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Research Article

Preparation of Silver Immobilised TiO_2-Hectorite for Phenol Removal and *Eschericia coli* Desinfection

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Abstract

Preparation of silver immobilized TiO_2-Hectorite and its application in phenol photooxidation and Eschericia coli bacteria desinfection has been conducted. Material was obtained by two steps of synthesis: preparation of TiO_2-Hectorite and silver immobilization into TiO_2-Hectorite. Physico-chemical characterization to the prepared material compared to raw hectorite was conducted by X-ray Diffraction, gas sorption analyzer, scanning electron microscope and DRUV-Visible spectrophotometry and for photoactivity study, phenol photo-oxidation and *Eschericia coli* desinfection were investigated. The results indicated that the modification to hectorite material improve the physico-chemical character related to its role as photo-catalyst. Kinetic study of phenol photooxidation revealed the role of TiO_2 pillarization and silver immobilization in enhancing rate of reaction as well as increased photoactivity of the materials in *E. coli* desinfection. © 2013 BCREC UNDIP. All rights reserved. (*Selected Paper from The 2nd ITB Catalysis Symposium 2012, Bandung, Indonesia*).

***Keywords*:** pillared clay; TiO_2; hectorite; photocatalysis; phenol photo-oxidation

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1. Introduction

Adsorption and photocatalytic degradation were recently reported as efficient process to eliminate organic pollutants in water. Compared to adsorption, photodegradation consisting photooxidation and/or photoreduction is evaluated as better technique. Degradation of molecules assisted by radicals generated by the interaction of photo-catalyst and photon is the basic principle of photocatalytic degradation. Titania is known as leading photocatalyst material with refer to its photoactivity and economist value. Due to its easy in loosing photoactivity in the bulk form, titania dispersion in a porous and stable inorganic supports are widely developed [1,2]. For this purpose, clay minerals are good adsorbents and suitable material. In phylosilicate classification, hectorite is a kind of clay mineral, being composed of alternative pairs of an expandable dioctahedral-smectite like layer at a ratio of 2:1 [3].

The physico-chemical properties of hectorite was reported as effective adsorbent and reported by many studies to reduce pollutants or as catalysts support for some photocatalysis and industrial catalysis [5-7]. Based on the structure of hectorite material that is rich in channels allows penetration and adsorption, the advantageous of adsorptivity is proposed to intensely improve a photoactivity as analogue to similar project in smectite clay utilization for supporting TiO_2. In advance, due to photocatalysis mechanism that

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contained both oxidation and reduction process on the surface of TiO_2 particles, the efficiency of photocatalytic reaction depends on the presence of photo-excited electron-hole during its interaction with photon. The loading of noble metal such as Ag was reported as new strategy to minimize the recombination [8-11]. Clay material including hectorite are used in human and veterinary health formulations like excipients or active substances. The interaction between active material and the excipients may delay the drug release and this can be more favorable. Refer to previous studies on the participation of silver to enhance activity of some photocatalyst, this work is aimed to develop a combination of TiO_2, silver and hectorite clay material. With a formulation of TiO_2-hectorite and silver particles deposition into TiO_2-hectorite, increased photo-efficiency compared to bulk TiO_2 is proposed. With higher thermal and chemical stability compared to other smectite class of clay that have been studied, the use of synthetic hectorite as clay matrix is proposed to give better physico-chemical character with an enhanced photoactivity efficiency [4,5].

Investigation on surface and physicochemical profiles of prepared material in relation with photoactivity is discussed. Some characteration by means of x-ray diffraction, diffuse reflectance UV-Visible, gas sorption analysis and scanning electron microscopy were utilised and the well known organic molecule degradation of phenol and photocatalytic desinfection of *Eschericia coli* were used to evaluate the significancy of material modification.

2. Experimentals

2.1. Materials

Synthetic clay of hectorite was obtained as commercial products from Rockwood international Co. Limited and was used as received without any pre-treatment. The cation exchange capacity of hectorite is 89-100 meq/100 g. As TiO_2 precursor, titanium isopropoxide dihydrate were purchased from Sigma Aldrich in pro analyst grade. Phenol, ethanol and isopropanol were obtained from Merck.

