Photocatalysis over N-doped TiO$_2$ driven by visible light as a new method for Pb(II) removal

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Abstract: The photocatalysis process over N-doped TiO$_2$ under visible light is examined for Pb(II) oxidation to form the less toxic and handleable PbO$_2$ suggesting a new method for Pb(II) remediation. The doping TiO$_2$ with N element was conducted by simple hydrothermal technique and using urea as the N source with various concentrations. The doped photocatalysts were characterized by DRUVS, XRD, FTIR and SEM-EDX instruments. Photocatalysis of Pb(II) through batch experiment was performed for evaluation of the doped TiO$_2$ activity under visible light, with applying various fractions of N doped, photocatalyst weigh, irradiation time, and solution pH. The research results attributed that N doping has been successfully performed, that shifted TiO$_2$ absorption into visible region, allowing it to be active under visible irradiation. The photocatalytic removal of Pb(II) under visible light over N-TiO$_2$ showed more effective than that of over the undoped photocatalyst. The removal of Pb(II) has notably taken place through oxidation, that may form PbO$_2$. The highest photocatalytic oxidation of Pb(II) 15 mg/L in 25 mL of the solution could be reached by using TiO$_2$ doped with 10%w of N, 15 mg of N-TiO$_2$ weight, 30 minutes of time, and at pH 8, suggesting a feasible method for Pb(II) remediation.

Keywords: doping N; TiO$_2$; Pb(II); photocatalytic-oxidation; visible light

1. Introduction

Lead (Pb), along with Cd, Hg, Cr(VI) and As, is categorized as the most toxic of the heavy metal. Lead as Pb(II) ion can be present intensively in wastewaters of many industries, such as storage batteries, mining, metal plating, painting, smelting, ammunition, oil refining and the ceramic glass [1-4]. Pb(II) ion is non-biodegradable and tends to accumulate in living tissues, causing various diseases and disorders [1-2]. Pb affects the functioning of the blood, liver, kidney and brain of the human being [1-4]. At high concentrations in human body, Pb is known to cause encephalopathy, cognitive impairment, kidney and liver damage, anaemia and toxicity to the reproductive system [2]. The permissible limit of Pb(II) in drinking water is 0.005 mg/L according to the current Environmental Protection Agency (EPA) standard, while WHO determines the limit is
0.01 mg/L [2]. In fact, the actual concentration of lead in wastewater is as high as several hundred milligram per liter. Therefore, the removal of lead from wastewater before they are contacted with unpolluted natural water bodies is important and urgent.

In recent years, adsorption is the most frequently method used for Pb(II) removal, because it is very effective technique in terms of initial cost, simplicity of design, ease of operation and insensitive to toxic substances [1-2, 5]. Several adsorbents that have been devoted for removal of Pb(II) included palm tree leaves [1], mesoporous activated carbon [2], modified natural zeolite [3], magnetic natural zeolite [5], and sulfonated polystyrene [6]. However, the adsorbent saturated with the concentrated Pb(II) ions becomes solid waste with higher toxicity, that will create new environmental problems.

Recently, remediation of Pb(II) containing water by photo-oxidation process through photo-Fenton method [4] and under TiO₂ photocatalyst [7] have also been developed. Oxidation of Pb(II) is the most interesting method since it resulted the non-toxic precipitate PbO₂ and easier to be handled [4, 7-9].

With respect to photocatalysis process, TiO₂ as a photocatalyst, has recently received considerable attention for removal of the persistent organic pollutants (POPs) including phenols [10], tetracycline [11], dyes [12], and linier alkyl benzene sulphonate [13] due to its cost-effective technology, non-toxicity, fast oxidation rate, and chemical stability. However, the wide band gap energy (Eg) of TiO₂, that is 3.2 eV for anatase type, leads it to be excited only by photons with wavelengths shorter than 385 nm emerging into UV region [14-16]. In fact, UV light only occupies a small portion (about 4%) of the sunlight spectrum, that limits TiO₂ application under low-cost sunlight or visible irradiation [14-18].

