the as-prepared TiO$_2$ in the range 200–700 cm$^{-1}$ shows the Raman signal of rutile phase at 451 (E$_g$) and 611 (A$_{1g}$). Then the N and V-doped TiO$_2$ samples show the Raman signal of anatase phase at 451 (E$_g$) and 611 (A$_{1g}$). The phase structure of these samples is suitable with XRD and Raman spectra.

3.5. Electron paramagnetic resonance (EPR) analysis

The electron paramagnetic resonance (EPR) spectra of the as-prepared TiO$_2$, N-TiO$_2$ and V-TiO$_2$ are shown in Figure 5. The EPR spectra of the as-prepared TiO$_2$ that has a rutile phase, showed some response of paramagnetic signal, although normally for the anatase and rutile phase they do not show any signal because Ti$^{4+}$ species is not an active paramagnetic. From some references, Ti$^{3+}$ is reported as one of the EPR active species that can be obtained from TiO$_2$. The presence of Ti$^{3+}$ can be found around 3.5 kG that is assigned to the defect of oxygen vacancy. In the EPR spectra of N-TiO$_2$, at 3.5 kG also can be found a broad signal that refers to the presence of Ti$^{3+}$ (Dogan, Chao, Peng, & Greenbaum, 2014). However, in the EPR spectra of N-TiO$_2$ the signals at 0.8 and 1.2 kG have disappeared; this happened because those signals are fingerprints for the rutile phase. Meanwhile, for the N-TiO$_2$, it has an anatase phase. The phase structure of these samples is suitable with XRD and Raman spectra.

3.6. Photocatalytic degradation of the dyes using UV-Vis light

The photoactivity of the as-prepared TiO$_2$, N-TiO$_2$ and V-TiO$_2$ was assessed by photodegradation of four dyes, such as acid yellow (AY), direct blue 71 (DB71), reactive black 05 (RB05), and methylene blue (MB). Photolysis was also performed to evaluate the possibility of the dyes degradation that were caused only by the UV-Vis source light. The photoactivity of the as-prepared photocatalyst was also compared to the photoactivity of TiO$_2$ anatase (Sigma-Aldrich). In Figure 6, after 45 min of treatment using UV-Vis source light, the impact of photolysis treatment among the dye samples is less than 5%. The photoactivity after correction of photolysis indicates that the photoactivity of N-TiO$_2$ is slightly increased after the doping process with nitrogen and it has the highest photoactivity, which can be the impact of the reduced band gap value. From the XRD data, the crystal structure of N-TiO$_2$ only consists of anatase phase, which has a better photoactivity than rutile. Moreover, N-TiO$_2$ has band gap value at $\sim$3.24 eV, which is lower than the band gap of TiO$_2$ anatase ($\sim$3.31 eV). The unique result was obtained on the photoactivity of V-TiO$_2$ that was almost similar to rutile. The band gap value of V-TiO$_2$ is $\sim$1.95 eV and the crystal structures are dominated with anatase phase. This phenomenon is caused by the presence of bulk vanadium (V$^{5+}$ or V$^{4+}$) on the surface of TiO$_2$ (Figure 2f) (Bettinelli et al., 2007).
the Figure 2f, the surface of TiO₂ is covered by black spot (vanadium species); the presence of vanadium on the surface of TiO₂ can increase the surface area and improve the photoactivity. However, here within the bulk amount of vanadium on the surface of TiO₂, the photoactive site of TiO₂ is covered by these particles and it reduces the photoactivity of TiO₂. The photodegradation of DB71 by anatase, the as-prepared TiO₂, N-TiO₂ and V-TiO₂ are 76.24; 52.95; 99.13 and 13.83%, respectively, while for acid yellow 96.57; 5.30; 91.38 and 5.80% are respectively for anatase, the as-prepared TiO₂, N-TiO₂ and V-TiO₂. In the photodegradation of methylene blue and reactive black 05, the photoactivity of N-TiO₂ is 98.34 and 100%, respectively, and the photoactivity of anatase is 96.25 and 72.21%.

