



Physicochemical Characteristics and Photocatalytic Activity of Silver Nanoparticles-decorated on Natural Halloysite (An aluminosilicate clay)

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ABSTRACT

Development of functional material for green chemistry applications become popular in recent years, and as part of these, preparation of nanoparticles for such application of organic contaminant is interesting topic. This research was aimed to prepare the chemical stable silver nanoparticles (AgNPs) for photocatalytic application over decorating onto natural clay mineral, halloysite. Prepared material was characterized using UV-Visible spectroscopy, x-ray diffraction (XRD), Fourier Transform Infra-Red (FTIR), gas sorption analysis, scanning electron microscope (SEM) and transmission electron microscope (TEM) studies. From TEM analysis, it is found that AgNPs present in the diameter range of 20-50 nm. The dispersed AgNPs slightly affect to increase the surface parameter of specific surface area and pore volume of the mineral. Photocatalytic activity test of the material exhibits that silver nanoparticle decorated halloysite shows excellent photocatalytic activity for photooxidation of rhodamine B.

Keyword: Photocatalytic study, Silver nanoparticles-decorated, Natural halloysite.

INTRODUCTION

Silver is widely known as functional metal in wide applications such as antibacterial agent, optical functionalizing, electrical applications and medical and chemical sensors. The growing interests are related to synthesis of Ag in nanosize or called as silver nanoparticles (Ag NPs) as there

is close relationship between the physical and chemical properties of nanomaterials for increasing activities in many applications. A material is categorized as nanoparticles as it has size of 1 – 100 nm. Basically nanoparticles synthesis can be conducted with top down (physics) and bottom up (chemistry) methods. Physics method is the manner of breaking metal solid into nano-sized



small particles, meanwhile chemistry method is conducted by forming nanoparticles from molecular precursor or ionic^{1,2}.

Some techniques that can be used to produce nanoparticles are chemical, photochemical, sonochemical reduction, etc. Nanoparticles synthesis with sonochemical technique is using ultrasonic tool to break metal solid into nano sized particles, meanwhile photochemical technique is using highly UV radiation. There are many techniques can be used for producing nanoparticles such as i.e chemical, photochemical, sonochemical reduction, etc. For these scheme, Ag NPs were reported to be produced by green chemistry method such as utilizing plant extract as reductor for the synthesis^{3,4}. In order to use Ag-NPs for water treatment purposes, the trouble will be gained as Ag-NPs used as it form, moreover the reused Ag-NPs will be a serious problem in treated water. Due to this limitation, another mechanism for increasing stability of Ag-NPs is supporting the nanoparticles onto a stable porous solid and usually called as decorating Ag-NPs. Some investigations reported the preparation of Ag-NPs in composite forms with zeolite, clay, graphene oxide, silica and other polymer-solid composites⁵⁻⁷. Clay minerals are kind of solid having modifiable properties and also sufficient porous structure for supporting antibacterial activity and photocatalytic activity of Ag-NPs. Shameli *et al.*, (2010) prepared immobilized Ag-NPs within the interlayer of montmorillonite⁸. It is found that the nanoparticle size was about 20-30 nm depend on the g-irradiation doses. By other varied parameters, Ahmad *et al.*, (2009) showed that the particle size of nanoparticles is depending on the AgNO₃ concentration. Using other kind of clay mineral, Pataklavi *et al.*, (2003) and Hashemian and Shahedi (2013) utilized kaolinite mineral as support^{9,10}.

In general, the basic principle of Ag-NPs synthesis was based on chemical reduction towards Ag⁺ before it anchored onto the solid support. Many researchers investigated the high potency of Ag NPs as photocatalyst dopant and photocatalyst itself. It is revealed that the combination of Ag with TiO₂ in

the composite form of kaolinite for example, the enhancement of dye degradation was obtained significantly. Beside on the potency of mineral clays for supporting photocatalytic activity of Ag-NPs application, exploration on other kind of clay as support is an interesting topic for low cost photocatalysis.

Natural halloysite is one of phyllosilicate found in some places in Indonesia. Chemically, halloysite can be utilized for catalysis and functional material applications even until right now the utilization of halloysite in Indonesia is still related with ceramic production only. Refer to its potency for Ag-NPs immobilizing solid, this research aimed to evaluate the preparation of Halloysite decorated with Ag-NPs or furthermore called as AgNPs-Hal and its activity as photocatalyst.

