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Application of TiO_2 Nano Particles Photocatalyst to Degrade Synthetic Dye Wastewater Under Solar Irradiation

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Abstract

Synthetic dyes are difficult to degrade in nature and contain hazardous material which can generate skin cancer and if not well treat, the synthetic dyes wastewater also can kill the organism live in the environment. One of alternative methods for handling the synthetic dyes wastewater is by using photocatalytic process as one of Advanced Oxidation Processes (AOPs). Semiconductor photocatalyst of TiO_2 under solar irradiation was chose in this process. The objective of this work is to study the application of Titanium dioxide (TiO_2) nano-particles photocatalyst to degrade the sample of synthetic dye wastewater with solar irradiation assistance. The anatase-powder and anatase-nano powder of TiO_2 used in this research was coated on the plastic media to prevent the cost of separation. The synthetic dye wastewater was made from Procion Redas a model of organic pollutant. The concentration of Procion Red was 100 mg/L. The TiO_2 concentration of the coating solution immobilized on the plastic material was varied between5-40% (w/v).The photocatalytic degradation of Procion Red synthetic dye was studied under solar irradiation within 3-12 hours, from 9 am until 3 pm for 2 days. The results show that the highest color degradation of 98% and COD degradation of 56% were achieved when using 40% anatase-nanopowder TiO_2concentration of coating solution under sunlight of 12 hrs. The nano-particles have a high interaction surface. As the interaction of particles increase, the catalyst activity will increases and inhibit the recombination reaction. In the nano-particle size, the TiO_2photocatalyst can absorb the UV vis from the sunlight to excite the electron and furthermore generate the hydroxyl radical as a strong oxidiser. The hydroxyl radicals oxidize the organic pollutant to be the less harmful compound and finally to carbon dioxide and water. As the generation of hydroxyl radical rise, the degradation of organic pollutant will increase. As the conclusion, it is feasible to apply the TiO_2nano-particles photocatalyst to degrade the sample of synthetic dye wastewater with solar irradiation assistance. In this research, the degradation of colour and COD increase as the nano-particles TiO_2photocatalyst concentration of coating solution and the exposure time increase. The colour degradation and COD degradation of 98% and 56%, respectively, was obtained under solar irradiation of 12 hours.

Keywords : Advanced Oxidation Processes (AOPs), photocatalytic, TiO_2 nano particles, synthetic dyes, solar irradiation

1. Introduction

Textile industrial development in Indonesia especially in South Sumatera at the recent time have a significant progress so give the positive affect to society's economic. On the other side, the activities in clothing production field also give the negative effect to environment. Today, the use of synthetic dyes in the textile industry has been inevitable, because of the cheap price, the durable colour, and much variety of colour availableifcompared with natural dyes. The untreated wastewater comes from the processes mostly contain the synthetic dyes which are difficult to degrade in nature. In Palembang city, generally, the textile home industries are located near the Musi River. In general, such kind of industries was not equipped with the wastewater treatment installation. So if the untreated wastewaters were discarded to the river, it can be worst the water body quality.

The wastewater treatment technology growth at this time still need a high cost of maintenance processes and much time of supervision. In recent decades a more promising approaches based on Advanced Oxidation Processes (AOPs) has been studied broadly for wastewater treatment. One of the AOPs methods is utilizephotocatalytic process of semiconductor material. Some kinds of semiconductor can be used for photocatalytic process are come from oxide group, such as TiO_2, Fe_2O_3, ZnO, WO_3, or SnO_2, whereas from sulfide group, such as

CdS, ZnS, CuS, FeS, etc. Among many kinds of semiconductor, until now TiO_2powder (mainly in anatase crystal form) has a high photocatalytic activity, stable, and not toxic. Comercially, TiO_2powder can be got easily and have been produced in huge quantity [1]. In addition, TiO_2 semiconductor photocatalytic presents various advantages: solar light may be used and TiO_2 is a relative cheap, reusable, and non-toxic material [2].

