The effect of iron doping on ZnO catalyst on dye removal efficiency

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Abstract. Dyes often being used in many manufacturing processes. Hence, the wastewater resulted from the manufacturing process contain colour which need to be removed before being emitted into any water bodies. Photocatalysis is a method which effectively treating wastewater using photocatalyst. ZnO is an example of semiconductor material which is use as a photocatalyst in the treatment method. Doping with transition metals can improve its properties to maximize its photocatalytic efficiency. In this study, the effect of zinc oxide (ZnO) and zinc oxide doped Fe (ZnO/Fe) photocatalyst for dye removal efficiency were investigated. The photocatalysts were successfully synthesized through sol-gel method and characterized by SEM, FTIR and EDX. The photocatalytic efficiency of ZnO and ZnO/Fe was studied by degrading methylene blue (MB) under the exposure of 3 hours of sunlight with varies operational condition. Optimal photocatalytic efficiency operating parameters were performed by Design Expert 10 using the Response Surface Method (RSM). ZnO appeared as regular shape compared to ZnO/Fe which most of the particles had clumped together. The removal efficiency of MB was increase when the dosage of catalyst increased. However, once the optimum dosage of catalyst exceeded, the removal efficiency of MB reduced. During the experiment, 30 mg of ZnO was capable to remove 90% of MB from the solution. While, ZnO/Fe exhibited better result as it could remove up to 95% of MB using only 10 mg of ZnO/Fe during the treatment. It can be concluded that doping the ZnO with Fe could improve the catalytic ability of ZnO to degrade MB in wastewater.

1. Introduction
Many industries consume a substantial amount of water in its manufacturing processes. The water mainly used in the dyeing and finishing operations of the products. Discharge of poorly treated dye wastewater into the environment could cause serious environmental issues and create public health problems [1]. In most factories, conventional treatment method such as activated sludge process is used to treat dye wastewater. However, due to its high stability, complex dyes required advanced treatment to ensure the complete removal of dyes from the wastewater.

Photocatalysis in one of the advanced treatment methods used to treat dye wastewater [2]. Many types of catalyst have been tested and ZnO is one of the proven effective photocatalyst in treating dyes wastewater [3]. ZnO has been reported to have stable wurtzite structure with the bad gap of 3.3 eV in room temperature [4] and large excitation binding energy (60 meV) [5]. Due to these characteristics, ZnO act better as a catalyst compare to other metal oxide.
However, because of the wide band gap of ZnO, the high chance of faster e⁻ and h⁺ recombination causes it weak in trigger the photocatalytic activity while in visible light region. Also, ZnO has a low quantum yield in photocatalytic reactions in aqueous solutions, which can obstruct the photocatalytic degradation process. Hence, doping the ZnO nanoparticles with iron ions can reduce the band gap of ZnO, and improve the chance of forming superoxide anion radicals (·O₂⁻) and hydroxyl radicals (·OH).

In this research, the main aim of this research was to find out the photocatalytic degradation efficiency of ZnO and ZnO nanoparticles doped Fe by degrading methylene blue. The characteristics of ZnO and ZnO doped Fe in terms of structure, morphology and size were studied in detail. Meanwhile, the photocatalytic degradation efficiency, chemical oxygen demand (COD) removal efficiency and adsorption capacity of ZnO and ZnO doped Fe in methylene blue with the effect of dosage photocatalyst and initial concentration of dye were examined in detail. Finally, the whole relationships were used to determine the optimum operating parameters to obtain maximum degradation of methylene blue using design of experiment (DOE).

2. Methodology

2.1. Materials and chemicals
Zinc acetate dehydrate (Zn (CH₂COO)₂·2H₂O) and iron (II) sulphate (FeSO₄·7H₂O) were purchased from the R&M Chemical, Malaysia. Ethanol approximate 96% (C₂H₅O) was obtained from Quality Reagent Chemical (QReC) Company. No purification was done when using these chemicals. Deionized water was used in all conducted experiments.

