

Solar Photocatalytic Degradation of Orange G Dye Based on Zinc Oxide

Muhammad Nasri Abdul Rahman¹, NurAisyah Hamzah¹, Wan Farahiyah Wan Kamarudin²,
Zildawarni Irwan², Mohd Rabani Yaafar³, Noor Erni Fazlina Mohd Akhir⁴

¹Faculty of Applied Science, Universiti Teknologi MARA, Jengka, Pahang, Malaysia

²Faculty of Applied Science, Universiti Teknologi MARA, Dungun, Terengganu, Malaysia

³Faculty of Applied Science, Universiti Teknologi MARA, Tapah, Perak, Malaysia

⁴Faculty of Computer and Mathematical Science, Universiti Teknologi MARA, Dungun, Terengganu, Malaysia

Received: June 11, 2017

Accepted: August 23, 2017

ABSTRACT

Under uncontrolled and unsatisfactory conditions, the wastewater released by the commercial enterprise is causing critical environmental issues. Wastewater treatment and pollution control are absolute to solve this environmental challenged. Photocatalytic has come to be considered one of the most important, clean chemical technologies, environmental friendly for green chemistry method. The main objective of this study was to evaluate the efficiency of degradation of Orange G (OG) dye by using Zinc Oxide (ZnO) as semiconductor illuminated by solar light. The study also comprises the effect of radical scavengers in different concentrations towards the solar photocatalytic degradation. It also to evaluate the efficiency of solar photocatalytic degradation in the presence of co-catalyst. A laboratory set-up was designed to evaluate the effectiveness of photocatalytic degradation process in the presence of radical scavengers, and also was operated in the presence of co-catalyst. The effect of different types and concentration of organic salts (NaCl, NaHCO₃ and Na₂CO₃) and co-catalyst (Mn²⁺, Cu²⁺ and Fe²⁺) on the degree of degradation efficiency were studied. The results showed that OG degrade under solar irradiation, while degradation was almost impossible in the absence of sunlight. The results also indicated that one of the effective way to degrade the OG dye is to add metals ions into the sample and Fe²⁺ metal ion was proved as an effective co-catalyst. Additionally, it was found that all salts in the sample inhibits the efficiency of OG degradation. The inhibition of OG dye by the salts are best at high pH value.

KEYWORDS: Solar Photocatalytic, Orange G Dyes, Radical Scavengers, Wastewater Treatment, Semiconductor, Co-Catalyst.

INTRODUCTION

The textile industry is very water intensive. Water is used for cleaning the raw material and for many flushing steps during the whole production. Produced waste water has to be cleaned from fat, oil, colour and other chemicals, which are used during the several production steps [1]. The most detrimental aspects for the discharge of textile wastewaters are the strong colour, high and unstable pH and high chemical oxygen demand (COD) [2]. Dye is substances that are used to change the colour from leather, paper, textile and other materials. Dyes are copious source of coloured organics emanating as a waste from the textile dyeing process [3]. Nowadays, the dyes have been used commercially in the industries with the large sum of quantities especially in textile industries. The industry is using more than 8000 chemicals in various processes of textile manufacture including dyeing and printing [4].

Azo dyes are the most widely used dyes and represent over 60% of the total dyes [5]. Azo dyes are characterized by the presence of one or more azo bonds ($-N\equiv N-$) in association with aromatic systems and auxochromes ($-OH$, $-SO_3$, etc.) [6]. Their properties are enhanced to provide a high degree of chemical, biological and photocatalytic stability and resist breakdown due to time, exposure to sunlight, microorganisms, water and soap. In other words, they are resistant to degradation. Azo dyes are resistant to degradation and remains persistent for long time due to its fused aromatic structure [7]. Textile industry wastewater is heavily charged with unconsumed dyes, surfactants and sometimes traces of metals. These effluents cause a lot of damage to the environment [8]. Dye wastewater pollution had become a severe problem in current times, which were contributed from the used of synthetic dye and the increased demand for textile product. These dyes can be hazardous when come into contact with human as well as it can be carcinogenic. To avoid this harmful effect, newer treatments of the wastewater are still in development.