Thephotocatalytic process needs electron (e^-) and hole (h^+) pairs as a result of light ray on a semiconductor material. Recombination of the electron-hole pair is possible occur in the process. The unwanted recombination reaction of the electron-hole pair within semiconductor particles is drastically reduced as particle size decreases. With decreasing particles size of semiconductor to nanometer scale, the band gap energy greatly increased, which is led to higher redox potentials in the system. Moreover, the nano-scale semiconductors have a higher surface area to volume ratio than their equivalent bulk, thus allow for greater photon absorption on the photocatalyst surface. Therefore, the nano-scale semiconductor is expected to have higher photocatalytiv activity than its bulk [3,4]. For this reason, TiO_2 nanoparticles were used in this study.

In previous application, TiO_2 powder has been used in suspended solution form. The separation and reuse of the TiO_2 powder from treated water or wastewater also limit its application. This separation need a further process and associate cost with it. In order to overcome this problem, TiO_2 immobilization appears as a possible alternative. Many researchers have coated TiO_2 on various materials in their study. TiO_2 was immobilized on glass fiber [5], activated carbon fiber [6] silicone rubber film [7], pebbles [8], ceramic tiles [9], and acrylic plastic [10]. However, polyethylene terephthalate (PET) bottles have been successfully used to expose drinking water to sunlight for solar disinfection [11]. These bottles appear to be an interesting support to reduced technologies cost for in situ water treatment, especially for isolated population in developing countries without access to municipal wastewater networks or unavailable municipal wastewater such as in several cities like Palembang. In this research, the PET plastic bottle taken from the soft drink bottle waste was used as media for TiO_2 coating on.

The light source could be used for TiO_2 photocatalytic process is the UV light comes from sunlight/solar irradiation or the artificial light. Application of the artificial light or often called UV light is more efective than the sunlight, because the electron-hole recombination can be avoided. Although the sunlight has only 5% of optimum energy for photocatalytic excitation and ultimately degradation of textile dyes, it could be safe and cost effective source. The UV light is not only hazardous but also expensive because of large input of electric power to generate UV irradiation [12]. The application of artificial UV light is not feasible and economical for the treatment of a huge quantity of industrial effluent.

However, the development of a practical application photocatalytic system focused on the cost effectiveness by the use of renewable solar energy source. Photocatalytic degradation of organic contaminants using solar irradiation could be highly economical compare with the processes using artificial UV irradiation which required significant electrical power input. In tropical country like Indonesia, intense solar irradiation is available through the years and hence, it could be used for photocatalytic degradation of pollutants in wastewater effectively. The present study focuses on the application of TiO_2 nano particles to degrade synthetic dye wastewater under solar irradiation.

2. Materials and methods

2.1. Materials preparation

Synthetic dye wastewater was made by using Procion Red (PR) as organic pollutant model. This commercial sample of common textile dye, obtained from Fajar Setia Dyestuff (Indonesia) was used as such. The PR concentration of 100 mg/l was prepared in distilled water. TheTiO_2anatase-powderwith particle size: -325 mesh, $\geq$ 99% trace metal basis and TiO_2anatase-nanopowder with particle size: < 25 nm, 99.7% trace metal basis were used as semiconductor photocatalyst (Sigma-Aldrich). The coating process was accomplished by mixing the TiO_2photocatalyst with acetone in the 250 ml beaker glass. The TiO_2 photocatalyst concentration of coating solution was varied 5-40% (w/v). The certain amount of catalyst was dissolved in 10 mL of acetone until a homogeneous solution recognized. Add a few drops of cyanoacrylate adhesive to the solution and stir slowly, followed by putting the plastic then stir until the thick solution obtained. Take the coated plastic immediately and place in the room air. Allow the entire surface of plastic dry in the room temperature.

2.2. Procedure

Solar irradiation was used as energy source to the photocatalytic process. The photocatalytic degradation of synthetic dye was carried out in batch operation in a cylinder glass type of reactor. The reactor capacity is 300 ml with 7 cm of inside diameter and 8.5 cm of height. For every experiment performed, the reactor was initially loaded with 250 ml of Procion Red aqueous solution, and then put TiO_2-coated plastic at the bottom of reactor. Reactor was placed under solar irradiation from 9 am until 3 pm, selection of time based on secondary data from BMKG South Sumatera during May-June of 2012. The data shown that the average intensity of sunlight reached the maximum between 9 am to 3 pm. COD and colour degradation was observed every 3 hours between 9 am until 3 pm under the sunlight for 2 days. The reactor was retained in the dark place when the experiment pending. All the solar photocatalytic experiments were carried out at the same conditions.

