Photocatalytic degradation of indigo carmine dye using α-Fe₂O₃/bentonite nanocomposite prepared by mechanochemical synthesis

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Abstract. Preparation of α-Fe₂O₃/bentonite nanocomposite has been successfully conducted by mechanochemical synthesis using iron sand from Syiah Kuala Beach, Banda Aceh and bentonite from Kuala Dewa, North Aceh as raw materials. The α-Fe₂O₃ was extracted using hydrochloric acid and precipitated using ammonium hydroxide as precipitation agent at pH 6 followed by calcination at high temperature in order to obtained α-Fe₂O₃. The α-Fe₂O₃/bentonite nanocomposite was prepared by milling the mixture of α-Fe₂O₃ and bentonite at 4:1 ratio in a planetary mill for 2 hours without any solvent. The XRD results showed that the main component of iron sand was magnetite (Fe₃O₄), while in α-Fe₂O₃/bentonite nanocomposite the main component was α-Fe₂O₃ and SiO₂. The photocatalytic activity of α-Fe₂O₃/bentonite nanocomposite was investigated on degradation of indigo carmine (IC) dye at various conditions of pH, photocatalyst mass, initial dye concentration and irradiation time. The results showed that the highest photocatalytic activity of α-Fe₂O₃/bentonite nanocomposite was obtained at the initial pH value of IC solution 1, 250 mg photocatalyst mass and initial concentration of IC 10 mg/L after irradiated for 90 minutes under ultra violet and solar light, respectively. The photocatalytic activity of α-Fe₂O₃/bentonite nanocomposite using UV light was almost the same as that of by solar light.

Keywords: α-Fe₂O₃; bentonite; hematite; indigo carmine: mechanochemical: photodegradation

1. Introduction

Hematite, a well-known of iron oxide with the narrow band gap (2.1 eV) has been used as photocatalyst in waste water remediation. Hematite is a nontoxic semiconductor material that exhibits good visible light response and high stability. In addition, α-Fe₂O₃ has great natural abundance and can obtain from iron sand or iron ore. However, the narrow band gap of α-Fe₂O₃ also limits its application due to the rate of recombination of electron and hole that implied low photocatalytic activity [1, 2]. Various attempts have been conducted to enhance the photocatalytic activity and to overcome these limitations, one of them was support or disperse of α-Fe₂O₃ within a porous matrix which has high specific surface area such as clay, bentonite and activated carbon. Bentonite, a low-cost material and abundant clay are often used as a good support to fabricate photocatalyst composites. Bentonite possess layered structure that consists of two silica tetrahedral sheets fused to one alumina octahedral sheet [3, 4]. The combination of α-Fe₂O₃ and high surface material will enhance the photocatalytic of α-Fe₂O₃ by the synergic effect of adsorption and photodegradation. It has been known that the first step of photocatalysis was adsorption of substrate or molecule to the surface of photocatalyst.
Photocatalysis is the acceleration of the rate of a chemical reaction by activating a catalyst by presence of light (ultraviolet (UV) or visible light). When photocatalyst absorbs light energy, transfer electron from the valence band (VB) to the conduction band (CB) take places and produce electron on CB and hole on VB. The resulting electron and hole can initiate redox reaction or react with oxygen (O₂) and water (H₂O) to form strong oxidizing agent superoxide anion (O₂⁻) and hydroxyl radical (·OH), respectively [5, 6]. Photocatalytic degradation of organic compounds such as dyes using semiconductor become an efficient method because it can be totally degraded these pollutant and mineralised into CO₂ and harmless inorganic anions [7, 8]. Indigo carmine (IC) dye is considered as a highly toxic indigoid class of dye which constitutes one of the largest groups of pollutants found in wastewaters from textile and other industries. IC can cause skin and eye irritation if contact with it. The discharge of this effluents into the ecosystem induced the environmental problems such as human health, aesthetic pollution and perturbation of aquatic life [9].

In this paper we reported the preparation of α-Fe₂O₃/bentonite nanocomposite using mechanochemical synthesis by milling of α-Fe₂O₃ and bentonite at the planetary mill. Mechanical milling is a simple and free solvent method that involved the mechanical activation of solid-state chemical reactions displacement. The main purpose of milling is to reduce the particle size and blending of particles in new phases [10, 11]. α-Fe₂O₃ used in this study was extracted from iron ore which is one of an abundant natural resources in Aceh province. In addition, Aceh province also has bentonite deposit. Characterization of as-prepared materials was conducted by X-ray diffraction (XRD) and scanning electron microscopy energy dispersive X-ray spectroscopy (SEM EDS).

