Hydrothermal Synthesis of Activated Carbon/α-Fe₂O₃ Nanocomposite and Its Application for Removing Tartrazine Dye

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Abstract. Hematite containing activated carbon (AC/α-Fe₂O₃) nanocomposite has been prepared by hydrothermal method and used as photocatalyst for removing tartrazine dye. Hematite was extracted from iron sand while activated carbon was derived from coffee waste which was activated using hydrochloric acid. The structure and morphology of photocatalyst was characterized by means of X-ray diffraction (XRD), nitrogen adsorption–desorption (BET) and Scanning Electron Microscopy-Energy-Dispersive X-Ray Spectroscopy (SEM-EDS). These techniques indicate that the AC/α-Fe₂O₃ nanocomposite has an average crystallite size of 35.47 nm and specific surface area of 41.52 m²/g. The photocatalytic activity evaluation showed that various factors influencing the removal of tartrazine dye including pH of dye solution, photocatalyst dosage, dye concentration and irradiation time. The results showed that AC/α-Fe₂O₃ nanocomposite can remove tartrazine up to 91.01% under UV light and 93.69% under solar light which were obtained at pH value of 2, photocatalyst dosage of 250 mg and initial concentration of tartrazine is 15 ppm with irradiation time for 210 min under UV light and 180 min under solar light. The AC/α-Fe₂O₃ nanocomposite also can remove tartrazine dye contained in noodle waste water up to 94.67% and 97.86% under UV light irradiation for 150 min and 120 min under solar light irradiation, respectively.

1. Introduction
Photocatalysis has been widely used in the degradation of organic pollutants such as dye effluents, phenols and pesticides in waste water. Semiconductor such as TiO₂, ZnO, ZnS and α-Fe₂O₃ could be used as photocatalyst under ultra violet or solar light. These processes are based on the generation of electron in the conduction band (CB) and hole in the valence band (VB) by light irradiation. The electrons and holes initiate reduction and oxidation reactions with species adsorbed on photocatalyst surface. Electron as reducing agent while hole as oxidizing agent. On the other hand, the electrons and holes can recombine, releasing the absorbed light energy as heat, without any chemical reaction occurring. On the semiconductor surface, the excited electron and the hole can participate in redox reactions with water, hydroxide ion (OH⁻), oxygen or organic compounds leading to mineralization of the pollutant [1,2].

Heterogeneous photocatalysis utilizing hematite (α-Fe₂O₃) is the most promising water treatment technology due to its low cost, chemical stability, nontoxicity, and high oxidation ability [3,4]. Hematite (α-Fe₂O₃) is one of the most stable iron oxides with the narrow band gap energy (E₀ ≈...
2.2 eV) which can be used with visible and solar light. However, there are some weakness of $\alpha$-$\text{Fe}_2\text{O}_3$ including low adsorption ability and flash recombination of photogenerated electron and hole which led to decrease its photocatalytic activity. It has been reported that activated carbon (AC) in combination with various iron oxide related materials is an excellent adsorbent for a various dangerous water pollutants [5,6]. The combination of activated carbon and iron oxide can increase adsorption and photodegradation and eliminate organic pollutants under UV and/or solar illuminations. Therefore, iron oxide and AC are able to effectively remove organic and inorganic substances by simultaneous adsorption-desorption in the water treatment process [7].

The aims of the present work were to synthesis the AC/$\alpha$-$\text{Fe}_2\text{O}_3$ nanocomposite and to investigate its photocatalytic activity on the removal of tartrazine dye (CI. No.19140). $\alpha$-$\text{Fe}_2\text{O}_3$ can be provided naturally from iron sand and iron ore. The high content of iron oxide in iron sand taken from Syiah Kuala Beach, Banda Aceh Indonesia has been reported [8]. Tartrazine is a synthetic dye with the formula $\text{C}_{16}\text{H}_{17}\text{Cl}\text{N}_3\text{Na}_2\text{Os}_2$ has a wide application in food, drug, pharmaceuticals, cosmetics and textile industry [9]. The full chemical name of tartrazine is trisodium 5-hydroxy-1-(4-sulfonatophenyl)-4-(4-sulfonatophenylazo)-H-pyrazol-3-carboxylate, with the structural formula was described in Fig. 1. Based on the national agency of Drug and Food Control of Republic of Indonesia the acceptable daily intake of tartrazine for humans is 0-7.5 mg/kg, while in food is 70 mg/kg. Tartrazine is very toxic in high concentration and is known to cause allergic reactions such as asthma, migraines, eczema, thyroid cancer, lupus, blurred vision, itching, hyperactive and fertility for human being [10, 11]. Thus, waste water containing tartrazine must be treated before discharge to environment. The degradation of tartrazine in TiO$_2$ fixed bed has been reported. The removal of tartrazine was only 30% under UV light irradiation for 200 min and 99% under solar light irradiation [12].