2.3. Characterization and Analysis

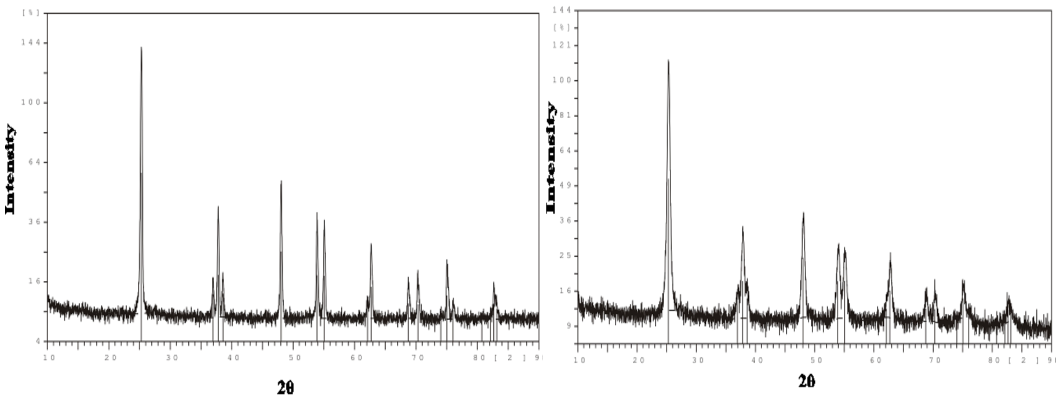
The intensity of solar light was measured using Light meter (Luxtron Lx-103, Lux, Taiwan) at various time intervals of 3 hours between 9 am and 3 pm. The mean intensity of solar irradiation was 128 W/m^2. The TiO_2 particles catalysts were characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). The crystalline phases were determined by using a X-ray diffraction measurements (PC-APD Philip) with Cu tube anode, operated at 40 kV and 30 mA. A Scanning Electron Microscope (SEM), JEOL SEM-330 JAPAN was used to examine the surface morphology of TiO_2-coated plastic. COD degradation was determined by titrimetric method and colour degradation was measured by HACH Spectrophotometer based on Platinum-Cobalt (PtCo) scale. COD and colour degradation percentage of dye is defined as follows:

$$\text{COD degradation percentage} = ((COD_o - COD_t)/COD_o) \times 100\% \quad (1)$$

$$\text{Colour degradation percentage} = ((C_o - C_t)/C_o) \times 100\% \quad (2)$$

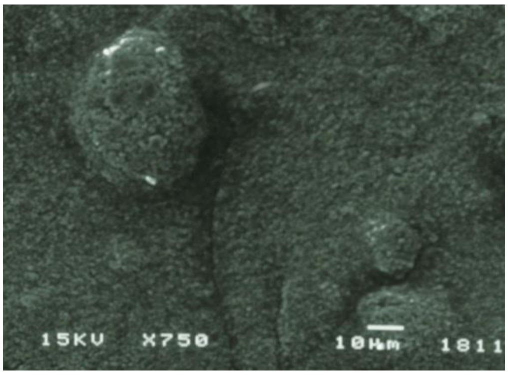
Where COD_o,C_o is the initial COD and colour, respectively. And COD_t, C_t is the COD and colour at reaction time t, respectively.

Figure 1 displays the X-Ray diffraction (XRD) pattern of anatase-powder and anatase-nadno powder of TiO_2 as prepared. All characteristic lines are attributed to the anatase phase in outstanding agreement with a reference pattern [13]. Photocatalytic process was examined by using the coated anatase-powder and anatase-nano powder TiO_2 photocatalyst on PET plastic material. Morphology of TiO_2-coated plastic surface by different TiO_2 concentration of coating solution can be exposed in Figure 2.