Therefore, an effort has been focused to overcome this deficiency by doping TiO₂ crystal structure with either metal elements [16, 18-21] and non-metal elements [14-15, 17, 22-25]. Non-metal dopant has been reported to give more effective in narrowing gap or decreasing Eg of TiO₂, compared to the metal dopant, because the size of non-metal elements are smaller than the metal dopants [14, 22-25], that easier to insert in the lattice of TiO₂ crystal. Among the non-metal dopants, N is the most interesting due to the very effective shift of Eg [14-15, 24]. Further, N-doped TiO₂ materials exhibit strong absorption of visible light irradiation and significant photocatalytic activity [14-15, 24].

Many studies of using N-doped TiO₂ have been frequently reported for degradation of dyes [15, 17], para-nitrophenol [24] and H₂ gas production [14]. However a research of using N doped TiO₂ for catalysis of the Pb(II) photo-oxidation under visible irradiation can not be traced. Under the circumstance, in this present paper, photo-oxidation of Pb(II) in the aqueous media over N doped TiO₂ by visible driven process is systematically studied. Operating parameters such as photocatalyst weight and irradiation time were optimized through laboratory scale experiment to obtain the best condition of the photo-oxidation process.

2. Results and Discussion

2.1 Characterization of TiO₂-N photocatalyst
2.1.1. By DRUV method

The DRUV/Visible spectra of the photocatalyst samples were displayed as figure 1. As expected, doping TiO$_2$ with N atom can shift the absorption into longer wavelength due to the narrowing their gaps. The narrowing was resulted from the insertion of N atom into the lattice of TiO$_2$ crystal. The evident of the narrowing gap was represented by decreasing $E_g$ values, as exhibited in Table 1.

![Figure 1. The DRUV Spectra of a) TiO$_2$, b) TiO$_2$-N(5) c) TiO$_2$-N(10), d) TiO$_2$-N(15)](image)

Table 1. The effect of N doped into TiO$_2$ on their band gap energy

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>$\lambda$ (nm)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>386</td>
<td>3.20</td>
</tr>
<tr>
<td>TiO$_2$-N (5)</td>
<td>405</td>
<td>3.06</td>
</tr>
<tr>
<td>TiO$_2$-N (10)</td>
<td>414</td>
<td>3.00</td>
</tr>
<tr>
<td>TiO$_2$-N (15)</td>
<td>417</td>
<td>2.97</td>
</tr>
</tbody>
</table>

It is also notable that increasing amount of N dopant has declined their Eg more effectively. It was considerably implied that N has successfully doped in the TiO$_2$ crystal. Some studies reported same findings [14-15, 24].

2.1.2. By XRD method

The XRD patterns of TiO$_2$ and TiO$_2$-N photocatalysts are displayed as figure 2. Several 2θ values of 25.25°, 37.52°, 48.02°, 53.58°, 54.88°, 62.61°, 68.78°, 70.33°, 75.07° and 82.68° are observed, which are assigned to anatase TiO$_2$ [15, 24]. In the XRD pattern of the N doped photocatalyst, additional phase, except anatase, is not observed.
Figure 2. The XRD patterns of a) TiO$_2$ (uncalcined), b) TiO$_2$ (calcined at 400 °C), c) TiO$_2$-N(5), d) TiO$_2$-N(10), and e) TiO$_2$-N(15)

It is also observable that doping N caused a decrease in the XRD intensities, and the intensities gradually declined as the enhancement of N amount. The decrease of the intensities assigned the partially TiO$_2$ crystallinity destroyed, due the insertion of N dopant in the TiO$_2$ lattice. The similar data was also reported by Li et al. [15] and Mahy et al. [24]. This data trend was in a good agreement with the Eg data.

2.1.3. By FTIR method

In the figure 3, it is seen that the FTIR spectra of all TiO$_2$-N samples are similar to that of un-doped TiO$_2$, where several peaks are observed at around 3400, 2450, 1630, and 700–500 cm$^{-1}$ of the wavenumbers. A study also reported the same IR spectra [15]. The peaks appearing at around 3400 and 2450 cm$^{-1}$ were attributed to the Ti–OH bond. In addition, the spectra also shows a sharp band at ∼1630 cm$^{-1}$ due to the OH bending vibration of chemisorbed and/or physisorbed water molecule on the surface of the catalysts [13]. The strong band in the range of 700–500 cm$^{-1}$ appearing was attributed to stretching vibrations of Ti–O–Ti bond.
The FTIR spectra of all TiO$_2$-N samples reveal a weak peak at about 1385-1280 cm$^{-1}$, which was not observed for the un-doped TiO$_2$. The intensity of this peak is seemed to increase with the increase of N amount doped in TiO$_2$. Moreover, the peaks at 1385 – 1280 cm$^{-1}$ were assigned tentatively to the interaction between N and TiO$_2$ particles [15], proofing that N atoms have been inserted in the TiO$_2$ structure.