2. Materials and Methods

2.1. Materials
The iron sand taken from Syiah Kuala Beach, Banda Aceh, Aceh Province, Indonesia was washed with distilled water, dried and separated using magnetic bar. The sample was ground in a porcelain ball mill (Planetary mill, Fritsch, P6) for 30 min using a rotational speed of 250 rpm to reduce the particle size up to 150 mesh sieve. Bentonite taken from Kuala Dewa, North Aceh Province, Indonesia. Hydrochloric acid (HCl), ammonium hydroxide (NH₄OH), sodium hydroxide (NaOH) and indigo carmine of analytical reagent grade were purchased from Merck and were used without further purification.

2.2. Extraction of α-Fe₂O₃ from iron sand and synthesis of α-Fe₂O₃/Bentonite Nanocomposite
Extraction and synthesis of hematite (α-Fe₂O₃) from iron sand using hydrochloric acid and ammonium hydroxide as precipitating agent was conducted according to previous works [12, 13]. Iron sand was dissolved in hydrochloric acid solution (6 M) with stirring and heating at 145°C for 30 min. The solution was filtered and ammonium hydroxide 25% was added by drop to the filtrated solution until the pH reaches~6 at which ferric hydroxide was obtained as a brown precipitate. The precipitate was filtered and washed with distilled water. The obtained sample was dried at 100°C for 3 h and calcined at 700°C for 5 h. The α-Fe₂O₃ obtained was mixed with bentonite in the 4:1 weight ratio by mechanochemical synthesis using Planetary mill for 2 h at the milling speed of 350 rpm with the balls to powder mass ratio was 10:1.

2.3. Characterization of materials
The chemical composition of iron sand was determined by X-ray fluorescence (PAN Analytical AXIOS Advance) and the results are represented in wt % of oxides. X-ray diffraction (XRD) analysis was conducted by using an X-ray diffractometer (Shimadzu) using Cu-Kα radiation (λ=0.154056 nm) at a scan speed 5° min⁻¹ with accelerating voltage and current were 40 kV and 30 mA, respectively and a monochromator at a 2θ angle between 10 to 80 degrees. Average grains sizes of materials were calculated by using the Scherer’s formula (equation 1), where D is the crystallite size, k is Debye
Scherrer’s constant (0.9), λ is the wavelength of X-ray diffraction radiation, FWHM is the full width at half maximum observed from XRD pattern and θ is the Bragg’s angle.

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

Morphological studies of materials were analysed using scanning electron microscopy (SEM; JEOL microscope model JSM6510LV) at an accelerating voltage of 15 kV, coupled with energy dispersive X-ray spectroscopy (EDS) for elemental analysis.

2.4. Photocatalytic determination of α-Fe₃O₄/bentonite nanocomposite

The photocatalytic activity of α-Fe₃O₄/bentonite nanocomposite was investigated on degradation of indigo carmine (IC) dye (Fig. 1), a group of dark blue indigoid dye, from solution in various initial pH, photocatalyst mass, initial dye concentration and UV irradiation time. The UV light source was a 6 W UV lamp (λ=365 nm) and was located 10 cm from the Pyrex glass vessel. The pH of dye solution was adjusted by addition of either 0.1 M HCl or 0.1 M NaOH solutions using a pH meter (HANNA instruments pHep). A mixture of 25 mL of IC solution and photocatalyst with the appropriate amount was magnetically stirred in the dark for 30 min to establish adsorption-desorption equilibrium of IC and the photocatalyst surface before the irradiation. The suspensions were exposed to UV light irradiation for another 120 min and a small aliquot was taken from the system within 30 min at different time intervals during the experiment and centrifuged. The remaining IC dye in the filtrate was determined using UV-Vis spectrophotometer (Shimadzu UV mini 1240) at λ_{max} of 610 nm. The experiment was also conducted without UV irradiation (dark condition) under the same parameter with UV irradiation. All experiments were repeated twice. The degradation percentage (%D) of IC was calculated using the formula of equation (2).

\[
IC \ degradation = \frac{(C_a-C_t)}{C_o} \times 100\% 
\]

Figure 1. Chemical structure of indigo carmine.

3. Results and Discussion

3.1. Characterization

The chemical composition of iron sand after being separated using magnetics rods was analysed using XRF. The results show that iron sand from Syiah Kuala beach, Banda Aceh is composed mainly of iron (III) oxide (92.56%), TiO₂ (3.77%) with small amount of V₂O₅ (0.74%), Cr₂O₃ (0.49%), CaO (0.44%), SiO₂ (0.42%), Al₂O₃ (0.39%), ZnO (0.33%), MgO (0.06%) and ZrO₂ (0.02%). Iron (III) oxide in iron sand was extracted with hydrochloric acid followed by precipitated using ammonium hydroxide and calcined at high temperature to obtained iron (II) oxide in hematite phase (α-Fe₂O₃) [14, 15]. Hematite was mixed with natural bentonite by mechanical synthesis to produce α-Fe₂O₃/bentonite nanocomposite. The chemical composition of natural bentonite analysed by SEM EDS showed that SiO₂ was the main component (55.76%) followed by Al₂O₃ (25.36%), Fe₂O₃ (10.29%), ZnO (3.89%) and some traces of MgO (1.86%), K₂O (1.25%), CaO (1.23%) and TiO₂ (0.36%) [16]. Fig. 2 shows the XRD patterns as prepared materials. X-ray diffraction patterns of natural iron sand at 2θ=31.89°, 35.41°, 38.75°, 43.08°, 53.44°, 56.15° and 62.55° showed that the main phase of iron oxide on iron sand is magnetite (Fe₃O₄)

