Preparation and Characterization of Titania/Bentonite Composite Application on the Degradation of Naphthol Blue Black Dye

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Abstract

A titania/bentonite (TiO_2/bentonite) composite was prepared by modification of natural bentonite with sodium chloride and ammonium chloride followed by the use of a titanium tetraisopropoxide in acidic solution as precursor of titania. The as-prepared materials were characterized by X-Ray Diffraction (XRD), Scanning Electron Microscope and Energy Dispersive X-ray spectroscopy (SEM EDX) and specific surface area. The specific surface area of TiO_2/bentonite composite was found to be higher than that of non-modified bentonite.

The TiO_2/bentonite composite was categorized as mesoporous with an average pore diameter of 9.34 nm. The photocatalytic activity of the porous material was evaluated via the photodegradation of naphthol blue black (NBB) dye at room temperature. The maximum degradation percentage of the NBB dye was 99.83% which was obtained at an initial pH of 3, a photocatalyst dosage of 0.4 g, and an initial dye concentration of 5 mg/L for 120 minutes of UV irradiation time. The same maximum degradation percentage of NBB was obtained under solar light irradiation but in only 90 minutes.

Keywords: Bentonite, titania, composite, naphthol blue black, degradation

Introduction

Titanium dioxide, titania (TiO_2) is a semiconductor well known as a photocatalytic material with a high capacity for photooxidative decomposition of organic compounds under UV light[1]. The fundamentals of photocatalysis consist of exposing the semiconductor to radiation energy near to or greater than its band gap energy, which generates high energy electron–hole pairs initiating a photocatalytic reaction. Titanium dioxide has been the dominant photocatalyst for environmental applications due to its stability, non-photocorrosive, non-toxic characteristics and its monetary price[2].

However, the use of titania has reduced efficiency under radiation within the visible region due to its high optical band gap (3.2 eV), small specific surface area and low adsorption capacity[3]. Additionally, in the bulk form it usually suffers from some practical problems including agglomeration and difficulty recovery which limits its use in practical applications[4].

Several attempts have been made to overcome these limitations including modifying and doping with non metal[5,6] doping with transition metal[7] and semiconductor coupling[8,9]. Other attempts involved the dispersion of TiO_2 particles onto the surface of material with a large surface area. This is because the photocatalytic reactions occur on the photocatalyst surface and pre-adsorption of target compounds is necessary for their degradation. This can be achieved by using supports with large surface areas for adsorption and high adsorption capacity for target substances[10].

It has been reported that TiO_2 dispersed on the surfaces of clay minerals improves the photocatalytic activity by providing more active surface sites and reducing agglomeration of TiO_2 particles[11].

There are a large number of natural clays that can be used in removal of organic pollutants like synthetic dyes from wastewater. These clays include halloysite, kaolinite, bentonite and zeolite[12]. Bentonite possesses a layer structure and large surface areas that can be used to disperse TiO_2 and adsorb pollutants. It has been reported that TiO_2 supported by bentonite is more active in the photodegradation of methylene blue than commercial TiO_2 P-25.[13]

The adsorption of naphthol blue black dye (NBB) using acid activated TiO_2/bentonite has been studied and the results show an adsorption capacity of NBB at 1.49 mg/g[14]. NBB is an azo dye that contains azo groups with sulfonate groups and aromatic rings. Most synthetic dyes are toxic, non-biodegradable and can be transformed into more hazardous substances[15,16]. Therefore, it is important to remove the dyes from wastewater before discharging into mainstream channels.

In this study, we modified natural bentonite by cation exchange with sodium chloride followed by ammonium chloride. The product obtained was further modified with titanium tetraisopropoxide as TiO_2 precursor by the use of sol gel method to produce TiO_2/bentonite composite. The TiO_2/bentonite composite and natural bentonite were characterized by X-ray diffraction (XRD), Scanning Electron Microscope Energy Dispersive X-ray spectroscopy (SEM EDS) and specific surface area respectively. The photocatalytic activity of the TiO_2/bentonite composite was examined by napthol blue black degradation.