2.1.4. By SEM

In order to investigate the surface morphology of the N doped TiO$_2$ photocatalyst, their SEM images were taken that are shown in figure 4. The particles of TiO$_2$-N seem to be covered with materials that is different from the particles of undoped TiO$_2$. The materials may be urea left on the photocatalyst. Then small particles are observable on the photocatalyst surface after used for photo-oxidation, that may be PbO$_2$ particles as the photo-oxidation products.

Figure 3. IR spectra of: a) urea, b) TiO$_2$, c) TiO$_2$-N (5), d) TiO$_2$-N(10), and e) TiO$_2$-N(15)

Figure 4. The SEM a) TiO$_2$, b) TiO$_2$-N (10), and c) TiO$_2$-N(10) after used for Pb(II) oxidation
2.2. Photocatalytic activity TiO$_2$-N under visible light in the removal of Pb(II)

2.2.1. Influence of N doping

The activity of the doped photocatalyst was evaluated by applying it in the photo-oxidation of Pb(II) under visible light process. The results of the Pb(II) photo-oxidation driven by visible and UV light, whether over un-doped and doped TiO$_2$, are illustrated in figure 5. The figure assigns that N-doped TiO$_2$ showed higher activity in the Pb(II) photo-oxidation both under visible and UV irradiations. The enhancement of the visible photocatalytic-oxidation was promoted by a decrease in the band gap energy (E$_g$), allowing TiO$_2$ to be activated by visible light to generate lot of OH radicals for oxidation. The reaction of the formation of OH radicals and Pb(II) photo-oxidation were presented as Eq.1 to Eq.3. In addition, a pair of $h^+$ and $e^-$ can naturally recombine to release heat (Eq.4) [15] that could deplete the number of OH radicals, that further declined the oxidation. The effective photocatalytic-oxidation of Pb(II) under visible light is a potential and promising method to be applied in the larger scale for industrial wastewater treatment.

![Figure 5. The effectiveness of the Pb(II) photo-oxidation over: 1) TiO$_2$, 2) TiO$_2$-N (5), 3) TiO$_2$-N (10), and 4) TiO$_2$-N (15). Both under UV and visible light expose](image)

\[
\begin{align*}
\text{TiO}_2\cdot\text{N} + h\nu &\rightarrow \text{TiO}_2\cdot\text{N} + h^+ + e^- \\
\text{H}_2\text{O} + h^+ &\rightarrow \cdot\text{OH} + \text{H}^+ \\
\text{Pb}^{2+} + 2\cdot\text{OH} &\rightarrow \text{PbO}_2 + 2\text{ H}^+ \\
\text{TiO}_2\cdot\text{N} + h^+ + e^- &\rightarrow \text{TiO}_2\cdot\text{N} + \text{heat}
\end{align*}
\]

Doping N could also considerably improve the photocatalyst activity under UV irradiation, since the dopant was found as electron-hole separation center [24] by capturing the electrons, that could prevent the recombination. The electron transfer from the TiO$_2$ conduction band to N atom at the interface is thermodynamically possible because
the Fermi level of TiO$_2$ is higher than that of N atom [24]. This doping resulted in the formation of a Schottky barrier at metal semiconductor contact region and improved the photocatalytic activity of TiO$_2$ [20, 24]. Hence, doping N atom essentially narrows the band gap of TiO$_2$ for the photo-excitation or red shift, and simultaneously delays the recombination rate of photogenerated electron–hole pair.

Moreover, the photo-oxidation of Pb(II) over un-doped TiO$_2$ photocatalyst under UV light is seen to be more effective than that of under visible light. The Eg of TiO$_2$ is 3.2 eV that is equal to UV light enabling TiO$_2$ to be activated by UV irradiation, and so more OH radicals could be provided. In contrast, the energy of visible light that is lower than the Eg of TiO$_2$, prevented TiO$_2$ in generation of OH radicals [17], that resulted in the lower photo-oxidation.