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according to JCPDS card no 96-900-6243, while the peaks at $\theta = 33.20^\circ$ and $49.50^\circ$ was in accordance with hematite ($\alpha$-Fe$_2$O$_3$) (JCPDS card no 96-900-9783). The XRD diffraction peaks indicated at $\theta = 24.17^\circ$, $33.20^\circ$, $35.66^\circ$, $40.89^\circ$, $49.50^\circ$, $54.11^\circ$, $62.49^\circ$, $64.03^\circ$, and $71.98^\circ$ (Fig. 2b) was in accordance with hematite ($\alpha$-Fe$_2$O$_3$) (JCPDS card no 96-900-9783). XRD pattern of natural bentonite (Fig. 2d) showed that the reflections corresponding to quartz ($\text{SiO}_2$) are present at $\theta = 20.96^\circ$, $24.17^\circ$, $29.89^\circ$, $40.88^\circ$, and $60.06^\circ$ (JCPDS file no. 96-900-5022). The diffraction patterns of $\alpha$-Fe$_2$O$_3$/bentonite nanocomposite (Fig. 2c) confirmed the presence of hematite and $\text{SiO}_2$ from bentonite but with the lower intensity due to coorporation of two materials in which bentonite only 25 wt%.

![X-ray diffraction patterns](image)

**Figure 2.** X-ray diffraction patterns of (a) Iron sand, (b) $\alpha$-Fe$_2$O$_3$, (c) $\alpha$-Fe$_2$O$_3$/bentonite and (d) bentonite.

The average crystallite size of materials calculated using Debye Scherer’s formula showed that there is no significant difference between iron sand and hematite extracted from iron sand. The average crystallite size of iron sand was 47.09 nm while hematite extracted from iron sand was 46.88 nm. The average crystallite size of $\alpha$-Fe$_2$O$_3$/bentonite nanocomposite was higher than that of other materials. This is might be due to the high-energy impact between milling balls and the mixture that caused agglomeration of hematite and bentonite. It has been reported that powder that was milled longer at 30 min had a higher surface energy, which facilitated the powder to reunite and reagglomerate in order to reduce surface energy and restabilize the system [17]. This observation was confirmed by the SEM EDS analysis in Fig. 3 which showed that the particles size of $\alpha$-Fe$_2$O$_3$/bentonite nanocomposite was higher than others. It can be seen from Fig. 3a that iron sand was irregular in size and shaped. From the SEM image, $\alpha$-Fe$_2$O$_3$ extracted from iron sand consisted of uniform spherical particles, smaller and regular in size. It can be seen that the morphology of natural bentonite consisted of flake-like and layered structure.
3.2. Photocatalytic activity determination

The effect of photodegradation environment was determined by varying the condition of initial dye solution from 1 to 5, photocatalyst mass from 50 to 250 mg, initial dye concentration from 5 to 25 mg/L for 120 min under UV or solar light irradiation. The pH of the initial dye solution was important parameters that affect the photocatalytic activity of α-Fe₂O₃/bentonite nanocomposite. The initial pH of solution will affect the ionization state, the acid base property of the photocatalyst surface and also the reactant dye [18]. The effect of initial pH of IC solution on the photocatalytic degradation in the presence of α-Fe₂O₃/bentonite nanocomposite is exhibited in Fig. 4. The lower the pH of initial dye solution the greater the degradation of IC. The highest percentage of degradation of IC was obtained at pH value 1. In the acidic environment, the surface of α-Fe₂O₃ change to the positive charge (FeOH⁺), on the other hand IC was an anionic dye due to the negatively charged of sulphonate (SO₃⁻) group [19], which can easily adsorbed on the positively charge of α-Fe₂O₃. On the other hand, bentonite has a net negative surface charge due to the isomorphous substitution of Al³⁺ for Si⁴⁺ in the tetrahedral sheet and Mg²⁺, Fe²⁺ and other cations for Al³⁺ in the octahedral sheet [20], but at a lower pH (<2) the surface of bentonite tend to positively charged an increase in adsorption takes place for IC molecule. Increasing of IC molecule on the photocatalyst surface lead to increase of photodegradation of IC [21]. 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 removal efficiency of IC due to photodegradation process decrease. A linear relation between degradation percentage of IC dye with irradiation time also has been observed.