There is a correlation between photoactivity and EPR spectra that is the influence of Ti³⁺ to the photocatalyst activity. The photoactivity of the as-prepared photocatalyst can be arranged as N-TiO₂ > TiO₂ (rutile) > V-TiO₂. From the EPR spectra, the Ti³⁺ can be found in the N-TiO₂ and TiO₂ (rutile), but not in V-TiO₂. The presence of Ti³⁺ in the surface of TiO₂ based photocatalyst can easily react with oxygen to form some radical species, such as •O₂, HO₂• and •OH. The presence of Ti³⁺ in the photocatalyst material can influence the photocatalyst activity of TiO₂ and the doped TiO₂. This argument is supported by some previous studies, such as that the high photoactivity of N-TiO₂ is the impact of the synergistic effect of Ti³⁺ and nitrogen (Ramchiary & Samdarshi, 2015; Wang et al., 2009; Xiong, Li, Yang, & Yu, 2012). The proposed mechanism of the formation of Ti³⁺ and those radical species may follow these equations:

\[
\begin{align*}
\text{e}^-_b + \text{Ti}^{4+} \text{OH} & \rightarrow \text{Ti}^{3+} \text{OH} \quad (1) \\
\text{Ti}^{3+} \text{OH} + \text{O}_2 & \rightarrow \text{Ti}^{4+} \text{OH} + \text{•O}_2^- \quad (2) \\
\text{•O}_2^- + \text{H}^+ & \rightarrow \text{HO}_2\text{•} \quad (3) \\
\text{HO}_2\text{•} + \text{H}^+ + \text{e}^-_b & \rightarrow \text{H}_2\text{O}_2 \quad (4) \\
\text{H}_2\text{O}_2 + \text{e}^-_b & \rightarrow \text{•OH} + \text{OH}^- \quad (5)
\end{align*}
\]

Based on the proposed mechanism for the formation of radical species, the photocatalyst of N-TiO₂ can produce more active species during the process of photoactivity. The production of these radical species can enhance the photoactivity of photocatalyst material.

The photocatalytic degradation of AY, DB71, RB05 and MB is shown in Figure 7. The plot of ln C/C₀ vs. time in Figure 7 illustrates that the reaction rate of all the as-prepared photocatalyst follows pseudo-first order kinetics. The N-TiO₂ shows the highest photocatalytic degradation which has 6.95 x 10⁻², 8.77 x 10⁻², 8.93 x 10⁻² and 9.03 x 10⁻² of k value for acid yellow, direct blue 71, reactive black 05 and...
methylene blue, respectively. The improvement of the N-TiO₂ photoactivity is attributed to the presence of Ti³⁺ on the surface of TiO₂ and the overlapping of p and 2p orbital of nitrogen and oxygen.

The influence of N-TiO₂ photocatalyst on the chemical structure of synthetic dyes AY, DB71, RB05 and MB during the photocatalytic process was investigated by observing the absorption spectral changes of the dyes every five minutes in the range of 400–700 nm wavelength. The photodegradation process of AY, DB71, RB05 and MB is shown in Figure 8. These processes show blue shift and the maximal peak broadens with the increase of the reaction time. From the absorption spectra pattern shown in Figure 8, the dyes decomposed quickly and no new absorption bands appeared in both visible and ultraviolet regions, which indicates that no aromatic moieties and other similar intermediates were produced (Gao & Liu, 2005).

3.7. Photocatalytic activity of DPNR/TiO₂ and doped TiO₂ composites

A disadvantage of photocatalyst material in powder form is the difficulty in the recovery process and reuse of the catalyst after treatment. Methods have been developed to overcome this, such as coating the photocatalyst as thin film, combination with polymer based on plastic, and magnetic material. However, all of these processes lack industrial application. To date, the research on elucidating the most suitable matrix for immobilized photocatalyst that can be applied for industrial purposes is still in a development process.

In the present work, the composite DPNR/TiO₂ and DPNR/doped TiO₂ were prepared by a blending process between deproteinized natural rubber DPNR (obtained from rubber latex with 30% dry rubber content) and the as-prepared TiO₂ (1 wt. %) using an internal mixer (Toyo Seiki, Labo Plastomil 4M150) for 10 min with a rotation speed 50 rpm. The morphology of DPNR composite and its photoactivity on several dyes, such as AY, DB71, RB05 and MB were evaluated.

The morphology analysis of DPNR composite is shown in Figure 9. Only few particles can be observed on the surface of DPNR and no aggregation was observed in any of the SEM microphotographs. Although not an aggregate, the distribution of the as-prepared TiO₂ and doped TiO₂ are not homogeneous. From Figure 9, it can be observed that the TiO₂ and doped TiO₂ particle centred at some points. This morphology result can give a negative impact to the photocatalytic degradation.
Figure 8. Wavelength shift of dyes during photocatalytic process.

Figure 9. The microphotograph of surface morphology of (a) DPNR/TiO₂, (b) DPNR/N-TiO₂ and (c) DPNR/V-TiO₂.
Results from the photocatalytic degradation of AY, DB71, RB05 and MB dye solution by the DPNR composite are shown in Figure 10. The photocatalytic degradation does not involve the adsorption process (data not showed). It implies that the photoactivity during the degradation process of dyes is caused by the as-prepared TiO₂ and doped TiO₂. The photoactivity of all DPNR composites has a lower value than the photocatalyst in powder form. The lower photoactivity of the composite is caused by the lack of material on the DPNR surface, it can be observed from the SEM images. Most of photocatalyst is well-dispersed in the DPNR matrix.

