Enhanced photocatalytic degradation of N-doped TiO$_2$-SiO$_2$ composite for degradation of phenol under simulated natural light assisted by S$_2$O$_8^{2-}$ anions

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Abstract: In recent years, TiO$_2$ photocatalyst has been studied to increase the overall efficiency in the degradation of organic pollutants in water. Several solutions have been proposed such as non-metal doping to reduce a high band gap energy (3.2 eV) of TiO$_2$ to increase absorption in the visible region and synthesis of composite photocatalyst to improve the efficiency of electron-hole separation and the specific surface area. Herein, the N-doped TiO$_2$-SiO$_2$ photocatalysts were investigated. Powder samples with three molar ratios of TiO$_2$/SiO$_2$ (95/5-TS5, 85/15-TS15, 75/25-TS25) were successfully synthesized, characterized, and estimated their photocatalytic activity toward the phenol degradation (initial concentration to be 10 ppm) under simulated natural light. N-doped TiO$_2$-SiO$_2$ samples were prepared with molar ratios of N to designed TiO$_2$ to be 3%, 5%, 7%. The 3N-TS5 photocatalyst (3 mol % N doped TS5) shows the highest phenol efficiency degradation, to be 95% in 4 h, photocatalytic degradation rate constant of $1.02\times 10^{-2}$ min$^{-1}$ due to its narrower band gap energy (3.05 eV). Furthermore, the addition of S$_2$O$_8^{2-}$ anions at a concentration of 1 mM is enhanced degradation efficiency and degradation rate. And phenol is almost completely degraded within 60 min and achieved a degradation rate constant of $7.65\times 10^{-2}$ min$^{-1}$, 7.5 times higher than that without the presence of S$_2$O$_8^{2-}$ anions. This attractive result is attributed to the generation of sulfate radical ($SO_4^{2-}$) during photolysis.

Finally, N-doped TiO$_2$-SiO$_2$ photocatalyst assisted by S$_2$O$_8^{2-}$ anions shows potential to design and improve manufacturing processes to obtain photoreactors for organic degradation from waste-water under natural light degradation.

Keyword: N-doped TiO$_2$, TiO$_2$-SiO$_2$ composite, S$_2$O$_8^{2-}$ anions, photocatalyst, sulfate radical.

1.Introduction

Phenol is one of the hazardous organic pollutants discharged into the environment. At low concentrations, phenol can also be a dangerous factor for human life and the ecosystem. Nowadays, many methods are studied to remove phenol in water such as chemical precipitation [1], photocatalyst [2], ion exchange [3], biological method [4], etc. Compare to various available methods, photocatalytic degradation based on titanium dioxide (TiO$_2$) has been considered as an effective method for phenol photocatalytic degradation [5] due to physical stability, nontoxicity, good photocatalytic performance, corrosion resistance and environmental friendliness [6]. Anatase phase of TiO$_2$ has a wide band gap...
energy (approximately 3.2 eV) [7] that shows only photocatalytic activity under UV irradiation. Modified TiO$_2$ issue was investigated by structural adjustment [8], self-doped TiO$_2$ [9], hybrid element doping [10], which have been shown to be effective in reducing TiO$_2$ band gap, to extend light absorption wavelength to the visible region which accounts for more than 40% of the solar spectrum [11]. Photocatalyst materials base on doping TiO$_2$ with nonmetal such as N [12], C [13], S [14], F [15] have been studied. N-doped TiO$_2$ with high photocatalytic activity in the visible region causes the hybridization of N(2p) and O(2p) orbitals to shift the valence band upward resulting in a reduction in the TiO$_2$ band gap [16]. In addition, the N-doping has formed an N(2p) middle band gap level between valance band O(2p) and conduct band Ti(3d), thereby visible light can be absorbed and active electron from valance band to conduct band [17].