2.2. Preparation of ZnO and Fe–ZnO nanoparticles
ZnO and ZnO doped Fe nanoparticles powders with 1g of weight composition of Zn(1–x)FeₓO [x = 0, 5%] were synthesized by a sol–gel method. Stoichiometry amount of zinc acetate and iron (II) sulphate were synthesized according Zn(1–x)FeₓO [x = 0, 5%]. Then the mixture was dissolved with 50 ml ethanol and stirred thoroughly until the solutes were dissolved completely. Then, the solution was stirred for 45 minutes in room temperature. In this stage, 1M of NaOH was titrated into the solution until pH 9 was obtained. After 45 minutes, the solution was stirred for another 1 hour under room temperature. After that, the solution was left for 24 hours undisturbed in room temperature. Then, the precipitation was formed at the bottom of container, then it was repeatedly washed with deionized water. After that, the washed precipitation was poured onto a petri dish and dried in an oven at 80°C for 24 hours to drive off the solvents. After that, the dry powder was going calcination under 500 °C to get nanoparticles.

2.3. Characterization study on photocatalyst
The quality and composition of the synthesized samples nanostructures were determined by the FTIR (Perkin Elmer spectrophotometer) in the range of 400–4000 cm⁻¹. The morphology and structure of the samples were characterized by using scanning electron microscopy (SEM) equipment (Hitachi TM 3000). Elemental analysis in terms of weight composition and atomic weight composition of the synthesized sample was carried out using an energy-dispersive X-ray spectrocope (EDX) (Hitachi TM 3000).

2.4. Photocatalytic degradation study
The photocatalytic activity of ZnO and ZnO doped Fe nanopowders was studied by degradation of methylene blue (MB) in continuous stirring solution under sunlight (UV light) at ambient temperature. Different dosage of photocatalysts was added to MB aqueous solution (10 ppm). To achieve the adsorption-desorption equilibrium, the sample solution was left in darkness for 20min with magnetic before being exposed to the sunlight radiation. 5ml of reaction mixture was collected at a regular interval of 30 min for a period of 3 hours.
Spectra measurement was done on the degraded solution by GENESYS UV spectrometer. The absorption spectra were then recorded and the rate of decolorisation was observed in terms of change in intensity at \( \lambda_{\text{max}} = 664 \) nm. The efficiency of degradation was calculated as in equation (1):

\[
\% \text{ Photocatalytic efficiency} = (C_0 - C_t/C_0) \times 100
\]  

(1)

Where:

- \( C_0 \) = initial concentration of MB dye in aqueous solution
- \( C_t \) = final concentration of MB at time of \( t \)

2.5. Chemical Oxygen Demand (COD) removal

The chemical oxygen demand (COD) use to determines amount of oxygen need to oxidize the organic matter in the sample solution. First, 2.5ml of sample solution was mixed with 3.5ml of sulphuric acid (H\(_2\)SO\(_4\)) and 1.5ml of potassium dichromate (low range) (K\(_2\)Cr\(_2\)O\(_7\)) in a vial, then it was heated up to 150 °C in a COD reactor for 2 hours. Afterwards, the sample was allowed to cool down in room temperature. The blank reagent was initially prepared by using distilled water to zero the reading in the COD spectrometer. The COD reading of sample was get from COD spectrometer (HACH DR 2800). The COD removal efficiency was calculated by using the equation (2).

\[
\text{COD Removal} \% = (1 - (\text{COD}_0 / \text{COD}_t)) \times 100\%
\]  

(2)

Where:

- \( \text{COD}_0 \) = COD value of the sample before testing
- \( \text{COD}_t \) = COD value of the sample after treatment

3. Result and discussion

3.1. Characteristics of ZnO and ZnO/Fe

The chemical composition of synthesized ZnO and ZnO/Fe were analysed by Fourier transform infrared (FTIR) spectroscopy as shown in Figure 1 and Figure 2. The peaks appeared at 540\,cm\(^{-1}\) and 543\,cm\(^{-1}\) in both Figure 1 and Figure 2 indicated the Zn-O, Fe-O, Zn-O-Fe and Zn-O-Zn bonds stretching which confirmed the formation of ZnO and ZnO/Fe from the ions zinc acetate and iron (II) sulphate [6]. This narrowing of peak at 543\,cm\(^{-1}\) in Figure 1 was the result of Zn-Fe-O lattice vibration. The peaks at 903 cm\(^{-1}\) and 937 cm\(^{-1}\) in both Figure 1 and Figure 2 indicated C-O-C bond stretching which mean the integration Zn ions and Fe ions respectively [7].

