Studies on Nitrate Reduction by Zinc-doped Titanium Dioxide Photocatalyst

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***Abstract*—The research aimed to prepare Zinc-doped TiO2 photocatalyst by impregnation to reduce nitrate ion by UVC irradiation. The effects of Zn loading, ethanol concentration and hydrogen peroxide addition were examined. During the reaction test, the nitrate concentration was determined by UV-vis spectrophotometry. Then, the conversion was analyzed to evaluate nitrate reduction for the catalyst performance. The catalyst characterization was measured for the surface area and particle size by BET and Laser particle size methods, respectively. Among various results, it was found that 12%wt. Zn-doped TiO2 photocatalyst with 0.06 M ethanol gave 31.62% for nitrate reduction. It had the surface area of 10.62 m2/g and the particle size about 7.62 microns. It was speculated that ethanol became the hole-scavenger reagent to increase the nitrate reduction while H2O2 enhanced the efficiency of photolysis. Therefore, it can be concluded that Zn-doped TiO2 photocatalyst can reduce nitrate ion. The chemical kinetic of this result will be studied further.**

***Keywords*— nitrate reduction, photocatalysis, wastewater Treatment**

I. INTRODUCTION

Nitrate is one of the important nutrients (NPK) from fertilizer for vegetation and agriculture in the farms. It is also available from nature in nitrogen cycle and in the animal waste [1], [2]. The excess amount of nitrate in agriculture can permeate to underground water and leach to public water resource. Then it caused water pollution as eutrophication and damage animals [3] including human threat on drinking water [4]. Then, the EU regulation for nitrate content in groundwater was limited at 50mg/L [5], and WHO had specified nitrate content at 50mg/L [6], [7]. In Thailand, Pollution control department had regulated the nitrate content at 4 mg/L for the bottled drinking water [8]. The allowed nitrate content is the important parameter for water quality control. Then, the method to reduce nitrate is the challenging issue.

One method to reduce nitrate is the application of photocatalysis. The well-known photocatalyst is TiO2 with various transition metals doping for water pollution control [9], [10]. The previous report on Ag/TiO2 photocatalyst for phenol photoconversion, it reduced phenol to 53.7% by H2O2 + 5% Ag/TiO2 photocatalyst [11]. The presence of Ag increased particle agglomeration and increased active sites for phenol adsorption. Zn/TiO2 clay photocatalyst could degrade methyl green in aqueous solution. And the various parameters played role on the catalyst activity such as pH, catalyst dosage, and the presence of oxidant [12]. In case of indigo carmine photodegradation [13], it was examined by Zn/TiO2 photocatalyst with Ti: Zn ratio of 5:1 had 12.3% conversion. And it was found that sunlight with unmodified TiO2 showed 87% conversion. Gold/Gold ion doping on TiO2 photocatalyst could photodegrade methylene blue with the visible light irradiation [14]. The presence of gold decreased energy band gap below 3.2 eV.

As mentioned above nitrate ion was the selected ion and the proper condition to find out for Zn/TiO2 photocatalyst became the crucial parameter for the optimum performance. The research aimed to prepare Zn-doped TiO2 photocatalyst by impregnation and to test its performance with nitrate ion. The effects of Zn/Ti ratio and the type of irradiation were also examined with the addition of ethanol and H2O2. It was postulated that ethanol had some function similar to that of H2O2 on photocatalysis. The results will show the optimum condition to reduce nitrate in the aqueous solution and it will be the solution to control water pollution.

II. EXPERIMENTAL PROCEDURE

The research consisted of 3 main sections. There were catalyst preparation, catalyst characterization and catalyst testing. The chemicals for catalyst preparation were TiO2 supplied by Carlo Erba and ZnCl2 by Fisher Scientific Co.Ltd. While ethanol and hydrogen peroxide (H2O2) were provided by Carlo Erba. The nitrate ion from NaNO3 solution was derived from Rankem Co.Ltd. P25 was the commercial TiO2 produced by Aeroxide-Evonik Pte.Ltd.

The catalys preparation involved ZnCl2 solution and the impregnation on 5 g of TiO2 powder. The weight percent of Zn was varied 12%, 6.38% and 1.0%, respectively. After impregnation, the conditon for drying occurred at 120oC 2 hr and calcination at 400oC 6 hr.
The catalyst testing was conducted in the photoreactor with UVC irradiation was produced from 15W*3 bulbs [15]. Using 100 ppm of nitrate solution, the solution from the beaker was transferrred to determine the absorbace by UV-vis spectrometer with λ 203 nm. Then, the nitrate conversion was calculated by Eq.1. And the list of experiment also tabulated in Table 1.

$$\%\ \text{nitrate reduction} = \frac{C_0 - C_1}{C_0} \times 100 \qquad \text{Eq.1}$$

Co and Ct represented the initial concentration and instantaneous concentration, respectively.

