USING NANO - SIZED CATALYTICAL MATERIAL OF ZnO IN THE OZONATION PROCESS FOR REMOVING ACID ORANGE II

SỬ DỤNG VẬT LIỆU XÚC TÁC NANO ZnO TRONG QUÁ TRÌNH ÔZÔN HÓA ĐỂ XỬ LÝ AXIT ORANGE II

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ABSTRACT

Sustainable development with green technology and management is appreciated in the 21st century. Advanced oxidation processes (AOPs) are considered as one of the green ways towards a sustainable future when using advanced materials to enhance the AOPs for complete pollutant treatment. The ozonation process using nano sized catalytical material of ZnO and investigation of the effect parameters such as initial pH, ZnO nanocatalyst concentration for removing different dye concentrations of acid orange II (AOII) have been presented through batch experiments in this study. The obtained results showed that the synergetic effect of ozone process and nanomaterial of ZnO for removal of AOII was investigated with optimal conditions. Hence, the highest AOII degradation efficiency with conditions at initial pH of 10.71; initial ZnO nanocatalyst concentration of 100mgL^{-1}, initial ozone concentration of 9.47mgL^{-1} for removal of the initial AOII concentration at 100ppm get 51.4% of the dye efficiency and COD efficiency of 43.7% for removal of AOII during 60 minutes of the batch experiments. Thus, this investigation demonstrated that the contribution of nano ZnO as catalyst to enhance the removal efficiency was appreciated by improvement of OH° generation for removing AOII in operational conditions.

Keyword: *Ozonation process, nano sized material, nano ZnO, degradation efficiency, acid orange II.*

TÓM TẮT

Phát triển bền vững với việc quản lý và công nghệ xanh đang được đánh giá cao trong thế kỷ 21. Các quá trình ô xy hóa tiên tiến được coi như là một trong cách đi xanh hướng tới một tương lai bền vững sử dụng các vật liệu tiên tiến để thúc đẩy các quá trình ôxy hóa tiên tiến trong việc xử lý chất ô nhiễm hoàn toàn. Quá trình ôzôn hóa sử dụng vật liệu xúc tác nano ZnO và điều tra các yếu tố ảnh hưởng như pH ban đầu, nồng độ nano ZnO để xử lý các nồng độ khác nhau của axit orange II (AOII) được trình bày xuyên suốt các thí nghiệm theo mẻ trong nghiên cứu này. Các kết quả đạt được chỉ ra rằng hiệu ứng cộng hưởng của quá trình ôzôn và vật liệu nano ZnO để xử lý AOII được phát hiện với các điều kiện tốt ưu. Thực vậy, hiệu quả xử lý AOII cao nhất với các điều kiện tại pH 10,71; nồng độ nano ZnO 100mg/L, nồng độ ôzôn ban đầu 9,74mg/L để xử lý nồng độ AOII ban đầu nồng độ 100ppm đạt hiệu quả xử lý chất màu là 51,4% và hiệu quả xử lý COD đạt 43,7% trong thời gian xử lý 60 phút trong các thí nghiệm theo mẻ. Do đó, nghiên cứu này đã minh chứng sự đóng góp của nano ZnO như là một chất xúc tác để thúc đẩy hiệu quả xử lý, và được đánh giá cao bởi sự tăng cường của nhóm OH° linh động sinh ra để xử lý AOII trong các điều kiện nghiên cứu.

Từ khóa*: Ôzôn hóa, vật liệu kích cỡ nano, nano ZnO, hiệu quả xử lý, axit orange II.*

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1. INTRODUCTION

Over the past year, the demand for organic dyes and pigments has been increasing according to the economic development. An American market analyst in Freedonia's, the demand for organic dyes and pigments increased 6% per year and reached $19.5 billion in 2019. The textiles and plastics markets, which are the main markets for organic dyes and pigments are developed. In which, the textile dyeing industry is currently the largest consumer of organic dyes and pigments. However, during the performance, a large volume of dyes and organic pigments has been lost through wastewater if not being managed and treated timely. Some studies found out that the volume of dyes and organic pigments lost during the dyeing process may be up to 50% of the total initial used volume [1,2]. These substances are very toxic and the main causes of negative impacts on the environment and human [3], without effective treatment.