Besides, the high surface area in photocatalytic process is an important factor which increases the adsorption capacity of organic substances onto materials. To increase surface area of materials, many methods have been proposed such as associating TiO$_2$ with absorbent [18], modified shape of nanoparticles [19], doping metal [10]. Especially, synthesis of nanocomposite photocatalytic TiO$_2$-SiO$_2$ is considered as a promising method to elevate specific surface area of materials [20]. Increasing the specific surface area corresponds to the creation of more contact sites between TiO$_2$ and the organic compounds in the bulk solution and provides more active site for photocatalytic reaction, thereby possibly improving the photocatalytic activity.

Advanced oxidation process for water treatment is related to the generation of highly reactive oxygen species with high redox potentials. Hydroxyl radical is one of the common reactive species with high redox potential $E_{\text{r}}=1.8–2.7$ V [21], and highly efficient to degrade toxic organic compounds in water throw Fenton reaction [22] or advanced oxidation process [23]. However, the disadvantages of hydroxyl radical are known as leaching of metal ions during reaction and require UV radiation. Sulfate radical is known to be another active species with a high oxidation potential $E_{\text{r}}=2.5–3.1$ V and a longer half-life than hydroxyl radical and other reactive radicals [21].

In this research, N-doped TiO$_2$-SiO$_2$ photocatalyst were prepared to increase surface area and improve visible light response through nitrogen doping. Furthermore, persulfate ions – $\text{S}_2\text{O}_8^{2-}$ were employed for the formation of sulfate radicals, which significantly increase the degradation efficiency and reaction rate. The molar ratio of TiO$_2$ to SiO$_2$, amount of nitrogen doping and initial concentration of persulfate were evaluated through the photocatalytic degradation efficiency of phenol under simulated natural light.

2. Experimental

2.1. Chemicals

Required chemicals such as tetraethyl orthosilicate (TEOS 99%) and urea (99%) were purchased from Merk, titanium n- butoxide (TNB, ≥ 98 %) and acid nitric (65 wt%) were supplied by Sigma Aldrich. Ethanol (EtOH, 99.5%, Comaco Viet Nam), polyethylene glycol 20000 (PEG, Macklin), acetyl acetone (AcAc, >99%, Indian) used as received without any purified step.

2.2. Photocatalyst preparation

The N-doped TiO$_2$-SiO$_2$ photocatalysts were synthesized by sol-gel method. Firstly, a mixture including 4.00 g of TNB, 1.2 mL of AcAc, 5.0 mL of ethanol and 0.5 mL of HNO$_3$ 65 wt.% was mixed at 80°C under magnetic stirring for 1 h to form homogeneous solution A. At the same time, a solution B including TEOS, 0.20 g of PEG, 5mL of ethanol,2.4 mL of deionized water and 0.5 mL of HNO$_3$ 65 wt.% was also prepared at room temperature under magnetic stirring for 1 h. The amount of TEOS was designed to synthesize TiO$_2$:SiO$_2$ photocatalyst with different molar ratios to be 95:5; 85:5 and 75:25. Subsequently, the solution A was added dropwise to the solution B, and kept stirring for 2h. The final solutions were aged for 2 days, then dried at 120°C for 3 h and then calcined at 500°C for 2 h. The samples were named as TS5, TS15 and TS25, corresponding to molar ratios of 95:5; 85:5 and 75:25, respectively. To prepare N-doped TS5, urea was added into the solution B to obtain molar ratio of N to calculated TiO$_2$ to be 3, 5 and 7% and named as 3N-TS5, 5N-TS5 and 7N-TS5.

2.3. Characterization

Anatase phase and crystal size were determined from the X-ray diffraction (XRD) results, which were
obtained from D2 Phaser – Bruker diffractometer using CuKα radiation (30kW, λ=0.15406 nm). XRD pattern was recorded over 2θ range from 20 to 90° with a step of 0.02° at the rate 0.2 °/s. The crystalline sizes were calculated using Sherrer’s equation by the following [24]:

\[ D = \frac{k\lambda}{\beta \cos \theta} \]

where where \( D \) is the crystallite size at (101) crystal plane, \( \lambda \) the wavelength of the radiation (nanometer), \( k \) is the shape factor (k=0.9), \( \beta \) is the Full Width at Half Maximum at crystal plane (101) (FWHM, radians), and \( \theta \) is the diffraction angle (radian).

