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SYNTHESIS OF ZnO-AC COMPOSITE AND ITS USE IN REDUCING TEXTILE DYES CONCENTRATIONS OF METHYLENE BLUE AND CONGO RED BY PHOTODEGRADATION

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ABSTRAK: Telah dilakukan penelitian mengenai minimalisasi konsentrasi zat warna tekstil metilen biru (MB) dan congo red (CR) melalui fotodegradasi menggunakan komposit ZnO-Arang aktif (ZnO-AC). Penelitian meliputi sintesis seng oksida (ZnO) dengan berbagai rasio pelarut (air:etanol), pembuatan komposit ZnO-AC, dan penerapan komposit untuk mengurangi konsentrasi MB dan CR dalam limbah buatan melalui proses fotodegradasi. Karakterisasi dari partikel ZnO hasil sintesis dilakukan dengan Fourier Transformed Infra Red (FTIR), X-Ray Diffraction (XRD), dan Scanning Electron Microscope (SEM). Fotodegradasi zat warna tekstil MB dan CR dilakukan dengan memaparkan campuran zat warna dan komposit di bawah radiasi sinar ultraviolet. Intensitas warna sebelum dan sesudah fotodegradasi ditentukan dengan menggunakan spektrofotometer sinar tampak. Hasil menunjukkan bahwa semakin besar rasio pelarut air:etanol yang digunakan dalam sintesis ZnO, semakin mudah, cepat dan semakin banyak jumlah ZnO yang terbentuk. Spektra FTIR dari ZnO hasil sintesis menunjukkan adanya gugus fungsi Zn-O, O-H, N-H, C-H, dan C-O. Semua puncak difraksi dari ZnO hasil sintesis yang pada 2θ 31,79-31,91°, 34,45-34,57°, dan 36,27-36,40° sesuai dengan ZnO Wurtzite fase heksagonal. Karakterisasi ZnO dengan SEM menunjukkan bahwa bentuk partikel ZnO adalah bulat dan ukuran partikelnya berkisar 220,5 nm sampai 1222 nm. Bentuk partikel yang paling mendekati bulat dihasilkan oleh perlakuan sintesis dengan rasio pelarut etanol: air sebanyak 150 mL:150 mL. Persentase fotodegradasi dari MB dan CR dengan komposit ZnO-AC lebih besar dibandingkan dengan kontrol (tanpa komposit ZnO-AC), dengan persentase tertinggi diberikan oleh komposit yang terbuat dari ZnO yang disintesis dengan rasio pelarut air : etanol sebesar 150 mL:150 mL.

Kata kunci: komposit ZnO-Arang aktif, fotodegradasi, metilen biru, congo red

ABSTRACT: Research on minimization of textile dyes concentration of methylene blue (MB) and congo red (CR) through photodegradation using ZnO-Activated Carbon (ZnO-AC) composite has been done. The research included synthesis of Zinc oxide (ZnO) with various solvent ratio (water: ethanol), synthesis of ZnO - AC composite, and the application of the composite to reduce the concentrations of MB and CR in the artificial waste by photodegradation process. The characteristics of the zinc oxide particle were determined by Fourier Transformed Infra Red (FTIR), X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM). Photodegradation of the textile dyes was carried out by exposing the mixture of the dyes and the composite to the Ultraviolet light. The colour intensities before and after exposure were determined by using visible spectrophotometer. The result show that the greater the

water:ethanol ratio is used, the easier, faster and more ZnO formed. FTIR spectra of the synthesized ZnO indicate the presence of the functional groups of Zn-O, O-H, N-H, C-H and C-O. All the diffraction peaks of synthesized ZnO that located at 2θ 31.79-31.91°, 34.45-34.57°, and 36.27-36.40° are consistent with the hexagonal phase wurtzite ZnO. Characterization of ZnO with SEM show that the particle shape of the synthesized ZnO is spherical and the sizes of particles are 220,5 nm to 1222 nm. The nearest spherical shape is resulted by water:ethanol ratio of 150 mL:150 mL. The photodegradation percentages of MB and CR with ZnO-AC composite are higher than those without ZnO-AC composite, with the highest percentages given by the composite made of ZnO that is synthesized with water:ethanol ratio of 150 mL: 150 mL.