The currently-applied technologies, such as coagulation - flocculation, aerobic biological treatment, membrane technology, etc. are incapable of complete treatment due to easily result in a large volume of sludge and prolonged treatment period. To resolve that problem, many studies applied advanced oxidation processes (AOPs) in removing dyes and organic pigments have shown high effectiveness. In which, the ozonation process has been much concerned because of the capability to directly oxidize pollutants by molecular O_3 or indirectly oxidize pollutants by OH° radical with a high reaction rate. Many studies have demonstrated during catalytic ozonation, ozone can be activated using transition

metal oxide catalysts to enhance the production of hydroxyl radicals. Moreover, nanomaterial based catalysts have shown a distinctive and signifcant potential for the enhancement of reaction kinetics and many nanomaterials have been investigated, including metal oxides, metals or metal oxides on supports.

In the study of Kaoutar El Hassani et al., catalytic ozonation use Ni-based layered double hydroxides nanomaterials has proven to provide significant improvement for azo dye removal when compared with ozone alone which follows a hydroxyl radical based mechanism. In optimized conditions, after 60 min reaction, COD removal has reached 72% in the catalytic ozonation process, while it reached only 30% in non-catalytic ozonation [4].

In another paper, Nikita et al. studied synthesis of Nano Ag-La-Co Composite Metal Oxide for Degradation of RB 5 Dye Using Catalytic Ozonation Process. The results showed the degradation efficiency of catalytic ozonation was 63% compared to 32% and 4% in ozonation without catalyst and adsorption on the catalyst, respectively [5].

ZnO is a catalytic material which is widely used during the treatment processes, with advantages of high catalytic activity. Typically, ZnO nanoparticles also have special advantages such as chemical stability, fast electron transfer and good absorption because of small nanoparticle size and large specific surface [6]. Therefore, the supplementation of ZnO nanocatalysts in ozonation process for dye treatment promises to bring positive effectivenesses. This article presents the preliminarily studied results in assessing the effect of some factors (pH, initial concentration of ZnO nano-catalyst, initial AOII concentration) on the treatment capicity of the chemical ozonation process using ZnO nanoparticles for removing acid orange 2 (AOII) of the batch experiments.

2. MATERIALS AND METHODS

2.1. Materials

Pigments: Orange acid II (AOII) $C_{16}H_{11}N_2NaO_4S$ is a direct dye of the group of azo pigments, produced by Aladdin - China, with a purity of 99%.

$Na_2S_2O_3$, glycerin use pure chemicals, made by Merck - Germany to stop the reaction over time. NaOH, HCl made by Merck - Germany are added to adjust the initial pH for each research condition.

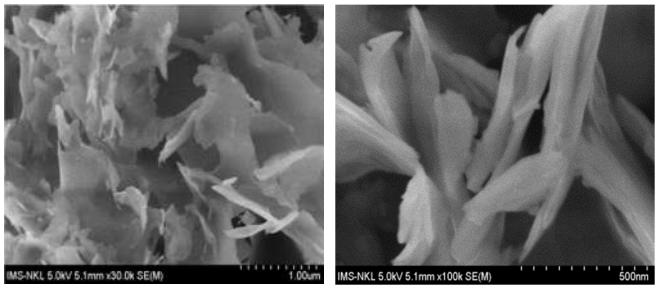

Figure 1. SEM images of nano - sized ZnO material

Nano - sized ZnO material is supplied from the Institute of Chemistry - Vietnam Academy of Science and Technology, with a surface area of $35.11 m^2g^{-1}$, purity greater than 99.9%, particle volume of $1.293x10^{-2}cm^3g^{-1}$, hole size of 1.838A°, determined by the BET method. SEM image of nano ZnO was determined by HITACHI S-4800, Japan at the Institute of Materials Science, Vietnam Academy of Science and Technology (Figure 1).

2.2. Methods

The experiments are conducted in the closed experimental systems, including an ozone generator connected with 1.5 liter glass of reactor in Figure 2.