UV-Visible diffuse reflection spectroscopy (UV Vis – DRS) was used to determine light absorption wavelength, UV – Vis DRS spectra were measured on JASCO V-550 instrument with the scanning wavelength is 250 – 800 nm and scanning speed of 400 nm/min. The band gap energies were obtained by converting absorbance data into Tauc plot using equation [24]:

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

where \( h \) is Planck’s constant, \( \nu \) is the frequency, \( \alpha \) is the absorption coefficient, \( A \) is constant, \( n \) is equal to 1/2 for direct band gap transition. The band gap energy is determined from the intersection of the tangent line with the horizontal axis.

2.4. Photocatalytic performance

The photocatalytic degradation phenol was carried out in laboratory scale slurry photoreactor containing 200 mL phenol solution (with a concentration of 10 mg/L, catalyst dosage of 1.0 g/L) under continuous stirring. Suspension was stirred in the dark condition for an hour to reaching the adsorption-desorption equilibrium. Suspension was then irradiated under simulated natural light for 4 h using the Exo Terra Natural Light with full spectrum daylight (from 290 to 740 nm). The lamp was placed above a liquid surface of the phenol solution about 5 cm.

Aliquots of suspension were withdrawn at selected times and filtered through a 0.45 µm nylon filter to remove photocatalyst. The residual concentration of phenol was determined by using the ASTM 9065 method on UV-Vis spectrophotometer (Hitachi U-2910) at absorbance wavelength of 510 nm. To investigate the effect of the initial concentrations of persulfate, a designed amount of K2S2O8 was mixed with 200 mL of 10 ppm phenol solution for 30 min before adding catalyst to the mixture. S2O82- anion to be 0.25, 0.50, 1.0, 2.0 and 4.0 mM.

Langmuir – Hinshelwood (L – H) model was used to describe kinetics of photocatalytic degradation. At the low concentration of phenol, the reaction can be simplified to pseudo first-order kinetics, which is presented by the following equation [10]:

\[-\ln\left(\frac{C}{C_o}\right) = kt\]

in which \( C \) is the concentration of phenol, \( C_o \) is the concentration at the time the lamp is turned on, \( k \) is the first-order reaction rate constant.

3. Results and discussion

3.1. Characterization

The XRD patterns of TiO2 and TiO2-SiO2 samples with various TiO2:SiO2 molar ratios are shown in figure 1. It is clear that all characteristic peaks approximate at 2θ = 25.33°, 37.90°, 48.08°, 54.58°, 62.72°, 75.25° on the pattern assigned with pure anatase phase TiO2 (JCPDS 21-1272). In particular, from the XRD results, the diffraction peaks of SiO2 are not clearly observed, indicating that SiO2 exists in an amorphous phase. Table 1 shows the increase of FWHM with increasing SiO2 content because of the change of the TiO2 surface charge in the composite and a suppressive effect on grain growth with the existence of SiO2 [25].
The XRD pattern of N-doped TS5 samples is shown in figure 2(a). The obtained result shows that the unchanged intensity and no shift peaks in the N-doped TS5 samples with N-dopant content. The unchanged crystal structure of TiO₂ is due to the low concentration of nitrogen dopant. However, the crystallite sizes of the N-doped TS5 samples increases with increasing nitrogen content. It may be contributed by the intercalation of nitrogen in the TiO₂ structure affecting the TiO₂ particle growth leading to increase in crystallite size of the N-doped TS5 samples [26].

