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Preparation and photocatalytic activity of hematite from iron sand modified ZnO for indigo carmine degradation

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Abstract. Modification of hematite (α -Fe₂O₃) with ZnO to produce ZnO/ α -Fe₂O₃ composites by sol gel method and their photocatalytic activity testing on the degradation of indigo carmine (IC) dye has been done. The hematite was extracted from iron sand using hydrochloric acid and precipitated using aqueous ammonia. The ZnO/α -Fe₂O₃ composites were prepared with the mole ratio of ZnO to α -Fe₂O₃ 1:1, 1:5 and 5:1. XRD pattern analysis showed that the average crystallite size of ZnO/α -Fe₂O₃ composites were greater than that of α -Fe₂O₃. The result of photocatalytic activity test showed that composite with the mole ratio of ZnO to α -Fe₂O₃ 1:5 has the highest photocatalytic activity under the optimized conditions, with the maximum degradation efficiency of IC are 91.75 % and 93.18 % under UV light and sunlight irradiation, respectively. These highest of photocatalytic activity was reached at the initial pH of dye solution =1, photocatalyst dosage of 300 mg, initial dye concentration 15 ppm and irradiation time 120 minutes under UV light and 90 minutes under sunlight irradiation.

1. Introduction

Hematite $(\alpha - Fe_2O_3)$ is the most stable iron oxide under ambient conditions, abundant in nature and has been widely used as photocatalyst [1]. Hematite exhibits chemical stability and the narrow band gap (1.9-2.2 eV) which can be used under low energy of visible light. However, the applied performance of hematite as photocatalyst is restricted by several factors including poor conductivity, photocorrosion and high rate of electron and hole recombination [2]. These disadvantage could be overcome by morphological controlled synthesis of α -Fe₂O₃, surface modification, formation of composites, and coupling by other semiconductor with higher band gap energy such as TiO₂ and ZnO. ZnO is a wide band gap semiconductor (3.37 eV), shows very strong optical properties in the UV range and widely used as photocatalyst [3]. Therefore, synthesis of composites consisting of α -Fe₂O₃ and ZnO is way interesting to combine optical properties of ZnO and magnetic properties of α -Fe₂O₃ in a single material. It has been reported that ZnO/a-Fe₂O₃ nanotube synthesized by photochemical deposition showed a much higher photocatalytic activity for methylene blue degradation compare with bare ZnO [4]. ZnO/Fe₂O₃ heterostructures prepared by atomic layer deposition of ZnO onto Fe₂O₃ nanosheets has been used as H₂S gas sensor and the response of ZnO/Fe₂O₃ heterostructures was 15-fold larger than the Fe₂O₃ and ZnO [5].

In this report, a simple method based on sol gel process using zinc acetate and hematite was employed for the formation of ZnO/α-Fe₂O₃ composites. Hematite has been extracted from iron sand by using precipitation method. The photocatalytic activity of ZnO/α -Fe₂O₃ composites were evaluated by the

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degradation of indigo carmine (IC) dye. IC is an acid dye and is categorized as a high-toxic synthetic dye that has a large application in many industries as an additive in pharmaceutical tablets and coloring agent in food [6] and as a textile dye [7].

2. Method

2.1. Preparation of ZnO/α -Fe₂O₃ composites

A certain amount of iron sand taken from Syiah Kuala Beach, Deah Raya, Aceh Province, was dissolved in 100 mL hydrochloric acid solution (6 M) with constant stirring and heating at 80°C for 30 min. The solution was filtered and aqueous ammonia was added to the filtrate solution until the pH reaches 6 at which a brown iron (III) hydroxide precipitate is obtained. The precipitated was filtered, dried and calcined in air at 700°C for 5 h at which transformed into hematite (α -Fe₂O₃) [8]. A quantity of Zn(CH₃COO)₂.2H₂O was disolved in ethanol at room temperature and hematite was added to the solution under continuous stirring for an hour and triethanolamine was put into it drop by drop. The mole ratio of triethanolamine to Zn(CH₃COO)₂.2H₂O was 1.0, while the mole ratio of Zn(CH₃COO)₂. 2H₂O to α -Fe₂O₃ were 1:1, 1:5 and 5:1. The reaction mixture was maintained at room temperature and was aged for 24 h. The obtained materials was filtered followed by drying in the oven at 80 °C for 5 h and finally was calcined in air at 700 °C for 5 h. The samples was designated as ZnO/ α -Fe₂O₃(X) where X corresponds to different mole ratio of ZnO to α -Fe₂O₃.

2.2. Characterization of ZnO/α -Fe₂O₃ composites

The X-ray diffraction (XRD) patterns of the samples were recorded on a Shimadzu X-ray diffractometer, equipped with Cu-K α radiation ($\lambda = 0.154056$ nm) employing a scan rate 5° min⁻¹ at a 2 θ from 10 to 80°. The samples also were analyzed by scanning electron microscopy using SEM JEOL microscope model JSM6510LV.

