Synthesis and characterization of novel TiO$_2$–ZnO–CoO nanocomposite photocatalyst for photodegradation of methylene blue dye

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Abstract. TiO$_2$–ZnO–CoO nanocomposite photocatalyst has been synthesized using sol-gel method. Titanium (IV) ethoxide, zinc acetate (Zn(CH$_3$COO)$_2$.2H$_2$O) and cobalt acetate (Co(C$_3$COO)$_2$.4H$_2$O) were used as precursors. TiO$_2$ and ZnO posses good photocatalytic ability in photodegradation of water pollutant. The disadvantage and weakness of photocatalytic reaction of TiO$_2$ and ZnO mostly happens at ultraviolet range and less at visible light. This research aimed to decrease the disadvantage of TiO$_2$ and ZnO, using cobalt oxide. TiO$_2$–ZnO–CoO nanocomposite photocatalyst was characterized by using SEM-EDS and XRD. SEM analysis showed homogenous and smooth morphology of TiO$_2$–ZnO–CoO nanocomposite photocatalyst. EDS analysis revealed the TiO$_2$–ZnO–CoO nanocomposite photocatalyst had O : Ti : Co : Zn = 32.64 : 37.39 : 11.85 : 18.12. In this study, we expose effect of amount of TiO$_2$–ZnO–CoO nanocomposite photocatalyst, pH, and irradiation time on methylene blue dye photodegradation. Novel TiO$_2$–ZnO–CoO nanocomposite photocatalyst was effective in photodegradation of methylene blue dye.

1. Introduction
Fast growing of industry influences the decrease of environment quality. For example; textile industry polluted water and reduced the water quality. Waste water from textile industry contain dyes such as methylene blue. There are many treatments to treat waste water such as membrane process, adsorption, chemical, biological, advanced oxidation, and photodegradation process. Photodegradation of methylene blue by nanometal oxide photocatalyst is one promising process [1].

Many researchers had been interested to study nanoparticle materials since nanoparticle materials can be designed to show a novelty and to increase physical and chemical properties from the materials significantly. Nanoparticle is particle with ranging in size from 1-100 nm. Presently, different metallic nanomaterials are being produced using copper, zinc, titanium, magnesium, gold, alginiate, and silver [2]. Nanoparticles such as metals, semiconductors and metal oxides are interesting materials for a wide variety of applications in the field of information, energy, environmental and medical technologies due to their unique or improved properties determined primarily by size, composition, and structure along with their selforganized film structures [3]. Among these metal oxides with semiconductor property, titanium dioxide (TiO$_2$) and zinc oxide (ZnO) have been extensively studied for their chemical stability dan efficient photocatalytic properties [4]. However, these two metal oxides show disadvantages for application in photodegradation such as hard for regeneration as well as photocatalytic reaction mostly occurs in ultraviolet light but less in visible light [4]. Aal et.al, 2008 [5] reported the coupling of semiconductors particles with different band-gap widths and carried out photocatalytic activity experiments using various coupled semiconductor particle systems such TiO$_2$ – CdS [6], TiO$_2$ – WO$_3$ [6], TiO$_2$ – SnO$_2$ [7], TiO$_2$ – MoO$_3$ [8] and TiO$_2$ – Fe$_2$O$_3$ [9]. However, few researcher focused on the photocatalytic activity of TiO$_2$ – ZnO coupled oxides [10]. This study aimed...
to synthesize nano photocatalyst to degrade methylene blue dye and to optimize photodegradation process of methylene blue dye.

2. Experimental

2.1. Materials
The chemicals used were titanium (IV) ethoxide (Merck), zinc acetate (Zn(CH₃COO)₂·2H₂O) (Merck), cobalt acetate (Co(CH₃COO)₂·4H₂O) (Merck), polyvinyl pyrrolidone (PVP) (Merck), methylene blue dye (Merck), ethanol pa (Merck) and demineralization water.