Keywords: ZnO-activated carbon composite, photodegradation, methylene blue, congo red.

1. INTRODUCTION

Environmental pollution from textile dye is continuously increasing along with the growing demand on the textile industries. Amongst so many different types of dye, methylene blue and congo red are the most frequently used. These synthetic dyes are not environmentally friendly since they are non-biodegradable, toxic, and carcinogenic. Therefore it is critically important that waste containing these dyes are treated prior to their discharge into the environment.

Photodegradation is an alternative method to minimize the dye contents from textile waste with the aid of a photo catalyst and UV light. In this report, ZnO is used as the catalyst because it has broad band gap of 3.17 eV [1-2], and high photo catalysis activity [3], and it is cheap. However, ZnO, which is a semiconductor, has a limitation in adsorbing the dye, and thus as a surface catalyst it cannot provide optimum reaction. To improve the adsorption, it is combined with activated carbon (AC). This substance can effectively adsorb synthetic organic materials including dyes, and in turn transfer them onto the ZnO. This will improve the photodegradation significantly [4].

In this research, ZnO-Activated Carbon (ZnO-AC) composite was prepared in the form of pellet to aid the separation after the degradation process. The ZnO was prepared by the precipitation method which has some advantages: it is conducted under low temperature with starting materials which are widely available [5]. $Zn(CH_3COO)_2.2H_2O$ was used as the precursor and a mixture of water and ethanol was used as the solvent. The variety of the water:ethanol ratios results in varied particle sizes of the catalyst produced.

The aims of this research are to: (i) characterize the ZnO produced using varied water:ethanol ratios, and (ii) determine the best ratio producing ZnO with best ability in degrading methylene blue (MB) and congo red (CR).

2. EXPERIMENTAL SECTION

2.1. Materials and Instrumentation

Materials: We use analytical grade of $Zn(CH_3COO)_2.2H_2O$, triethanol amine (TEA), n-propylamine, activated carbon (AC), congo red (CR), methylene blue chloride (MB), demineralised water, and 99.5% ethanol.

Instrumentation: Glass wares, refluxing apparatus, magnetic stirrer, analytical balance, oven, irradiation box with Philip TUV 15 W/ G15 T8 lamp, UV-Vis spectrophotometer (Shimadzu 1800), FTIR (Shimadzu Ir Prestige-21), X-Ray Diffraction and SEM (PEI Inspect 550).

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2.2. Procedure

The synthesis of ZnO

ZnO synthesis method in this study is modified from the Hsieh method [6]. Five portions of 0.15 mole of $Zn(CH_3COO)_2.2H_2O$ were dissolved in 90, 120, 150, 180, and 210 mL of demineralised water. Meanwhile, 5 portions of 0.30 mole of TEA and 0.30 mole n-propylamine were dissolved in 90, 120, 150, 180, and 210 mL of 99.5% ethanol. Each of the ZnO solution in 90, 120, 150, 180, and 210 mL water was then mixed with the TEA solution in 210, 180, 150, 120, and 90 mL ethanol in round bottom flask attached to a condenser to maintain vapor pressure saturation. These mixtures were labeled as P1, P2, P3, P4, and P5 and thus P1 has a water:ethanol ratio of 90:210, P2 120:180, etc. The mixtures were the refluxed for 8 hours under 65-77^{0}C.

White precipitates resulted were filtered through a glass fiber micropore filter, rinsed 3 times with ethanol to remove remaining reagents, and dried at 60^{0}C. The solids were characterized using FTIR, XRD and SEM.

