



Preparation of TiO₂ nano –material coating on rice husk ash and application for nitrogen compound removal from water

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ABSTRACT

This article reports the results of initial research on synthetic process of nitrogen modified TiO₂ nano-material and coating on the rice husk ash by the sol-gel method. Nitrogen modified TiO₂ nano-material has anatase crystalline properties. The particle size has relative uniformity, about 25nm, and covers quite evenly on the surface of the husk ash. The specific surface area of the prepared material is 109.7 m²/g. The efficiency of NH₄⁺, NO₃⁻ and NO₂⁻ removal from industrial wastewater was found to be promising, in natural lighting conditions with the reaction time of 60 minutes, the concentrations of NH₄⁺; NO₃⁻ and NO₂⁻ decreased from 20.00 to 0.053 mg/l; 1.02 and 0.87 mg/l, respectively. The removal efficiency ranged from 77 to 97%. However, in dark conditions, the removal efficiency attained was very low.

Introduction

Nitrogen polluted industrial wastewater discharged into the environment will cause the growth of aquatic plants such as moss, algae and the reduction of dissolved oxygen in recipient. Nitrogen compounds including nitrite have high toxicity. Nitrite absorbed into the blood will consume the oxygen and incapability of receiving the oxygen of hemoglobin, resulting in anemia. Nitrite in combination with amino acids in foods will produce nitrosamine that can cause genetic trauma and cancer [1-5].

Currently, there are number of technologies applied to remove nitrogen compounds in wastewater, groundwater as well as drinking water such as biological methods, adsorption methods, ion exchange, membrane filtration technology, reverse osmosis, etc. Generally, these methods require high investment, long-residence time, and are produced by-products and secondary pollutants that all required

additional cost. Therefore, low cost and environment - friendly technologies that use available material sources, durable and low-operating costs for treatment effectiveness as well as economic, got interested in researching and applying.

Nano size TiO₂ is a low cost of photo catalyst, with chemical inert, photochemical durable and non-toxic to humans and the environment that is then widely and commonly used. Nano size TiO₂ is proven as the photo catalyst with the remarkable advantages of economic and technological effectiveness in the removal of organic, inorganic, and biological infectious pollutants from water.

Husk and husk ash are agricultural waste accounting for about 1/5 rice yield in the world (about 545 million tons per year). Globally, there are over twenty million tones of husk ash disposed annually [6-7]. Husk ash is used as adsorption materials to remove a variety of inorganic substances, organic pollutants. Also, the husk

ash is used as a bearing substance for catalytic materials because of its good mechanical durability, chemical inert. Further, when it is used as a bearing substance, it can be easily separated from the solution after the reaction.

Therefore, utilizing husk ash as a bearing and filter in material to remove the nitrogen compounds, combined with the photosynthesis of the modified TiO₂ catalyst to convert nitrogen compounds such as nitrate, nitrite, and ammonium into N₂ (non-toxic substance) has been much concerned. This has led to the proposal of solutions to minimize environmental pollution from agricultural waste; and to increase the efficiency of nano material application. It invents a new method in the treatment of nitrogen compounds as well as being able to deploy the application in other industries [8-9].

Experimental setup

Chemical and materials

Chemicals used in research include: TiCl₄, NH₄NO₃, PVA, (NH₂)₂CO, standard solutions: NH₄⁺, NO₃⁻, NO₂⁻, HgCl₂, KI, NaOH, KNaC₄H₄O₆.4H₂O, H₂SO₄, NH₄Cl, KNO₃, NaNO₂, CH₃COOH, NaOH, phenol, sulfanilic acid, α-naphthylamine, EDTA, methylene blue. The chemical compounds have a purity of PA, produced by the Merck, German, distilled water and super clean water. Husk is taken from the Rice enterprise in Hoai Duc, Ha Noi.