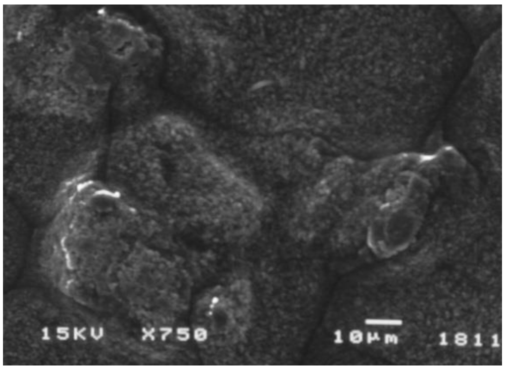


(a) (b)

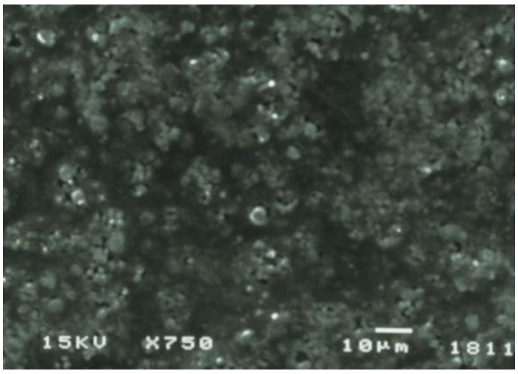
Figure 1. TiO_2 XRD pattern of (a) anatase-powder as prepared (b) anatase-nano powder as prepared



(a)



(b)



(c)

Figure 2. SEM images of TiO_2 coated on PET plasticby using (a) 10% of anatase-powder TiO_2 concentration of coating solution (b) 40% of anatase-powder TiO_2 concentration of coating solution and (c) 40% of anatase-nano powder TiO_2concentration of coating solution

3. Results and Discussion

3.1. Effect of TiO_2 concentration of coating solution on colour and COD degradation

Colour degradation in this photocatalytic process happened in the presence of oxidation reaction by hydroxyl radical which could decomposed the synthetic dye compound to the more simple compound. The colour measured based on PtCo scale by comparing the colour of sample with the standard colour. The initial colour concentration is 1750 PtCo, whereas the initial COD is 191 mg/l. Figure 3 illustrated effect of anatase-powder TiO_2 concentration of coating solution on colour degradation of the dye.

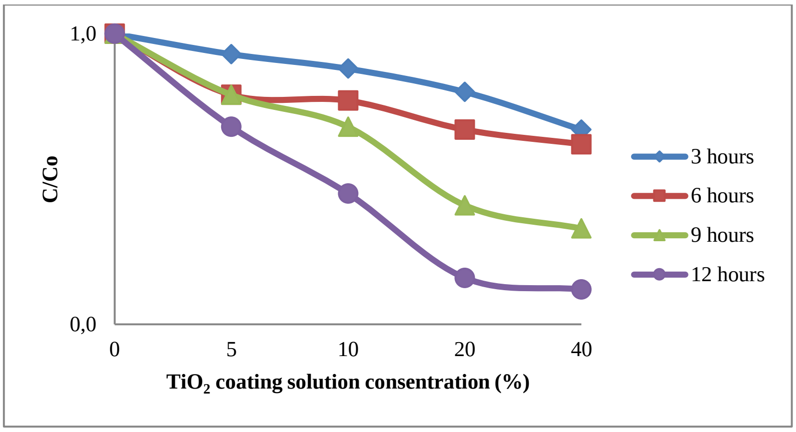


Figure 3. Effect of anatase-powder TiO_2 concentration of coating solution on colour degradation (C/C_o)

The figure shows that the highest colour degradation was reached when using the highest TiO_2 concentration of coating solution. As the concentration of coating solution increase, the amount of TiO_2 photocatalyst available also increase which generated more electron-hole pairs and more hydroxyl radicals subsequently. It must be highlighted in this case, increasing TiO_2 concentration would increase the surface area and improve the oxidation efficiency as reported by Fostier et al. in their study on arsenic removal from water employing heterogeneous photocatalysis with TiO_2 immobilized in PET bottles [14]. By means of 40% anatase-powder TiO_2 concentration of coating solution, the final colour of 214 PtCo and COD of 102.4 mg/l were obtained. According to eq. (1) and (2), the COD degradation of 46% and colour degradation of 88% were found under solar irradiation of 12 hours.