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Material and Methods

Materials: Bentonite was taken from Kuala Dewa, North Aceh, Indonesia and was sieved to sort different particle size fractions using 100 mesh ASTM standard sieves. The bentonite was composed of 55.76% SiO_2, 25.36% Al_2O_3, 10.29% Fe_2O_3, 3.89% ZnO, 1.86% MgO, 1.25% K_2O, 1.23% CaO and 0.36% TiO_2. The titanium tetraisopropoxide $(Ti(C_3H_4O_2)_4)$, sodium chloride (NaCl), ammonium chloride (NH_4Cl), hydrochloric acid (HCl) and naphthol blue black (Fig. 1), an anionic dye with the chemical formula $C_{22}H_{14}N_6Na_2O_9S_2$ (C.I. = 20470 and MW= 616.49 g/mole) were purchased from Merck.

Methods: Dried bentonite was modified through cation exchange with a saturated sodium chloride solution to obtain Na-Bentonite followed by an ammonium chloride solution to obtain H-Bentonite. The TiO_2/Bentonite composite was prepared from H-Bentonite by adding a sol solution of titanium hydrate drop by drop. The sol of titanium hydrate was obtained by the hydrolysis of $Ti(C_3H_4O_2)_4$ in 1 M hydrochloric acid solution with the molar ratio of HCl to titanium tetraisopropoxide at 4:1. The mixture was magnetically stirred at room temperature for 12 h and then the solids were separated by a Hettich-EBA III microcentrifuge at 1000 rpm for 10 minutes. The solids were dried at 100 °C for 12 h and calcined at 500 °C for 5 h.

Characterizations: The morphology observations and chemical composition analysis of natural bentonite and TiO_2/bentonite composite were characterized using a scanning electron microscope (SEM, JEOL-JSM-6510LV) at an accelerating voltage of 15 kV equipped with an energy dispersive X-ray spectrometer (EDX). The structure characterizations were performed with an X-ray diffraction (XRD, Shimadzu X-ray diffractometer) equipped with Cu Kα radiation (λ = 0.15405 nm 30 kV, 15 mA). The specific surface area and average pore size of the samples were analyzed using the BET and BJH methods. The determinations of the surface area and pore size were based on isotherms of adsorption and desorption of nitrogen at 77 K using a Quantachrome Nova 3200E instrument.

Photocatalytic Activity Test: The photocatalytic activity of the prepared composite was determined by the degradation of NBB, a diazo dye widely used in the textile and soap industries at room temperature. The experiment was performed under UV irradiation using a 6 W UV lamp (λ_{max} = 365 nm) in various initial pH, photocatalyst dosage and initial dye concentration. First mixtures of 25 mL NBB solutions with the apropriate concentration, photocatalyst dosage and initial pH were mixed into 100 mL glass vessel. The mixtures were stirred in the dark for 30 min to establish an adsorption/desorption equilibrium between the dye and the photocatalyst surface. Then, the suspensions were exposed to UV light irradiation for another 120 min.

During the reaction, samples were collected at selected time intervals. The adsorption experiment was performed under the same conditions without irradiation. The supernatants were analyzed at 618 nm with a UV-Vis spectrophotometer (Shimadzu UV mini 1240) to record the characteristic absoption peak of NBB. The percent degradation (% degradation) of NBB was calculated using the following formula:

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

where C_0 and C_t refer to the concentration of the NBB solution before and after irradiation.

