One-step Synthesis of TiO_2/ZnO Nanocomposites by Refluxing Methods for Photochemical Degradation of Humic Acid

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Abstract
Synthesis of TiO_2/ZnO nanocomposites (TZN) through the one-step refluxing method for photochemical degradation of humic acid (HA) in aqueous solution has been studied. Titanium isopropoxide (TTIP) and $ZnSO_4.7H_2O$ were used as a starting material under base solution at 120 ^oC for 24 hours. TZN materials were characterized by x-ray diffraction (XRD), scanning electron microscope (SEM), the thermogravimetric analysis and differential thermal analysis (TG-DTA). The characterization showed that there is a specific diffraction peak from TiO_2 (2θ = 25.30) and ZnO (2θ = 36.33) as a composite with the crystal size 41.55 and 15.76 nm, respectively. The material morphology showed the granular shape of the composite and have good thermal stability. The photochemical activity was evaluated by photocatalytic degradation of HA under UV_{254} light. The optimum condition was found at pH 4.0, and times at 30 minutes. This study confirmed that the TZN material can decrease the HA concentration. Furthermore, the maximum result of the experiment was a 95-98% degradation of HA in aqueous solution.
Keywords: degradation, humic acid, photochemical, TiO_2, ZnO

1. Introduction

Humic acid (HA) is one of large molecules, easily soluble, and also have dangerous effects at a high concentration in the water. High concentration of the HA can decrease the quality of the water and also affects many quality watertreatment. Numerous studies have been studied for removal of HA in the water, including adsorption, membranes separation, sedimentation, ion exchange and photoelectrodegradation (Wang et al., 2011; Zhou et al., 2019). Some previous studies have reported some of the semiconductor material for photochemical degradation such as SiO_2, ZnO, TiO_2, SnO_2, Fe_2O_3, and etc (Wahyuningsih et al., 2016; Begum et al., 2016). However, some of these results do not show a maximum degradation value. Currently, the combination of two metal oxide materials is interesting topics to study due to the synergistic properties of two metal oxide materials.

Generally, the synthesis of nanomaterials uses the hydrothermal method. But the method requires the higher temperatures so this method is considered less green chemistry. In this work, TiO_2/ZnO nanocomposites were synthesized via one-step synthesis with refluxing methods. TiO_2 has widely used for the photocatalytic process but the material still has low efficiency for photochemical reaction due to the higher bandgap. Therefore, some studies are still needed for improving TiO_2 performance as photocatalyst materials. One approach is to combine some metal oxides such as ZnO. ZnO has been reported as good performance because it has a lower band gap. The crystalline structure, thermal stability, and surface morphology were studied by XRD, DTA, and SEM. The photocatalytic study of nanocomposites was investigated in aqueous solution under UV_{254} radiation.

2. Experimental

2.1 Synthesis of TiO_2/ZnO

The starting materials, 5 mmol TTIP 95% was added into 2.5 mL ethanol 99% (sol. A), then 5 mmol zinc sulfate was added into 2.5 mL ethanol 99% (sol. B). The sol. B was slowly dropped into sol. An under magnetic stirring for 30 minutes. The mixed solution was added 12 M NaOH and refluxed at 120 ^oC for 12 hours. The mixed gel was washed with 0.1 M HCl, and the mixed gel was dried and calcined at 400 ^oC for 2 hours. The TiO_2/ZnO nanocomposites were characterized by SEM (JEOL JSM-6510A), XRD (Rigaku, Cu Kα), and TG-DTA (PerkinElmer).

2.2 Photocatalytic study

0.1 g powder of TiO_2/ZnO nanocomposites were put into 50 mL HA 2 mg L^{-1}. A 145 W Philips UV lamp was used as a light source, with the working distance of 5-10 mm and the voltage of 20 kV. The degradation of HA was analyzed by spectrophotometry UV-Vis at the wavelength 255 nm.