Water samples: water samples containing nitrogen are prepared from the chemicals NH₄Cl; KNO₃; NaNO₂ with concentration of NH₄⁺-N, NO₃⁻-N, NO₂⁻-N about 20.00 mg/L.

Dispense TiCl₄ 3m by mixing TiCl₄ in cold water then diluting to 0.5 M solution by cold water.

Preparation of nitrogen doped TiO₂ nano material coated in husk ash

+ Preparation of nitrogen doped TiO₂ nano material (step 1)

Nitrogen modified TiO₂ nano material was prepared according to the procedures of Nguyen HN et al (2016): Mixing 60 ml NH₄NO₃ 1M with 450 ml(NH₂)₂CO 1M+ 180 ml PVA 1M + 60 ml TiCl₄ (0,5M); heating to 70°C, stirring continuously in 24 hrs., 1200 rpm, then heating up to 90°C, and stirring for 12 h. Sol-gel solution obtained was dried at 120°C for 12 h, then the temperature was increased to 250°C for 3 h until no more white smoke was released, and black powder

was generated. Finally, materials were put in furnace at 600°C for 3 h with a heating rate of 10°C/min. Materials after the furnace were washed 4-5 times with distilled water and super clean water, then dried at 120°C for 2 h.

+ Preparation of husk ash bearing material (step2)

The husk is washed with distilled water to eliminate impurities, dried at temperatures of 105°C for 2 h, then put in furnace at temperatures of 800°C for 3 h in N₂ gas environment to have ash bearing material.

+ Coating TiO₂ nano material on husk ash (step 3)

Husk ash was added into sol-gel solution prepared in section (step 2) to have the concentrations of TiO₂ in husk ash corresponding 0.1; 0.2; 0.3; 0.4 and 0.5% w/w. The thermal modification process started with well stirring the mixture at 90°C for 12 h then was followed by similar processes as in the preparation of nitrogen modified TiO₂ nano materials in section (step 1).

Investigation of nitrogen compound removal efficiency of TiO₂ nano material/huskash

Experiments were conducted on the column (volume: 25.0 ml with 4.1 g of TiO₂ material/husk ash, porous volume: 14 ml). Inlet water is continuously pumped to the column and control the flow rate of 28.00; 14.00 and 9.36 ml/h. The system is operated at 3 residence times 30, 60 and 90 min. Inlet and outlet water samples were taken hourly for NH₄⁺-N, NO₃⁻-N, NO₂⁻-N analyzing.

Analysis methods

The surface area of the husk ash is determined by the BET analysis in N₂ environment at 196°C using NOVA 1200 Quanta chrome-USA. Surface structure of husk ash and TiO₂ material/husk ash defined by the SEM method (Jeol 5410 LV, Japan). Purity of a TiO₂ material defined by X-ray diffraction method (XRD), Siemens D5005, Germany. Nano TiO₂ particle size determined by TEM, LIBRA120, Germany. The element compositions are analyzed by Energy dispersive analysis of X-rays (EDX), JEOL 6490JED 2300, 2300, Japan. Compounds of nitrogen: NH₄⁺-N, NO₃⁻-N, NO₂⁻-N are analyzed by spectral methods of molecular absorption, UV-VIS Optizen 2120 UV, England.