Figure 5 also illustrates that higher amount of N doped raised the photo-oxidation efficiency and reached maximum at 10% of N. The improvement was promoted by increasing their activity under visible light due to the lower Eg. Additionally, more amount of N dopant may improve the retardation of the recombination, that further enhanced the Pb(II) oxidation. On the contrary, at the N content beyond its optimum value, the Pb(II) oxidation seems to be detrimental. With further increasing N content, the N particles could also act as recombination center of e$^-$ and h$^+$ or promoted the recombination, that should reduce the number OH radicals available. The excess of N dopant might also cover the active sites on the TiO$_2$ surface, thereby inhibiting the OH radical formation. These conditions explained the decrease in the photo-oxidation. Same finding was also found by some studies [14-17, 20, 24]. Based on their Eg, 15% of N doped posed the lowest Eg suggesting the highest visible light absorption, and it was supposed to show highest photo-oxidation effectiveness. In fact the highest result is shown 10% of N content. It is obvious hence that both Eg and amount of N dopant plays role in the photocatalysis process and amount of N dopant showed larger role.

2.2.2. Influence of irradiation time

As seen in figure 6, prolong irradiation time up to 30 min could improve of the photo-oxidation but further expansion of the irradiation time longer than 30 min, there was no influence on the photo-oxidation that could be observed. Irradiation more than 30 min led to the photocatalyst exhausted in the OH radical formation, that was unable to improve the photo-oxidation [13]. Similar trend was also found by Wahyuni et al. [16]. Moreover, the short optimum time for the most effective Pb(II) removal is benefit in term of the application in the industrial scale.
2.2.3. Influence of photocatalyst weight on the photo-oxidation of Pb(II)

The photo-oxidation of Pb(II) sharply enhances with the elevation weight of the photocatalyst as demonstrated by figure 7. The increase of the photocatalyst weight provided more OH radicals, that could enhance the photodegradation. The larger weight that exceeded the optimum level caused a detrimental in the photodegradation. The excessive photocatalyst made the turbidity of the mixture increased that could inhibit the penetration light [16]. As a consequence, the OH radical formation was prevented and the less photo-oxidation efficiency was obtained. The mass giving maximum photo-oxidation is found as 15 mg for 25 mL of the Pb(II) solution that is equal to 0.6 g/L of the photocatalyst dose. Such dose is believed to be cost-effective in the larger scale.
2.2.4. Influence of solution pH

It can be notable in figure 8, raising solution pH up to 8 is found to improve the oxidation, but the photodegradation declines when the pH is further elevated. In the solution with low pH, the surface of TiO$_2$ was protonated to form positive charge (TiO$_2$:H$^+$), reducing the OH radicals formation [16]. In addition, the cationic of Pb$^{2+}$ was formed predominantly in the solution, the interaction of Pb$^{2+}$ with the protonated N-doped TiO$_2$ was repulsed. These simultaneous condition led to the less effective oxidation. When the pH was gradually increased, the protonation of TiO$_2$ gradually depleted, that generated greater amount of OH radicals. Additionally, large number of Pb$^{2+}$ were available, enabling it to interact with TiO$_2$ surface effectively. At pH higher than 8, the surface of TiO$_2$ was found as TiO$^{-}$ that was prevented to release OH radicals. In addition, Pb(OH)$_2$: precipitate may be formed in the solution that screened the entering light, leading to the less OH radicals formed [4, 7]. The most effective process taking place at neutral pH, is closely applicable for industrial scale.

![Figure 8. The influence of solution pH on the Pb(II) photo-oxidation](image)

2.2.5. Detection of PbO$_2$ formed from the photo-oxidation

In order to detect the result of Pb(II) oxidation, the EDX analysis of TiO$_2$-N before and after being used for Pb(II) photo-oxidation was executed, and the EDX data is displayed as figure 9. From the figure, the composition of the doped photocatalyst before and after being used could be formulated as displayed in Table 2.
Figure 9. The EDX data of a) TiO$_2$-N before, and b) TiO$_2$-N after used for Pb(II) photo-oxidation