![Figure 1. Chemical structure of tartrazine](image)

2. Experimental

2.1. Materials

Tartrazine, a water soluble dye, was purchased from PT. Karya Muda Indochem, Indonesia while waste water containing tartrazine was taken from the noodle industry in Banda aceh, Indonesia. Hematite ($\alpha$-$\text{Fe}_2\text{O}_3$) was extracted from iron sand taken from Syiah Kuala Beach, Banda Aceh, Indonesia. Coffee waste was taken from some coffee shops in Banda Aceh, Indonesia. Other chemicals such as HCl, NH$_4$OH and NaOH were purchased from Merck.

2.2. Preparation of Hematite ($\alpha$-$\text{Fe}_2\text{O}_3$) and activated carbon

The hematite was extracted from iron sand according to previously report [13]. Hydrochloric acid was used to dissolve the iron oxide, following by adding NH$_4$OH as precipitation agent to the solution. The precipitate obtained was filtered and rinsed until it reached pH 7 (neutral), dried in an oven at 100 °C for 12 h and calcined in air at 700 °C for 5 h to produce $\alpha$-$\text{Fe}_2\text{O}_3$. Activated carbon was obtained from coffee waste by hydrothermal carbonization process on a Teflon-lined stainless steel autoclave at 170 °C for 5 h. The resulting product was dried at 100 °C for 5 h. In order to activate the carbon material obtained, the sample was immersed in 1 M HCl solution for 24 h. The resulting solid product was washed with water to neutralize its acidity. The sample was dried and calcined at 250 °C for 3 h.
2.3. Production of AC/α-Fe₂O₃ nanocomposites

The hematite containing activated carbon (AC/α-Fe₂O₃) nanocomposite was prepared by hydrothermal method. Briefly, 2.5 g of activated carbon and 7.5 g of α-Fe₂O₃ were mixed in 75 ml of distilled water under magnetic stirring. The mixture was transferred into a Teflon-lined stainless steel autoclave and then hydrothermally treated at 170 °C for 5 h. The resulting solid was filtered, washed with distilled water, dried at 100 °C for 5 h and calcined at 250 °C for 3 h.

2.4. Characterization of materials

X-ray diffraction (XRD) patterns were recorded with a Shimadzu X-ray diffractometer (XD-7000) equipped with Cu-Kα radiation source (λ = 1.54056 Å) operating at 40 kV and 30 mA. The scan rate is 5° min⁻¹ with Bragg angle 2θ varied from 10 to 80°. The crystallite sizes of as-synthesized samples (D) were examined from broadening of diffraction peaks according to Scherrer’s formula [14], where k is shape factor (the value is 0.9), λ is the X-ray wavelength, β is the full width at half maximum (FWHM) measured in radians of the reflection peak and θ is the Bragg’s angle.

\[
D = \frac{k\lambda}{\beta \cos \theta}
\]

The morphologies of the samples surface were examined by Scanning Electron Microscope (SEM) (JEOL JSM6510LV) operated at an acceleration voltage of 15 kV. The nitrogen adsorption-desorption isotherms were carried out by Quantachrome instruments (Nova touch 4LX). The Brunauer–Emmett–Teller (BET) surface area was measured at 77 K. Prior to measurement, the samples were out-gassed at 100 °C under a N₂ flow for 2 h.