Preparation of ZnO-AC composites

Into 0.75 grams of gypsum, 0.75 grams of AC and 0.425 grams of ZnO were added and mixed till homogenous. The mixture was transferred into the composite mold. One mL of demineralised water was added dropwise, molded into a 1.5x0.45 cm composite, dried, and stored in a desicator.

Photodegradation

Into six 250 mL beaker glasses, 100 mL of 100 mg/L of MB were added. One composite of P1, P2, P3, P4, and P5 was added into each beaker glass. The sixth beaker glass was used as a control and was labeled P0. They were then placed in the irradiation box, stirred and irradiated for 5 hours. The suspension were then filtered and the absorbance of the filtrates was measured at 664.2 nm (that is the λ_{max} of MB). The same process was applied to CR, with λ_{max} of 497.6 nm.

3. RESULTS AND DISCUSSION

It was apparent during the refluxing process, that the higher water:ethanol ratio was used, the faster the precipitates formed, and concequently, the more ZnO was resulted. Table 1 shows the amount (in grams) of ZnO produced as a function of water:ethanol ratios.

The theoretical yield was expected to be 12.20 grams. The P5 resulted dry solid with a mass larger than this number, presumably because of residual water or reagents entrapped in the precipitates.

The possible reaction taking place during the reflux is as follows:

- Zinc acetate was ionized in the water, while n-propylamine was hydrolysed:

  $$Zn(OAc)_2 \rightarrow Zn^{2+} + 2\ OAc^-$$

  $$C_3H_7NH_2 + H_2O \rightarrow C_3H_7NH_3 + OH^-$$

  This was supported by the pH of the mixture which ranged 8.05-8.34
- The zinc ions reacted with the hydroxide resulted to form white precipitates of zinc hydroxide which was then separated and oven dried to produce zinc oxide:

  $$Zn^{2+} + 2\ OH^- \rightarrow Zn(OH)_2$$

  $$Zn(OH)_2 \xrightarrow{\Delta} ZnO + H_2O$$

Table 1. Mass of ZnO Produced by Different Solvent Ratios

Sample	water:ethanol ratio	mass of ZnO (grams)
P1	90:210	7.7043
P2	120:180	10.2945
P3	150:150	11.3941
P4	180:120	11.6480
P5	210:90	13.6405

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The characteristics of the ZnO

The FTIR spectra of the ZnO (one of them is presented in Figure 1) resulted by the different solvent ratios reveal that they all similar, shown by the wide band absorption between 400-600 cm^{-1} indicating Zn-O stretching. Absorption at 3373 cm^{-1} shows the presence of O-H and N-H. Peaks at 2853 and 2959 cm^{-1} suggest the absorption of C-H, whose stretching vibration is shown by the valley of the band at 1412 cm^{-1}. Bands around 889 and 1575 cm^{-1} indicate the stretching of N-H, while at 1026 and 1074 the stretching of C-O. These spectra is also similar to that of commercially available ZnO, which mean that the synthesis process conducted in this research has produced the expected ZnO.