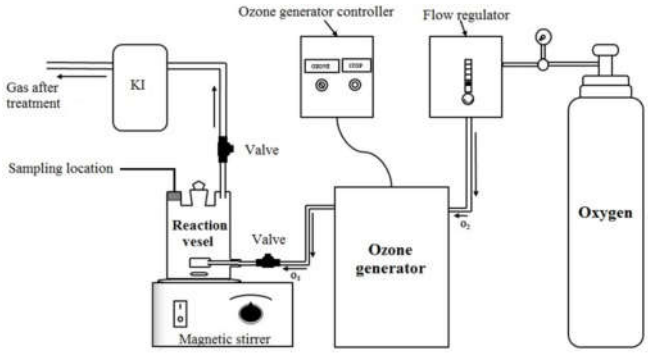

Figure 2. Experimental system diagram

Ozone is produced by Ozone D-10S generator with the capacity of 10g O_3/h from pure oxygen (99%). Gaseous ozone is generated by the closed pipeline system and then that is transferre in the 1.5 liter of reactor and evenly distributed from the gas phase to the liquid phase. Through the conversion system from the gas to liquid phase in the reactor, the part of outgas ozone will be run through a KI solution containing reducer before being discharged. The valves installed at the reactor connections to the ozone generator are non - return valves.

Experimental Setup

Install reactor in the experimental system. Add ultra-pure distilled water to the reactor, add a determined amount of nano ZnO depending on each experiment, turn on the stirrer so that the ZnO is evenly dispersed in the water. Adjust the solution pH to 3, start the ozone generator system and conduct ozone generation for 15 minutes to reach saturation. the dissolved ozone concentration in the solution reaches $9.47 \pm 0.03 mgL^{-1}$.

Initial AOII dye concentrations in the experiments are expected to be 50, 100 and 200ppm, prepared by injecting from the $10gL^{-1}$ stock solution into the reactor with controlling desired pH by NaOH solution 1N immediately after turning off the ozone generation process in the reactor.

Samples for analysis of pH, ozone concentration, AOII concentration, COD concentration are taken versus by time with a 10 - 20ml syringe to ensure that the sample is taken out in a completely closed system during the experimental process.

Analytical method

The concentration of AOII is determined by photometric method at the wave length of 481nm on UH5300 dual beam visible spectrometer - made by Hitachi - Japan.

COD concentration in the samples over time is determined by oxidizing $K_2Cr_2O_7$ measured at the wave length of 600nm, on a two-beam visible spectrometer UH5300 [7].

3. RESULT AND DISCUSSION

3.1. Effect of pH on removal of AOII

In the catalytic ozonation process, solution pH plays an important role, affecting on the properties of the surface active positions of the catalyst and the ozone decomposition reaction in the aqueous phase [8], affecting on the treatment efficiency of the selected dye. The experiments studied the effect at the three pH values 3.41, 7.57 and 10.71 with initial AOII concentration of 100ppm, initial ZnO nanocatalyst concentration of 100mgL^{-1}, initial ozone concentration of 9.47mgL^{-1}. The results of these experiments are shown in Figure 3.

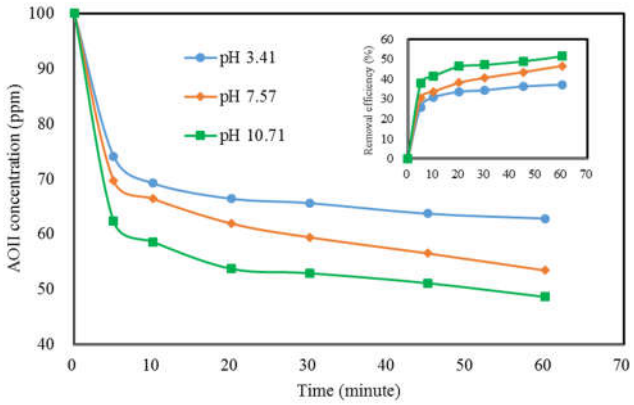

Figure 3. Effect of pH on the ozonation of AOII. Experimental conditions: $[O_3]_o = 9.47mgL^{-1}$, $[AOII]_o$=100ppm, $[ZnO]_o$=100mgL^{-1}