2.5. Photocatalytic experiment

The study of photocatalytic degradation of tartrazine was carried out under ultra violet (using a 6-W UV lamp, λ = 365 nm) or solar light irradiation. The effect of various parameters, such as pH of tartrazine solution, photocatalyst dosage and tartrazine concentration were investigated. The entire arrangement was placed in a box to avoid the passage of other light from outside. The pH of tartrazine solution was measured on HI98107 pHep pH tester and was adjusted to desired pH value by adding small amount of 0.5 M HCl or 0.5 M NaOH solution. Typically, 250 mg of AC/α-Fe₂O₃ nanocomposite was added to 25 mL of 15 ppm tartrazine solution on the Pyrex glass vessel. The mixture was placed about 10 cm from the UV lamp. The experiments were carried out for 120 min consisting of 30 min in darkness and 90-180 min under UV light irradiation. After regular time interval of 30 min, the suspensions were collected and centrifuged for 10-15 min to completely remove the photocatalyst. The concentrations of tartrazine were determined with a UV–vis spectrophotometer (Shimadzu UV mini 1240 spectrophotometer) at λ_{max} = 427 nm. The removal (%) of tartrazine was estimated using the following equation (eq. 1), where C₀ and C₁ were represented the initial and final dye concentration (ppm) [15].

\[
\text{Removal} (%) = \left(\frac{C₀-C₁}{C₀}\right) \times 100
\]

The experiment was also performed using AC/α-Fe₂O₃ nanocomposite and 25 mL of tartrazine solution in the absence of UV-light.

3. Result and Discussion

3.1 Characterization of Materials

3.1.1 XRD analysis

The XRD patterns of iron sand, α-Fe₂O₃ samples before and after addition of activated carbon are shown in figure 2. The iron sand mainly composed of magnetite (Fe₃O₄) (JCPDS card no. 96-900-6243) and a small amount of hematite (α-Fe₂O₃) (JCPDS card no. 96-900-9783). After being extracted and calcined at high temperature almost all of magnetite converted into hematite (α-Fe₂O₃) phase. The activated carbon (Fig. 2c) showed a broad peak at 2θ = 10 - 20°, corresponding to the diffraction
of amorphous carbon. The AC/\(\alpha\)-Fe\(_2\)O\(_3\) nanocomposite (Fig 2d) exhibited XRD patterns almost similar to those of \(\alpha\)-Fe\(_2\)O\(_3\). There is no clear reflection corresponding to amorphous carbon was observed. This is might be due to the low amount of carbon because of the decomposition of some carbon after calcination at high temperature (250 \(^\circ\)C). Thus, only few of carbon remain on the surface of \(\alpha\)-Fe\(_2\)O\(_3\).

The average crystallite sizes of samples was estimated from XRD peaks broadening using Scherrer formula. The \(\alpha\)-Fe\(_2\)O\(_3\) exhibited the smallest crystallite size (27.54 nm), which size increased after addition of activated carbon (35.47 nm). This observation was confirmed that activated carbon has been added to the surface of \(\alpha\)-Fe\(_2\)O\(_3\). Larger crystallite size were belong to iron sand (47.09 nm) and activated carbon (44.57 nm).

![Figure 2. XRD patterns of a) Iron sand, b) \(\alpha\)-Fe\(_2\)O\(_3\), c) Activated carbon and d) AC/\(\alpha\)-Fe\(_2\)O\(_3\)](image)

