STUDY ON 2-DIAZO-4,6-DINITROPHENOL IN WASTE WATER USING UV-H_2O_2/TiO_2

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Abstract: *This article focuses on researching the possibility of applying Nano TiO_2 photocatalyst in an advanced UV-H_2O_2 oxidation process to decompose 2-Diazo-4,6-dinitrophenol (DDNP) in wastewater of propellant and explosives production facilities. Effects of reaction time (0-120 minutes), pH, UV light, molar ratio of H_2O_2/TiO_2, reaction temperature and initial DDNP concentration on DDNP treatment efficiency were evaluated. The results showed that at C^o_{DDNP} = 370.9 mg/L, the molar ratio of H_2O_2/TiO_2 = 20, pH = 3, λ = 185 nm, 99.41% of DDNP was treated after 120 minutes of reaction. Temperature does not significantly affect DDNP processing speed and efficiency.*

Keywords: DDNP; UV- H_2O_2; Nano TiO_2.

1. INTRODUCTION

2-Diazo-4,6-dinitrophenol (DDNP) has a molecular formula $C_6H_2N_4O_5$; Molecular weight: 210.104 g/mole, with nitro (-NO_2) and diazo (-N=N) groups connect to benzene ring. DDNP exists in the form of yellow crystals but the technical product's color can range from dark yellow, green to dark brown, its density is 1.63 g/cm^3. DDNP is a poison, causes eye, skin or respiratory irritation, leading to headaches, dizziness, nausea, vomiting, diarrhea, and decreased vision. Long-term exposure to nitro compounds of aromatic hydrocarbons causes damage to the liver, kidneys, toxic hepatitis and kidney fat degradation [1].

Every year, explosive manufacturers produce a large amount of waste water contains DDNP. This type of waste usually contains elements that are highly toxic to the environment and difficult to decompose. Therefore, the detoxification technology for water sources contaminated with these compounds is an issue of interest to study. In order to treat DDNP in waste water, there are many research and application works. Methods have been studied and applied are advanced oxidation methods (fenton, UV fenton), electrochemical methods; ozonation method; method of using plants [2,3,4]. However, most of these technologies when applied are inconvenient and do not have high efficiency due to unstable operation or high processing costs. In order to treat DDNP in waste water, the technique of using photocatalyst oxidation process is widely applicable and highly effective, low cost and easy to implement [6].

The use of Nano TiO_2 a catalyst in advanced oxidation processes to treat DDNP is one of the interested research directions. Moreover, TiO_2 is a typical, non-toxic, non-polluting nano material, chemically stable and reusable, less affected by other inorganic salts. Especially, it opened a new prospect in the catalytic photochemical processes by taking advantage of the available infinite radiation source from the sun using UV-A radiation [4,5,7,8]. Photocatalytic oxidation is a newly developed technology. UV radiation is used as an energy source to stimulate the creation of photon-optical holes pairs. These two agents are very flexible, they can combine with H_2O and O_2 in the atmosphere to produce $^{\bullet}OH$ and $O_2^{\bullet}$ free radicals. These free radicals react with other organic substances (RH) to form highly reactive organic bases, these products continue to participate in secondary reactions. The result is forming of CO_2, H_2O, N_2 molecules and NO_3^- radical [7,8,9]. Therefore, this method produces strong oxidants, which is promising for the treatment of persistent pollutants.

This study introduces the research results on the effects of factors such as H_2O_2/TiO_2 molar ratio, pH, temperature, wavelength of UV light, initial concentration of DDNP to the efficiency of treatment in waste water.

2. BACKGROUND

2.1. Experimental preparation

2.1.1. Equipment

- Analytical balance PA214, Ohaus (USA), accuracy of ± 0,0002 g.
- PH meter HI 2211, Hanna Instrument (USA).
- Heating Magnetic Stirrer 03403-15, Cole-Parmer Instrument Company (USA).
- Quartz tubes, UV lamps, aerator.
- High performance liquid chromatography system (HPLC) HP Model 1100, using chain detector (DAD) manufactured by Agilent (USA), placed at the Environmental Technology Department, Institute for New Technology, Academy of Military Science and Technology.