To find an economic and proficient approach to treat the textile dyeing wastewater, numerous methods have been developed including physicochemical, biochemical, combined treatment processes and other methods in the past several decades [9]. The conventional oxidants has been used for years for the standard chemical method for the treatment of azo dye wastewaters. It is because the biological treatments methods are not efficient for dye degradation as the chemical structures of dyes are rather complicated [2]. The latter

improvement of chemical treatment of waste waters brought forth a change of the oxidative degradation of the organic compounds. Advanced Oxidation Process (AOPs) is an alternative methods used to disintegrate the dyes and other organics in industrial effluents [3]. Among the new oxidation methods, the photocatalysis oxidation has been more researched and applied currently. This technology can effectively destroy a lot of organic pollutants whose structure is stable and difficult to biologically degrade [9].

Heterogeneous photocatalytic degradation is considered as one of the AOPs technique. Photocatalytic degradation mechanism occurs on the top layer of catalyst. Photocatalysis is a light induced catalytic process that reduces or oxidize organic molecules through redox reactions on the surface of metal oxide semiconductors upon beyond band gap light illumination [10]. Photocatalysis has come to be considered one of the most important, clean chemical technologies, environmental friendly for green chemistry method [11]. For the degradation of resistant pollutant, this process is being developed rapidly. Recently the use of combining photocatalysis and solar technologies has attracted increasing attention [12]. This technique has attracted a lot of attention as efficient process in the reduction of environmental deterioration.

Photocatalytic environmental reconciliation, especially wastewater cleansing have been widely used the heterogeneous photodegradation mechanism involving metal-oxide semiconductors and light as the irradiation sources. Instead of manufactured light sources such as ultraviolet radiation (UV) that is pricey and dangerous, solar energy can be used since it is a sufficient natural energy source. Zinc oxide (ZnO) displays high photocatalytic efficiencies for the degradation in aqueous systems and has become a favourable catalyst as a solar light photocatalytic material. For the past few years, degradation of dye pollutants using ZnO-mediated photocatalysis process has been used effectively. Due to their unique electronic band structure, semiconductors act as photocatalyst for the light induced photochemical reactions [13]. Zinc oxide (ZnO) is a favourable applicant as a solar light photocatalytic material, since it indicates high photocatalytic efficiencies for the degradation of pollutants [10]. As one of the proven semiconductors photocatalysts, ZnO has been widely utilize as photocatalysts, due to its high activity, low cost and environmentally friendly properties [11].

As we know, photocatalytic reaction will occur on the surface of photocatalyst and the presence of co-catalyst will act as a reduction or oxidation active site in promoting the separation of photogenerated electrons and holes. The various types and characteristics of co-catalyst somehow play a big and effective role in determining the efficiency of photocatalytic [14]. This is because co-catalyst will speed up the reaction of photocatalytic degradation better than the presence of catalyst alone. Some of the transition metal such as Cu^{2+} , Fe^{2+} and Mn^{2+} which known as metal ion in characteristics also added to ZnO catalyst to show the improvement of response in photocatalytic degradation.

Radical scavengers are antioxidants which have the ability to donate electron, thus inactivates the free radical. It is believed that these radical scavenge $\bullet\text{OH}$ radicals, which are supposed to attack the organics. However, the anion salts presence in the wastewater may affect the organics degradation. Chloride, carbonate and bicarbonate have been the sources of inorganics anions that are very common in textile wastewater. These scavenger may be originated from various waste chemical pollutants such as wetting agents, dyes, softening agent, oils, wax and others additives which are used throughout the processes.

This study focused on photocatalytic process by using ZnO as a semiconductor with the presence of ultraviolet (UV) irradiation for the treatment. The target pollutant in this study is OG, which is widely used in textile dyeing processes. OG dye is a synthetic Azo dye and it is in the form of orange crystalline powder. OG dye is a reactive dye that contains two groups SO_3Na , which are soluble in water. One of the most important, clean chemical technologies, environmental friendly for green chemistry method. The main objective of this study was to evaluate the efficiency of degradation of Orange G (OG) dye by using Zinc Oxide (ZnO) as semiconductor illuminated by solar light. The influence of different types and concentration of organic salts (NaCl , NaHCO_3 and Na_2CO_3) and different experimental conditions for co-catalyst (Mn^{2+} , Cu^{2+} and Fe^{2+}), which affect the efficiency in OG dye degradation were investigated.

