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Removal of Hydrogen Sulfide in Terms of Scrubbing Techniques using Silver Nano-Particles

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Abstract**—**Silver nano-particles have been used for antibacterial purpose and it is also believed to have removal of odorous compounds, oxidation capacity as a metal catalyst. In this study, silver nano-particles in nano sizes (5-30 nm) were prepared on the surface of $NaHCO_3$, the supporting material, using a sputtering method that provided high silver content and minimized conglomerating problems observed in the common $AgNO_3$ photo-deposition method. The silver nano-particles were dispersed by dissolving Ag-$NaHCO_3$ into water, and the dispersed silver nano-particles in the aqueous phase were applied to remove inorganic odor compounds, H_2S, in a scrubbing reactor. Hydrogen sulfide in the gas phase was rapidly removed by the silver nano-particles, and the concentration of sulfate (SO_4^{2-}) ion increased with time due to the oxidation reaction by silver as a catalyst. Consequently, the experimental results demonstrated that the silver nano-particles in the aqueous solution can be successfully applied to remove odorous compounds without adding additional energy sources and producing any harmful byproducts

Keywords**—**Silver nano-particles, Scrubbing, Oxidation, Hydrogen sulfide, Ammonia

I. INTRODUCTION

MALODOR is affected by various factors such as characteristic of society, culture, area, a level of life, age and health condition. One of the representative malodorous compounds, hydrogen sulfide causes an unpleasant and repulsive feeling when human is exposed to this compound. Also, it can be easily adsorbed on eyes and respiratory organs and impairs human health since hydrogen sulfide has a high solubility[1]. In addition, in recent days, due to the problems such as Sick House Syndrome and Sick Building Syndrome, the concern for indoor air quality has been increased continually.

The treatment technologies have been developed for removal of odorous compounds by using physical, chemical and biological methods. Especially, it was shown that hydrogen sulfide could be treated by scrubbing or biofilter[2]. Also, several researches have been conducted using activated carbon or photocatalyst for the removal of odorous compounds[3]. However, these kinds of general methods have shown the problems of high energy consumption, high cost and inefficient removal of odorous compounds. Therefore, effective and economical methods need to be proposed and applied for effective removal of odorous compounds.

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Silver (Ag^0) or Silver ion (Ag^+) has a feature of antibacterial ability and was known as harmlessness to human body. Silver has been widely used to make spoon and accessory in many countries. Recently, silver was also utilized to produce fibers, construction materials, baby products, medical products and various household items showing the characteristic of antibiotic. Therefore, many studies of silver were conducted on antibacterial ability in biological science and environmental engineering area. Also, many studies have been conducted with respect to sterilization of *Escherichia co*li and *staphylococcus aureu*s by using silver nano-particles to prove antibacterial ability [4].

Silver has removal capability for malodorous compounds such as gaseous hydrogen sulfide, ammonia and volatile organic compounds (VOCs). Basically, removal efficiency of silver nano-particles is dependent on catalytic oxidation of metal surface. Even though oxidation degree of silver nano-particles was lower than the other catalytic metals (platinum, nickel), it could be widely used for human life since it did not show bad effects in human health. Catalytic oxidation of silver nano-particles was strongly connected with adsorption and reaction of molecular oxygen in the air. At room temperature, molecular oxygen on the surface of silver decomposes into oxygen atom or ions showing high oxidation rate. Meanwhile, since reactive oxygen ions attached unstably on the surface of silver particles[5],[6], silver nano-particles induced oxidation/reduction reaction on malodorous compounds floating in the air. It was verified that organic compounds were oxidized by oxygen ions on the surface of silver [7]. As a result, the structure of silver nano-particles retained reactive oxygen for the effective removal of malodorous compounds [8].

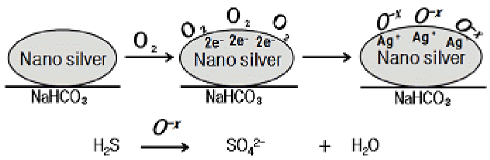

Fig. 1 Mechanism of inorganic compounds oxidation on silver nano-surface

According to the further studies of oxidation reaction on silver nano-particles, atom or molecule of oxygen adsorbed on the surface of silver particles provides or accepts electron leading to the formation of active oxygen. Silver nano-particle itself produces free radical of oxygen that oxidized organic compound [9]. The estimated reaction mechanism of hydrogen sulfide oxidation is shown in Fig. 1 [10],[11],[12].