3.1.2 SEM-EDS analysis

The surface morphology and elemental composition of the samples were investigated employing SEM and EDS. SEM images of \(\alpha\)-Fe\(_2\)O\(_3\), carbon from coffee waste, activated carbon and AC/\(\alpha\)-Fe\(_2\)O\(_3\) at 20,000 x magnification are shown in figure 3 which is show a clear change of the carbon and \(\alpha\)-Fe\(_2\)O\(_3\) morphologies. \(\alpha\)-Fe\(_2\)O\(_3\) has the smallest particle size which was accordance with XRD data. The small particle size leads to the agglomeration of particles [16] which can be prevented by adding the activated carbon. It can be seen from SEM image of AC/\(\alpha\)-Fe\(_2\)O\(_3\) nanocomposites (Fig 3d.) that the agglomeration of \(\alpha\)-Fe\(_2\)O\(_3\) particles was decreased. The results of the elemental analysis of \(\alpha\)-Fe\(_2\)O\(_3\) and AC/\(\alpha\)-Fe\(_2\)O\(_3\) indicated that Fe is the main constituents of the materials, which is estimated to be 87.96 and 69.98\%, respectively. Furthermore, carbon content in AC/\(\alpha\)-Fe\(_2\)O\(_3\) is 4.19\% and no carbon content was observed in \(\alpha\)-Fe\(_2\)O\(_3\). EDS analysis also reveals that activated carbon contain only C and O element.
3.1.3 Nitrogen adsorption-desorption analysis
The nitrogen adsorption–desorption was applied for determination of BET surface area of activated carbon derived from coffee waste, α-Fe₂O₃ and AC/α-Fe₂O₃. It can be observed from Table 1 that the addition of carbon to the α-Fe₂O₃ changes the value of surface area, pore radius and pore volume of α-Fe₂O₃. The results show an increasing of specific surface area of α-Fe₂O₃ due to the combination with activated carbon which has large specific surface area. The result also show that the addition of activated carbon cause a decreasing of average pore diameter of α-Fe₂O₃. Based on IUPAC classification all the materials prepared are categorized as mesopores materials with the pore diameter 2 – 50 nm [17].

| Samples       | Specific surface area (m²/g) | Pore volume (cc/g) | Pore diameter (nm) |
|---------------|------------------------------|-------------------|--------------------|
| AC            | 160.463                      | 0.110             | 2.754              |
| α-Fe₂O₃       | 22.005                       | 0.057             | 10.450             |
| AC/α-Fe₂O₃    | 41.528                       | 0.037             | 3.596              |

3.2 Photocatalytic Activity
3.2.1 Effect of initial pH of solution
pH has an important role in dye photodegradation process because it will influence the ionic state of dye molecule or surface of photocatalyst in the aqueous media. The photodegradation experiments were conducted at pH value of tartrazine solution 1, 2, 3, 4 and 5. The results showed that the photocatalytic activity of AC/α-Fe₂O₃ increased from pH 1 to 2 and then decreased from 3 to 5 (Fig. 3).
4). Tartrazine is anionic in nature and at the low pH value the positive charge site of AC/α-Fe₂O₃ surface increase, which contributed to the electrostatic interactions between the dye molecules and the AC/α-Fe₂O₃ surface. The increasing of tartrazine molecule on the photocatalyst surface leads to the greater amount of tartrazine molecule which reacts with photogenerated electron, hole, *OH, or O₂*- in photocatalysis. Thus, the photocatalytic degradation increases at low pH value. At higher pH value the positive charge site of AC/α-Fe₂O₃ surface decreases and the contribution to the photodegradation process will decrease. The photocatalytic activity was also evaluated at different time points (30–120 min) and the data show that tartrazine photodegradation increased with the increase of time. At the pH value of 2 and irradiation time 120 min, the maximum dye removal was 50.14% (Fig. 4), so the further experiments were conducted at pH value of 2.

![Figure 4. Removal of tartrazine vs time for different pH of dye solution, using 250 mg AC/α-Fe₂O₃ nanocomposite, C₀ = 15 ppm, UV light](image)

3.2.2 Effect of photocatalyst dosage

The amount of the photocatalyst is also an important parameter which influences the photodegradation process. In this study, the photocatalyst dosage used are 150 to 350 mg and the experiments were conducted at pH value 2. The results illustrated that, with an increase in photocatalyst dosage, the removal of tartrazine increased. This can be explained by more active sites being available for dye photodegradation at higher photocatalyst dosages [18]. The maximum dye removal (%) was achieved at a photocatalyst dosage of 250 mg. A further increase in the photocatalyst dosage resulted in a decrease in photocatalytic activity, which can be correlated to the limited light penetration through the tartrazine solution decreasing the photocatalytic activity [19].

![Figure 5. Removal of tartrazine vs time for different photocatalysts dosage, pH of dye solution = 1, C₀ = 15 ppm, UV light](image)
3.2.3 Effect of dye concentration

To evaluate the effect of the concentration of tartrazine, experiments were conducted for dye concentration from 5 to 15 ppm. The experiments were performed under pH value of 2 and photocatalyst dosage of 250 mg (Figure 6). The results showed that the dye photodegradation increased with an increase in dye concentration. The photodegradation was proportional to the concentration, in agreement with an increase in the molecules adsorbing on the surface of the photocatalyst [20].