Table I List of the experiments

Item	Light	Condition	Symbol
1		UVC	-
2		EtOH+UVC	EtOH
3		H2O2+UVC	H2O2
4		TiO2+EtOH+UVC	TiO2+EtOH
5		P25+EtOH+UVC	P25+EtOH
6	UVC	Zn/TiO2+UVC	Zn/TiO2
7		Zn/TiO2+EtOH+UVC	Zn/TiO2+EtOH
8		Zn/TiO2+H2O2+UVC	Zn/TiO2+H2O2
9		Zn/TiO2+EtOH+H2O2+UVC	Zn/TiO2+EtOH+H2O2
10	Dark	Zn/TiO2+EtOH+Dark	Zn/TiO2+EtOH

Note EtOH represented ethanol.

The catalyst characterization comprised of surface area (BET) and the laser particle sizer. The BET measurement by nitrogen adsorption, it was conducted byAutosorb1MP from Quanta chrome Co.Ltd. While, Laser particle sizer was carried out from Mastersizer S from Malvern Co.Ltd. The results of BET and Particle size, they possibly clarified the photocatalyst performance in the research.

III. RESULT AND DISCUSSION

The results of this research divided into 3 sections. There were the nitrate calibration, the catalyst characterization, and the catalyst testing, consecutively.

III.I CALIBRATION OF NITRATE SOLUTION

The nitrate concentration range was 0.25 to 3.0 mg/L at 203 mn as shown in Fig 1.The graph showed the linearity between the concentration and the absorbance so it was valid to use further procedure.

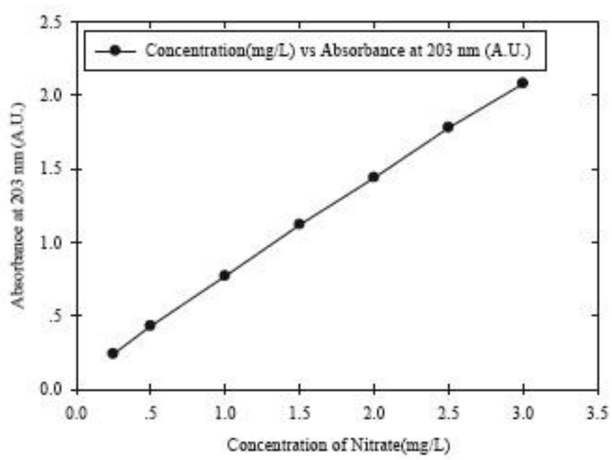

Fig. 1 Calibration of nitrate solution

III.II CATALYST CHARACTERIZATION

The catalyst characterization was shown in Table 2. Surface area was decreased from 14.64 m2/g to 10.62 m2/g as the %wt Zn increased conversely. While D [4,3] as the particle size, it increased as %wt Zn increased. This was due to Zn oxide, 6.38%Zn/TiO2 photocatalyst, on the TiO2 surface increased more agglomeration so the bigger particles formed. On the other hand, 12% Zn/TiO2 photocatalyst, it redispersed the particle by repulsive force and it obtained smaller particles. Compared to P-25, it was found that the prepared catalyst had less surface area of 4.3 times and much bigger particle size of 14.2 times. The presence of Zn changed surface area and particle size compared to undoped Zn/TiO2 catalyst. It possibly changed the catalytic performance on nitrate reduction in the next section.

Table II Determination of surface areas and particle size

catalyst	Surface area , m2/g	D[4,3], micron
P-25	63.02	51.7
TiO2	14.64	3.63
6.38% Zn/TiO2	12.75	17.23
12% Zn/TiO2	10.62	7.62

III.III CATALYST TESTING

Testing of nitrate reduction, it had the constant condition with 100 mg/L of 500 mL nitrate solution and 120 min for reaction time. Fig. 2, it was found that the presence of 12% wt Zn increased the nitrate reduction to 31.62% compared to 25.76 % for that without Zn. But at the catalyst with 6.38 % wt Zn, it decreased nitrate reduction to 23.62%. From Table 2, it indicated that 6.38% Zn/TiO2 had the larger particle size than the other. Its particle blocked the UVC light to reduce nitrate. Whereas the surface area of the catalyst, it showed slight difference. The presence of Zn on TiO2 for nitrate reduction followed the similar results of Mo/TiO2 for phenol photodegradation [16] and Cr/TiO2 photodegradation for acetonitrile [17].