3.2. Effect of exposure time on colour degradation

Effect of exposure time on the final concentration of Procion Red synthetic dye solution can be demonstrated in Figure 4. The figure shown that the exposure time has a significant effect on the colour degradation of the dye after 12 hours of illuminating under solar irradiation. On the first day, the colour change was observed. But on the second day, degradation of the dye solution was very substantial. After 12 hours of exposure time, the colour of dye changes to become nearly clear and the colour degradation of 88% was achieved when using 40% anatase-powder TiO_2 concentration of coating solution. Increasing the exposure time will enhance electron-hole formation and hence, the electron-hole recombination is negligible and in turn increases the construction of hydroxyl radicals, thereby, causing more effect on the percentage degradation of the dye.

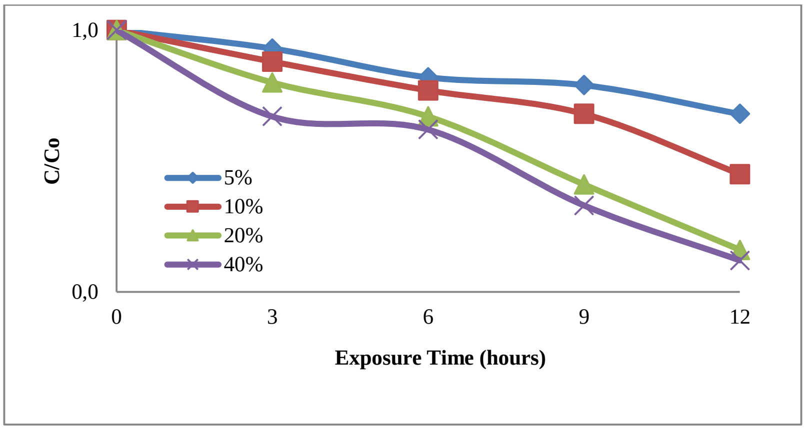


Figure 4. Effect of exposure time on colour degradation (C/C_o) by using different anatase-powder TiO_2 concentration of coating solution

As can be seen in Figure 4, degradation of colour increase as increasing the exposure time. This result was in agreement with Neppolian et al. in 2002 who found that degradation of commercial textile dyes increase with increasing irradiant time. The degradation of Reactive Yellow 17 and Reactive Red 2 were almost 100% after 12 and 6 hours of solar irradiation time, respectively. Whereas the degradation of Reactive Blue 4 was about 70% after 12 hours of solar irradiation time. Bhosale et al. in 2014 also reported that decomposition of Methylene Blue (MB) obviously increase with increasing solar irradiation time. In their research about solar photocatalytic degradation of MB using doped TiO_2 nanoparticles, among the different metal and non-metal incorporated samples, C-TiO_2 sample exhibited the highest photocatalytic activity, only 5-7% of MB remained, and in the case of Fe-TiO_2, N-TiO_2 10% of MB remained after exposure to solar light for 60 minutes.

3.3. Effect of TiO_2photocatalyst type on colour and COD degradation

From the previous results, it was found that the TiO_2anatase-powder coating solution of 40% and the exposure time of 12 hours were the best condition for COD and colour degradation. In that condition, the colour degradation of 88% and COD degradation of 46% were attained. It is expected to have a higher pollutant degradation by generate more electron-hole pairs and prevent the recombination of electron-hole pairs. Various methods have been developed to avoid that recombination. Photocatalyst modification and the effort to get a larger active surface area were the possible alternative methods. One of TiO_2 modification is by design the nano particle in composite. The nano particles have a high interaction surface area. The more interaction between particles will give a higher photocatalytic activity, thus prevent the recombination reaction. In nano state, the particles of TiO_2photocatalyst might use visible light from the sun to excite the electron [8].

Figure 5 shows a comparison of final colour degradation reached between anatase-powder and anatase-nano powder of TiO_2.It can be seen from the figure, the final colour degradation by using anatase-nano powder was higher than by using anatase-powder of TiO_2. Initial colour concentration of dye solution was 1750 PtCo and after the process by using anatase-nano powder of TiO_2, the colour concentration decrease to 30 PtCo or the colour degradation of 98% was obtained. In this case, the environmental quality standard for wastewater has been fulfilled, whereas the maximum concentration of colour in the wastewater must be less than 50 PtCo.