The proposed research is focused on the examination of removal efficiency by hydrogen sulfide oxidation of silver nano-particle. In addition, the morphology and optical properties of the silver nano-particle are investigated.

II. EXPERIMENTAL

A. Synthesis of silver nano-particles

To composite the silver nano particles, photo-deposition method that use liquid $AgNO_3$ aqueous solution on the surface of basic materials has been usually used. But this method has several disadvantages. The first one is disadvantageous on mass production. Second one is adding dispersing agent because of silver nano particles condensation.

Accordingly, stirring and sputtering methods for deposition of silver nano-particles on surface of solid support materials were used in this study. Stirring and sputtering methods are effective to make silver nano-particles because it is possible to make more purity and ensure higher quality of silver nano-particles than $AgNO_3$. Method of manufacture needs to make plasmas when flowing argon gas. To make silver nano-particles, a plasma making condition by adding argon gas and high voltage at once in the making device was set and the silver nano-particles deposited to solid material ($NaHCO_3$) were stirred simultaneously. To synthesis silver nano particles, the stirring rate at 10~30 rpm has been maintained. In order to make particles to nano size, sputtering was stopped before silver formed thin film.

In this study, the silver nano-particle aqueous solution was made by dissolving the silver nano particles to attach them on sodium bicarbonate. The concentration of silver nano-particles attached with sodium bicarbonate was 1000 mg-Ag/kg-$NaHCO_3$ and silver nano-particles concentration was 50 mg-Ag/L.

B. Batch scrubbing test of silver nano-particle

Basic operation factors for assessment of silver nano-particle scrubbing to remove the odorous substance were determined by batch test. In batch experiment, scrubbing reactor (volume=60L) was made by the stainless steel tightly filled with the odorous gas at the consistency. And then aqueous solution of silver nano-particles was circulated continuously and sprayed out using the nozzle. The volume of silver nano-particle aqueous solution added in batch reactor was 2L (58L contaminant gas volume) and the flow of recirculation solution was 4L/min (2 time circulation per minute). To compare the effects of silver nano-particle in distilled water, sodium bicarbonate aqueous solution was used for the same experiment.

C. Continuous scrubbing test of silver nano-particles

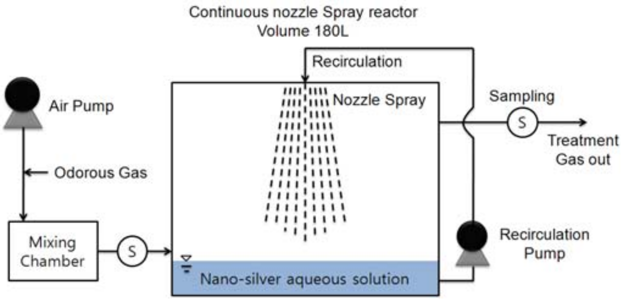

Fig. 2 Schematic of silver nano-particles scrubbing reactor.

The continuous scrubbing reactor (Fig. 2) used in this study was consisted of stainless steel and has 180 L of total volume. The continuous scrubbing reactor was operated at 90 L/min of gas flow rate corresponding to retention time of 2 minutes. The 4L of silver nano-particle aqueous solution was sprayed out by installation of 4 nozzles on top of reactor. Then the flow rate of silver nano-particle aqueous solution was 6L/min. In order to make silver nano particles to react with odorous compounds effectively, reactor was designed to spray the solution tidy and micro water droplets was made by nozzle. The tube of inlet and outlet parts was made by teflon to prevent loss of mass due to adsorption.

D. *Analysis methods*

The concentrations of sulfate and sulfide ion in liquid were measured for the confirmation of oxidizing of gaseous hydrogen sulfide. S^{2-} and SO_4^{2-} ion concentrations in liquid phase were analyzed using ion chromatography (DX-80 ion analyzer, DIONEX, USA). Gas phase compound (H_2S) was measured using detector tube (Gastec co. Japan) and exclusive measure instrument (MultiRAE plus, RAE system. USA).