MATERIALS AND METHODS

Materials

All materials in this experiment were prepared in the laboratory and of analytical grade. The model dye, Orange G was purchased from manufacturing company and a stock solution of the dye (1 M) was prepared in distilled water. The instrument UV-Vis Spectrophotometer-UV 1800 Shimadzu was used in this experiment. All materials was prepared in the laboratory.

Methods

The photodegradation of azo dye (Orange G) process was operated in the presence of solar light. The experiment was also operated in the presence of radical scavenger and metal ion. The degradation of azo dye was analyzed with UV-Vis spectrometer by tabulating the absorbance reading of the dye solution. The rate of degradation for the condition was also studied.

To Study the Effect of Solar Irradiation in Rate of Degradation

100 mL of 5 ppm OG solution was poured into a 250mL conical flask and the initial pH for 5 ppm OG solution was recorded. Control the pH by dropping H₂SO₄ solution prepared earlier. Dipped the pH meter into the solution to ensure the pH was around 3.5. The acidified solution then was added with 0.1 g of zinc oxide (ZnO) and stirred with magnetic stirrer. The solution then was exposed under the sunlight for a period of time. Obtain a small amount of sample solution in a time interval of 0 min, 1 min, 5 mins, 10 mins, 15 mins and 20 mins. Use the UV/Vis spectrophotometer for monitoring the decolourization of the samples. Repeat the steps in the absence of sunlight.

To Study Effect of Radical Scavengers in the Rate of Degradation

100 mL of 5 ppm OG solution was poured into a 250mL conical flask and the initial pH for 5 ppm OG solution was recorded. Control the pH by dropping H₂SO₄ solution prepared earlier. Dipped the pH meter into the solution to ensure the pH was around 3.5. The acidified solution then was added with 0.1 g of Zinc Oxide (ZnO) and 10 mL of 10⁻¹ M CO₃²⁻ salt solution and stirred with magnetic stirrer. The solution then was exposed under the sunlight for a period of time. Obtain a small amount of sample solution in a time interval of 0 min, 1 min, 5 mins, 10 mins, 15 mins and 20 mins. Use the UV/Vis spectrophotometer for monitoring the decolourization of the samples. Repeat the above steps using different concentrations of CO₃²⁻ salt solution which were 10⁻² M, 10⁻³ M and 10⁻⁴ M respectively, followed by the presence of other types of scavengers which were HCO₃⁻ and Cl⁻ salt solution in the concentration of 10⁻¹ M, 10⁻² M, 10⁻³ M and 10⁻⁴ M respectively.

To Study Effect of Metal Ions in the Rate of Degradation

Use 5 ppm of OG in the degradation process. Then transferred 100 mL of OG solution into 250 mL conical flask. The initial pH for 5 ppm OG solution was recorded. Control the pH by dropping H₂SO₄ solution prepared earlier. Dipped the pH meter into the solution to ensure the pH was around 3.5. Add 0.1 g of the ZnO into the flask that contained OG solution and followed by 10 mL 10⁻² M of metal ion. The solution then was exposed under the sunlight for a period of time. Obtain a small amount of sample solution in a time interval of 0 min, 1 min, 5 mins, 10 mins, 15 mins and 20 mins. Use the UV/Vis spectrophotometer for monitoring the decolourization of the samples.

RESULTS AND DISCUSSION

Based on the experiment, orange G dye can degrade by using catalyst zinc oxide (ZnO) with solar light, oxidizing agent which is metal ion and radical scavenger sodium salts. The radical scavenger that had been used is CO₃²⁻, HCO₃⁻ and Cl⁻ while the metal ion used are Mn²⁺, Fe²⁺ and Cu²⁺. Furthermore, the degradation also happened under the solar light. The differentiation of the degradation can be seen after compared the process that did not used the metal ion and radical scavenger on the orange G dye. The degradation efficiency was calculated by using the following formula:

$$\text{Degradation efficiency (\%)} = \frac{C_0 - C_t}{C_0} \times 100$$

where C₀ and C_t are the initial concentration of OG and concentration at time.