2.1.2. Chemicals

- 2-diazo-4,6-trinitrophenol (DDNP) in crystal form with analytical purity (Merck - Germany).
- H_2O_2 with analytical purity, concentration of 30% (Merck - Germany).
- High purity Nano TiO_2 (Japan).
- Solvents: Acetonitrile, ethanol, methanol, n-hexane have high purity for HPLC analysis (Merck - Germany).

2.1.3 Experimental models

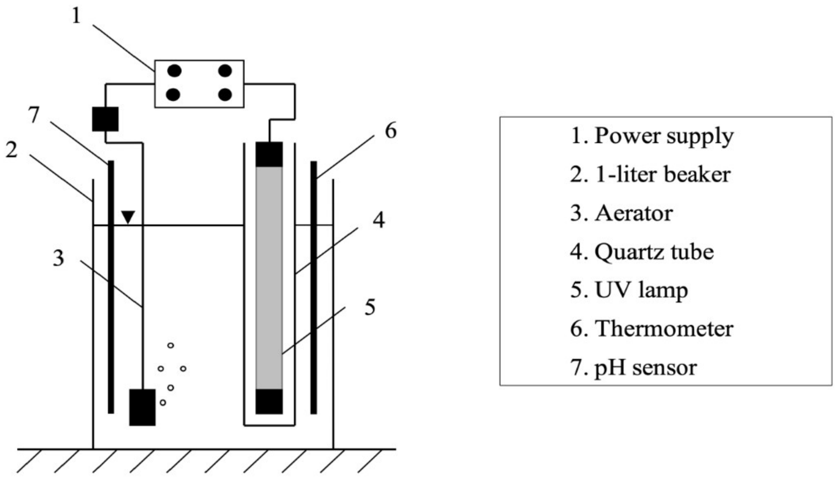

Figure 1. *Experimental device model of DDNP/UV-H_2O_2/TiO_2 system.*

The advanced oxidation reactions were conducted in the batch test model, shown in Figure 1. Reaction system consists of a glass bottle (2) with a capacity of 1 liter, it can control temperature and monitor pH changes during reaction. The reaction solution container (2) is left open to saturate oxygen in the air. 15W UV lamps with wavelengths 185, 254 and 313 nm were protected by quartz tube and placed inside the reaction system. The experimental system was aerated by aerator (3) to enhance the oxidation processes.

2.2. Sample preparation method

Experiments to study the effect of H_2O_2/TiO_2 ratio on the decomposition of DDNP in UV-H_2O_2/TiO_2 systems were conducted at the same conditions C^o_{DDNP} = 370.9 mg/L, pH= 3, C_{TiO2} = 8.75x10^{-4}M, λ = 185 nm, change the ratio of H_2O_2/TiO_2 by 5; 10; 15; 20.

Experiments to study the effect of pH on the decomposition of DDNP in UV-H_2O_2/TiO_2 systems were conducted under the same conditions C^o_{DDNP} = 370.9 mg/L, C_{TiO2} = 8.75x10^{-4}M, λ = 185 nm, H_2O_2/ TiO_2 ratio = 20, change pH by 3; 7; 9.

Experiments to study the effect of wavelength on the decomposition of DDNP in UV-H_2O_2/TiO_2 systems were conducted at the same conditions C^o_{DDNP} = 370.9 mg/L, pH = 3, C_{TiO2} = 8.75x10^{-4}M, H_2O_2/TiO_2 ratio = 20, changing wavelength by 185; 254; 313 nm.

Experiments to study the effect of temperature on the decomposition of DDNP in UV-H_2O_2/ TiO_2 systems were conducted at the same conditions C^o_{DDNP} = 370.9 mg/L, pH = 3, C_{TiO2}= 8.75x10^{-4}M, λ = 185 nm, H_2O_2/TiO_2 ratio = 20, changes the temperature by 30^{o}C, 40^{o}C and 50^{o}C.