3.8. pH dependence in the N-TiO₂ synthesized

The preparation condition, e.g. pH, is one factor that has a big influence on the properties of photocatalyst material. For example, in the previous study about the preparation of TiO₂, the temperature, synthesis method, precursor, and reaction time have an important role in determining the crystal phase. The current work took a study of the influence of pH to the properties of N-TiO₂ – as the most active photocatalyst material in this work. The N-TiO₂ has been prepared in pH 2 and 4 by a combination method between hydrothermal and sol-gel as explained in the Methods section.

In Figure 11, the as-prepared N-TiO₂ at pH 2 and 4 has a different morphology, especially on the size of the agglomerate. At pH 4, the N-TiO₂ cannot be found as single particle, and all of the TiO₂ particle is found as agglomerate. The agglomerate size of N-TiO₂ prepared in pH 2 is less than 160 nm, but at pH 4 it is up to 1-micron size. The different result on the morphology may has an influence on the photoactivity.

The XRD analysis has been performed to determine the phase structure of the as-prepared N-TiO₂. Based on XRD spectra (Figure 12), photocatalyst N-TiO₂ that is prepared at pH 2 and 4 has different signals. The as-prepared N-TiO₂ at pH 2 is the anatase phase.

However, at pH 4, the N-TiO₂ consists of two kinds of crystalline phase and from the XRD spectra at this pH the crystalline phase was dominated with rutile (85%) and anatase (15%) phases. The obtained
TiO$_2$ crystalline phase is highly dependent on the chosen synthesis method. As shown in the previous work, nanoparticle TiO$_2$ was prepared using the sol-gel method at varying pH (3, 7 and 9) and it has varying results in which the anatase phase is only found at pH 3 and the mixture phase at pH 7 and 9 with a different composition of rutile and anatase (Santana-Aranda, Moran-Pineda, Hernandez, & Castillo, 2005). The composition of the mixture phase is an important factor in the context of photoactivity. In several studies, the TiO$_2$ with mixture phase will give a higher photoactivity than the pure anatase, but the percentage composition is mostly dominated with the anatase phase. Here, the mixture phase is dominated with rutile. The change of crystalline phase structure of N-TiO$_2$ that is prepared at pH 4, from anatase to amixture phase of anatase/rutile, will cause a change on the band gap value of this material. Figure 13 shows the optical transmittance profile of N-TiO$_2$ prepared at pH 4. The absorption onset of the band gap appeared at 424 nm with a band gap value 3.02 eV. The band gap value of this photocatalyst is between the as-prepared TiO$_2$ (rutile, 2.99 eV) and N-TiO$_2$ prepared at pH 2 (3.24 eV).

The photoactivity of the as-prepared N-TiO$_2$ is shown in Figure 14. The as-prepared N-TiO$_2$ at pH 4 has the lowest photoactivity in both kinds of dyes, MB and RB05. This result is the impact of the high composition of rutile in the mixture phase of N-TiO$_2$. After 45 min of photocatalytic process, the N-TiO$_2$ at pH 4 only showed 72.42% and 20.73% of the degradation ratio for MB and RB05, respectively. The kinetic rate constants of N-TiO$_2$ on the photocatalytic process of MB and RB05 are $2.65 \times 10^{-3}$ and $4.63 \times 10^{-3}$, respectively. That constant value is lower than the kinetic rate constant of N-TiO$_2$ prepared at pH 2.

4. Conclusion

The as-prepared TiO$_2$ and doped TiO$_2$, using a combined hydrothermal and sol-gel method resulted in rutile and anatase phases. The presence of anatase and rutile phases of TiO$_2$ and doped TiO$_2$ has been
confirmed using UV-DRS, XRD, Raman spectroscopy, and EPR. The N-TiO$_2$ showed the highest photoactivity in powder form compared with the as-prepared TiO$_2$ (rutile), anatase and V-TiO$_2$. The influence of pH during the preparation of N-TiO$_2$ has a big effect on the morphology and photoactivity of the photocatalyst. The N-TiO$_2$ at pH 2 showed a higher photoactivity than N-TiO$_2$ at pH 4 and it also showed a fine morphology. The N-TiO$_2$ also showed the highest photoactivity when it was immobilized in the DPNR matrix. However, after being immobilized, the photoactivity of the as-prepared photocatalyst decreased to 0–30%.

Disclosure statement

No potential conflict of interest was reported by the authors.

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