Meanwhile, the wide peaks at 1454 cm\(^{-1}\) in Figure 1 and narrowed 1380cm\(^{-1}\) in Figure 2 indicated the C-O bond stretching. In Figure 1, the peak at 1631 cm\(^{-1}\) indicated the formation of ZnO [8]. There was an O-H bond which gave a very broad signal on IR spectrum which appeared in the range from 2900 cm\(^{-1}\) to 3500 cm\(^{-1}\). It was due to oxygen which was more electronegative while the hydrogen became more electropositive on the other side of the bonding. Due to this, oxygen and hydrogen will be attracted by another hydrogen and oxygen respectively with resulting the original O-H bond itself weaken. So, different amount of weaken O-H bond gave different signal on IR spectrum which resulted a broad signal that overlapped over the C–H stretching (sp3 hybridize) at the range of 2800 cm\(^{-1}\) to 3000 cm\(^{-1}\)[9].
To ensure that the synthesized ZnO and ZnO doped Fe did not had any impurities, EDX was used to measure the compositions of the sample. From the Figure 3, elemental analysis showing there was no appearance of other peaks except of Zn and O were found, it was confirmed that was pure ZnO without any impurities infiltration. All the EDX spectral peak of O could be found at 0.5 keV, meanwhile Zn appears at 1 keV and 8.6 keV. The weight percentages (wt %) of Zn and O were 83.17% and 16.83% respectively without other element content. The atomic percentages (at %) of Zn and O were 54.74% and 45.26% respectively.

In Figure 4, once again the analysis of EDX was confirmed there was no other impurities inside ZnO doped Fe except for O, Zn and Fe. There were three different spectral peak which indicated element Zn, O and Fe. The spectral peak of O could be found at 0.5 keV, spectral peak of Zn appeared at 1 keV and 8.6 keV while Fe signal appears at 0.7 keV and 6.4 keV. The weight concentration (wt %) of Zn, O and Fe were 73.49%, 20.34% and 6.17% respectively. It shown that more Fe was doped on ZnO surface which increasing the Fe concentration in the sample which contained more than 5% of Fe. Meanwhile, the results shown the atomic wt% compositions of Zn, O and Fe were 44.85%, 50.73% and 4.41% respectively.
In Figure 5, ZnO appeared to be more evenly dispersed, and the size of the particles were fine, and the aggregated particles are not particularly large. Compared with ZnO, the particles of ZnO/Fe in Figure 4 polymerize into a large block and are unevenly distributed.

3.2. Effect of dosage on the photocatalytic efficiency

Figure 7, it shows that 30 mg of ZnO was the optimum dosage use to obtain the highest degradation efficiency of ME. The figure also shows that 10 mg and 20 mg of ZnO managed to degrade about 92% and 96% of 10ppm of dye. By increasing the dosage of photocatalyst, the number of the active site was also increased, and more sites were exposed to photon energy from sunlight hence generated more OH• and boosted the photocatalytic process [10].

Figure 8 shows that at dosage of 10 mg, 20 mg and 30 mg of ZnO/Fe, the degradation efficiency of MB was almost the same. The degradation efficiency was increased from 98% to 99% when using 10 mg to 20 mg of ZnO/Fe. This initial result shows that by increasing the ZnO/Fe catalyst in the treatment, the degradation efficiency could be improved.

However, further increment of ZnO/Fe could deter the degradation of MB inside the solution. The degradation efficiency was decreasing to 96% when 30 mg of ZnO/Fe was used during the treatment. In expectation, increasing dosage of ZnO/Fe will eventually raise the total surface area of active sites in MB solution and increased the number of hydroxyl and superoxide radicals produced.