The Effect of Solar Irradiation in Rate of Degradation

Results showed that OG could be degrading under the solar irradiation while degradation was almost impossible in the absence of sunlight. The addition of ZnO are only slightly affected the degradation efficiency of the OG dye. The percentages of degradation or degradation efficiency became lower when put early in the morning because the intensity of the irradiation is small. It concludes that the present of the sunlight can affect the degradation efficiency of OG dye compared to the condition were the sunlight was absence. The percentage degradation efficiency of OG dye in different condition is shown in Figure 1.

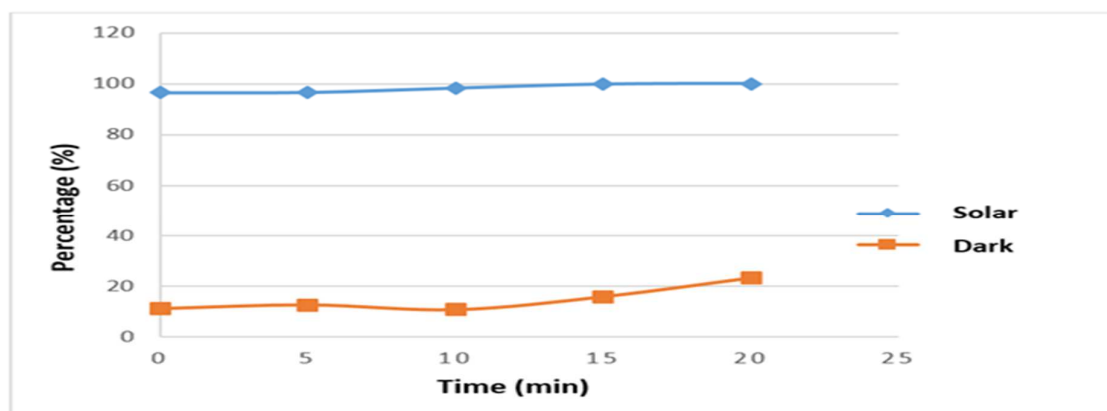


Figure 1: The percentage degradation efficiency of OG dye in different condition

The Effect of Radical Scavengers in the Rate of Degradation

In textile effluents huge amounts of inorganic salts are present with dyes [15]. A variety of reaction mechanisms have been proposed to describe the photodegradation of organic molecules on ZnO. Consequently, the adsorption is believed to play a prominent role in photocatalytic degradation to explain a photocatalytic disappears of organic substrate [16]. In the literature, the inhibition of photocatalytic properties in presence of ions is often explained by the scavenging of $\text{OH}\bullet$ radicals by ions [17].

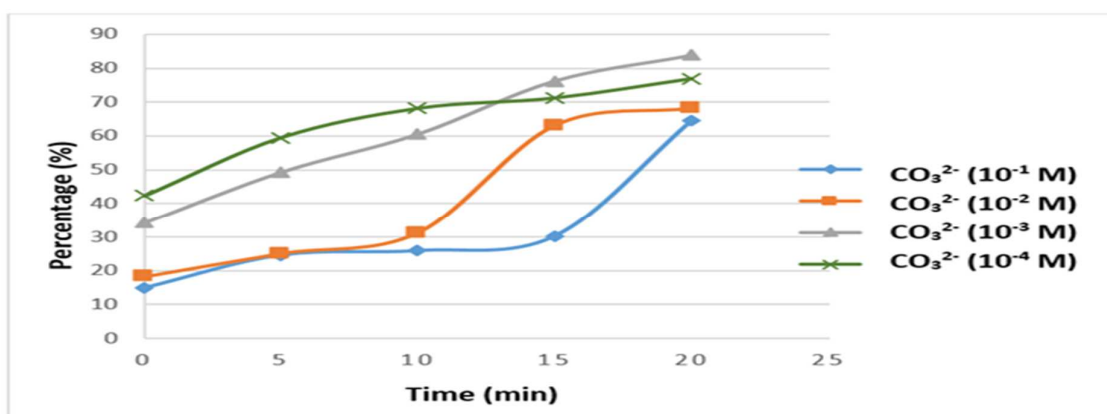


Figure 2: The percentage degradation efficiency of OG dye solution in the presence of different concentration of Na_2CO_3 salt