2.2. Synthesis of TiO₂-ZnO-CoO nanocomposite
0.2 M zinc acetate solution was added to 2% PVP solution under vigorous stirring. Cobalt acetate solution of 0.2 M was added drop by drop to the mixture. The mixture was stirred magnetically at room temperature until a homogeneous solution was obtained. Titanium ethoxide in ethanol of 1M was added to the homogeneous solution and stirred for 12 hr then separated using filter to get the precipitate product. The product was dried in oven at 105°C for 6 hr and calcined in furnace at 800°C for 2 hr.

2.3. Characterization of TiO₂-ZnO-CoO nanocomposite
The structural characterization of nanocomposite were investigated by X-Ray Diffraction (XRD). The morphology of the product was characterized by Scanning Electron Microscopy (SEM/EDS).

2.4. Photodegradation of methylene blue dye using TiO₂-ZnO-CoO nanocomposite
The photodegradation of dye using nanocomposite was evaluated by degradation of a model aqueous solution of methylene blue (MB) after subjection to UV-radiation. The initial concentration of MB aqueous solution was 4 ppm. TiO₂ nanocomposite sample was added to 25 mL dye solution then magnetically stirred in the dark for 30 min. The irradiation source was a UV-C lamp (Philips 15 watt, λ = 253.7 nm). All photocatalytic tests were performed at constant stirring. The parameters for the photodegradation were pH, photodegradation time and nanocomposite mass. After irradiated, mixture were centrifuged. The absorbances of clear filtrate were measured by an Agilent 8453 UV-Vis spectrophotometer at 664 nm, the maximum absorption wavelength of MB.

3. Result and Discussion

3.1. Characterization of TiO₂-ZnO-CoO nanocomposite
The XRD patterns of TiO₂-ZnO-CoO nanocomposite are shown in Figure1 - Figure 3. Figure 1 shows that there is titanium dioxide (TiO₂) in the product in rutile form (JCPDS 21-1276). The XRD pattern in 2θ from TiO₂-ZnO-CoO has a similar pattern with that of ZnO. Figure 3 shows the formation of cobalt oxide. The XRD pattern from TiO₂-ZnO-CoO nanocomposite shows similar pattern with that of CoO (JCPDS 42-1300).
Figure 1. XRD pattern of TiO$_2$ standard and TiO$_2$-ZnO-CoO nanocomposite.

Figure 2. XRD pattern of ZnO standard and TiO$_2$-ZnO-CoO nanocomposite.
SEM image of morphology of the TiO$_2$-ZnO-CoO nanocomposite is presented in Figure 4. We can observe shape of nanoparticle and its aggregation. Shape of nanoparticle is in spherical form with diameter less 1 µm. Nanoparticle size is relatively homogenous. The EDS analysis shows in Figure 5. The EDS analysis reveals that TiO$_2$-ZnO-CoO nanocomposite has mass ratio of O : Ti : Co : Zn was 32.64 : 37.39 : 11.85 : 18.12, respectively.
3.2. Photodegradation of Methylene Blue dye using TiO$_2$-ZnO-CoO nanocomposite

Figure 6 shows the effect of pH on photodegradation of methylene blue. Photodegradation was carried out with and without TiO$_2$-ZnO-CoO (TZCo) as the photocatalyst. Both photodegradation reach the highest value at pH 7 indicated that TiO$_2$-ZnO-CoO played a role in optimum condition for photodegradation of methylene blue dye at pH 7.
Figure 7. Effect of photodegradation time on photodegradation of methylene blue.

Figure 7 shows that the degree of degradation increased with longer photodegradation time. Sixty minutes was the optimum condition on photodegradation of methylene blue. At 90 min, degradation value similar with of 60 min.

Figure 8. Effect of TiO$_2$-ZnO-CoO nanocomposite mass on photodegradation of methylene blue.

Figure 8 shows the effect of nanocomposite mass on photodegradation of methylene blue. Addition of nanocomposite mass from 0.01 to 0.04 gr increased the degree of degradation but decreased with the addition of 0.05 gr of nanocomposite mass. The photodegradation of methylene blue can reach its optimum condition at addition of 0.04 gr of nanocomposite mass.
4. Conclusion
TiO$_2$-ZnO-CoO nanocomposite has been successfully synthesized for photodegradation of methylene blue dye. The optimum condition for photodegradation of methylene blue was achieved at pH 7 with degree of degradation was of 36.98% for 60 min.

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