Effect of sonication on ZnO and ZnO-Fe catalyst for colour and COD removal from Methylene Blue solution

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Abstract. Textile and cosmetics industries are among the industries which produce huge volume of dyes wastewater. Photocatalysis is of the methods that effectively treating dye wastewater. Semiconductor such as zinc oxide (ZnO) is one of the photocatalyst which is widely used in photocatalysis treatment method. In this research, removal of chemical oxygen demand (COD) and colour from Methylene Blue (MB) solution using ZnO were compared with ZnO doped with Fe. In addition, ultrasonic cavitation was also applied during the preparation of the catalyst. The catalysts were successfully synthesized through sol-gel method. By comparing all catalysts, sonocatalyst ZnO doped Fe produced the highest efficiency for colour removal. During the experiments, the colour removal from MB solution with 10 ppm and 30 ppm concentration were 99.65% and 51.3% respectively. This study concluded that the presence of ultrasonic cavitation during the catalyst preparation did change the physical and chemical characteristics of ZnO doped Fe. As a result, the catalyst worked better during the treatment system to remove colour from MB solution.

1. Introduction

Many types of catalyst have been used by researchers to treat different kind of wastewater using varieties of treatment methods. Few of the examples are nano-zero valent iron (NZVI) to treat palm oil mill effluent (POME) using Fenton process [1] and manganese oxide [2] to treat dye wastewater using microbial fuel cell.

Zinc Oxide (ZnO) is a photocatalyst which is very popular in wastewater treatment process. ZnO are cheap, environmentally friendly as well as biocompatible. Zinc Oxide is a semiconductor which have a band gap of 3.37 eV [3] and a large excitation binding energy of 60 meV [4] which indicates it is able to activate photocatalytic activity under visible light region.

When ZnO nanoparticles exposed to sunlight, the nanoparticles absorb sufficient photon energy which exceeds its own band gap energy. The ZnO nanoparticles will form electron-hole pair when they absorb enough energy from the sunlight and form O2− and OH radicals. Formed O2− and OH radicals can convert organic substances and pollutants into harmless compounds for example, H2O and CO2 which can be degrade easily.

Furthermore, ZnO nanoparticles could doped with Fe ions to decrease the band gap energy by forming electron traps, thus the charge separation between hole and electron can be improve. The optical
properties of ZnO also improved after being doped with Fe. Due to its high compatibility, Fe is widely used to dope with ZnO nanoparticles [5].

Expansion and destruction of tiny air bubbles during sonolysis create high temperature and pressure. Due to this, the characteristics of produced ZnO or ZnO doped Fe might change when they are expose to ultrasonic cavitation during the preparation process. Hence, this study will investigate the effect of ultrasonic cavitation on the ZnO and ZnO dope Fe in removing the COD and colour from MB solution.

2. Methodology

2.1 Raw materials and chemicals
Zinc Acetate Dehydrate (Zn (CH\(_2\)COO)\(_2\)2H\(_2\)O) and Iron (II) Sulphate (FeSO\(_4\)7H\(_2\)O) were purchased from the R&M Chemical, Malaysia while the Ethanol (C\(_2\)H\(_6\)O) (96%) was obtained from Quality Reagent Chemical (QReC). Deionized water was prepared for experiments purposes.

2.2 Preparation of ZnO and Fe-ZnO nanoparticles
ZnO and ZnO doped Fe nanoparticles powders with weight composition of Zn(1– x)Fe\(_x\)O, [x = 0, 1%] were synthesized by a sol–gel method. Stoichiometry amount of Zinc Acetate and Iron (II) Sulphate were synthesized according to Zn(1–x)Fe\(_x\)O [x = 0, 1%]. The mixture was dissolved with 50ml ethanol and stirred thoroughly until the solutes were dissolved completely. Then, the solution was stirred for 45 minutes. In this stage, 1M of NaOH was titrated into the solution until pH 9 was obtained. The solution was stirred for another 1 hour under room temperature. At this stage, the solution was sonicated using Utrasonic Homogenizer instead of using the magnetic stirrer when ZnO and ZnO doped Fe sonocatalyst to be produced. Next, the solution was leaved for 24 hours undisturbed under room temperature. Precipitates which formed and settled at the bottom of the beaker were collected and repeatedly washed with deionized water. The washed precipitates were poured onto a petri dish and dried in an oven at 80°C for 24 hours to drive off the solvents. Next, the produced dried powder was calcinated for 4 hours under 500°C.

2.3 Colour removal study
30 mg of silent and sonicated ZnO and ZnO doped Fe nanoparticles was added into 300 ml of two different concentration of methylene blue aqueous solution (10mg/L and 30mg/L). The mix solutions were stirred continuously under the sunlight for 3 hours. 5 ml of MB solution was collected at a regular interval of 30 min. Collected samples were tested for its colour concentration. Spectra measurement was done on the degraded solution by using GENESYS UV spectrometer. The absorption spectra were then recorded and the rate of decolorisation was observed in terms of change in intensity at \(\lambda_{\text{max}}=664\text{nm}\).