I. RESULTS

A. silver nano-particle aqueous solution

Scanning Electron Microscope (SEM) images of the silver nano-particles were presented in Fig.3. SEM was used to verify the attachment of silver nano-particle on sodium bicarbonate of the certain deposition and determine the sizes of particles.

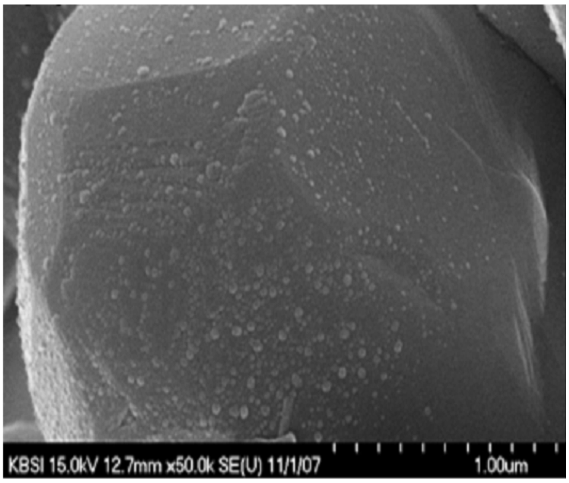

Fig. 3 SEM images of the silver nano-particles on the surface of support solid.

According to the SEM pictures, the diameters of particles were approximately 10~30nm. In order to examine the uniformed distribution of the silver nano-particles in the aqueous solution containing silver particles, TEM (transmission Electron Microscope) and SEM were utilized. From the SEM and TEM analysis, the sizes of particles used in this study were about 5-30nm.

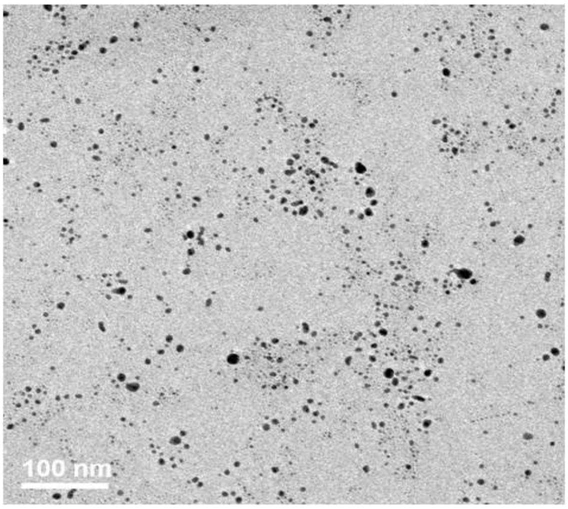

Fig. 4 TEM images of the silver nano-particles at the concentration of 100 mg-Ag/L in the liquid phase

B. Batch scrubbing test of silver nano-particles

To consider the solubility of hydrogen sulfide and experimental reproducibility, the initial concentration of hydrogen sulfide was maintained to 20 ppm in the batch scrubber system. Fig. 5 shows changes of hydrogen sulfide concentration in batch scrubbing system against time. Distilled water was used as control group. After 5 minutes, we can't see changes of hydrogen sulfide concentration since equilibrium of hydrogen sulfide between liquid phase and gas phase was made in 5minutes.

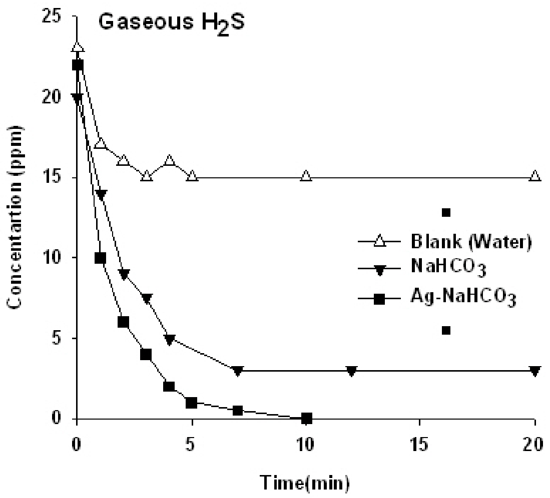

Fig. 5 Change of hydrogen sulfide concentration in the gas phase of the batch nano-silver scrubbing reactor.