![Figure 6](image1.png)

**Figure 6.** Removal of tartrazine vs time for different concentration of dye solution, using 250 mg AC/α-Fe₂O₃ nanocomposite, pH of dye solution = 1, UV light.

![Figure 7](image2.png)

**Figure 7.** Comparative degradation of tartrazine \(C₀ = 15\) ppm with 250 mg of photocatalyst under 180 min of ultra violet (UV) or solar light (SL) irradiation.
3.2.4 Effect of photocatalyst type and light source

Figure 7 shows the photodegradation of tartrazine dye over different photocatalysts for 180 min at optimum conditions (pH = 2, photocatalyst dosage = 250 mg and dye concentration = 15 ppm). It is obvious that AC/\(\alpha\)-Fe\(_2\)O\(_3\) nanocomposite has higher photocatalytic activity than that of bare \(\alpha\)-Fe\(_2\)O\(_3\). This confirms that addition of activated carbon can enhance the photocatalytic activity of \(\alpha\)-Fe\(_2\)O\(_3\). Activated carbon has the important role to enhance the adsorption of tartrazine molecule to the photocatalyst surface thus enhance the photodegradation. It can be seen from experiment which was conducted in the dark condition. In addition, the photogenerated electrons can easily transfer from the \(\alpha\)-Fe\(_2\)O\(_3\) conduction band to carbon and thus inhibited the recombination of photogenerated electrons and holes [21]. Figure 7 also exhibits that AC/\(\alpha\)-Fe\(_2\)O\(_3\) nanocomposite has higher photocatalytic activity under solar light irradiation than that of under UV light. This observation was accordance with the previously report that tartrazine was more efficiently degraded by TiO\(_2\) under solar radiation than with UV lamp radiation [12]. The photolysis of tartrazine dye under UV light in the absence of photocatalyst were very low, and which can be neglected.

![Graph showing photodegradation of tartrazine dye](image)

**Figure 8.** Comparative degradation of tartrazine contained in noodle waste water with 250 mg of AC/\(\alpha\)-Fe\(_2\)O\(_3\) nanocomposite under ultra violet (UV) or solar light (SL) irradiation

The photocatalytic activity of AC/\(\alpha\)-Fe\(_2\)O\(_3\) was also evaluated on photodegradation of tartrazine contained in noodle waste water. The experiments were conducted at pH value of noodle waste water using 250 mg of AC/\(\alpha\)-Fe\(_2\)O\(_3\) (Fig. 8). It was observed that AC/\(\alpha\)-Fe\(_2\)O\(_3\) can remove tartrazine up to 94.67% under UV light irradiation for 150 min and 97.86% under solar light irradiation for 120 min.

4. Conclusions

In the present study, AC/\(\alpha\)-Fe\(_2\)O\(_3\) nanocomposite was prepared through a hydrothermal method. XRD analysis confirms that the prepared AC/\(\alpha\)-Fe\(_2\)O\(_3\) was nano structure and size of the particle was calculated as 35.47 nm. SEM-EDS analysis also confirms the carbon content in AC/\(\alpha\)-Fe\(_2\)O\(_3\) nanocomposite which was supported by the increasing of specific surface area of \(\alpha\)-Fe\(_2\)O\(_3\) obtained from nitrogen-desorption isotherm analysis. Photocatalytic acitivity of prepared sample was tested on degradation of tartrazine dye. The results showed that AC/\(\alpha\)-Fe\(_2\)O\(_3\) has the high photocatalytic activity compare to bare \(\alpha\)-Fe\(_2\)O\(_3\). The highest photocatalytic activity of AC/\(\alpha\)-Fe\(_2\)O\(_3\) was achieved at pH value
of tartrazine solution is 1, photocatalyst dosage is 250 mg and tartrazine concentration is 15 ppm. The maximum removal of tartrazine for the optimal conditions is 91.01% and 93.69% after being irradiated for 210 min under ultra violet light and 180 min under solar light, respectively. AC/α-Fe₂O₃ nanocomposite also showed high photocatalytic activity on degradation of tartrazine dye contained in noodle waste water.

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