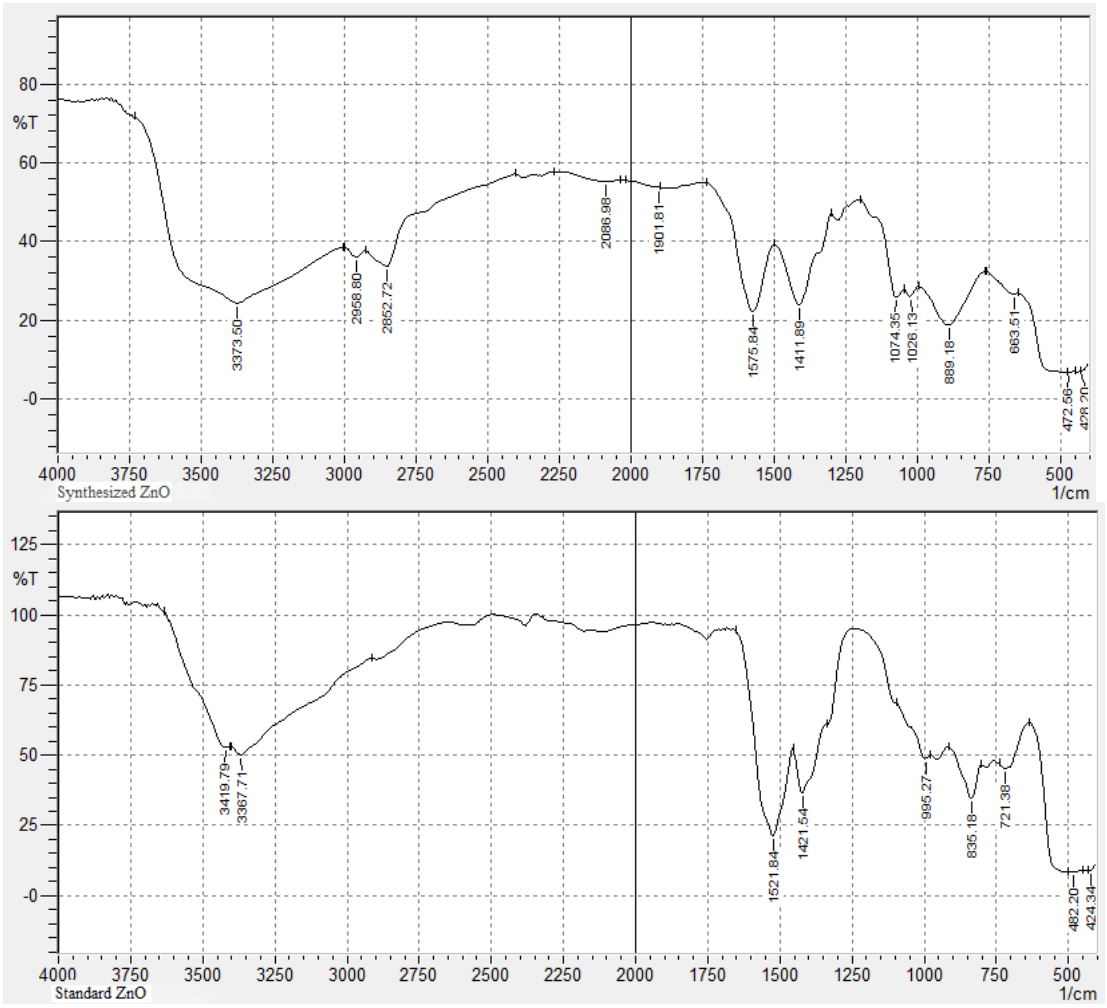

Figure 1. FTIR spectra of the synthesized ZnO (top) and the standard ZnO (bottom)

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The XRD pattern of synthesized ZnO with different solvent ratio (P1-5) were shown in Figure 2. All the diffraction peaks of synthesized ZnO are consistent with the hexagonal phase wurtzite ZnO (JCPDS No. 36-1451). The diffraction peaks of synthesized ZnO located at 31.79-31.91°, 34.45-34.57°, and 36.27-36.40°.

SEM is used to study the morphological structures and measure the diameter of particles. The characterization of the synthesized ZnO using SEM (Figure 3) suggests that all particles are spherical, with those resulted by the water:solvent ratio of 1:1 (P3) showing the most spherical and having the smallest size variation. The diameter of particles of the photocatalyst were measured to range from 220.5 to 1222 nm.