The optical properties of TS5 and N-doped TS5 samples were investigated using UV–Visible absorbance spectra and Tauc plot method as shown in figure 3(a) and 3(b). As depicted in figure 3(a),

![Figure 1. XRD pattern of TiO₂ and TiO₂-SiO₂ samples.](image)

![Figure 2. (a) XRD pattern of TS5 and N-doped TS5 samples, (b) enlarged (101) peaks.](image)

![Table 1. Crystal and optical properties of TS and N-doped TS5 samples.](table)

| Sample  | 2θ (degree) | FWHM (degree) | Crystallite size (nm) | Band gap energy (eV) |
|---------|-------------|---------------|----------------------|---------------------|
| TiO₂    | 25.34       | 0.513         | 15.89                | -                   |
| TS5     | 25.34       | 1.2162        | 6.63                 | 3.18                |
| TS15    | 25.33       | 1.408         | 5.79                 | -                   |
| TS25    | 25.32       | 1.557         | 5.23                 | -                   |
| 3N-TS5  | 25.33       | 1.1351        | 7.18                 | 3.05                |
| 5N-TS5  | 25.27       | 0.8919        | 9.13                 | 3.11                |
| 7N-TS5  | 25.19       | 0.8919        | 9.13                 | 3.12                |
the absorbance at the short wavelength region decreases along with the increased amount of nitrogen content, which means extension of visible light range. The lowest band gap energy of 3N-TS5 sample is determined to be 3.05 eV. It can be seen the absorbance spectra of 3N-TS5 samples in the range of 400 to 600 nm, the stronger absorbance is due to the formation of the shallow-level state, which is attributed to the orbital interaction of N(2p) state and O(2p) state in the band gap region of TiO$_2$ [27]. The band-gap energy of the samples decreases slightly with the increase of nitrogen dopant to coincide with Ravidhas’s report [24].

Figure 3. (a) UV–visible spectra of TS5 and N-doped TS5 (x=3, 5, 7%), (b) Tauc plot of TS5 and N-doped-TS5 samples.

3.2. Photocatalytic activity

3.2.1. Effect of TiO$_2$:SiO$_2$ molar ratio
Photocatalytic activity of TS samples with different TiO$_2$:SiO$_2$ molar ratio is shown in figure 4(a). It can be seen that the photocatalytic performance of TiO$_2$, TS5, TS15, TS25 were calculated approximately 50%, 82%, 60% and 40% under irradiation for 240 minutes, respectively. Among them, TS5 exhibited the highest efficiency may be due to the associated improvement of the specific surface area and band gap energy. A higher amount of SiO$_2$ content lead to higher band gap energy of composite. On the other hand, as shown in figure 4(b), reaction rate constant decreased from: $0.675 \times 10^{-2} > 0.355 \times 10^{-2} > 0.318 \times 10^{-2} > 0.155 \times 10^{-2}$ corresponding to TS5, TS15, TiO$_2$ and TS25 sample. The highest degradation rate constant obtained in sample TS5 may be due to the improvement of surface area resulting in increased adsorption capacity and providing more active sites for degradation process [28].

Figure 4. (a) Effect of TiO$_2$:SiO$_2$ molar ratio on photocatalytic degradation of phenol, (b) Plot of $- \ln(C/C_0)$ versus time of TiO$_2$ and TS sample.
3.2.2. Effect of amount of N dopant

Figure 5 shows the effect of nitrogen dopant to phenol photocatalytic degradation efficiency. Particularly, the 3N-TS5 photocatalyst achieve phenol degradation efficiency and first-order reaction rate constant to be 94.5 % and 1.022×10⁻² min⁻¹ while non-doped sample TS5 was only to be 82 %, and 0.675×10⁻² min⁻¹, respectively. The enhanced photocatalytic activity of 3N-TS5 sample can be explained by the substitution of oxygen atoms in TiO₂ structure by nitrogen atoms led to narrow down band gap to 3.05 eV, and thereby enhancing light absorption in the visible region. The higher band gap energy can also be the reason for the efficiency reduction in 5N-TS5 and 7N-TS5 samples.

![Figure 5](image)

**Figure 5.** (a) Effect of various amount nitrogen doped TS5 on photocatalytic degradation of phenol, (b) Plot of −ln(Ct/C₀) versus time of TS5 and N-doped TS5 (x=3,5,7%) samples.