2.2. Method

Preparation of silver immobilised TiO_2-Hectorite (further called as Ag/TiO_2-Hectorite) consist of two main steps; preparation of TiO_2 – Hectorite by pillarization process and Ag immobilization onto TiO_2-Hectorite by ion exchange process. Supporting of TiO_2 into hectorite sample was engaged by using titanium isopoxide as precursors obtained from dilluting titanium isopropoxide in isopropanol sovent under the addition of acetic acid at the concentration of 0.001 M followed by stirring for 4 h. At theoretical content of 7.0 wt%, titanium isopropoxide solution was dropped slowly into hectorite mineral suspension in water (5 %) and then the mixture was kept stirred for 24 h. After the dispersion, the suspension was filtered, washed several times with distilled water before drying at 105 °C for 24 h and calcinations at 450 °C as [12]. The samples produced by these step is specified as TiO_2-Hectorite. Furthermore, TiO_2-Hectorite was used to produce Ag/TiO_2-Hectorite by dispersion of silver ion onto TiO_2-Hectorite material performed by mixing $AgNO_3$ solution and 200 mesh of TiO_2-Hectorite powder at room temperature stirring for 24 hours in a batch reactor. Filtration and neutralization to find acid-free solid of Ag/TiO_2-Hectorite were the next steps. Characterization of materials were performed by gas sorption analysis to determine specific surface are, pore volume and pore radius parameters, Scanning Electrone Microscope-Energy Dispersive x-ray (SEM-EDX) for elemental analysis and surface profile identification, XRD for crystallinity identification and Diffuse Reflectance UV-Visible spectrophotometry analysis (DRUV-Vis) to specify UV-Visible absorbance of solid material. Specific surface area, pore radius and total pore volume of material were acquired with NOVA 2000 Gas Sorption Analyzer and for XRD analysis Shimadzu X6000 was employed. Ni-filtered Cu-Kα was used as radiation source and diffractogram obtained at the measurement range of 2-60°, step size 0.4 °/min. For DRUV-Vis spectra measurement, a range of 200-600 nm wavelenght was choosen and $BaSO_4$ was used as reference material.

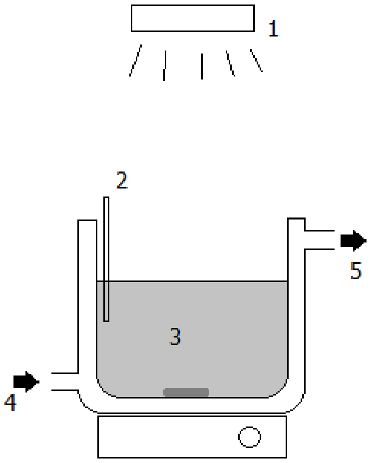

Figure 1. Scheme of photocatalytic reactor. (1) UV lamp; (2) Sampler syringe; (3) tested solution + photocatalyst; (4) water inlet; (5) water outlet

Photoactivity test of materials in phenol photooxidation was conducted in a thermo-stable batch reactor at room temperature (Fig.1). Materials in powder form was mixed with phenol solution at the concentration of 40mg/L and the addition of H_2O_2 at the concentration of 1mM as oxidant. Reaction was performed by stirring the mixture under UVB illumination and air flow and sampling of treated phenol was collected after certain time sequentially. As comparison, photodegradation treatment to the solution was conducted at the similar condition but without the addition of H_2O_2 as oxidant source. Concentration of phenol and possible reaction products in each sampling time was determined by high performance liquid chromatography (HPLC). Specified condition of HPLC analysis were acetonitrile: water as mobile phase, C30 as stationary phase and UV detector.

Photoactivity of material was also examined in photo-inactivation of bacteria. Material in powder form was layered in glass slide before it contacted with bacteria culture solution and under UVB illumination. Photoactivity was defined as percentage of bacteria colony reductin after the treatment. The test organism; *Eschericia coli*, is pathogenic gram-negative bacteria, originally cultivated from the stored pure cultures of bacterial species in the Microbiology Laboratory, Pharmacy Department, Islamic University of Indonesia. The stock cultures were kept in a biological refrigerating room at 4 °C. The concentrations of cells was determined by the spread plate method, in which the cells are plated on nutrient agar, incubated at 37 °C as similar method used in similar studies [13,14]. Bacteria counter of Thermoscience X500 was used for calculation. Detail of antibacterial test was similar to that was reported in utilization of TiO_2-montmorillonite [10].