Experiments to study the effect of the initial concentration on the decomposition of DDNP in UV-H_2O_2/TiO_2 systems were conducted at the same condition pH = 3, λ= 185 nm, C_{TiO2} = 8.75x10^{-4} M, H_2O_2/ TiO_2 ratio = 20, changing DDNP concentration with values of 222.5 mg/L; 370.9 mg/L; 450.8 mg/L; 550.5 mg/L; 722 mg/L.

2.3. Research methods

Determining the concentration of DDNP in the experiment using UV-Vis measurement method. The formulas for calculating the efficiency and reaction speed are as follows [1,5]:

$$H\% = \frac{C_0 - C_t}{C_0} x\ 100\ (\%);$$

In which: H is the processing efficiency, C_o and C_t are the concentration of DDNP at the initial time and reaction time t, mg/L.

3. RESULTS AND DISCUSSION

3.1. The effect of H_2O_2/TiO_2 ratio on DDNP decomposition efficiency

Research results of the effect of H_2O_2/TiO_2 ratio on DDNP decomposition efficiency are presented in Figure 2. The results in Figure 2 show that when the TiO_2 concentration is fixed, increasing H_2O_2 concentration from 4.375x10^{-3}M to 17.5x10^{-3}M (C_{H2O2}/C_{TiO2} ratio = 20), the efficiency of DDNP decomposition process also increases. When increasing the concentration of H_2O_2 to $21.875x10^{-3}M$ (the ratio of C_{H2O2}/C_{TiO2} = 25), the treatment efficiency of DDNP changed insignificantly compared with the concentration of H_2O_2 = $17.5x10^{-3}M$ (C_{H2O2}/C_{TiO2} = 20).

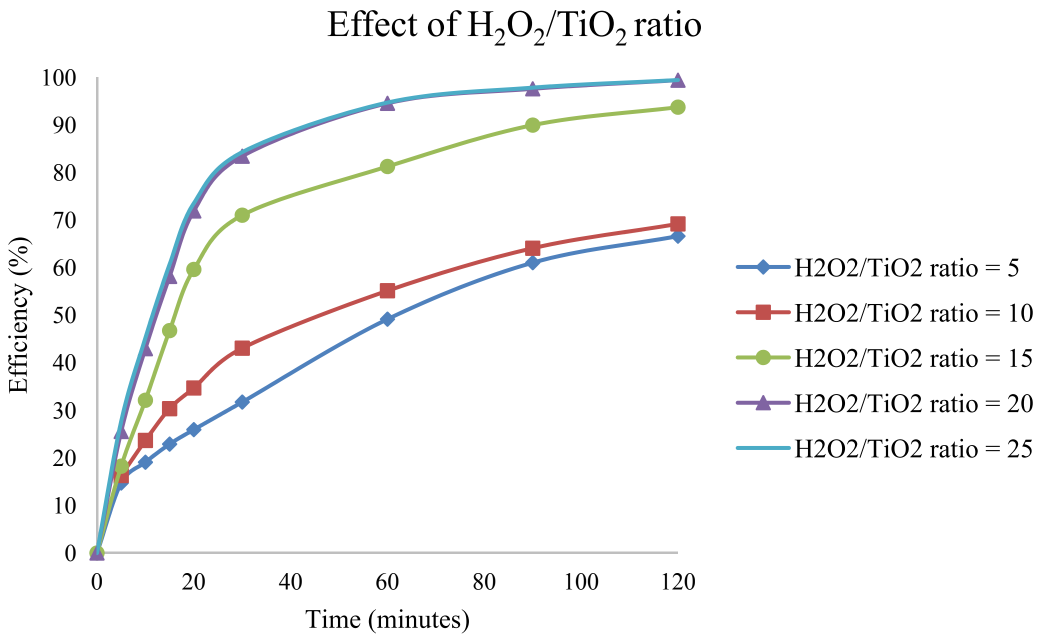

Figure 2. *Effect of H_2O_2/TiO_2 ratio on DDNP decomposition efficiency in UV-H_2O_2/TiO_2 system.*

From the above results, with the ratio of C_{H2O2}/C_{TiO2} = 20 and 25, the efficiency and decomposition rate of DDNP after 60 minutes of reaction are the same and both higher among the others.