Figure 2 showed the percentage degradation efficiency of OG dye solution in the presence of different concentration of Na_2CO_3 salt. From the graph, the rate of degradation were increases over time for all different concentration of CO_3^{2-} . The purpose of adding the Na_2CO_3 is to inhibit the degradation process of the OG dye. As clearly from the graph, we can see that the inhibition by the salt are failed. It is because for the inhibition by the salt on the OG dye to occur, it requires natural and basic pH environment [15]. However, in this experiment, acidic pH environment was applied. The OG dye has its adsorption inhibited by high pH values because of its negatively charged sulfonate ($-\text{SO}_3^-$) function [15].

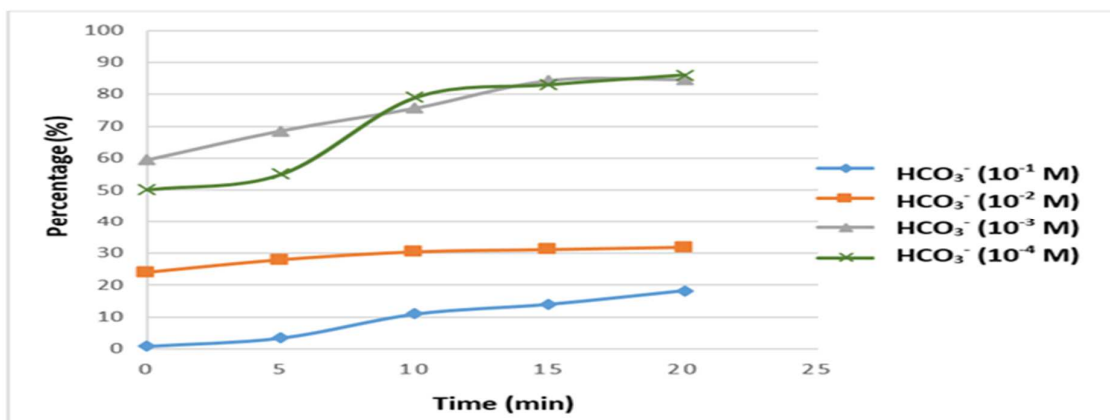


Figure 3: The percentage degradation efficiency of OG dye solution in the presence of different concentration of NaHCO_3 salt

Figure 3 showed the percentage degradation efficiency of OG dye solution in the presence of different concentration of NaHCO_3 salt. The effect of hydrogen carbonate in the mixture on the photodegradation of OG was measured by using UV-Vis Spectrometer. The degradation efficiency on the OG dye by HCO_3^- salt were increases over time for all of the concentration applied. The inhibitory effect of hydrogen carbonate on photocatalytic degradation can be elucidate by the scavenging character of these anions on the OH^\bullet photogenerated radicals during the photocatalysis [16]. However, from the data above the efficiency of the OG degradation are increases as the inhibitory effect was prevented. It is because the concentration of the HCO_3^- that had been used are diluted, so the amount of the anions to inhibit the degradation process is less.