3. Results and Discussion

Figure 1a shows the XRD pattern of the synthesized TiO_2/ZnO nanocomposites using refluxing methods. From the XRD pattern, it can be confirmed that the phase of TiO_2 is anatase phase (2θ=25.30) with the crystal size 41.55 nm (ICSD standard no. 63711), while the ZnO is found as zincite phase (2θ=36.33) with the

crystal size 15.76 nm (ICSD standard no. 67454). The results show that the composites have a high crystallinity. Figure 1b has shown the surface morphology of the nanocomposites. The characterization shows that the TiO_2/ZnO has a granular morphology. However, it can be seen that the TiO_2 particles are more dominant than the ZnO particles.

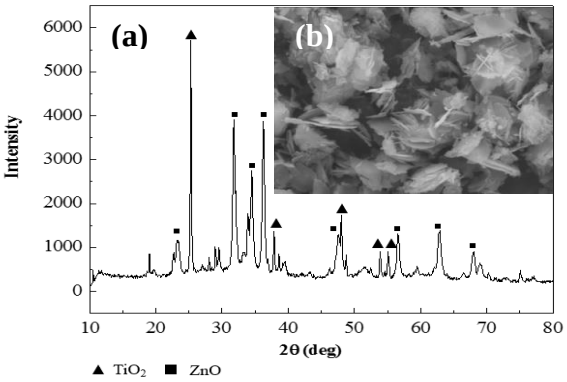

Figure 1. (a) XRD pattern, and (b) surface morphology of the prepared TiO_2/ZnO

The thermal stability of the TiO_2/ZnO was observed by TG-DTA. When the temperature is increased to 300 ^oC, it can be found an exothermic peak in the DTA curve and it is a corresponding with the TG curve. It proved that the hydroxylation of the precursor and formation of anatase phase TiO_2 have occurred. In addition, a widening DTA curve is obtained. This indicates that the growth of TiO_2 crystals is influenced by the presence of ZnO.The Photocatalytic test was found optimum at pH 4.0 and times at 30 minutes with removed 97.52%. at the low pH, the presence of acidic ions (H^+) can be generated the formation of H radicals and dissociation of protons that caused the surface charge will be negative, while the metal oxide nanocomposites will be positively charged (Wang et al., 2011). As shown in Figure 2, the rate constant degradation of HA using TiO_2/ZnO has a value higher than TiO_2 and ZnO. The plot ln (C/C_o) vs time (t) shows that the degradation followed the pseudo first-order kinetics mechanism. The rate constant was found at 0.0651, 0.0261, and 0.0154 for TiO_2/ZnO, ZnO, and TiO_2, respectively.

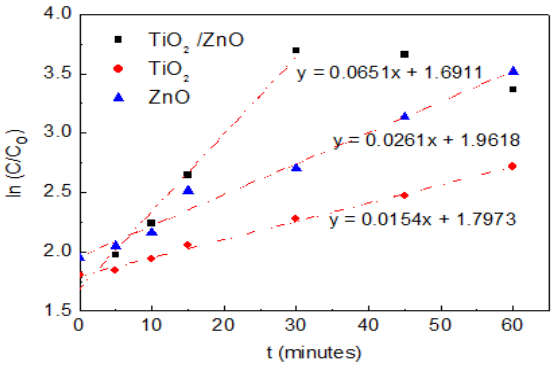

Figure 2. Effect of degradation time of HA 2 mg L^{-1} at pH 4.0

Because the nanostructure of TiO_2/ZnO has high adsorption activity for HA on its surface, the photoelectrons and photo holes can rapidly react with the HA, thus resulting in significant degradation of molecules. The degradation of HA can be described as follows:

$$(ZnO_2\text{-}TiO_2) \xrightarrow{hv} (ZnO_2\text{-}TiO_2) + e^-_{CB} + h^+_{VB}$$

$$HA_{ads} + h^+_{VB} \longrightarrow R^{\bullet +}_{ads} \longrightarrow \text{degradationproducts}$$

4. Conclusions

In this study, the nanocomposites TiO_2/ZnO has been successfully synthesized by refluxing methods. The materials have good crystallinity and thermal stability. The photocatalytic performance showed that the TiO_2/ZnO has the highest rate constant value by following pseudo first-order kinetics. It revealed that the combination of two metal oxide nanocomposites could improve the catalytic performance for organic molecules degradation.

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