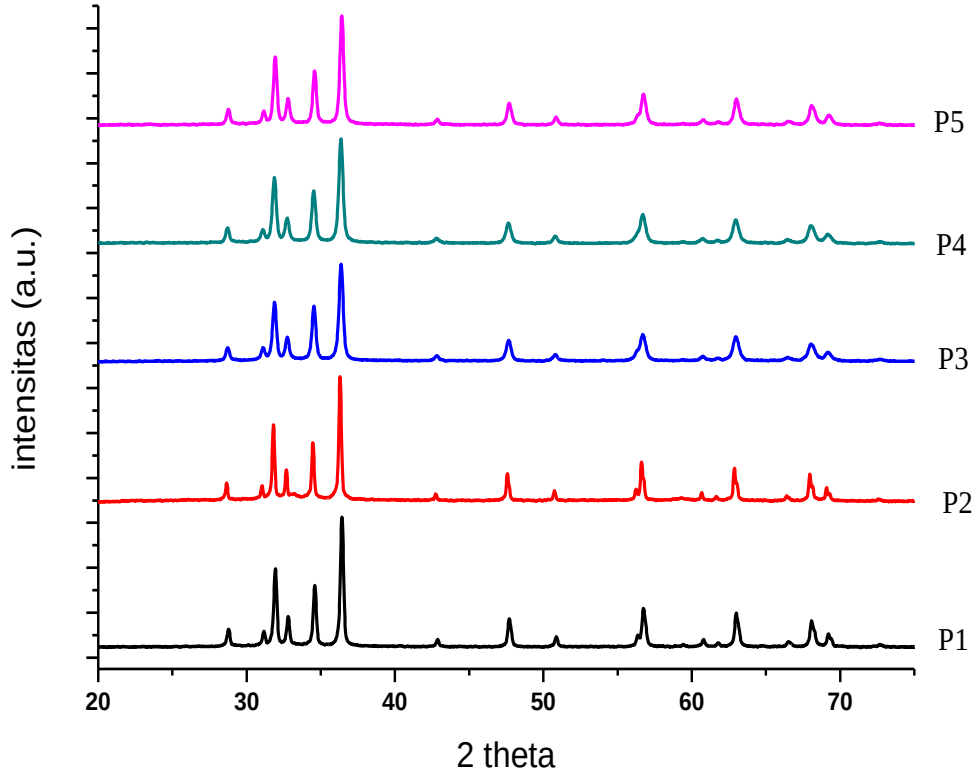

Figure 2. XRD pattern of synthesized ZnO with different solvent ratio

The photodegradation ability of the ZnO-AC composite

Figure 4 shows the photodegradation percentages of MB and CR by UV light with and without the composite. It is clear that all of the composites improve the degradation by at least a factor of five. Activated carbon (AC) assist the adsorption, and accumulate the dyes onto the composite surface. When the composite is exposed to UV light, the electron of ZnO is excited from the valence

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band to the conductance band, leaving a hole at the valence band (h_{vb}^+). The electron at the conductance band (e_{cb}^-) reacts with oxygen to form superoxide, and the hole reacts with hydroxide to form hydroxyl radical (·OH). This radical reacts with the dyes and degrades them, as the radical is produced continuously as long as the irradiation occurs. The mechanism is as follows [2,7-10]:

$$ZnO + h\upsilon \rightarrow h_{vb}^+ + e_{cb}^-$$

$$h_{vb}^+ + OH^- \rightarrow \cdot OH$$

$$\cdot OH + \text{dye} \rightarrow CO_2 + H_2O$$

The result also shows that the ZnO prepared by water:ethanol ratio of 1:1 (i.e. P3) provides the best composite, in terms of the degradation percentage achieved (76.6% for MB and 99.6% for CR).