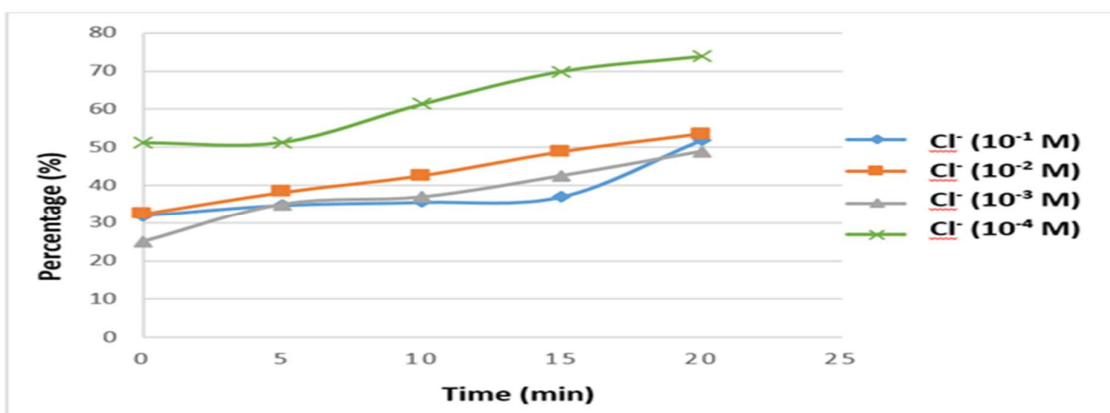


Figure 4: The percentage degradation efficiency of OG dye solution in the presence of different concentration of NaCl salt

Figure 4 shows that the degradation efficiency of OG dye by the Cl^- salt are increases over time. The role of NaCl in this experiment is same with the role of other salts used, which is to inhibit the photodegradation of OG dye. However, the inhibitory effect is not successful. The photodegradation efficiency of OG decreases in the presence of Cl^- and is pH dependent if the inhibition take placed [18]. As stated in the above discussion, the inhibition by the salt on the OG dye to occur, it requires natural and basic pH environment [15]. However, in this experiment, acidic pH environment was applied. The other reasons is the concentration of the Cl^- that had been used are diluted, so the amount of the anions to inhibit the degradation process is less.

The Effect of Metal Ions in the Rate of Degradation

The presence of metal ion in the photodegradation system can cause the rate of OG degradation increases. The metal ion can block an excited electron when the positive charges was combined together at the surface of the catalyst [19]. An electron will be trapped by the metal ion that act as co-catalyst to block the combine process between electron and positive charges, resulting the degradation process be retarded. The concentration used in this experiment are same for all types of metal ion used, which is $1 \times 10^{-2} \text{ M}$.

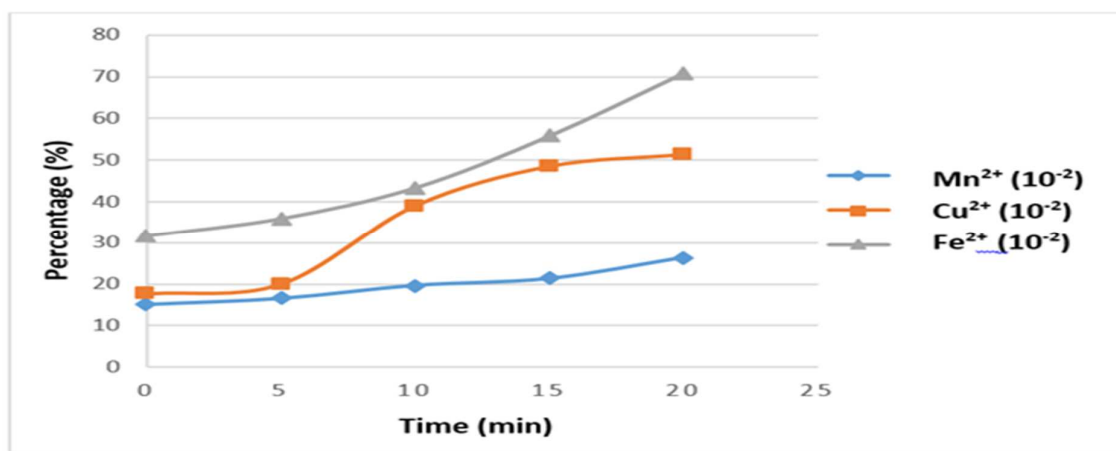


Figure 5: The percentage degradation efficiency of OG dye solution in the presence of different type of co-catalyst (Mn²⁺, Cu²⁺ and Fe²⁺)

According to the Figure 5, the degradation efficiency on the OG dye are increases. As previously stated, the role of the metal ions are to speed up the process of photodegradation on the OG dye. However, based on the Figure 5, the degradation efficiency of Mn²⁺ process are still considered as at normal speed. It is because the concentration of Mn²⁺ metal ion used is diluted making the amount of metal ion needed to speed up the degradation process is less.