AOII concentration decreased rapidly immediately after the catazone process started. At the 5th minute of the treatment process, at pH 3.41 the AOII concentration dropped to 70.1ppm; at pH 7.57 the AOII concentration fell to 69.7ppm and at pH 10.71 the AOII concentration declined to 62.3ppm. Over time, the difference in the decline of AOII concentration among formula was increasing and the difference on the treatment efficiency also rised. In which, formula pH 10.71 has the highest treatment efficiency, reaching 51.4% after 60 minutes, followed by the formula pH 7.54, with the treatment efficiency of 46.6% and the lowest was the formula pH 3.41 with the treatment efficiency of 37.2%.

It is explained by the fact that the nature of ZnO catalyst contains an alkaline active core. These active cores will enhance the absorption of dissolved O_3 on the surface, then react with O_3 molecules generate free radicals $ZnO-s^{O^\circ}$. These radicals continue to react with H_2O and O_3 to generate OH° (Reactions 1, 2, 3).

$$ZnO - s + O_3 \rightarrow ZnO - s^{O=O-O} \quad (1)$$

$$ZnO - s^{O=O-O} \rightarrow ZnO - s^{O^\circ} + O_2 \quad (2)$$

$$ZnO - s^{O^\circ} + 2H_2O + O_3 \rightarrow ZnO - s^{OH^\circ} + 3\,OH^\circ + O_2 \quad (3)$$

Meanwhile, AOII is an anionic dye, so in an acidic medium, AOII will be more strongly adsorbed on the surface of ZnO, which can compete with O_3 molecules to generate OH° radicals.

On the other hand, the self-decomposition of O_3 to generate OH° in alkaline medium occurs faster than in acidic and neutral medium [9].

Accordingly, the efficiency of AOII treatment in acidic environment is highly dependent on the direct decomposition of O_3 and the adsorption capacity of ZnO nanoparticles. Meanwhile, in alkaline medium, AOII decomposition efficiency mainly comes from indirect decomposition via OH° radical. Many studies found that in comparison of the direct O_3decomposition and the adsorption capacity of ZnO, the indirect decomposition process through the radical OH° occurs faster and stronger, so the ability to oxidize dyes is also higher, the results in the above experiments have once again proved this [10].

The results of the effect of pH on COD removal efficiency were shown in Figure 4.

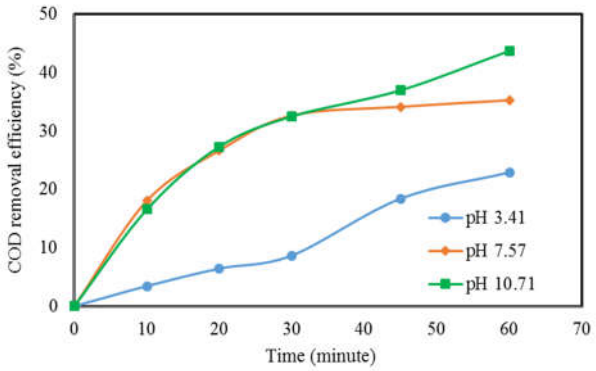

Figure 4. Effect of pH on the COD removal efficiency. Experimental conditions: $[O_3]_o = 9.47mgL^{-1}$, $[AOII]_o$=100ppm, $[ZnO]_o$=100mgL^{-1}

Different from AOII, the COD concentration changed gradually and the treatment efficiency increased over time. In which, at pH 3.41, the COD removal efficiency was significantly lower than the other two pH values, reaching only 22.9% after 60 minutes of treatment.

There was no significant difference in COD removal efficiency at the two pH values 7.57 and 10.71 in the first half of the treatment (from the start to 30 minute). After the 30th minute, the processing efficiency between the two formulas had a clear difference and increased gradually over time. By the 60th minute, at pH 7.57 the COD removal efficiency was 35.25%; and at the pH 10.71 the COD removal efficiency was 43.7%.

Thus, the ozonation process using ZnO nanocatalyst, the best suitable medium for the treatment was alkaline condition at pH 10.71.