Results and discussion

The result of TiO₂ nano material preparation from husk ash

+ Preparation of bearing material rice husk

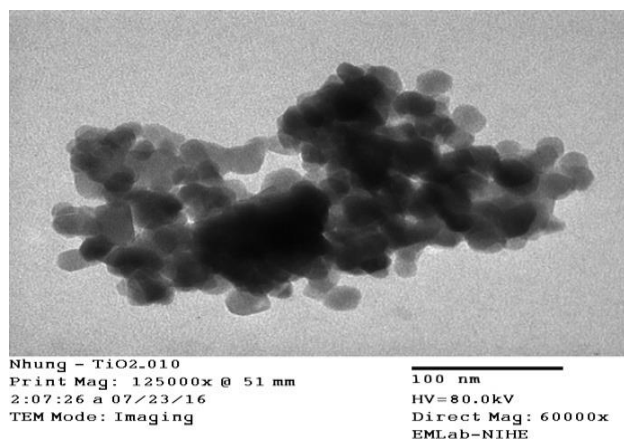


Fig5. TEM image of TiO₂ nano-material

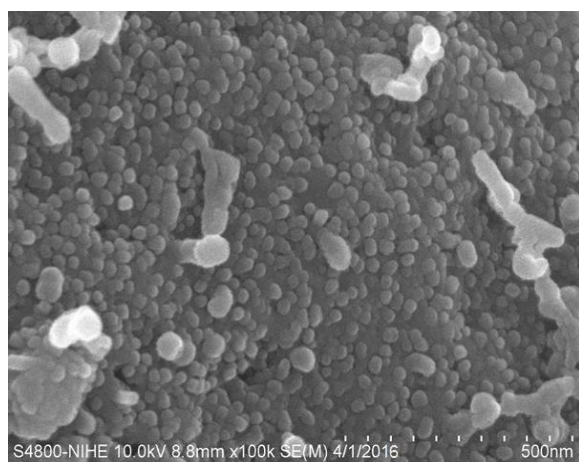


Fig 6. SEM image of TiO₂ nano material/husk ash with magnification 500 nm

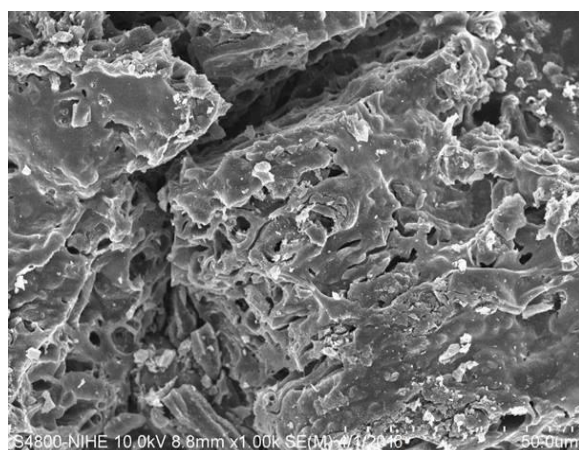


Fig 7. SEM image of TiO₂ nano-material/husk ash with magnification 50 μm (b)

XRD schema of TiO₂ nano-material/husk ash (Figure 8) shows the characterized peaks appeared at the 2θ position = 25.3 ° of TiO₂, and 22° of SiO₂ ensuring the presence of TiO₂ and SiO₂ particles on the surface of nano material/husk ash material. Mass and percentage

of elements found in TiO₂ nano-material/husk ash presented in Fig 9 shows that the material consists mainly of Si, accounting for 83.13%, also the O and C respectively make up 6.33 and 5.64%.

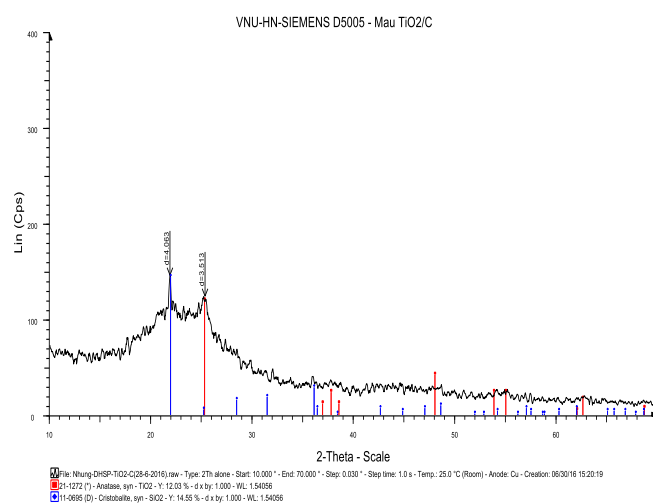


Fig 8. XRD schema of TiO₂ nano-material/husk ash

However, Ti only occupies a small amount (0.19% w/w). Also, a small amount of other elements like K, Cl and Ca were found to derive from husk ash.