Figure 5 shows that the degradation efficiency of OG dye by Cu²⁺ are higher compared to the degradation efficiency of OG dye by Mn²⁺. Even though the efficiency is higher, but it is still degrade at normal speed similar with the Mn²⁺ process. The reasons for this to happened is same with the Mn²⁺ process, which is the concentration of metal ion used is diluted, making the amount of metal ion needed to speed up the process is less.

Figure 5 also shows that the degradation efficiency of OG dye by Fe²⁺ are higher compared with the other metal ions. This reactive reaction can be shown from the colour changing of the OG. The OG colour remain when the ZnO was added, but changing when Fe²⁺ was added. The efficiency of the photodegradation of OG by Fe²⁺ can be even higher, if the concentration of the metal ion used is not diluted. When compared with the other metal ions, Fe²⁺ is more suitable to be co-catalyst in the degradation photocatalytic process.

The Effect of pH to Orange G Dye

One of the parameter that effect the photodegradation process is pH value. It is difficult for the pH to be effective on dye photodegradation process because of the element functions. The ionization state of the surface is connected to the reactant dyes and product. It is an important step to encourage the absorption of coloured pollutant particles upon the ZnO surfaces in pH changes [20]. Except for OG, other types of dyes favors the increase of pH for their degradation [15]. The negatively charged sulfonate (–SO₃[–]) function in the OG dye, become the reasons of its absorption inhibited by high pH values.

CONCLUSION

The photocatalytic degradation of the Orange G dye proved to be effective under the solar irradiation based on ZnO. Results showed that OG degrade under the solar irradiation while degradation was almost impossible in the absence of sunlight. The solar energy proven that it can replace the artificial light sources that is expensive and hazardous also maintained as a powerful sources supply for the photocatalysis degradation process. Trait to a photosensitization process that engaging the ZnO catalyst and absorbed the OG dye itself under the sunlight, leading the formation of OH• radical and the degradation efficiency was promoted. Furthermore, one of the effective ways to degrade the organic compound, which in this experiment is the OG dye is to add metal ions into the sample and Fe²⁺ metal ion was an effective co-catalyst. Opposite to the role of metal ions that speed up the degradation process, the presence of salts in the sample inhibits the degradation, as it act as scavenger in the process. Increasing the concentrations of salts in the dye solution reduced the degradation efficiency of the dye, to varying degrees depending on the type of salts used and the concentration of the salts. The pH value is one of the factors that affecting the degradation efficiency and the pH depends on the presence of the salts. The inhibition of the OG by the salts are best at high pH value.