Figure 3. SEM images of (a) Iron sand b. α-Fe₂O₃ extracted from iron sand (c) Natural bentonite and (d) α-Fe₂O₃/bentonite nanocomposite.
Figure 4. Effect of initial pH of solution on degradation of IC over \(\alpha\)-Fe\(_2\)O\(_3\)/bentonite nanocomposite. Initial dye concentration of 15 mg/L and photocatalyst dosage 150 mg after irradiated by UV light for 120 min.

Fig. 5 shows the effect of photocatalyst mass on photocatalytic degradation of IC. When the mass of \(\alpha\)-Fe\(_2\)O\(_3\)/bentonite nanocomposite was increased from 50 mg to 250 mg an increase in the degradation percentage of IC was observed. The maximum degradation percentage of IC was achieved by using 250 mg of \(\alpha\)-Fe\(_2\)O\(_3\)/bentonite nanocomposite. The increase in degradation percentage is obviously due to the increase of the \(\alpha\)-Fe\(_2\)O\(_3\) active site, resulting in enhanced \(\cdot\text{OH}\) and superoxide ion (O\(_2\)\(^{-}\)) generation.

Figure 5. Effect of photocatalyst mass on degradation of IC over \(\alpha\)-Fe\(_2\)O\(_3\)/bentonite nanocomposite. (Experimental conditions: pH=1, initial IC concentration=15 mg/L).

The effect of initial concentration on the degradation of IC was investigated by using different initial concentration of IC for 120 minutes. The results in Fig. 6 indicate that when the initial concentration of IC was increased from 5 mg/L to 10 mg/L an increase in the degradation percentage was observed. However, as the initial IC concentration was further increased, the degradation percentage tended to decrease. The result may be due to the decrease in the number of photogenerated electron and hole because more IC ions covered the photocatalyst surface. In addition, at a high IC concentration, a significant amount of light can be absorbed by the IC molecule rather than by the photocatalyst resulting
in a decrease in photogenerated electron and hole and also the formation of \(^*\)OH and superoxide ion (O\(_2^*\)) as well as the photocatalytic activity [22].

![Figure 6](image6.png)

**Figure 6.** Effect of initial dye concentration on degradation of IC over \(\alpha\)-Fe\(_2\)O\(_3\)/bentonite nanocomposite. (Experimental conditions: pH=1, photocatalyst mass=250 mg).

Fig. 7 shows the degradation profiles of IC with initial concentration of 10 mg/L at pH value of 1 in different processes for 90 minutes. The results revealed that the degradation of IC in the presence of \(\alpha\)-Fe\(_2\)O\(_3\)/bentonite nanocomposite is higher than that of \(\alpha\)-Fe\(_2\)O\(_3\). The presence of bentonite led to the increase of IC molecule adsorbed on the photocatalyst surface and reacted with photogenerated electron or hole and active species such as \(^*\)OH and superoxide ion (O\(_2^*\)) when the \(\alpha\)-Fe\(_2\)O\(_3\)/bentonite nanocomposite irradiated by UV or solar light. Fig. 7 also shows that photocatalytic activity of \(\alpha\)-Fe\(_2\)O\(_3\)/bentonite nanocomposite under solar light irradiation was almost the same as that of UV irradiation. All of IC molecule was completely degraded after irradiated with solar light for 90 minutes. Blank test (no photocatalyst) was also performed as IC is a kind of light sensitive dye and the result showed that degradation percentage of IC were 5.75% and 17.62% under UV and solar light irradiation, respectively.

![Figure 7](image7.png)

**Figure 7.** Degradation of IC on the different processes for 90 minutes’ treatment (Experimental conditions: pH=1, photocatalyst mass=250 mg, initial IC concentration=10 mg/L, UV=ultra violet, SL=solar light).
4. Conclusions
Preparation α-Fe$_2$O$_3$/bentonite nanocomposite using α-Fe$_2$O$_3$ extracted from iron sand has been done by mechanochemical synthesis. The results showed that the mechanochemical synthesis led to increase in size of nanoparticle of α-Fe$_2$O$_3$ due to the agglomeration between α-Fe$_2$O$_3$ and bentonite. The α-Fe$_2$O$_3$/bentonite nanocomposite exhibited significantly higher photocatalytic activity on degradation of indigo carmine (IC) dye than those of bare α-Fe$_2$O$_3$. The degradation of IC solution increased with the increasing α-Fe$_2$O$_3$/bentonite nanocomposite mass. The optimal pH value and the initial IC solutions were observed at 1 and 10 mg/L, respectively for 90 minutes both under UV and solar light irradiation.

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