MATERIALS AND METHOD

Silver nitrate (AgNO₃, >99.9% purity), sodium borohydride (NaBH₄, >99% purity), methylene blue, K²Cr²O₇, H₂O₂, and rhodamine B were purchased Merck-Millipore, Germany. Natural halloysite (Hal) was obtained from Sukabumi, West Java, Indonesia.

Procedures

Preparation of AgNPs-Hal

Natural halloysite powder was dissolved with 250 ml of water followed by stirring for 4 hours. a solution of 1x10⁻³M AgNO₃ was added into the halloysite suspension and the stirring was kept for 1 h before the slow addition of NaBH₄ 0,1M. The mixture was then kept for overnight and the Ag-NPs formation can be observed visually that it looks yellow to reddish. The mixture was filtered and the obtained powder was dried at the oven at 60 °C for activity tests and characterization.

Characterization of materials (Halloysite and AgNPs-Hal) was performed by x-ray Diffraction (XRD), gas sorption analysis, Fourier-Transform Infra-red (FTIR) and Transmission Electron Microscope (TEM). XRD Shimadzu X6000, Quantachrome gas sorption analyzer, Perkin-Elmer FTIR and Transmission electron microscope (TEM) of JEOL-JSM 6360 were employed for the analyses.

Photocatalytic activity test of AgNPs/Hal

Photocatalytic activity of prepared material was evaluated as photocatalyst in photo-oxidation of rhodamine B solution. The solution and photocatalyst was mixed in a photocatalytic reactor (Fig. 1). For photooxidation process, H_2O_2 was added as oxidizing agent and 20 watt UV Lamp was employed as photon source in the photocatalytic mechanism. Reduction of rhodamine B concentration was calculated based on UV-Visible spectrophotometric analysis of treated solution by using following equation 1:

$$C/C_0 = \frac{Abs_t}{Abs_0} \quad (1)$$

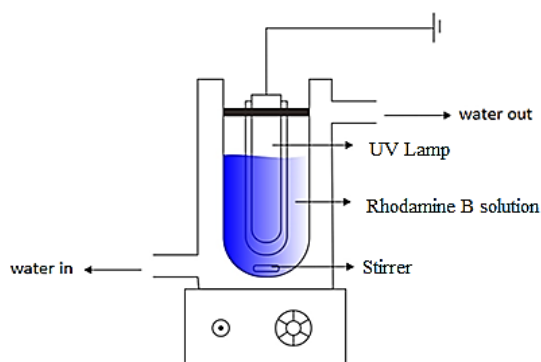


Fig. 1. Schematic representation of photocatalytic reactor

With Abs_t and Abs_0 are absorbance of treated solution and the absorbance of initial solution, respectively.

Spectrophotometer HITACHI U-2010 was utilized for the analysis.

Evaluation of photooxidation kinetics and mechanism was also studied by chemical oxygen demand (COD) measurement. The COD value was determined by using reflux method of the samples with $K_2Cr_2O_7$ followed by calculation based on spectrophotometric method.

RESULTS AND DISCUSSION

Figure 2 shows the XRD patterns of Hal and AgNPs-Hal. Both materials demonstrate the peaks can be indexed to the characteristic peaks of halloysite refer to JCPDS No. 04-0783. The pattern of Halloysite shows the basal spacing

reflections indicating a sharp peak at 12° (2θ) which translate to a (001) basal spacing of 7 Å and there is no peak at 8.8° (2θ) indicating the absence 10 Å form, which are indicative of hydrated halloysite. As shown by the patterns, it is confirmed that there is no significant different reflection peaks of both material assigning that there is no AgNPs patterns detected. This is assumed that the dispersed silver is in very low content with homogeneous distribution so there is no silver aggregate crystalline formed on surface.

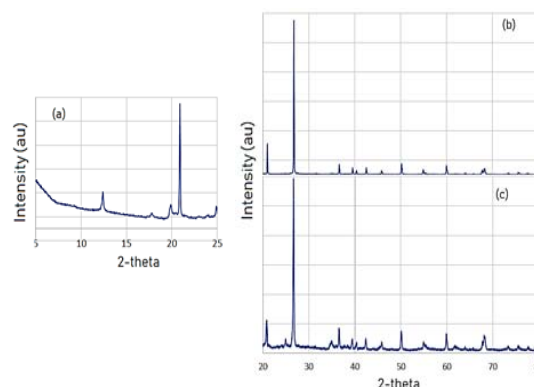


Fig. 2. XRD pattern of (a) Halloysite at low range of 2-theta (b) Hal (c) AgNPs/Hal

The presence of Ag is proofed by SEM-EDX analysis (Figure 3).