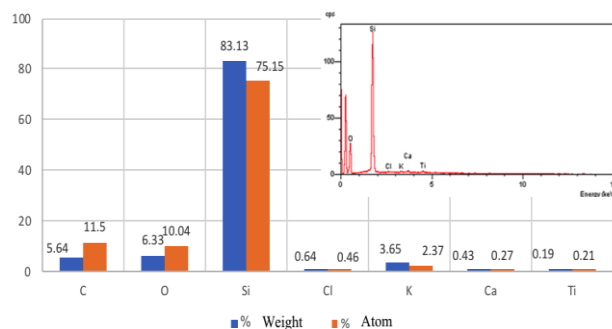


Fig 9. EDX schema of TiO₂ nano material/husk ash and percentage of the elements.

As can be seen in Fig 9, the TiO₂ nano material/husk ash has a high base line, above 20 cps. This showed that prepared materials have a low crystal structure. The reasons are a high percentage of Si and low percentage of O in material will form TiO₂ that is mainly in crystal structure. However, since Si and O elements exist mainly in atomic form, the crystal structure is not dominant. Therefore, base line is still high. This in accordance with the study of Hongliang Li et al. (2016).

Efficiency of nitrogen removal of prepared materials

Prepared TiO₂ nano material/husk ash had been used to remove some compounds of nitrogen in water (NH₄⁺, NO₃⁻ and NO₂⁻) under natural light condition

(sunlight) and darkness (no light) at different residence time.

+ The efficiency of ammonium removal in dark condition

The ammonium removal efficiency of TiO₂ nano material/husk ash in darkness for 24h processing, residence time 60 minutes (section 2.4) showed that ammonium concentration reduction within 14 hrs. from 23.927 initial to 9.979 mg/l corresponding to loading rate reduction of 7.8 g/m³.h. After 19 and 24h of operating, the ammonium concentration in the outlets gradually increased and reached 16.41 and 18.93 mg/l, respectively. At the same time, other nitrogen compounds like NO₃⁻ and NO₂⁻ have not been detected. It can be explained that in dark conditions, ammonium removal occurred only through the adsorption process and there was no reaction to convert ammonium to NO₃⁻, NO₂⁻. When the adsorption capacity of material reduced, the adsorption rate of NH₄⁺ on the surface of the TiO₂ nano material/husk ash was lower than the rate of desorption. Therefore, the concentration of the NH₄⁺ in the outlets gradually increased until it reached the equilibrium.

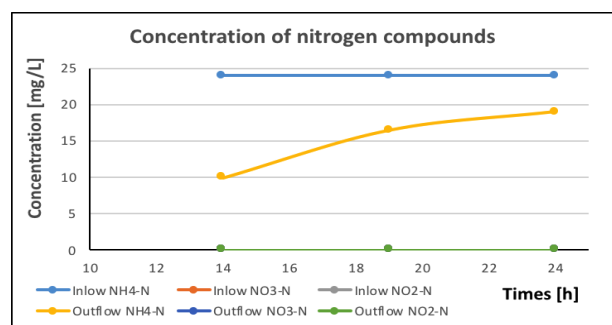


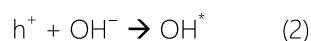
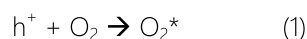
Fig10: Concentrations of the nitrogen compounds during the NH₄⁺ removal process using TiO₂ nano material/husk ask in dark conditions

Thus, in dark condition, TiO₂ nano material does not promote its photochemical properties because there is no radiation energy to form electrons and holes. Then both TiO₂ nano material and husk ash play the same role as the adsorbents to remove NH₄⁺ in water.