3.2. Effect of ZnO nanocatalyst concentration

Assess the effect of the ZnO nanocatalyst concentration on the dye removal efficiency, the experiment was conducted at three initial concentrations of 50, 100 and 200mgL^{-1} of nano ZnO with pH 10.71, the initial concentration of AOII dye of 100ppm, the results were illustrated in Figure 5.

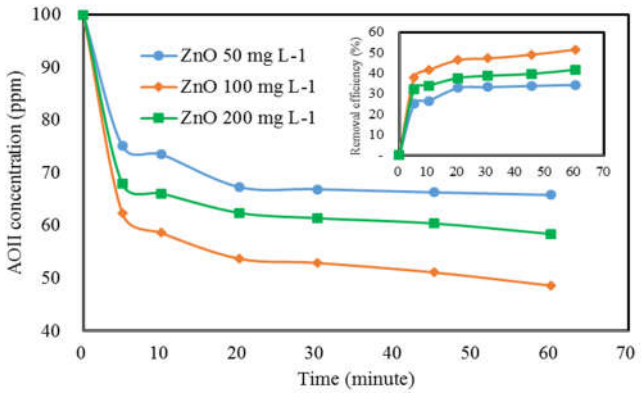

Figure 5. Effect of ZnO nanocatalyst concentration on the ozonation of AOII. Experimental conditions: $[O_3]_o = 9.47mgL^{-1}$, $[AOII]_o$=100ppm, pH_o= 10.71

The results in Figure 5 showed that in the ozonation process using ZnO nanocatalyst to treat AOII, when increasing the concentration of ZnO nanoparticle from 50mgL^{-1} to 100mgL^{-1}, the dye removal efficiency increased significantly. This was explained because the higher catalyst loading provided the higher rate of OH° generation, combined with the increase in adsorption of ZnO nanocatalysts, making the AOII treatment process take place faster.

However, when continuing to increase the concentration of ZnO nano to 200mgL^{-1}, the processing efficiency tended to decrease. The reason was that when the concentration was too high, the nanoparticles tended to agglomerate, narrowing the contact surface area, reducing the activation ability of the nanoparticles, thereby reducing the adsorption and decompose O_3 into OH° radicals.

The results of the effect of catalyst concentration on COD removal efficiency were shown in Figure 6.

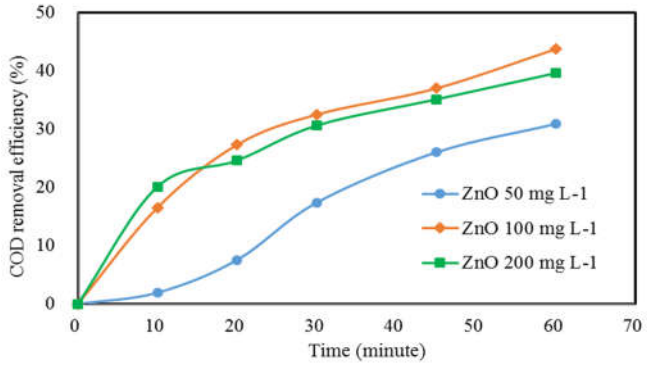

Figure 6. Effect of ZnO nanocatalyst concentration on the COD removal efficiency. Experimental conditions: $[O_3]_o = 9.47mgL^{-1}$, $[AOII]_o$=100ppm, pH_o= 10.71

The results showed that, at the 15th minute, the COD removal efficiency at the 200mgL^{-1} ZnO nano concentration formula reached the highest value. However, at the next time, the highest COD removal efficiency at the 100mgL^{-1} ZnO, by the 60th minute, COD removal efficince of 43.7%.

Thus, under experimental conditions $[O_3]_o = 9.47mgL^{-1}$, $[AOII]_o$=100ppm, pH_o= 10.71, the formula of 100mgL^{-1} ZnO nano concentration gave the best AOII removal efficiency.

3.3. Effect of initial AOII concentration

The effect of the initial AOII concentration on the treatment efficiency was studied at three AOII concentration values (50, 100 and 200ppm), the results were shown in Figure 7.