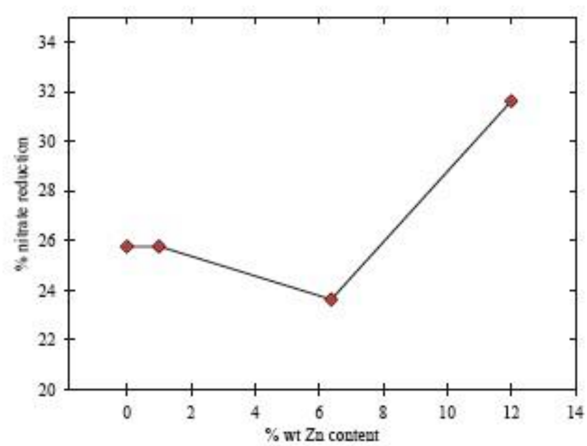

Fig. 2 The effect of % wt Zn on nitrate reduction
Reaction condition: 0.06M EtOH, 0.25 g catalyst, 120 min.

The EtOH concentration was varied from 0 to 0.10 molar as shown in Fig. 3, it was found that the nitrate reduction increased from 24.65% to 31.62% directly with EtOH increased from 0 to 0.06 M. But more than 0.06 to 0.1M of EtOH, it decreased the nitrate reduction to 25.10%, and then the optimum point of EtOH was 0.06 M. The EtOH interacted on the catalyst surface as in the reaction Eq. 2. The excessive ethoxide from ethanol and

H+ ions, they both suppressed nitrate reduction with UVC photodegradation.

$$C_2H_5OH \xrightarrow{\text{dissociation}} C_2H_5O^- + H^+ \quad \text{Eq.2}$$

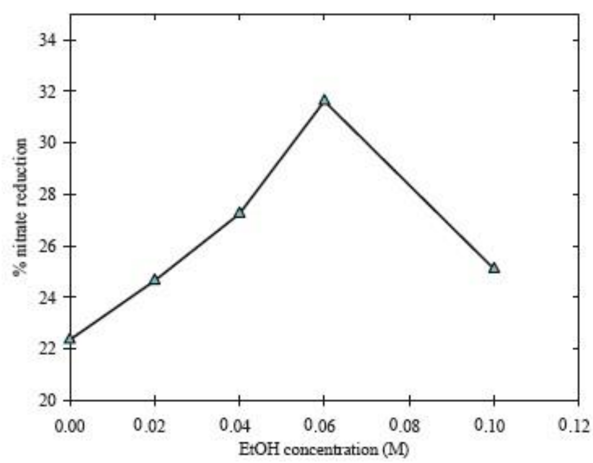

Fig. 3 The effect of ethanol on nitrate reduction
Reaction condition: 12%wt Zn/TiO2 0.25 g, 120 min

In Fig. 4, it showed that effect of H2O2 on nitrate reduction. With 1 mM H2O2, it had 31.08% nitrate reduction which was higher than that without H2O2 of 8.73%. But at 5 mM H2O2, it had 28.6% nitrate redcution. So 1 mM H2O2, it exhibited that highest nitrate reduction. The excessive H2O2, it reacted hydroxyl free radical (OH*) to hydrogen peroxide radical (HO2*) as in Eq. 3.

$$H_2O_2 + OH^* \longrightarrow H_2O + HO_2^* \quad \text{Eq.3}$$

So the reactive hydroxyl free radical decreased and it decreased nitrate reduction as well. The optimum amount of H_2O_2 on TiO_2 photocatalyst was the important factor to find as in previous researchs of Lutterbek [18] and Zurro [19]. Both EtOH and H_2O_2 are the important factors to combine and to increase the nitrate reduction. Therefore, more experiments will clarify the doubtful pointw.