REFERENCES

1. Chang, M.H., H.Y. Shu, T.H. Tseng and H.W. Hsu, 2013. Supported Zinc Oxide Photocatalyst for Decolorization and Mineralization of Orange G Dye Wastewater under UV365 Irradiation. *International Journal of Photoenergy*, 2013: 1-12.
2. López Cisneros, R., A. Gutarra Espinoza and M. Litter, 2002. Photodegradation of an Azo Dye of the Textile Industry. *Chemosphere*, 48 (4): 393-399.
3. Thennarasu, G., S. Kavithaa and A. Sivasamy, 2012. Photocatalytic Degardation of Orange G Dye Under Solar Light Using Nanocrystalline Semiconductor Metal Oxide. *Environmental Science and Pollution Research*, 19 (7): 2755-2765
4. Kant, R., 2012. Textile Dyeing Industry an Environmental Hazard. *Natural Science*, 4 (1): 22-26.
5. Fu, Y. and T. Viraraghavan, 2001. Fungal Decolorization of Dye Wastewaters: A Review. *Bioresource Technology*, 79 (3): 251-262.
6. Niu, C., Y. Wang, X. Zhang, G. Zeng, D. Huang, M. Ruan and X. Li, 2012. Decolorization of an Azo Dye Orange G in Microbial Fuel Cells Using Fe(II)-EDTA Catalyzed Persulfate. *Bioresource Technology*, 126: 101-106.
7. Xu, M., J. Guo, G. Zeng, X. Zhong and G. Sun, 2005. Decolorization of Anthraquinone Dye by *Shewanella Decolorationis* S12. *Applied Microbiology and Biotechnology*, 71 (2): 246-251.
8. Hachem, C., F. Bocquillon, O. Zahraa and M. Bouchy, 2001. Decolourization of Textile Industry Wastewater by the Photocatalytic Degradation Process. *Dyes and Pigments*, 49 (2): 117-125.
9. Z. Wang, K. Huang, M. Xue and Z. Liu, 2011. Textile dyeing wastewater treatment. INTECH Open Access Publisher.
10. Danwittayakul, S., M. Jaisai and J. Dutta, 2014. Efficient Solar Photocatalytic Degradation of Textile Wastewater Using ZnO/ZTO Composites. *Applied Catalysis B: Environmental*, 163: 1-8.
11. Tang, C.W., 2013. Study of Photocatalytic Degradation of Methyl Orange on Different Morphologies of ZnO Catalysts. *Modern Research in Catalysis*, 2 (2): 19-24.
12. Wang, Y., 2000. Solar Photocatalytic Degardation of Eight Commercial Dyes in TiO₂ Suspension. *Water Research*, 34(3):990-994.
13. Devi, L. and R. Kavitha, 2013. A Review on Non Metal Ion Doped Titania for the Photocatalytic Degradation of Organic Pollutants Under UV/Solar Light: Role of Photogenerated Charge Carrier Dynamics in Enhancing the Activity. *Applied Catalysis B: Environmental*, 140: 559-587.
14. Yu, H., R. Liu, X. Wang, P. Wang and J. Yu, 2012. Enhanced Visiblelight Photocatalytic Activity of Bi₂WO₆ Nanoparticles by Ag₂O Cocatalyst. *Applied Catalysis B: Environmental*, 111: 326-333.
15. Guillard, C., H. Lachheb, A. Houas, M. Ksibi, E. Elaloui and J. Herrmann, 2003. Influence of Chemical Structure of Dyes, of pH and of Inorganic Salts on Their Photocatalytic Degradation by TiO₂ Comparison of the Efficiency of Powder and Supported TiO₂. *Journal of Photochemistry and Photobiology A: Chemistry*, 158 (1): 27-36.
16. Wiszniowski, J., D. Robert, J. Surmacz-Gorska, K. Miksch, S. Malato and J. Weber, 2004. Solar Photocatalytic Degradation of Humic Acids as a Model of Organic Compounds of Landfill Leachate in Pilot-Plant Experiments: Influence of Inorganic Salts. *Applied Catalysis B: Environmental*, 53 (2): 127-137.
17. Bahnemann, D.W., J. Cunningham, M.A. Fox, E. Pellizetti, P. Pichat, N. Serpone, N., R.G. Zeep, G.R. Helz and D.G. Crosby, 1994. *Aquatic surface photochemistry*. Lewis Publishers.
18. Rincon, A. and C. Pulgarin, 2004. Effect of pH, Inorganic Ions, Organic Matter and H₂O₂ on E. Coli K12 Photocatalytic Inactivation by TiO₂ Implications in Solar Water Disinfection. *Applied Catalysis B: Environmental*, 51 (4): 283-302.
19. Butler, E. and A. Davis, 1993. Photocatalytic Oxidation in Aqueous Titanium Dioxide Suspensions: The Influence of Dissolved Transition Metals. *Journal of Photochemistry and Photobiology A: Chemistry*, 70 (3): 273-283.
20. Akpan, U. and B. Hameed, 2009. Parameters Affecting the Photocatalytic Degradation of Dyes Using TiO₂-Based Photocatalysts: A Review. *Journal of Hazardous Materials*, 170(2): 520-529.