+ The efficiency of ammonium removal in natural light condition

Varying residence time of 30, 60 and 90 minutes, the low NH₄⁺ removal efficiency was found at 30 minutes. The NH₄⁺ concentration reduced from 24.19 mg/l (loading 27.09 g/m³.h) to 23.86 mg/l after 14 h. of operating. Similarly, in dark condition, other nitrogen compounds like NO₃⁻, NO₂⁻ have not been detected.

This is probably because of the short residence time, the high flow rate through column which then reduce the contact time and photocatalytic reactions. When increasing the residence time to 60 and 90 minutes, the efficiency of NH₄⁺ removal markedly increased after 14h of operating (the inlets 24.58 and 23.88 mg/l, respectively, dropped to 5.53 and 5.34 mg/l in the outlets). In addition, ion NO₃⁻ was detected in the outlets at low concentrations (0.184, 0.125 and 0.095 mg/l, respectively, after 14, 19 and 24h of operating). However, NO₂⁻ was only detected in the outlet with residence time of 90 minutes at the concentration range of 0.037 - 0.085 mg/l. These results were in accordance with theoretical basis under radiation/light conditions:



These products continuously oxidized NH₄⁺ in material surface to higher oxidation level compounds like NO₂⁻, NO₃⁻ and gas forms like N₂, NO, NO₂. As a result, the content of NH₄⁺ at the outlets kept significantly reducing. Also, on the material surfaces began to appear the bubbles because NH₄⁺ partly was converted to gases by the following reactions:

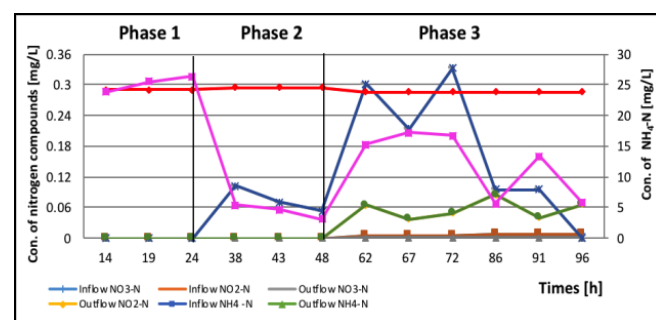
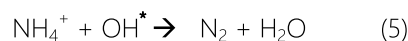
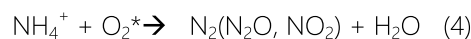


Fig 11. Concentrations of the nitrogen compounds during the NH₄⁺ removal process using TiO₂ nano material/husk ash in natural light conditions.

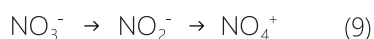
Based on the results of the NH₄⁺ removal process, the denatured TiO₂ nanoparticles obtained by this method have the ability to separate h⁺ very well under the effect of natural light (in natural light). only 4% of UV radiation. This can be explained by the fact that

when the material is denatured by nitrogen, the area of the forbidden zone ($E_g = 3.16$ V) is lower than the untreated TiO_2 ($E_g = 3.26$ V). By illuminating the visible light on the material, it is also possible to separate h^+ and electron from the material so that it can oxidize the reducing agent to a higher oxidation level. At the same time, undenatured TiO_2 nanoparticles were separated by h^+ and e^- when illuminated by ultraviolet light, which had greater energy than visible light.

Compared with other technologies in ammonium processing such as biotechnology, or membrane technology, the retention time of 60 minutes is relatively short, in addition it does not produce byproducts such as sludge and does not require separation. suspended solids, which reduces the cost of processing [13-15].