The mechanism of DDNP reaction rate raises as H_2O_2 concentration increases can be explained as follows: When increasing the H_2O_2 (C_{H2O2}/C_{TiO2} ratio increases), the number of free $^{\bullet}OH$ radicals are formed more. On the other hand, TiO_2 under the effect of UV light also produces a significant amount of $^{\bullet}OH$, contributing to improve the reaction efficiency. However, when the concentration of H_2O_2 is too high, the amount of residual H_2O_2 reacts with $^{\bullet}OH$ radicals reduces the reaction agents:

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O$$

$$HO_2^{\bullet} + {}^{\bullet}OH \rightarrow H_2O + O_2$$

The nature of the photocatalytic process is indirect photochemical process, TiO_2 catalyst receives UV radiation energy forming photogenic electrons and bio-optical holes. These two agents are very flexible, they can participate with water and air oxygen to produce hydroxyl free radicals $^{\bullet}OH$ and $O_2^{\bullet}$:

$$TiO_2 \rightarrow e^- + h^+$$

$$h^+ + H_2O \rightarrow {}^{\bullet}OH + H^+$$

$$h^+ + OH^- \rightarrow {}^{\bullet}OH + H^+$$

H_2O_2 is also affected by photochemical process of UV radiation, producing $^{\bullet}OH$ radicals:

$$H_2O_2 \rightarrow 2^{\bullet}OH$$

These free radicals react with other organic substances (RH) to form highly reactive organic bases, these products continue to participate in secondary reactions. The result is forming of CO_2, H_2O, N_2 molecules and NO_3^- radical [5].

From the results obtained, we see that at the ratio of C_{H2O2}/C_{TiO2} = 20 and 25, the decomposition efficiency of DDNP is almost equivalent. If the ratio of C_{H2O2}/C_{TiO2} = 25 is applied, even though the reaction efficiency is slightly higher in the early stages, the amount of H_2O_2 residual in the solution might reduce the reaction agents. Therefore, we choose the molar ratio of H_2O_2/TiO_2 = 20 to be optimal for next experiments.

3.2. The effect of pH on DDNP decomposition efficiency

Research results of the effect of pH on DDNP decomposition efficiency are shown in Figure 3.