3. Result and Discussion
At lower MB concentration, results show that the colour removal efficiency for all catalysts were increasing over time. After 30 minutes of treatment, about 32% to 45% of colour was removed from the MB solutions. More colour was removed as the treatment continues. The degradation efficiency showing a plateau trend towards the end of the treatment process because the active sites of the catalysts reduced over time thus decreased the active sites available to react with the dye particulate. However, all catalysts were able to reach a degradation efficiency above 90% at the end of the experiment. However, sonicated ZnO doped Fe catalyst shows the best result when approximately 99% of the colour was removed after 3 hours of treatment. The colour removal efficiency from MB solution (10 ppm) using different type of ZnO catalyst is shown in figure 1.
Initially, the colour removal efficiency shows a similar result although more concentrated MB solution (30 ppm) were used in the treatment process. However, the removal efficiencies were not increase although the treatment was prolonged for 3 hours. One of the reasons that the degradation efficiencies were stagnant after 30 minutes was due to the high concentration of the methylene blue solution which contains higher amount of dye particulate. This high amount of dye particulate quickly covered all the active sites of the catalysts in the early of the experiment and causes the degradation efficiency decreases greatly. In addition, limited sunlight irradiation received by catalyst due to concentrated coloured solution also contributed to this problem. The colour removal efficiency from MB solution (30 ppm) using different type of ZnO catalyst is shown in figure 2.

**Figure 1.** Colour degradation of Methylene Blue (10ppm).

**Figure 2.** Colour degradation of Methylene Blue (10ppm).
Similar trend was also noticed for COD removal where ZnO doped Fe worked better compared to ZnO during the treatment. Almost 90% of COD was removed especially when sonicated ZnO doped Fe we used during the treatment. Presence of small concentration of Fe ions which can function as photo-generated hole and trap, helping the recombination of hole-electron [6] (Zhou et al., 2005). These ions can react with oxygen and hydroxyl ions adsorbed onto the catalyst surface and produce superoxide (O$_2^-$) and hydroxyl (OH) radicals. With higher concentration of these radicals in the methylene blue solution it can react with more of the dye particles thus increases the degradation efficiency.

In addition, with its alternated physical and optical characteristics due to synthesizing with ultrasound irradiation and addition of Fe ions presence in the nanoparticles, the sonicated ZnO doped Fe was able to increase the surface area for the reaction. Thus, more superoxide (O$_2^-$) and hydroxyl (OH) radicals were produced. Ba-Abbad et. al. [7] reported that both ZnO and ZnO doped Fe which are not exposed to ultrasonic cavitation were mostly in spherical shape. However, the photocatalyst ZnO doped Fe was less agglomeration compare to photocatalyst ZnO. While for sonicated type, ZnO was in hexagonal rod shaped and most of the ZnO doped Fe nanoparticles were in flaky shapes [8].

4. Conclusion
The capability of ZnO to produce superoxide (O$_2^-$) and hydroxyl (OH) radicals was increased when Fe was doped into the catalyst. The potential of ZnO doped Fe was further enhanced when it was exposed to ultrasonic cavitation during the preparation process. As the catalyst need sufficient sunlight, ZnO doped Fe produced its best result when it treat less concentrated MB solution.

Reference
[1] Ong Y P, Ho L N, Ong S A, Banjuraizah J, Ibrahim A H, Thor S H & Yap K L 2021 A highly sustainable hydrothermal synthesized MnO$_2$ as cathodic catalyst in solar photocatalytic fuel cell Chemosphere 263 128 - 212
[2] Taha M R, Ibrahim A H, Amat R C & Azhari A W, 2014 ScieTech 495 (Institute of Physics Publishing) 012010
[3] Shohel M, Miran M S, Susan M A B H & Mollah M Y A 2016 Calcination temperature-dependent morphology of photocatalytic ZnO nanoparticles prepared by an electrochemical–thermal method Res Chem Intermediat 42(6) 5281–5297
[4] Ong C B, Ng L Y & Mohammad A W 2018 A review of ZnO nanoparticles as solar photocatalysts: Synthesis, mechanisms and applications Renew Sust Energ Rev 81 536–551
[5] Li C, Banerjee P, Maitra S, Liu X, Swihart M T & Chakrabarti S 2015 Synthesis of iron-doped zinc oxide nanoparticles by simple heating: influence of precursor composition and temperature Int J Mater Eng Innov 6(1) 18
[6] Zhou M, Yu J, Cheng B, & Yu H 2005 Preparation and photocatalytic activity of Fe-doped
mesoporous titanium dioxide nanocrystalline photocatalysts *Mater Chem Phys* 93(1) 159–163

[7] Ba-Abbad M M, Kadhum A A H, Mohamad A B, Takriff M S, & Sopian K 2013 Visible light photocatalytic activity of Fe$^{3+}$ doped ZnO nanoparticle prepared via sol–gel technique. *Chemosphere* 91(11) 1604–1611

[8] Anirban R, Sobhan G, Saikat M & Sampa C 2015 Sonochemical Synthesis and Characterization of Iron (Fe) Doped Zinc Oxide (ZnO) Nanoparticles *NANOSPECTRUM: A Current Scenario* 55–61