Results and Discussion

Characterization of the solids: The X-ray powder diffraction patterns of the bentonite and TiO_2/bentonite composite are depicted in figure 2. The 2θ angle of (001) reflection corresponding to the basal spacing was 5.69° for montmorillonite on the bentonite clay. This peak was not observed in the TiO_2/bentonite composite pattern due to the insertion of polynuclear cationic titanium in the galleries of the bentonite, indicating disordered structure. However, the presence of TiO_2 in the prepared TiO_2/bentonite composite was not observed. The absence might be due to the low TiO_2 content which was homogeneously dispersed on the surface of the bentonite. Other peaks at 2θ angle 8.98°, 12.16° and 13.86° were attributed to anorthite $((Al_2CaO_8Si_2)_8$, number: 96-100-0035).

SEM analysis was carried out to evaluate surface morphology of the non-modified and modified bentonite. The results are given in figure 3. As shown in figure 3, the surface morphologies of both bentonite samples are different. The natural bentonite shows massive, aggregated morphology, some large flakes and a layer structure. After modification with TiO_2 species, the bentonite surface changed, resulting in a large number of small particles with a barely observable layer structure. The composition of the materials was evaluated via EDX analysis. The results showed that the content of titania increased from 0.36% in the natural bentonite to 5.29% after being modified with titania.

The nitrogen adsorption–desorption isotherms of the prepared samples showed that the BET surface area of modified bentonite (18.33 m^2/g) was slightly larger than that of natural bentonite (15.88 m^2/g), suggesting that the introduction of the titania (approximately 4.93%) slightly increased the porosity of the bentonite layers. That conclusion is supported by the data that the average pore diameter of the TiO_2/bentonite composite was smaller (9.34 nm) than that of natural bentonite (10.74 nm). Based on the average pore diameter, modified and non-modified bentonite were categorized as mesoporous materials.

Photocatalytic degradation of NBB under UV irradiation Effect of pH: The effects of pH on the photodegradation of NBB over TiO_2/bentonite composite were investigated at pH

values of 3, 5, 7, 9 and 11. The initial pH of dye solution is one of the most important parameters in influencing photocatalytic activity. This is due to the fact that the pH of solution not only influences the surface-charge-properties of the photocatalyst but also the ionic species of dye in the solution[17]. Figure 4 revealed that the percentage degradation of NBB decreased from 62.30 to 12.49% as the pH value raised from 3 to 11. It should be noted that the photodegradation of NBB is favored in acidic solutions. As an anionic dye, the adsorption and degradation of NBB were favored at lower pH levels because of the positive charge of TiO₂ in acidic solution.

The adsorption and degradation decreased as the pH increased because of the negative charge of TiO₂ in basic solution. At high pH values, the surface site of bentonite is also negative and induces the electrostatic repulsion between anionic dye. Furthermore, the photocatalyst surface prevents the adsorption of NBB. The surface properties of TiO₂ under acid and base condition can be written as follows[18]:

pH acid (pH < 7) : Ti-OH + H$^+$ → TiOH₂$^+$
pH base (pH > 7) : Ti-OH + OH$^-$ → TiO$^-$ + H₂O

Effect of Photocatalyst Dosage: The photocatalyst dosage is an important parameter in the suspended photocatalytic degradation process[11]. Therefore, various amounts of TiO₂/bentonite composite (0.2–1.0 g) were used to determine the optimal dosage of photocatalyst on the photodegradation of NBB. As depicted in figure 5, percent degradation of NBB was developed with photocatalyst dosages ranging from 0.2 to 0.4 g. This is because more photocatalyst provides more activated centers and can adsorb more of the reactant.

However, increasing the photocatalyst loading from 0.4 g to 1.0 g resulted in a decrease in the percent degradation of NBB. That result is due to the increased turbidity of the mixtures, which reduces the amount of light transmitted through the solution, blocking the penetration of light onto all available surface particles. According to the results (Fig. 5) that 0.4 g of photocatalyst dosage gave the maximum percent degradation (96.57%), the TiO₂/bentonite composite dosage of 0.4 g is selected for further studies.