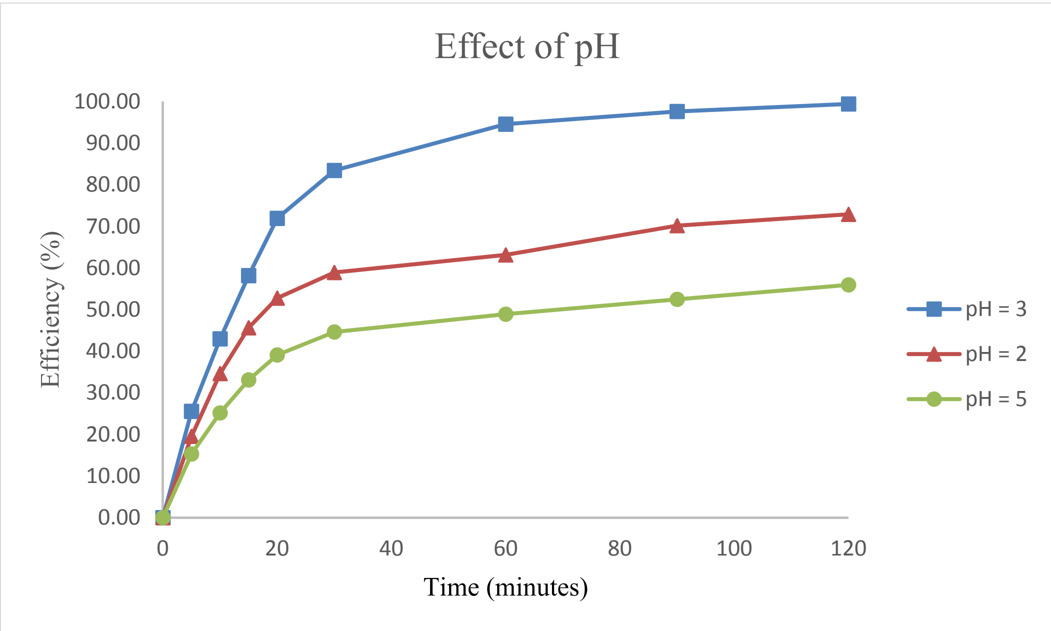

Figure 3. *Effect of pH on DDNP decomposition efficiency in UV-H_2O_2/TiO_2 system.*

The results show that at the condition of pH = 3, the decomposition rate of DDNP is fast and the processing efficiency reaches 99.41% at 120 minutes with DDNP concentration = 370.9 mg/L. With pH = 2 and pH = 5, the reaction speed is slower, the reaction efficiency is 72.89% and 55.94% after 120 minutes, respectively.

The increase of DDNP metabolism in acidic environment (pH = 3) can be explained as follows: O_2 in water receive electrons from TiO_2 surface to form $O_2^{\bullet-}$, $O_2^{\bullet-}$ continue to reacts with one proton H^+ and one electron creating H_2O_2. Then

H_2O_2 reduces one electron to produce free $OH^•$ radical. These free $^•OH$ radicals react with DDNP molecules to form highly reactive organic bases, these bases continue to participate in secondary reactions to form CO_2, H_2O, N_2 molecules and NO_3^- radical. At pH below 2, hydroxyl free radicals can be consumed by H^+ ions themselves:

$$H_2O_2 + H^+ \rightarrow H_3O_2^+$$

$$OH^· + H^+ + e^- \rightarrow H_2O$$

At pH above 4, hydrogen peroxide is degraded quite quickly and this is the main reason for reducing the efficiency of the decomposition process.

3.3. The effect of temperature on DDNP decomposition efficiency

Research results of the effect of temperature on DDNP decomposition efficiency are shown in Figure 4.

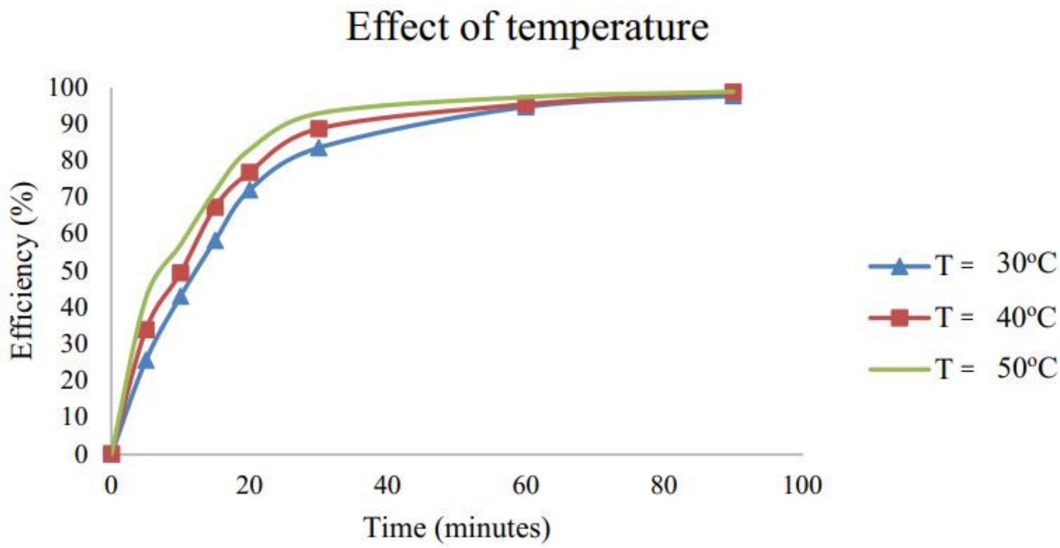

Figure 4. *Effect of temperature on DDNP decomposition efficiency in UV-H_2O_2/TiO_2 system.*

Although the thermal energy is not sufficient to activate TiO_2 surface, most studies suggest that the increase in temperature promotes the recombination and adsorption of organic compounds to the surface of TiO_2. Because of that, when the temperature increases, the decomposition process of DDNP is also more effective. Figure 4 shows that the decomposition efficiency of DDNP is maximum at the temperature of 50°C, when the temperature drops to 40°C and 30°C, the DDNP decomposition speed and efficiency decrease. However, the increase of temperature does not significantly affect DDNP decomposition efficiency.