Unfortunately, the situation was not as expected when the photocatalytic efficiency decreased as the amount of photocatalyst used was increased. It was believed that when dosage of photocatalyst exceeded the optimum value, the reverse effect happened. When the presence of catalyst was too much
inside the treatment system, the transmittance of sunlight to the active site might reduce and affected the production process of superoxide anion radicals (O$_2^-$) and hydroxyl radicals (OH).

![Figure 7. Photocatalytic efficiency against dosage of ZnO.](image1)

![Figure 8. Photocatalytic efficiency against dosage of ZnO/Fe.](image2)

3.3. Effect of initial dye concentration on photocatalytic efficiency

According to Figure 9, it showed that the initial concentration of the solution affected the degradation efficiency of methylene blue (MB). The trend shows that the degradation efficiencies of MB was decrease when the initial concentration was increased. It was obviously shown when the MB concentration was increase from 10 ppm to 30 ppm. The overall photocatalytic efficiency decreased because most of the dye particulate had covered up the ZnO surface and it reduced transmittance of sunlight to the active site hence reduced the production of the radicals. Hence, ZnO can only degraded certain amount of MB particulate since there was limited active sites of ZnO existed inside the solution could generate hydroxyl radicals [11].

In general, the ZnO worked better in treating low dye concentration which was 10ppm because the availability of surface of photocatalyst was not covered by dye particulate so the ZnO could operating at maximum efficiency. Compare to treatment of 30 ppm of MB dye, the excess untreated dye particulate started to accumulate on the surface of ZnO which restrained the photocatalytic process.

Figure 10 shows the initial concentration of dye had an impact on the ability of ZnO/Fe to degrade the MB. Similar trend was observed where the degradation efficiencies was decrease when the initial concentration was increased. In comparison, ZnO/Fe reduced only 60% while ZnO reduced up to 80% of 30 ppm MB. This may be explained there was too many dye molecules existed in that particular MB solutions which occupied the active sites of ZnO/Fe and slowing down of the generation of radicals to degrade the dye.

This situation even worse when the initial MB concentration was high because high amount of MB particulate remained in solution without treated will make the solution darker and inhibit the sunlight to pass through the dye solution and illuminate the surface of ZnO/Fe [12, 13]. Consequently, the promotion of electron to empty conduction band (CB) was more difficult because lesser photon energy than the excitation energy (Eg). Failure promotion of electron will fail to further produces electron-hole that can undergoes further process to degrade the dye, which decreased the photocatalytic efficiency at the end.

Therefore, 10 ppm which represented lower dye concentration was easier to treat by ZnO/Fe due to lighter colour of the dye solution which allowed the penetration of sunlight through the solution. Furthermore, low concentration of dye will also reduce the attachment of MB particulate onto ZnO/Fe and resulted more active sites could generate more hydroxyl radicals to treat the dye.
4. Conclusion
The ZnO and ZnO/Fe nanoparticles had successfully synthesized by the sol-gel method. The EDX analysis was confirmed that Fe was successfully doped into ZnO nanoparticles. Meanwhile, FTIR analysis were proved that Zn-O and Zn-O-Fe bonds existed in ZnO and ZnO/Fe respectively. In addition, ZnO appeared to be fine particles compared to ZnO/Fe which the particles had clumped together and in irregular shape. It was expected had a weak photocatalytic efficiency because most of the surface had been saturated. With the dosage of ZnO increased up to 30mg, the overall photocatalytic efficiency increased and achieve 95% and above because the total active sites generation of hydroxyl had increased. ZnO/Fe achieved the best photocatalytic efficiency by using 10 mg to treat the dye. Further addition of ZnO/Fe into dye solution will decreased its efficiency. Meanwhile when initial concentration of dye increased, the photocatalytic efficiency decreased due to excessive MB particulate accumulated in the solution which will scatter the sunlight. Both ZnO and ZnO/Fe having low efficiency when treating the dye concentration at 30ppm compared to 10ppm which both photocatalytic efficiencies performed by both photocatalyst were both achieved 95% and above in overall.

Acknowledgement
The authors would like to thank Universiti Malaysia Perlis (UniMAP) for the financial support towards this study.

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