2.3. Photocatalytic degradation

The photocatalytic activity of the prepared samples was evaluated by determining indigo carmine degradation in aqueous solution. The photocatalytic degradation was conducted under UV irradiation with constant stirring of the solution mixture and ZnO/ α -Fe₂O₃ composite. At the first step, the mixture was magnetically stirred in the dark for 30 min to establish the adsorption-desorption equilibrium followed by exposing to the UV light by using 6 W UV lamp (λ = 365 nm) which was located 10 cm from the Pyrex glass vessel for certain interval time. The experiments were conducted on the different of initial pH of dye solution which was adjusted by addition of either 0.1 M HCl or 0.1 M NaOH solutions, photocatalyst dosage, initial dye concentration and irradiation times. The IC suspension was collected after regular intervals during the irradiation times and centrifuged for 10 min to completely remove the photocatalyst. The concentration IC dye in the solution was determined with a UV-Vis spectrophotometer (Shimadzu UV mini 1240) at $\lambda_{max} = 610$ nm. The percentage of IC degradation (D%) was calculated using the formula of Eq. (1).

IC Degradation % =
$$\frac{(C_o-C_t)}{C_o} \times 100\%$$
 (1)

Where C_0 is the initial concentration of IC dye in the solution and C_t is the concentration of IC dye in solution at different times.

3. Result and discussion

3.1. Photocatalyst characterization

Fig. 1 indicates the XRD pattern of iron sand, α -Fe₂O₃, α -ZnO/ α -Fe₂O₃ composites and pure ZnO. It has been observed that diffraction peaks in iron sand indicates the presence of magnetite (Fe₃O₄) phase (Fig. 1a) corresponding to (211), (310), (311), (400), (421) and (533) planes according to JCPDS card no. 96-

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900-2317. Iron sand also contained iron (III) oxide in hematite (α -Fe₂O₃) phase. On the other hand, the diffraction peak in Fig. 1b correspond to the (110), (211), (101), (210), (202), (312), (310) and (211) reflection planes of hematite (α -Fe₂O₃) according to JCPDS card no. 96-900-9783. Fig. 1b also indicate that some of magnetite peak dissapeared and some how show a decrease in intensity suggested that iron oxide in iron sand has been converted to hematite (α -Fe₂O₃) phase. When ZnO is added to hematite with the mole ratio of ZnO to α -Fe₂O₃ 1 : 1 and 1: 5 (Fig. 1c-d) no peaks corresponding to zinc oxides can be observed but the XRD pattern of ZnO/ α -Fe₂O₃ (5:1) composite has revealed the presence of zinc oxide. The crystalline phase of zinc oxide is zincite which is accordance with JCPDS card no.96-900-8878.



Figure 1. XRD patterns of a. Iron sand b. α -Fe₂O₃ c. ZnO/ α -Fe₂O₃ (1:1) d. ZnO/ α -Fe₂O₃ (1:5) e. ZnO/ α -Fe₂O₃ (5:1) composite and f. Pure ZnO.

The average size of crystalline particles determined using Debye-Scherrer equation showed that the average size of crystalline particles in the ZnO/α -Fe₂O₃ (1:5) and ZnO/α -Fe₂O₃ (5:1) composites were almost the same approximately 44.25 nm and 44.99 nm [9]. On the other hand, the average size of crystalline particles in the ZnO/α -Fe₂O₃ (1:1) composite was 55.26 nm which was greater than that of two other composite. The average size of crystalline particles in the α -Fe₂O₃ was 39.47 nm which indicates that the presence of zinc oxide contributed to the increase in the average size of crystalline particles in ZnO/α -Fe₂O₃ composites.



Figure 2. SEM images of a. α -Fe₂O₃ b. ZnO/ α -Fe₂O₃ (1:5), c. ZnO/ α -Fe₂O₃ (1:1) and d. ZnO/ α -Fe₂O₃ (5:1) composite.

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SEM photographs of materials presented in Fig. 2 show that the hematite particle was spherical in shape and almost homogeneous in size. SEM photograph of ZnO/α -Fe₂O₃ composites exhibited the combination of ZnO and α -Fe₂O₃ particles with the larger size compare to α -Fe₂O₃. These observation was in accordance with the calculation of average size of crystalline particles from XRD data.

3.2. Photocatalytic activity

The photocatalytic efficiencies of the prepared samples were evaluated on degradation of IC dye under UV light irradiation. Fig. 3a show the influence of the initial pH of IC solution which was adjusted from 1 to 5 on its degradation. The results shows an increase in degradation efficiency at lower pH and the highest degradation efficiency was achieved at pH =1. IC is an anionic dye due to the negatively charged of sulphonate group [10], which can easily adsorbed on the positively charge of α -Fe₂O₃ (at acidic pH environment). Increasing the IC molecule on the photocatalyst surface causes an increase in IC degradation. It has been reported that adsorption process on the photocatalyst surface is an important step in degradation [11]. The greater the molecule adsorbed, the greater amount of IC molecule will react with 'OH, hole, electron or O₂[•] in photocatalysis. At higher pH values the adsorption decrease due to repulsion between the anionic dye molecules and negatively charged surface, as the result the degradation efficiency of IC decrease.