+ The efficiency of nitrite and nitrates removal in dark condition

After 14h of operating, NO_2^- -N concentration in inlet water of 18.748 mg/l was reduced to 16.313 mg/l. However, when the operating time lasts up to 19 and 24h, the concentration of NO_2^- -N in the outlets were increased 20.78 and 21.35 mg/l respectively, which was higher than the concentration in the inlets. Similar to ammonium removal, this was due to the adsorption process which was dominant in dark conditions. In addition, after 24h of operating, NH_4^+ and NO_3^- were found in the outlets of concentration of 3.522 and 7.126 mg/l, respectively, which were higher than that in the inlets. This can be explained as in dark conditions, with the presence of husk ash (carbon) material, TiO_2 and SiO_2 might act as a catalyst for the transformation of $NO_2^- \rightarrow NH_4^+$ and $NO_2^- \rightarrow NO_3^-$ (Fig12-13). These findings also indicate that ion NO_3^- was converted to lower oxidation level compounds as the following:



+ The efficiency of nitrite and nitrates removal in natural light condition

Under natural light condition at residence time of 30 minutes, similar to NH_4^+ removal process, the concentration of NO_2^- -N significantly reduced from 21.18 mg/L in inlet to 11.252 mg/l in the outlet after 14h. However, by operating time of 19 and 24h, the concentration of NO_2^- -N kept increasing and reaching 12.261 and 17.772 mg/l, respectively. At the same time, NO_3^- -N concentration also ascended in the outlets reaching 0.688 mg/l after 24h, which was higher than the inlets (0.419 mg/l).

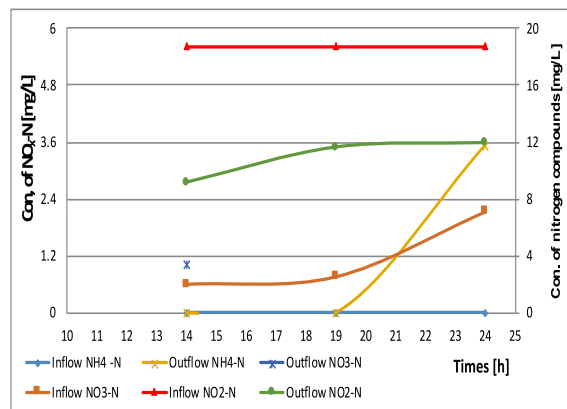


Fig 12. Concentrations of the nitrogen compounds during the NO_3^- and NO_2^- removal process using TiO_2 nano material/husk ash in dark condition

In phase 2 with residence time of 60 minutes, after 14h, the concentration of NO_2^- -N remarkably dropped from 20.25 to 2.76 – 0.99 mg/l. At the same time, NO_3^- appeared in the outlets at lower concentrations and less bubbles in comparison to phase 1.

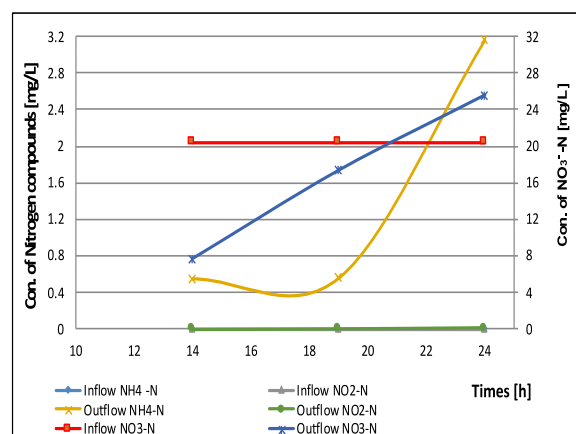
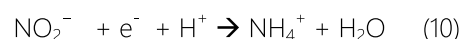


Fig 13. Concentrations of the nitrogen compounds during the NO_3^- and NO_2^- removal process using TiO_2 nano material/husk ash in dark condition

In phase 3, after 90 minutes, the NO_2^- removal efficiency reached 100%. However, when continuing the operation, the efficiency found the descending (Figure 14-15). As the results, NH_4^+ , NO_3^- were found in both the inlets and the outlets with higher concentration in outlets. This showed that the photochemical process was strong. It occurred and reduced NO_2^- to NH_4^+ as the following reaction equation:



For NO_3^- the removal process occurred similar to NH_4^+ and NO_2^- in 3 phases. In the light condition, removal

efficiency depended on the residence time in which the highest efficiency was found in 60 minutes.