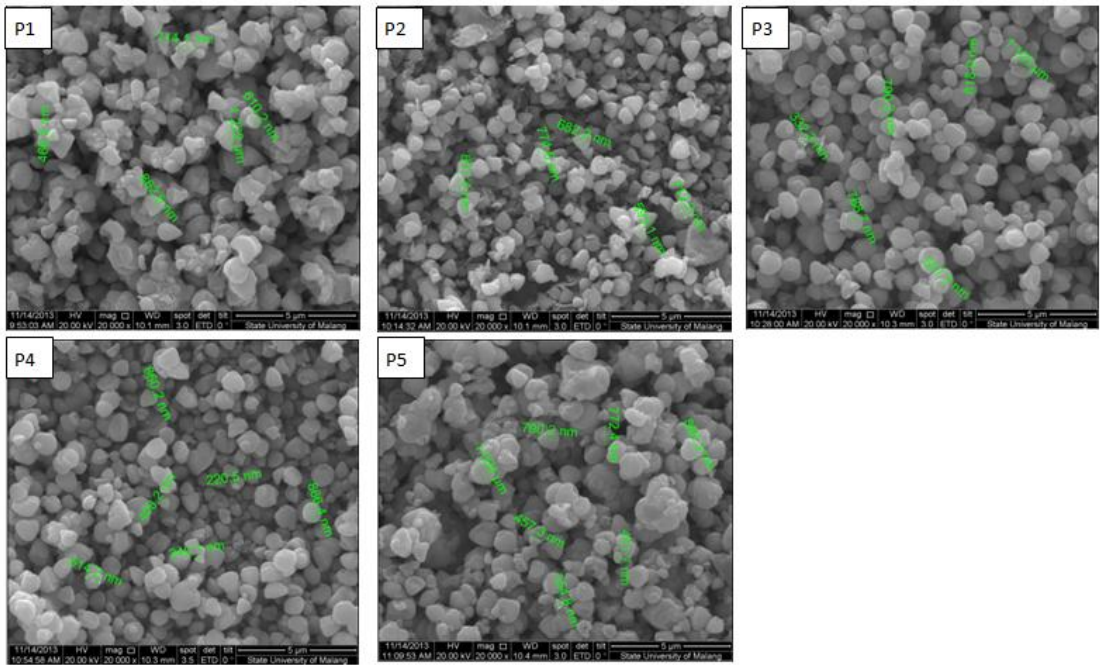

Figure 3. The morphology of synthesized ZnO with different solvent ratio, magnified 20.000x

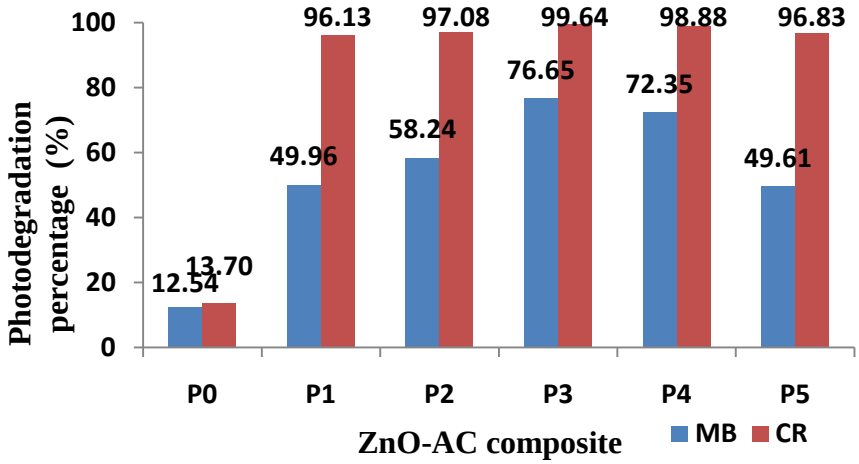

Figure 4. The photodegradation of MB and CR by UV light, with ZnO-AC composite (P1-5) and without composite (P0)

4. CONCLUSION

The ZnO synthesized in this research has the same FTIR spectra as that commercially available, thus it can be suggested that the synthesis is successful. The particles resulted are spherical with diameter varied from 220.5 to 1222 nm. Water:ethanol ratio of 1:1 (i.e. 150:150 mL ratio) results the most spherical particles with the smallest size and variation. The photocatalyst produced by this ratio also perform the best photodegradation by giving the highest percentage.

5. ACKNOWLEDGEMENTS

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