3.2.3. Effect of initial concentration of S₂O₈²⁻

As shown in figure 6(a, b), the 3N-TS5/S₂O₈²⁻ systems show significant enhancement in reaction rate and degradation efficiency. At a concentration of 1.0 mM, Phenol is completely degraded after only 60 min and the reaction rate constant to be 7.65 ×10⁻² min⁻¹. The highest of reaction rate constant was obtained at S₂O₈²⁻ concentration to be1 mM (Figure 6(c)). The improvement in the reaction rate is due to the contribution of the sulfate radical formed by reaction (1) during the degradation process. However, a decrease in the reaction rate was observed at a concentration of S₂O₈²⁻ of 2 mM, which may be due to the adsorption of generated SO₄²⁻ anions onto photocatalyst surface to lead to the decrease of active sites [29]. Another reason may be due to the generated SO₄²− to react with the oxidative species according to reactions (2) and (3) [29].

\[
\begin{align*}
S₂O₈²⁻ + e_{vb} & \rightarrow SO₄²⁻ + SO₄⁺ \\
SO₄²⁻ + h^+ & \rightarrow SO₄⁺ \\
SO₄²⁻ + OH⁺ & \rightarrow SO₄⁺ + OH⁻
\end{align*}
\]

The summary of this study and recent research using phenol as a model pollutant are listed in table 2. The 3N-TS5 samples have excellent phenol degradation compared to other photocatalysts. The results have confirmed the influence of the surface area increase by SiO₂ and the N-doping process. Furthermore, the reaction rate is enhanced by the persulfate anions through the generation of sulfate radicals.
Figure 6. (a) Effect of initial concentration of $\text{S}_2\text{O}_8^{2-}$ on photocatalytic degradation of phenol, (b) Plot of $-\ln(C/C_0)$ versus time of TiO$_2$ and TS sample, (c) Plot of reaction rate constant versus concentration of $\text{S}_2\text{O}_8^{2-}$.

Table 2. Table of results of phenol degradation study of this and previous studies

| Catalyst                        | Photocatalytic condition | Degradation results               | Ref.   |
|---------------------------------|--------------------------|-----------------------------------|--------|
| N-doped TiO$_2$-SiO$_2$         | 10 ppm, 1 g/L            | 95% after 240 min, $k=1.02\times10^{-2}$ min$^{-1}$ | This work |
| N-doped TiO$_2$-SiO$_2$/S$_2$O$_8^{2-}$ | 10 ppm, 1 g/L            | 100% after 60 min, $k=7.65\times10^{-2}$ min$^{-1}$ | This work |
| N-doped TiO$_2$                 | 100 ppm, 1 g/L           | 79.6% after 180 min               | [30]   |
| Ti$^{4+}$ self-doped P25        | 10 ppm                   | 87.5% after 300 min, $k=0.413\times10^{-2}$ min$^{-1}$ | [31]   |
| Fe$_3$O$_4$-TiO$_2$             | 50 ppm, 0.5 g/L          | 75% after 180 min, $k=1.72\times10^{-2}$ min$^{-1}$ | [32]   |
| (Fe-S) codoped TiO$_2$          | 20 ppm, 1 g/L            | 100% after 600 min, $k=0.370\times10^{-2}$ min$^{-1}$ | [33]   |

4.Conclusion
The N-doped TiO$_2$-SiO$_2$ photocatalysts were prepared by the sol-gel method. The crystal structure formation of TiO$_2$-SiO$_2$ (TS) and N-doped TS5 samples was confirmed by XRD patterns.
photocatalytic degradation of N-doped TS5 samples under the light visible condition was demonstrated by DRS data due to the reduction of band-gap energy. The N-doped TiO\textsubscript{2}-SiO\textsubscript{2} synthesized with the molar ratio of TiO\textsubscript{2}:SiO\textsubscript{2} to be 95:5 and 3% nitrogen doping showed the highest phenol degradation efficiency. Moreover, phenol was completely degraded in the presence of S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-} anions with a concentration of 1.0 mM. And the reaction rate constant was determined to be 6 times higher than that of the experiment without S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-} anions.

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