In the case of sodium bicarbonate aqueous solution, more hydrogen sulfide was transferred to liquid phase than distilled water because of increased solubility of hydrogen sulfide caused by the increased salt concentrations. In silver nano-particle aqueous solution, most of hydrogen was removed in batch nano-silver reactor. The reason is due to not only increasing of hydrogen sulfide solubility by salt ions in liquid but also oxidizing of hydrogen sulfide ion by silver nano-particles.

C. Continuous scrubbing test of silver nano-particles

To estimate the removal efficiency of hydrogen sulfide in the study, experimental results between sodium bicarbonate aqueous solution and silver nano-particle aqueous solution were compared. Fig. 6 shows changes of gas phase hydrogen sulfide, and liquid phase hydrogen sulfide and sulfate concentration in batch scrubbing system, respectively.

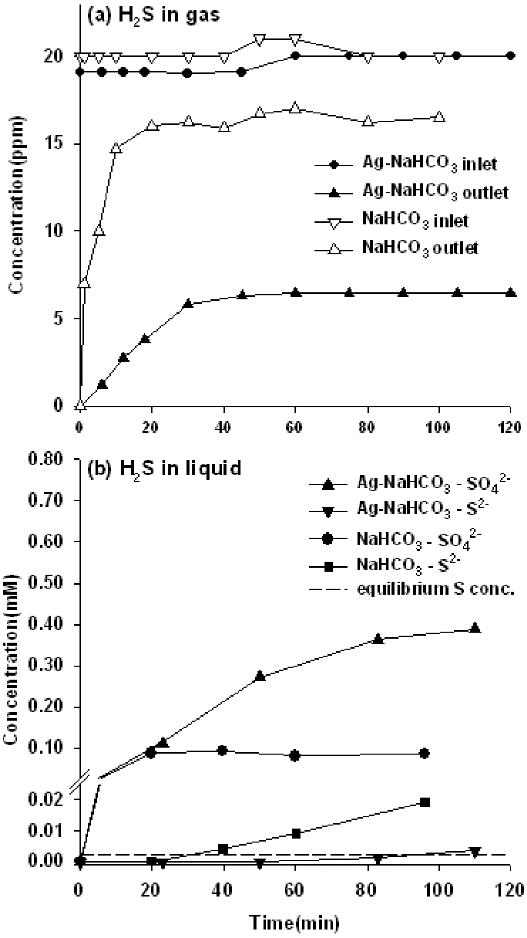

Fig. 6 Change of H_2S concentration in the gas phase, and SO_4^{2-} and S^{2-} ion concentration in the liquid phase of the continuous nano-silver scrubbing reactor.

At the same influent hydrogen sulfide concentration, changes of hydrogen sulfide concentration with sodium bicarbonate aqueous solution reached the steady state after 20 minutes. In contrast, with the silver nano-particle aqueous solution, steady state was achieved after 40 minutes. Also, we found that the equilibrium concentration of hydrogen sulfide in silver nano-particle aqueous solution scrubbing system was 6 ppm. This equilibrium concentration was 3 times less than in sodium bicarbonate aqueous solution scrubbing system showing 17 ppm. The increase of sulfate concentration in liquid phase indicated oxidation of hydrogen sulfide ion by silver nano-particles in aqueous solution scrubbing system. But sulfate concentration was maintained at a certain concentration in sodium bicarbonate aqueous solution scrubbing system. It showed the reason that hydrogen sulfide ions were oxidized by oxygen free radicals on surface of silver nano-particles. On the other hand, in case of sodium bicarbonate aqueous solution scrubbing system, some portions of hydrogen sulfide ions were accumulated in liquid because the oxidation of hydrogen sulfide ion was not achieved effectively.

Scrubbing system using the silver nano-particles can oxidize odorous compounds without additional energy consumption and this system also showed higher odor removal efficiency. In addition this technique did not make secondary by-products and required low maintenance costs. More gas phase hydrogen sulfide was removed than soluble hydrogen sulfide. The increase of sulfate ion indicated oxidation of hydrogen sulfide in scrubbing system using the silver nano-particles. Meanwhile, oxidation of odorous compound by silver nano-particles was progressed slowly. Therefore, enough operating time is required for the effective removal of odorous compound. Consequently, the experimental results indicated that this system could be used for the effective removal of malodor and the long-range odor improvement.

ACKNOWLEDGMENT

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