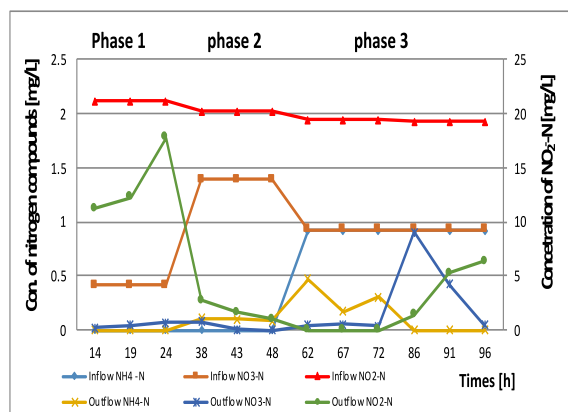


Fig14. Concentration of nitrogen compounds in water the inlets and the outlets during the NO_2^- removal on the process (3 phases) using TiO_2 nano material/husk ash under natural light

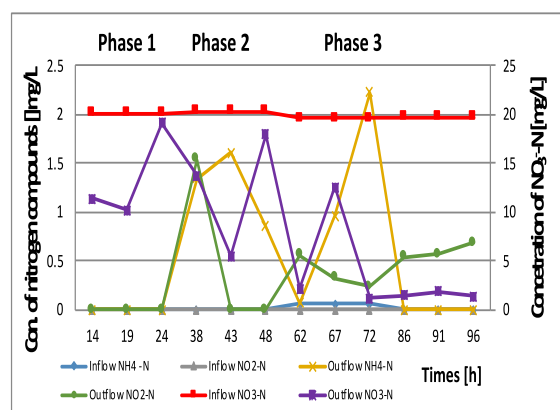


Fig15. Concentration of nitrogen compounds in water the inlets and the outlets during the NO_3^- on the process (3 phases) using TiO_2 nano material/husk ash under natural light

During the operation, there were times when the concentrations of NO_3^- -N in the outlets were increased because the adsorption was dominant under darkness light. During daytime with sun light, the photochemical reaction had advantage that NO_3^- removal process took place better. This mechanism also occurred when using TiO_2 nano material to decompose other pollutants such as persistent organics and dyes [12,13].

The results show that TiO_2 denatured nanoparticles prepared by this method can be separated even under conditions exposed to natural light, and the removal efficiency of nitrite and nitrite compounds is quite high, whereas TiO_2 nanoparticles are not modified to perform photochemical reactions in ultraviolet light conditions. In addition to other methods of treatment

such as biological methods, wetland technology, the retention time of this reaction is much shorter, the treatment is thorough and the material is used for a long time. Create secondary pollution products, no need to separate and recover materials after treatment, continuous operation, bringing economic efficiency for processing [14,15].

Conclusion

TiO_2 nano materials were successfully prepared by the sol-gel hydrothermal method. Materials had relative uniformity nano particle size, about 20-25 nm and anatase crystalline properties. The specific surface area of the prepared material was $109.7 \text{ m}^2/\text{g}$. The material had good capacity in adsorption and catalysis for photochemical to convert and remove nitrogen compounds like NH_4^+ , NO_2^- and NO_3^- in natural light condition. This indicates that the prepared materials had ability of separating e^- better than h^+ . However, the NO_2^- removal efficiency was the highest, followed by NO_3^- and NH_4^+ . Removal mechanism of NH_4^+ , NO_2^- and NO_3^- mainly based on the photochemical reduction and oxidation to form N_2 , which is the final product. In natural light conditions with the residence time of 60 minutes, the concentrations of NH_4^+ , NO_3^- and NO_2^- decreased in the outlets. The removal efficiency ranged from 77 to 97%.

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