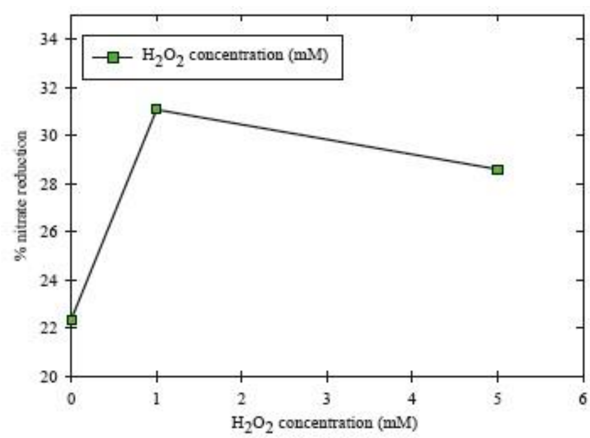

Fig. 4 The effect of H2O2 on nitrate reduction
Reaction condition: 12%wt Zn/TiO2 0.25 g, 0.06 M EtOH

From Fig 2-4, the best condition required 12 %wt Zn/TiO2 photocatalyst with 0.06M EtOH and 1 mM H2O2. The unclear points to examine are the effect of UVC, and the combination effect of EtOH+UVC including Zn/TiO2 + UVC during photodegradation for nitrate.

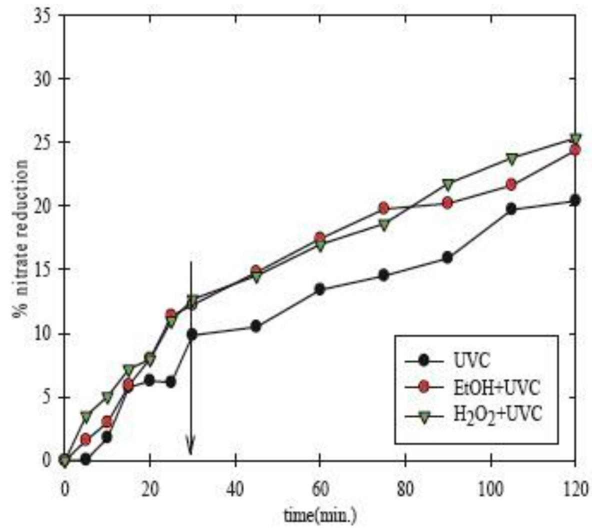

Fig. 5 Effect of UVC on nitrate reduction
Reaction condition: 1 mM H2O2, 0.06M EtOH

From Fig. 5, it compared 3 experiments as UVC, EtOH+UVC and H2O2 + UVC without Zn/TiO2 photocatalyst. At the first 30 min., the nitrate reduction increased abruptly and then increased linearly to 120 min. Among them, UVC had 20.40 % nitrate reduction. While EtOH+UVC and H_2O_2+UVC, they reached 24.39 % and 25.34%, respectively. They both had slight difference on nitrate reduction as it meant that EtOH gave the same function as H2O2 in nitrate reduction. The supportive reactions were shown in Eq. 4-5. Nitrate ion changed to nitrite with UVC irradiation. And Eq. 6-7, they described the interaction of ethoxide ion from EtOH with nitrate ion. So nitrogen and nitrite were the products after nitrate reduction. This evidence showed that EtOH and H_2O_2 increased nitrate reduction.

$$NO_3^- \overset{h\gamma}{\rightarrow} NO_2^- + O \quad \text{Eq.4}$$

$$NO_3^- \overset{h\gamma}{\rightarrow} O^{\circ -} + NO_2^{\circ} \quad \text{Eq.5}$$

$$2NO_3^- + CN_3CH_2O^- + 3H^+ + \frac{1}{2}O_2 \rightarrow N_2 + 2CO_2 + 4H_2O \quad \text{Eq.6}$$

$$NO_3^- + CH_3CH_2O^- + H^+ + \frac{3}{2}O_2 \rightarrow NO_2^- + 2CO_2 + 3H_2O \quad \text{Eq.7}$$

So the paper reported that EtOH enhanced NO reduction and it gave the reactive species from EtOH photolysis to promote the NO degradation [20] as we found in the research. This does not occur with the presence of H2O2. And the relevant paper was about V/TiO2 photocatalyst for ethanol photooxidation [21]. The reactive species from ethanol possibly interacted with nitrate ion and increased the reduction.