3. Results and Discussion

Data elemental analysis of materials is summarized in Table 1. It is shown that the main components of hectorite are dominantly Si and Mg. It refer to that the basic structure of hectorite that consist of silica in tetrahedral and magnesia in octahedral form in a layer. From the presence of sodium in the material it is confirmed that material is in a sodium hectorite in which sodium is major cations within the interlayer space of silica-magnesia sheets .

The titanium content in TiO_2-Hectorite and in Ag/TiO_2-Hectorite are 7.60 wt% and 7.30 wt% respectively. The existence of titania is demonstrated by SEM profile (Fig.2).

Table 1. Elemental analysis of materials

Component (%wt.)	Hectorite	TiO_2 - Hectorite	Ag/TiO_2 - Hectorite
SiO_2	61.62	61.21	60.45
MgO	29.67	26.11	23.45
Na_2O	1.55	1.58	2.23
Zn	-	-	9.26
Ti	-	7.60	7.30
Ag	-	-	0.13

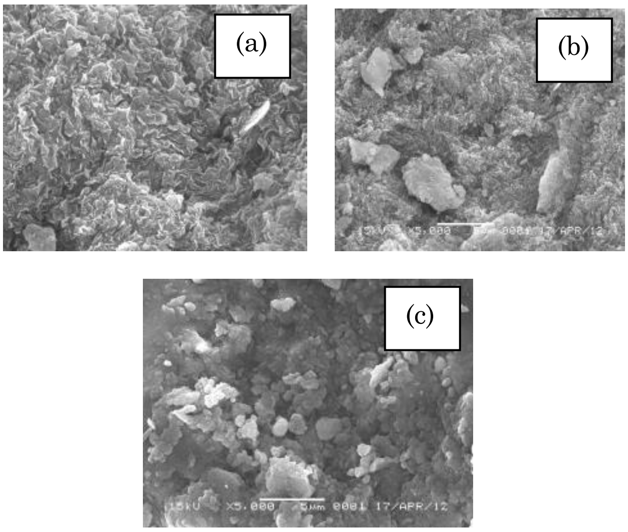

Figure 2. SEM profile of (a) Hectorite (b) TiO_2-Hectorite (c) Ag/ TiO_2-Hectorite

From the picture also, it can bee seen that there is change on surface profile of materials in that a rougher surface was formed after titania pillarization and there are some spots created after silver attachment. The dispersed titania is also confirmed from XRD patterns (Fig.3). Compared to hectorite as raw material, all significant and characteritic peaks from pure hectorite are still maintaned in both TiO_2-Hectorite and Ag/TiO_2-Hectorite suggesting that the dispersion of TiO_2 and Ag did not affect the main structure of hectorite as a support. The basal spacing of hectorite, TiO_2-hectorite and Ag/TiO_2-Hectorite are 14.97Å (6.06°), 15.50 (5.70°) and 15.44 (5.72°) respectively. The increase of the basal spacing for the both TiO_2-Hectorite and Ag/TiO_2-Hectorite two modified hectorites confirms the insertion of TiO_2 intercalated into the interlayer space. The presence of TiO_2 created higher space between silicate layers and it is also indicated by reflection at 25.2° refer to titania crystalline formation in anatase phase. After silver addition, there is no additional peak observed in Ag/TiO_2-Hectorite inform that silver incorporation does not give any crystalline formation.

The dispersion of TiO_2 produced higher specific surface area compared to raw hectorite as well as pore volume and pore radius (Table 2). The data confirmed the creation of TiO_2 particles in interlayer space as indicated by higher basal spacing from the XRD measurement. However after was dispersed with silver, parameter of specific surface area and pore volume were reduced. From Fig.4 depicting the pattern change of N_2 adsorption-desorption profile of materials it is noted that adsorption capacity of Ag/TiO_2-Hectorite is lower compared to TiO_2-Hectorite but mantained higher than Hectorite. The presence of Ag aggregates in porous structure of TiO_2-Hectorite material is the main reason for the specific surface area and pore volume reduction. It is also shown by the higher pore radius of Ag/TiO_2-Hectorite compared to TiO_2-Hectorite in that non homogeneous or aggregate distribution of silver potentially produce large narrow controbute to higher value of pore radius.