Table 2. The composition the doped photocatalyst based on the EDX data

<table>
<thead>
<tr>
<th>Element</th>
<th>TiO$_2$-N (20%) before photo-oxidation</th>
<th>TiO$_2$-N (20%) after photo-oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>6.6</td>
<td>4.7</td>
</tr>
<tr>
<td>N</td>
<td>9.4</td>
<td>7.0</td>
</tr>
<tr>
<td>O</td>
<td>25.9</td>
<td>27.3</td>
</tr>
<tr>
<td>Ti</td>
<td>58.1</td>
<td>60.8</td>
</tr>
<tr>
<td>Pb</td>
<td>0.2</td>
<td></td>
</tr>
</tbody>
</table>

From the table, it is observed the presence of Pb atoms and enhancing oxygen content in the TiO$_2$-N photocatalyst after used in the Pb(II) photo-oxidation, which is not found in the TiO$_2$-N before used. It may be proven that the photo-oxidation yielded PbO$_2$, by following the reaction in Eq.4. The formation of PbO$_2$ from Pb(II) oxidation is in agreement with the finding that was reported previously [8-9]. The formation of the solid PbO$_2$ is beneficial in terms of solid waste treatment due to the less toxic and handleable waste.

3. Materials and Methods

4.1. Materials

The chemicals used in this research were TiO$_2$, urea, Pb(NO$_3$)$_2$, HCl, and NaOH, that were purchased from E. Merck and were used without any purification.

4.2. Methods

4.2.1. Doping process of N on TiO$_2$

Doping was performed by hydrothermal method following reported previously [16]. TiO$_2$ powder about 1 gram was dispersed in 100 mL of urea solution 1 g/L. The mixture was placed in autoclave, then was heated at 150 °C for 24 h. The doped TiO$_2$-N resulted was dried at 100 °C for 30 min, and continued by calcination at 400 °C for
2 h. The sample was kept for characterization and activity evaluation. With such amount of urea, theoretically, N content in TiO$_2$ was about 5%w. The same procedure was repeated for urea with 2 g/L and 3 g/L of the concentrations, giving around 10%w and 15%w of N content in the doped TiO$_2$ respectively. Therefore, the doped photocatalyst samples were coded as TiO$_2$-N(5), TiO$_2$-N(10) and TiO$_2$-N(15).

4.2.2. Characterization of N-doped TiO$_2$

The doped photocatalysts obtained were characterized by using Pharmaspec UV-1700 DRUV spectrophotometer, Shimadzu 6000X-XRD, 8210 FTIR spectrophotometer, and JSM-6510 LA SEM-EDX machines.

4.2.3 Photosensitization of Pb(II) in the solution over TiO$_2$-N photocatalyst

The photosensitization of Pb(II) was conducted by batch technique in the apparatus seen in figure 10. The Pb(II) solution 15 mg/L 25 mL in an Erlenmeyer flask was mixed with 15 mg of TiO$_2$-N(5) then the flask was put in the photocatalysis apparatus. Next, the Erlenmeyer in the apparatus was irradiated with the visible lamp accompanied by magnetic stirring for 30 min. The Pb(II) left in the solution was analyzed by Perkin-Elmer 110 AAS machine. The concentration of the Pb(II) was determined by extrapolation on the corresponding standard curve. The same procedure was copied for processes with TiO$_2$-N containing N of 10% and 15%, and various irradiation time (5, 10, 20, 30, 45, 60 min), photocatalyst weight (1, 5, 10, 15, 20, 25 mg), and solution pH (4, 6, 8, 10, 12). When one parameter was varied, other parameters were kept to be constant.

![Figure 10. A set of apparatus used for Pb(II) photo-oxidation processes composed of: a) melamine box, b) visible lamps, c) magnetic stirrer plate, d) photocatalyst powder, e) magnetic stirrer bar, and f) sample solution.](image-url)
4. Conclusions

It has been successfully prepared the N-doped TiO$_2$ photocatalyst by hydrothermal method, that has narrowed the band gap energy, allowing it to absorb visible light. It was found that doping N on TiO$_2$ structure could improve its activity in the Pb(II) photo-oxidation under visible light irradiation. The most effective Pb(II) photo-oxidation (98%) from Pb(II) 15 mg/L in 25 mL solution was reached by using TiO$_2$-N with 10 % of N fraction, by applying condition of 15 mg of the doped photocatalyst, 30 minutes, and pH 8. It may be also evident that PbO$_2$ is produced from the Pb(II) photo-oxidation. The low photocatalyst dose, short reaction time and neutral pH effective process are beneficial factors allowing the method to be applied for the treatment of industrial Pb(II) containing wastewater.

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References