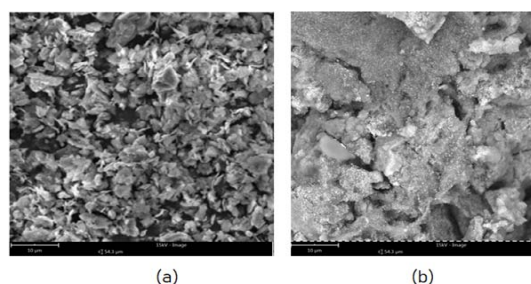


Fig. 3. SEM profile of (a) Hal (b) AgNPs/Hal

From the morphology profile, it is seen that the dominant forms in Hal is flaky structure. The surface is changed after Ag-NPs dispersion in that some dots appeared on surface. TEM analysis image (Fig. 4) reveals that the silver particles size are about 10-70 nm in diameter.

The FT-IR spectra of the Hal and AgNPs/Hal were furthermore used to investigate the the resultant of functional groups of samples before and after AgNPs dispersion (Fig. 5). The spectra at

around 3400-3600 cm^{-1} are the indication for O-H vibration and found for both samples. Generally, the O-H refer to either silica-alumina structure or adsorbed H_2O in the pores. The stretching spectra related to Al-O of halloysite structure are appeared in the range of 3620.47 cm^{-1} - 3696,07 cm^{-1} that are coincided with the spectra at around 1033.65 cm^{-1} and 913,48 cm^{-1} . The band at 1,032 cm^{-1} is the indication of caused by the stretching vibration of Si-O-Si while the band observed at around 538 cm^{-1} was due to the vibration of Al-O-Si.

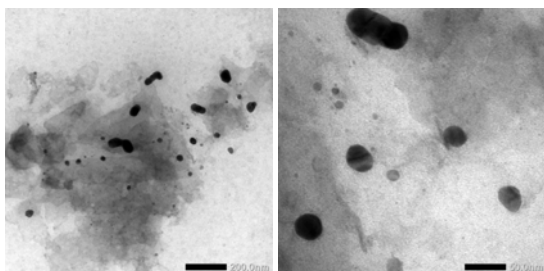


Fig. 4. TEM profile of AgNPs/Hal

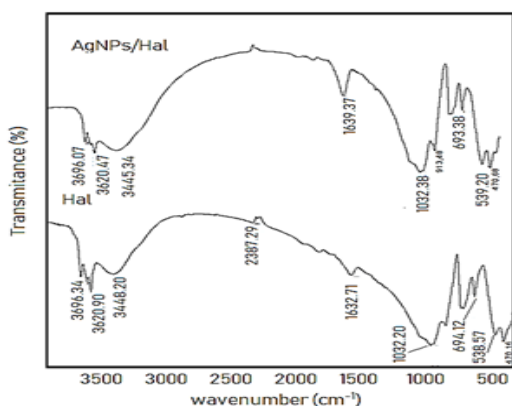


Fig. 5. FTIR spectra of Hal and AgNPs/Hal

By comparing the spectra of Hal and AgNPs/Hal it is found that there are some shifts of the spectra at higher wavenumber are found for AgNPs/Hal i.e. at around 1032 cm^{-1} . The shifts may be related with the interaction between AgNPs and Halloysite structure case the higher energy required for the vibration.

The dispersion of AgNPs slightly affects to the surface profile as shown by adsorption-desorption pattern (Fig. 6) and the calculated specific surface area, pore volume and pore radius are listed in Table 1. AgNPs/Hal exhibits the higher capability in adsorption as shown by the higher volume of adsorbed N_2 in all range of P/Po compared to Hal.

Due to the increasing adsorption-desorption profile the surface parameters of AgNPs/Hal suggest that the decorated AgNPs reflects the higher surface area from the dispersed particles.