Figure 3. Degradation of IC solution at initial concentration 15 ppm under UV light irradiation for 120 minutes a. by using 250 mg ZnO/ α -Fe₂O₃ (1:5) as a function of initial of dye solution and b. At initial pH of dye solution is equal to 1 as a function of ZnO/ α -Fe₂O₃ (1:5) dosage.

Effect of photocatalyst mass on the degradation of IC dye was studied with different ZnO/α -Fe₂O₃ composite dosage ranging from 150 to 350 mg (Fig. 3b). Results showed that degradation efficiency increases with increasing of photocatalyst dosage and the highest degradation efficiency was achieved by using 300 mg of ZnO/ α -Fe₂O₃, which confirmed that the greater number of active sites leads to the generation of more reactive radicals (-HO[•], O₂[•]), which in turn leads to higher rates of IC degradation. However, increasing the photocatalyst dosage from 300 mg to 350 mg resulted in a slightly decrease in the degradation efficiency of IC. That result is due to the increased turbidity of the mixtures, which reduces the amount of light transmitted through the solution and blocking the penetration of light onto all available surface particles [12].

Fig. 4a represents the effect of initial IC concentration on its degradation over ZnO/α -Fe₂O₃ (1:5) composite. Five different of IC concentrations were selected to evaluate the effect of initial dye concentration on the degradation while keeping constant photocatalyst mass (300 mg). It can be seen that the highest degradation efficiency was achieved at the initial IC concentration of 15 ppm with the degradation of IC 91.75%. Increasing the initial IC concentration to 20 until 25 mg/L caused the decreasing in the degradation efficiency of IC. This observation can be explained because the higher the IC concentration, the more IC molecules can react with active site (holes, electrons or -OH[•]) on photoacatalyst surface after being irradiated by UV light. However, at higher IC concentration the dye molecules prevented the UV light reaching the photocatalyst surface, so decreasing the production of

electrons and holes leading to less generation of reactive -•OH on the photocatalyst surface [13,14] and lower extents of degradation.



Figure 4. Degradation of IC as a function of UV light irradiation time at initial pH of IC solution is equal to 1 and photocatalyst dosage is 300 mg a. Over ZnO/α-Fe₂O₃ (1:5) with different initial IC concentration, b. Over ZnO/α -Fe₂O₃ at initial dye concentration is 15 ppm with the different mole ratio of ZnO to α-Fe₂O₃

Fig. 4b shows the degradation of IC dye over different photocatalysts under UV irradiation for 120 minutes at optimum conditions (pH = 1, photocatalyst dosage = 300 mg and initial dye concentration = 15 ppm). It is obvious that ZnO/α -Fe₂O₃ (1:5) has the highest photocatalytic activity than that of other composite. This observation was achieved might be due to the lower rate of recombination of photogenerated hole and electron in the photocatalysis process.



Figure 5. Degradation of IC as a function of UV and solar light irradiation over different photocatalyst and condition. Initial pH of IC solution is equal to 1, photocatalyst dosage is 300 mg and initial dye concentration is 15 ppm.

Fig. 5 shows the degradation of IC dye over different photocatalysts under UV and solar light (SL) irradiation for 120 minutes at optimum conditions (pH = 1, photocatalyst dosage = 300 mg and initial IC concentration = 15 ppm). It is obvious that combination of ZnO and α -Fe₂O₃ can enhance the photocatalytic activity of α -Fe₂O₃. In addition, ZnO/ α -Fe₂O₃ composite has high photocatalytic activity both under UV and solar light irradiation. Fig. 5 also exhibited that ZnO/α-Fe₂O₃ is a good adsorbent which can generate synergistic effect to the photocatalytic activity. Since hematite has been widely considered as a photocatalyst, the experiment also conducted using hematite extracted from iron sand. The result shows that hematite has a higher photocatalytic activity under UV light irradiation but still lower photocatalytic activity than bare ZnO and ZnO/α-Fe₂O₃ composite. The photolysis of IC dye under UV and solar light in the absence of photocatalyst were very low, and which can be neglected. The increasing of photodegradation ZnO/α -Fe₂O₃ can be arises the decreasing of electron hole pair recombination rate due to the addition of ZnO with the wide band gap energy.

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4. Conclusions

 ZnO/α -Fe₂O₃ composites were prepared by sol gel method and evaluated their characteristics and photocatalytic activity on degradation of indigo carmine dye. The average size of crystalline particle in ZnO/α -Fe₂O₃ composites were higher than that of α -Fe₂O₃. The photocatalytic activity of ZnO/α -Fe₂O₃ composites were higher than that of α -Fe₂O₃ and pure ZnO. Degradation investigation showed that ZnO/α -Fe₂O₃ (1:5) composite has the highest photocatalytic activity on the experiment conditions: initial pH of IC solution 1.0; photocatalyst dosage 300 mg; initial IC concentration 15 ppm and 120 minutes under UV and 90 minutes under solar light irradiation times.

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