3.4. The effect of UV wavelength on DDNP decomposition efficiency

Research results of the effect of UV wavelength on DDNP decomposition efficiency are presented in Figure 5. After 120 minutes, the decomposition efficiency of DDNP at λ = 185 nm, 254 nm and 313 nm was 99.41%, 48.95% and 47.35% respectively. From this result, we can conclude that the system reached its highest efficiency at wavelength λ = 185 nm. It can be explained that the shorter wavelengths produced more $^{\bullet}OH$ radicals, therefore increases the efficiency of the decomposition process.

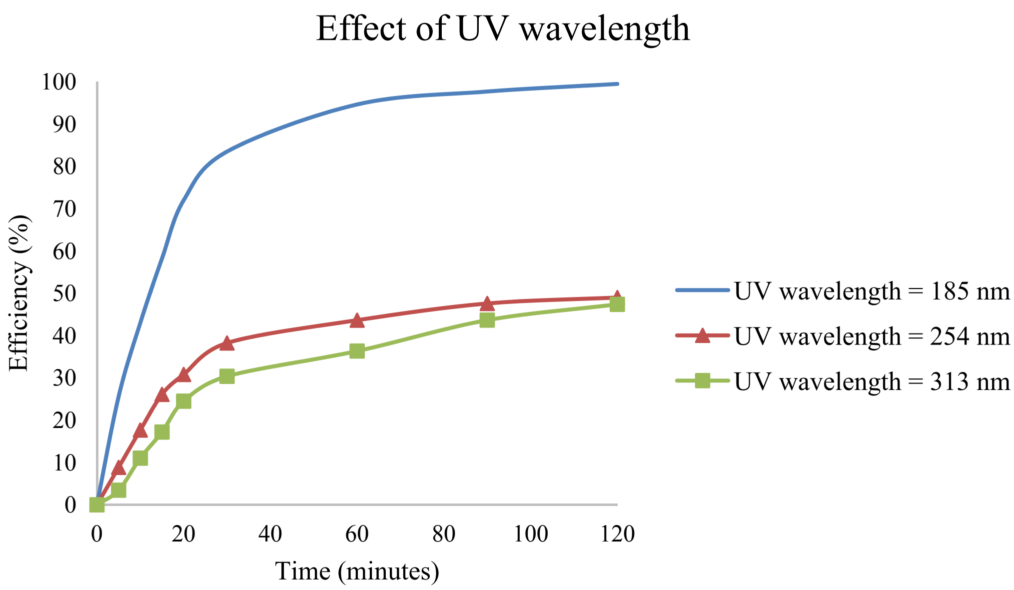

Figure 5. *Effect of UV wavelength on DDNP decomposition efficiency in UV-H_2O_2/TiO_2 system.*

3.5. The effect of initial DDNP concentration

Research results of the effect of initial DDNP concentration on DDNP decomposition efficiency are shown in Figure 6.