Diffuse Reflectance UV-Vis (DRUV) spectra (Fig.5) were collected for all the samples. It is seen that after TiO_2 attachment on hectorite, there is a change in spectra profile in that TiO_2-Hectorite demonstrate the edge wavelength at around 400 nm correspond to the band gap (E_g) value of 3.2 eV. The important change is obtained after silver dispersion as shown by increasing absorbance in all range wavelength. From the spectra, E_g value seems increased due to edge wavelength shift to lower wavelength, but there is another peak at higher wavelength. This presummable come from visible absorption for the rest nanomaterial related with the presence of silver oxide, due to change in color from white (pure TiO_2) to grey. This assumption is refered to that was reported in previous study similar with in this study [15].

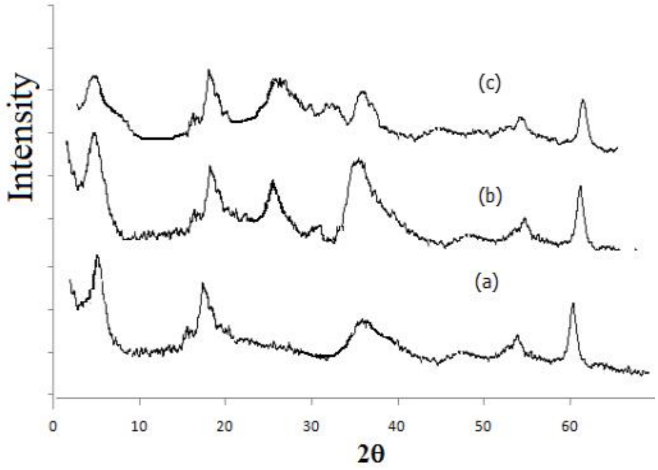

Figure 3. XRD peaks of titania (a) Hectorite, (b) TiO_2-Hectorite (c) Ag/ TiO_2-Hectorite

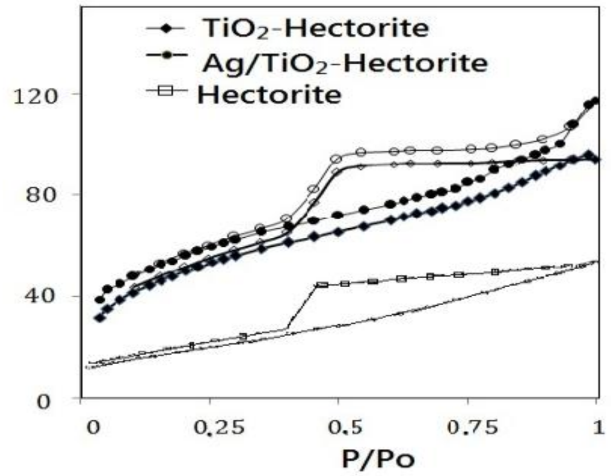

Figure 4. N_2 Adsorption-desorption profile of materials

Table 2. Specific surface area, pore volume and pore radius of prepared materials compared to raw hectorite

Material	Specific surface area (m^2/g)	Pore volume (cc/g)	Pore Radius (Å)
Hectorite	77.80	9.56×10^{-3}	11.33
TiO_2-Hectorite	164.18	3.37×10^{-2}	16.11
Ag/TiO_2-Hectorite	78.67	2.21×10^{-2}	24.33

3.2. Photoactivity Test

Photoactivity test of materials in phenol photodegradation is presented by the kinetics phenol degradation at varied process (Fig.6). From the data, it is noted that the presence of Ag in TiO_2-Hectorite significantly accelerate the photooxidation as indicated by lower concentration of phenol was gained on either the addition or the absence of H_2O_2. The addition of H_2O_2 enhace the rate of photodegradation come from silver sensitizing towards photocatalyst. From the kinetic simulation it is concluded that kinetics of phenol photooxidation over TiO_2-Hectorite and Ag/TiO_2-Hectorite fit to third order kinetics. The kinetic constant of phenol photooxidation over Ag/TiO_2-Hectorite is about 700 times respect to TiO_2-Hectorite indicate the role of silver during photocatalytic mechanism (Table 3).