Effect of Initial Dye Concentration: The effect of initial dye concentration on the photodegradation of the dye was studied by using different initial NBB concentrations (C_0 = 5, 10. 15, 20 and 25 mg/L). Figure 6 shows that there is a decrease in dye degradation as the dye concentration increases. The increase in initial dye concentration results in a greater amount of dye molecules attached on the surface of the photocatalyst and covers the active sites of TiO₂. As a result, there will be fewer photons that can reach the photocatalyst surface. Therefore, fewer •OH radicals will be formed and subsequently fewer •OH radicals that can attack the dye molecules.

Another possible cause is the UV-screening effect of the dye itself. A significant amount of UV may be absorbed by the dye molecules rather than the TiO₂ particles, reducing the efficiency of the photocatalytic reaction because the concentrations of OH and O₂ decrease. At a NBB concentration of 5 mg/L, 99.83% of NBB is removed within 120 min and decreased to 76.82% when the initial NBB concentration is 25 mg/L. The results reveal that photocatalytic degradation is rather promising at low NBB concentrations.
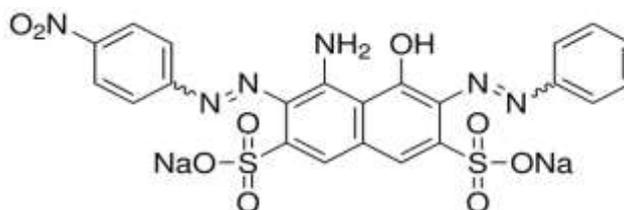
Figure 1: The structure of naphthol blue black (NBB) dye
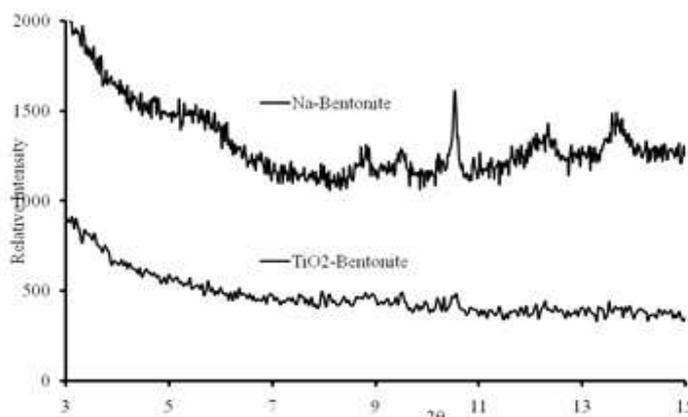
Figure 2: XRD pattern of the natural bentonite and TiO₂/bentonite composite
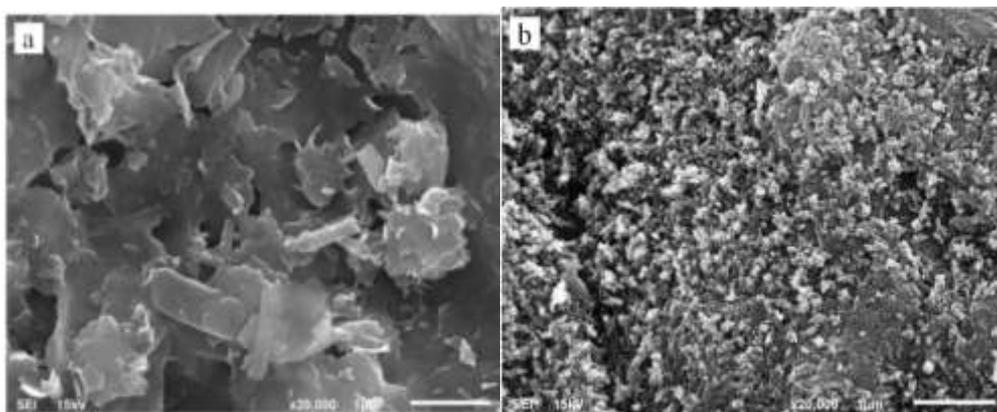
Figure 3: SEM image of a. Natural bentonite and b. TiO₂/bentonite composite
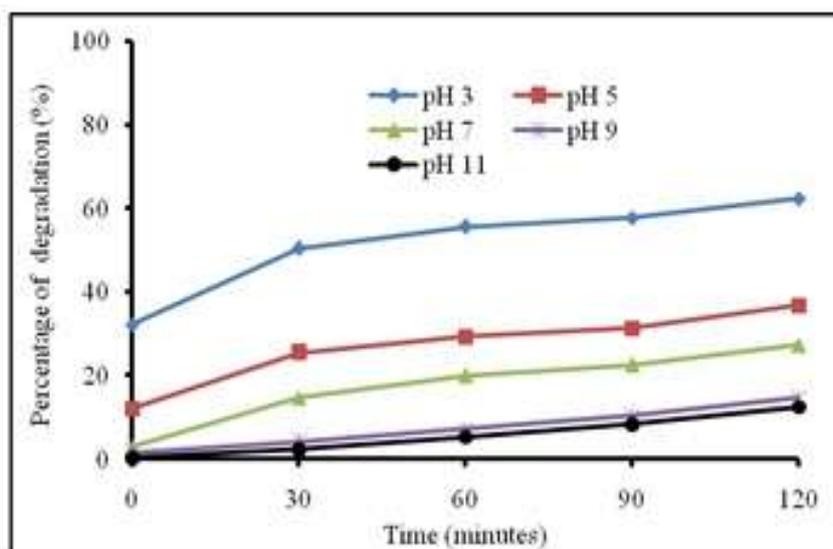
Figure 4: Photocatalytic degradation of NBB under UV light irradiation at various initial pH solutions. Initial dye concentration is 15 mg/L, photocatalyst dosage is 0.2 g.
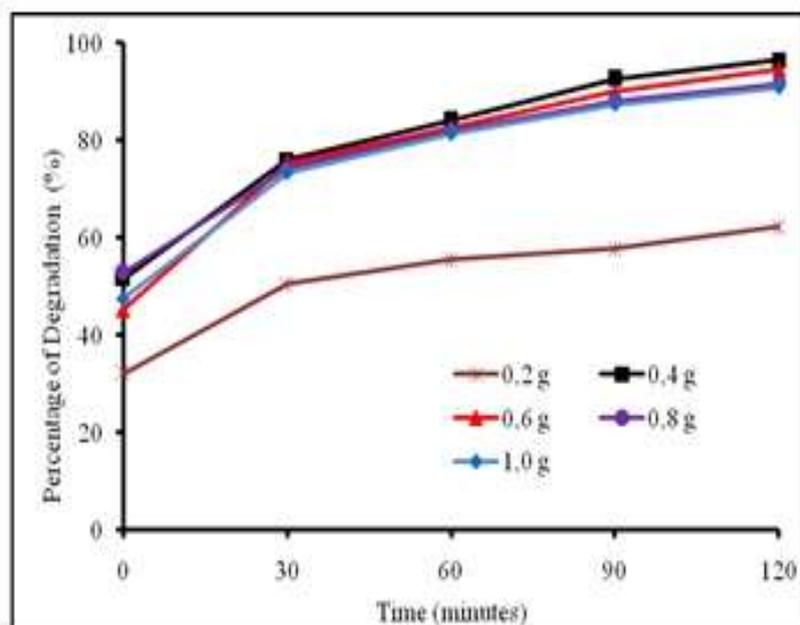
Figure 5: Photocatalytic degradation of NBB under UV light irradiation at various photocatalysts dosage. Initial dye concentration is 15 mg/L, initial pH solution is 3.
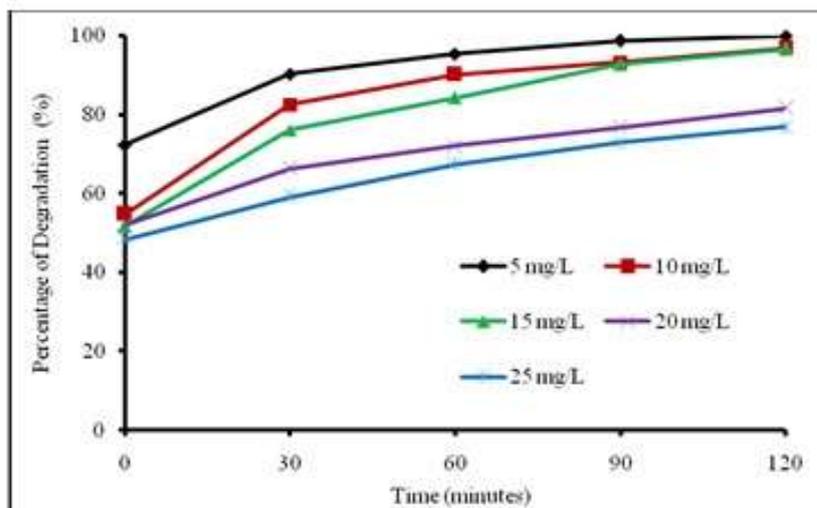
Figure 6: Photocatalytic degradation of NBB under UV light irradiation at various initial dye concentration. Initial pH solution is 3 and photocatalyst dosage is 0.4 g.
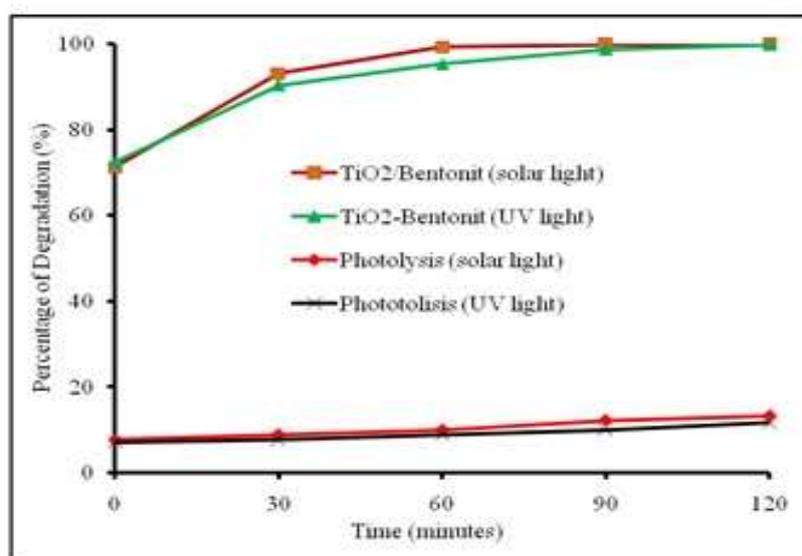
Figure 7: Photocatalytic and photolysis degradation of NBB. Initial dye concentration is 5 mg/L, initial pH solution is 3 and photocatalyst dosage is 0.4 g.

The effect of different light source on photodegradation of NBB was studied using solar light irradiation. It can be seen from figure 7 that the photocatalytic activity of the TiO$_2$/bentonite composite using solar light was higher than with the UV light. Figure 7 also reveals that the photolysis of NBB by UV and solar light in the absence of a photocatalyst is only 11.63% and 13.31% respectively which can be neglected.

Conclusion
The modification of natural bentonite into TiO$_2$/bentonite composite has been successfully performed by sol gel method using titanium tetraisopropoxide in hydrochloric solutions as TiO$_2$ precursor. The synthesized TiO$_2$/bentonite composite was categorized as mesoporous material. The TiO$_2$/bentonite composite is an effective photocatalyst for degradation of naphthol blue black dye under UV and solar

light irradiation. The highest photocatalytic activity of the TiO$_2$/bentonite composite was achieved at an initial dye solution pH equal to 3, a photocatalyst dosage of 0.4 g, an initial dye concentration of 5 mg/L, and 120 minutes of UV irradiation and 90 minutes under solar light irradiation.

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