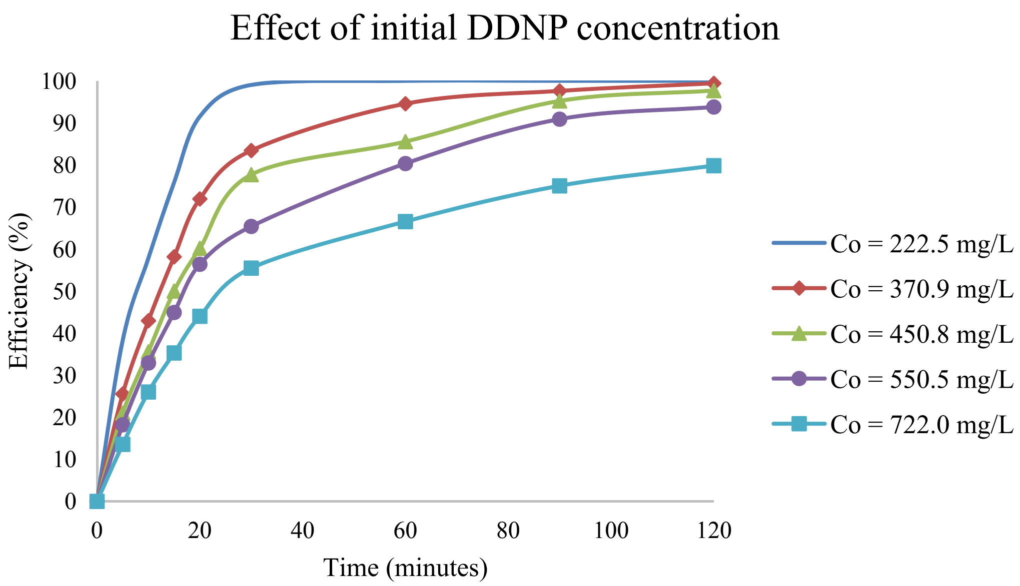

Figure 6. *Effect of initial DDNP concentration on DDNP decomposition efficiency in UV-H_2O_2/TiO_2 system.*

Figure 6 shows that at an initial concentration of 222.5 mg/L, DDNP decomposes the most quickly and takes the least time. When the initial concentration increased, the efficiency and decomposition rate decreased. At C^{o}_{DDNP} = 722 mg/L, in the first 30 minutes, DDNP decomposition efficiency was 55.47%, while 99.02% DDNP was decomposed (nearly doubled) with an initial concentration of 222.5 mg/L.

With the fixed ratio of H_2O_2/TiO_2, pH, wavelength and temperature, DDNP decomposition efficiency also depends on the initial concentration of DDNP in the waste water.

4. CONCLUSION

The effects of initial DDNP concentration, pH, H_2O_2/TiO_2 ratio, UV light wavelength and temperature showed that the DDNP decomposition efficiency in UV-H_2O_2/Nano TiO_2 system at concentration C^{o}_{DDNP} = 370.9 mg/L reaches 99.41% with optimal condition of pH = 3, ratio of H_2O_2/TiO_2 = 20, UV wavelength λ= 185 nm. Temperature does not have a considerable effect on performance and decomposition rate of DDNP in waste water.

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TÓM TẮT

NGHIÊN CỨU XỬ LÝ 2-DIAZO-4,6-DINITROPHENOL (DDNP) TRONG NƯỚC BẰNG HỆ UV-H_2O_2/Nano TiO_2

Nghiên cứu này tập trung vào việc khảo sát khả năng ứng dụng chất xúc tác quang Nano TiO_2 vào quá trình oxy hóa nâng cao UV- H_2O_2 để xử lý 2-Diazo-4,6-dinitrophenol (DDNP) trong nước thải của các cơ sở sản xuất thuốc phóng, thuốc gợi nổ quốc phòng. Các ảnh hưởng bởi thời gian phản ứng (0-120 phút), pH, bước sóng đèn UV, tỉ lệ mol H_2O_2/TiO_2, nhiệt độ, nồng độ chất ban đầu đến hiệu suất xử lý DDNP được đánh giá. Kết quả nghiên cứu cho thấy tại điều kiện C^o_{DDNP} = 370.9 mg/L, tỉ lệ mol H_2O_2/TiO_2 = 20, pH = 3, λ = 185 nm, 99.41% DDNP bị xử lý sau thời gian phản ứng 120 phút. Nhiệt độ không làm ảnh hưởng tới hiệu suất xử lý DDNP.

Từ khóa: DDNP; UV- H_2O_2; Nano TiO_2.

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