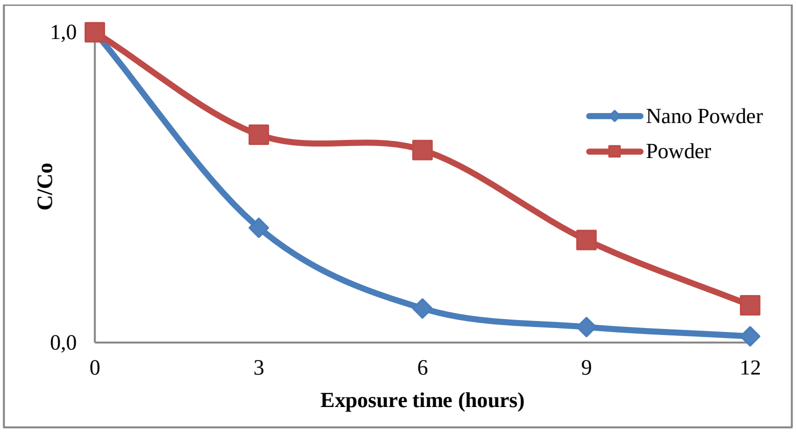


Figure 5.Effect of TiO2photocatalyst type on colour degradation (C/Co)

COD degradation achieved by using anatase-nano powder TiO_2 was higher than by using anatase-powder TiO_2, as can be demonstrated in Figure 6. The figure displays relationship between exposure time and COD degradation by using different type of TiO_2 photocatalyst, where TiO_2 concentration of the coating solution was 40%. Initial COD of the Procion Red was 191 mg/l.

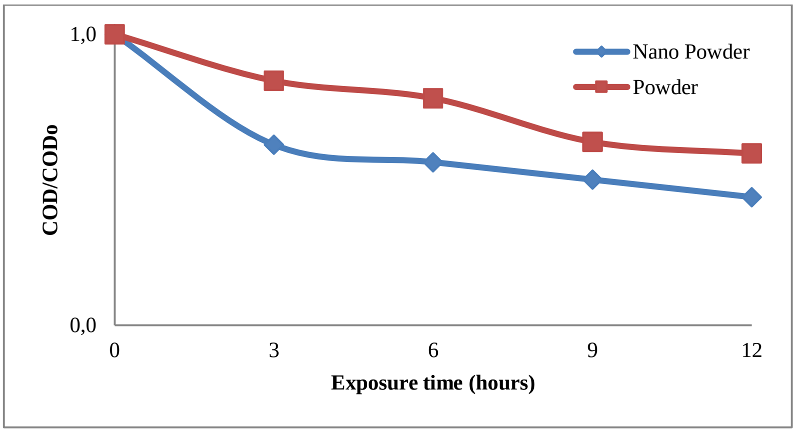


Figure 6. Effect of TiO_2catalyst typeon COD degradation(COD/COD_o)

In the nano-particle size, the TiO_2 photocatalyst can absorb the UV vis from the sunlight to excite the electron and furthermore generate the hydroxyl radical as a strong oxidator. The hydroxyl radical oxidize the organic pollutant to be the less harmful compound and finally to carbon dioxide and water. As the generation of hydroxyl radical rise, the degradation of organic pollutant will increase.At the end of the photocatalytic process, the final COD was 84 mg/l or COD degradation of 56% was obtained when using anatase-nano powderTiO_2, which it means that the environmental quality standard for wastewater have been accomplished. However, by using anatase-powder TiO_2 the final COD was 102.4 mg/l or COD degradation of 46% was reached.

4. Conclusion

As the conclusion, it is feasible to apply the TiO_2nano-particles photocatalyst to degrade the sample of synthetic dye wastewater with solar irradiation assistance. In this research, the degradation of colour and COD increase as the TiO_2 photocatalyst concentration of coating solution and the exposure time increase. The colour degradation and COD degradation of 98% and 56%, respectively was obtained by using 40% anatase-nano particles TiO_2 concentration of coating solution and exposure time of 12 hours.

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