Table 1: Surface parameters of AgNPs/Hal and Hal

Parameters	AgNPs/Hal	Hal
Specific surface area (m^2/g)	14.27	11.02
Pore volume (cc/g)	2.18×10^{-3}	1.94×10^{-3}
Pore Radius (nm)	1.49	1.51

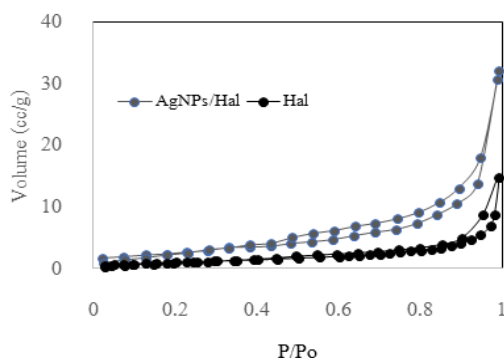


Fig. 6. Adsorption-desorption profile of Hal and AgNPs/Hal

Photocatalytic activity of AgNPs/Hal shows by kinetics of rhodamine B photooxidation in Fig. 7. The plots demonstrate the different kinetics of rhodamine B concentration along time of varied treatments: with the addition of AgNPs/Hal, the addition Hal with and without UV exposure. From the compared patterns, the rhodamine B reduction is obtained fastest by the treatment of the AgNPs/Hal addition with UV exposure while the kinetic profiles from other treatments are at similar values of C/Co in the same range of time. The patterns confirm the photocatalytic activity of AgNPs/Hal that is closely related with the presence of decorated-AgNPs since the Hal itself does not give photocatalytic activity¹¹. Furthermore, the treatment without UV is also does not give excessive reduction, means that the oxidation occurs only over the presence of photon source from UV lamp.

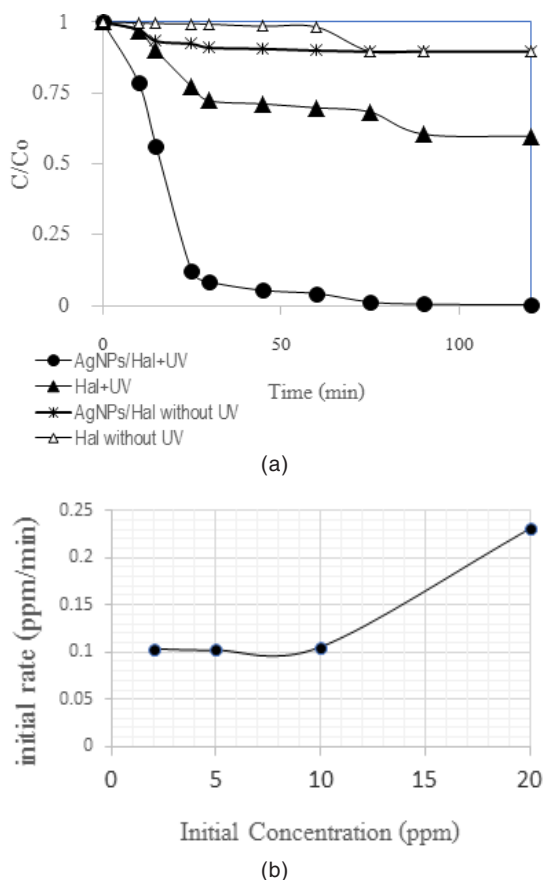


Fig. 7(a). Kinetics of rhodamine B photooxidation over varied treatments (b) Effect of initial concentration on initial rate of photooxidation

As shown in Fig. 7b, initial rate of rhodamine B oxidation is a function of initial concentration. The data is in line with general theory in that the concentration of reactant is the main factor for the

reaction rate. As the oxidation process toward organic compounds, the photooxidation of rhodamine B is reflected by the reduction of chemical oxygen demand (COD) values after the treatment. The reduction of COD value indicates that rhodamine B content in water is not only converted into other organic compounds but also removed (Figure 8).

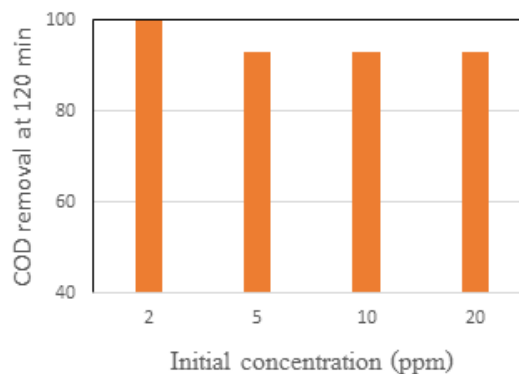


Fig. 8. COD removal for varied concentration at 120 min. of treatment

CONCLUSION

Silver nanoparticles decorated halloysite is an alternative method for the synthesis of stable nanoparticles for photocatalytic purposes. Prepared silver nanoparticles decorated halloysite were characterized by using, XRD, FTIR, SEM and TEM techniques. From the studies, it is found that the synthesized material showed the formation of silver nanoparticles at the range of 20-50 nm on halloysite surface. The material demonstrated photocatalytic activity in rhodamine B photooxidation.

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