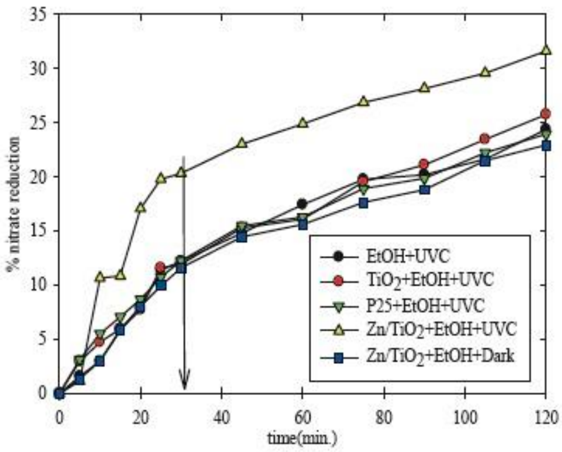

Fig. 6 Effect of EtOH on nitrate reduction
Reaction condition: 12%wt Zn/TiO2 0.25 g, 0.06 M EtOH

The results of Fig.6 indicated the EtOH+UVC effect with Zn/TiO2 photocatalyst. They were 2 groups. The first one was Zn/TiO2+EtOH+UVC with 31.62% nitrate reduction with highest reduction. And the second ones, they were EtOH+UVC, P25+EtOH+UVC, TiO2 +EtOH +UVC and Zn/TiO2+EtOH+Dark. Comparison of nitrate reduction, there were 24.3%, 23.9%, 25.7% and 22.9%, respectively. It meant that the dark condition as the control experiment, it had the lowest performance of ethanol photolysis. Opposed to that with Zn/TiO2+ EtOH+UVC, it had 8.72% higher. The Zn/TiO2 is the important component to reduce nitrate. The optimum condition to find out in more details was shown in Fig. 7.

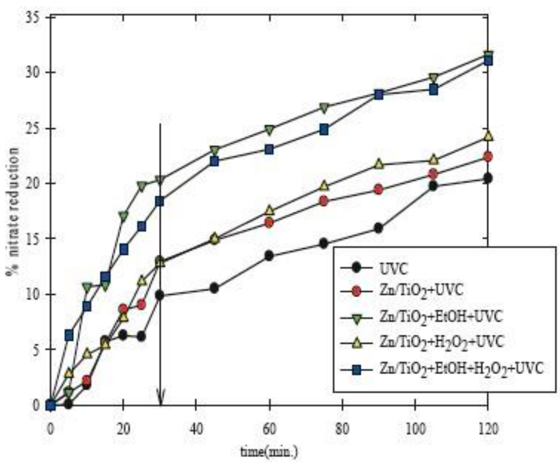

Fig.7 Effect of Zn/TiO2 photocatalyst on nitrate reduction
12%wt Zn/TiO2 0.25 g, with 1 mM H2O2, 0.06M EtOH

Based on UVC as the control system, it had 20.4% nitrate reduction compared to that of Zn/TiO2 +EtOH +UVC and Zn/TiO2+EtOH+H2O2+UVC sytems with 31.6% and 31.0%, respectively. It has 10% higher of nitrate reduction because of Zn/TiO2 and EtOH+H2O2 involvement. For more details, the results of Zn/TiO2+ H2O2+UVC and Zn/TiO2+UVC had 24.1% and 22.3% of nitrate reduction. The presence of H2O2+UVC, it gave the higher performace as the hydroxyl free radicals formation in Eq. 8. Then, nitrate ion reacted with hydroxyl free radicals in Eq.9. The presence of EtOH+H2O2, they were both important factors to increase the nitrate reduction.

$$H_2O_2 \xrightarrow{h\gamma} 2HO^{\circ} \qquad \text{Eq.8}$$

$$2NO_3^- + 2HO^{\circ} + 2H^+ \rightarrow N_2 + 2H_2O \qquad \text{Eq.9}$$

IV.CONCLUSIONS

From various results, it was found that 12% wt Znmodified TiO_2 photocatalyst gave 31.62% for nitrate reduction as the highest value. With the presence of 0.06 molar EtOH, it showed 31.62 % of nitrate reduction and it had the hole scavenger function. On the same way, it occurred with the addition of H_2O_2 during photoreduction. Without Znmodification, TiO_2 photocatalyst showed only 25.76% of nitrate reduction with respect to 22.35% from P25 photocatalyst. The effect of UVC irradiation, it had 31.62% of nitrate reduction compared to 22.95% from the dark condition. The best condition was from Zn-TiO_2+ EtOH+UVC system. The comparison of rate constant (k) and half-life time ($t_{1/2}$) will be included in the future. The Zn-TiO2 photocatalyst+EtOH+UVC system, it could remove nitrate from the aqueous solution. Not only H_2O_2 for photocatalysis, but EtOH acted as the hole scavenger and it enhanced photocatalytic performance.

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