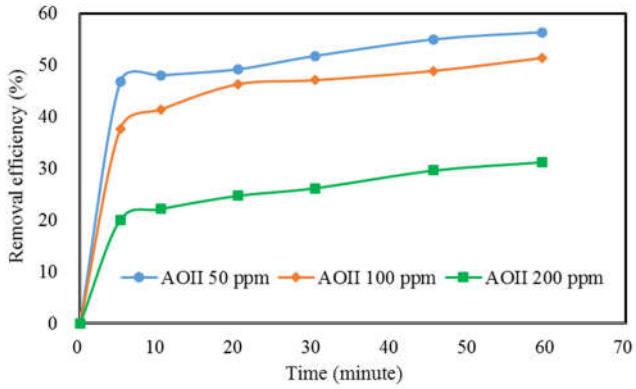

Figure 7. Effect of initial AOII concentration on the ozonation of AOII. Experimental conditions: $[O_3]_o = 9.47mgL^{-1}$, $[ZnO]_o$=100mgL^{-1}, pH_o= 10.71

The research results showed that when increasing the initial dye concentration, the treatment efficiency decreased. The reason was that under the same initial conditions, when the concentration of dye increased, the percentage of OH° radical generated per molecule of dye decreased, reducing processing efficiency.

On the other hand, although in alkaline medium, the adsorption of AOII on ZnO surface was limited, but when increasing the concentration of AOII, this process still increased passively, leading to competition for ZnO nanosurface active sites between dye molecules and O_3 molecules, thereby reducing the formation speed of OH° radicals [11-13]. It was explained that when doubling the initial dye concentration (from 50mgL^{-1} to 100mgL^{-1}), the treatment efficiency decreased insignificantly. But when increasing the initial dye concentration to 200mgL^{-1}, the treatment efficiency fell sharply.

The results of COD removal efficiency were shown in Figure 8.

As seen in Fig. 8, when the initial dye concentration was doubled from 50 to 100ppm, the difference in COD removal efficiency was not significant. At the 60th minute, the COD removal efficiency of the two formulations reached 45.14% and 43.7%, respectively.

When continuing to increase the dye concentration to 200mgL^{-1}, the COD removal efficiency was markedly

reduced. At the 10th minute, the COD concentration in the solution was almost unchanged, it was not varied until the 20th minute that the COD concentration started to decrease and by the 60th minute, the COD removal efficiency in this formula only reached 3.31%.

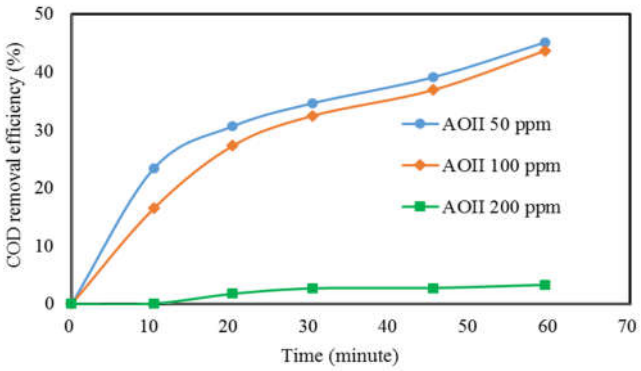

Figure 8. Effect of initial AOII concentration on the COD removal efficiency. Experimental conditions: $[O_3]_0 = 9.47 mgL^{-1}$, $[ZnO]_0 = 100 mgL^{-1}$, $pH_0 = 10.71$

Therefore, the most suitable initial AOII concentration for the ozonation process using ZnO nanocatalyst was 100ppm considered as the best condition for removal efficiency.

4. CONCLUSION

The ozonation process using ZnO nanocatalyst for removing AOII dye was effective in alkaline medium because this favorable condition promoted the capability of OH° generation.

The best conditions for AOII dye treatment process by ozonation process using nanocatalyst ZnO were at pH 10.71, ZnO nano concentration of $100 mgL^{-1}$; the initial concentration of AOII dye was $100 mgL^{-1}$ during the treatment time of 60 minutes in which AOII treatment efficiency of 51.4%, COD removal efficiency of 43.7% was studied.

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THÔNG TIN TÁC GIẢ

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