Data from *E. coli* inactivation listed in Table 4 shows the significant difference of varied treatment. The use Ag/TiO_2-Hectorite and TiO_2-Hectorite as photocatalyst demonstrated

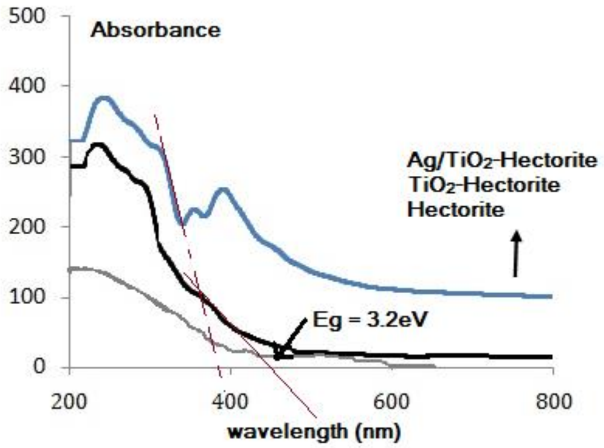

Figure 5. DRUV-Vis spectra of Ag/TiO_2-Hectorite compared to TiO_2-Hectorite and Hectorite

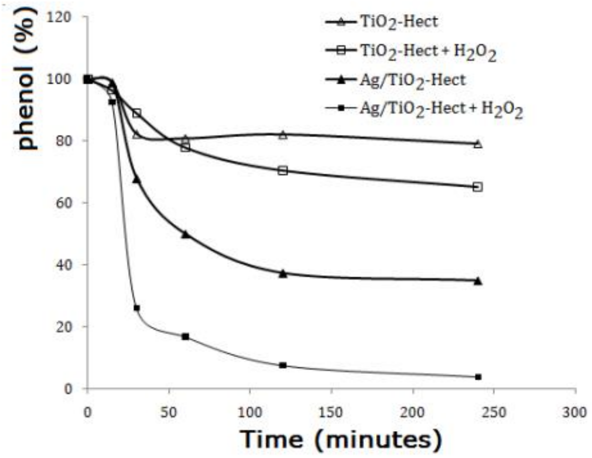

Figure 6. Kinetics phenol degradation at varied process

Table 3. Kinetic simulation data of phenol photooxidation using varied photocatalyst

Kinetic Order Simulation	Photocatalyst	
	TiO_2-Hectorite	**Ag/TiO_2-Hectorite**
1st order	R^2= 0.9484	R^2= 0.9537
2nd order	R^2=0.9484	R^2= 0.9769
3rd order	R^2=0.9789, k = $8.596.10^{-5}$/$mg^{-3}L^3min^{-1}$	R^2= 0.9858, k= 1.14910^{-3}/$mg^{-3}L^3min^{-1}$

Table 4. Bacteria count in photocatalytic treatment

Photocatalyst Material	E.coli in treated solution (CFU/mL)*
-	1801
UV	1462
Hectorite+ UV	1007
TiO_2-Hectorite+ UV	2
Ag/TiO_2-Hectorite+ UV	0

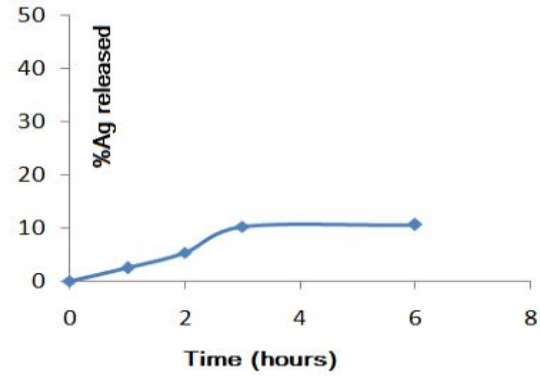

Figure 7. Released Ag in treated solution of *E. coli* at varied contacting time

inactivation excellently compared to UV ilumination and hectorite utilization. Kinetics study revealed that the antibacterial activity of prepared material is directly related to the presence of Ag particles. Refer to some studies, the most possible mechanism consists of the potentially released Ag ions and reacting Ag with water in generating activated peroxide. Furthermore the peroxides formed cause damage to bacteria [16-18]. This assumption is related to released Ag in treated solution of *E. coli* at varied time as presented in Fig.7.

4. Conclusions

Silver immobilized TiO_2/Hectorite has been succesfully prepared in this research. Identification using XRD, BET surface area, DRUV-Vis spectrophotometry and SEM-EDX confirm the presence of dispersed TiO_2 and Ag in increasing physico-chemical character of material as photocatalyst. Photoactivity test of material revealed that prepared material has high activity performance in phenol photooxidation and *E. coli* inactivation.

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