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Preparation of Silver Nano-Particles and Use as a Material for Water Sterilization

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Abstract

High dispersed nanodimensional silver metal (nanosilver) solution of concentration ranging from 40 to 400 mg/L was prepared from silver nitrate in water media with and without dispersing reagent. The reduction process was initiated by ammonium hydroxide and glucose was used as a reductive reagent.

The nanosilver solution was characterized by color changing from light-yellow to yellow, brown, red-brown, brown-green, dark-green, blue, dark-blue and those were depending on silver concentration and dimension of silver metal particles. The nanosilver solution was possibly used as a direct sterilizing reagent or coating on calcinated laterite grains to create sterilizing material in bacterial removing filter.

Direct sterilization ability of nanosilver solution and nanosilver coated material was investigated. The results showed that with 10 ppb nanosilver in supplied water, all bacteria will be removed within 25–30 min. 10 mm thick layer of silica gel or 20 mm of calcinated laterite coated nanosilver could remove all bacteria in water flowed though with maximum flow rate of 100 $L.m^2$/min. Moreover, sterilizing material was nontoxic and applicable for drinking water production.

Keywords: Nanosilver Preparation; Water Sterilizing Materials

1. Introduction

A thousand years ago silver and silver furniture were used for sterilizing and disinfecting purpose in the courts of the kings. Because of expensiveness, valuable properties of silver were not outspread used. Nanotechnology came out into society reduced consumption of silver quantity in use while its properties were not only preserved but in most cases increased (Sondi, 2003; Tien *et al*., 2008; Juehne, 2005). According to previous studies, very small quantity of 10 to 20 mg nanosilver metal per a cubic meter of water or about 200 mg per kilogram plastic material can avoid all bacterial infects (Con, 2009). Those affairs were explained by nanodimensional effects.

Preparation of nanosilver was realized by different methods (Sondi, 2003; Tien *et al*., 2008), but method of chemical reduction of silver cation from its solution brought high effect (Libor, 1998). The chemical reduction process could realize in water solution of organic silver compounds (Ivan Sondi, 2003) or in water – organic solvent solution of inorganic silver nitrate (Pastoriza-Santos, 2000; Kwon, 2005). In order to increase of dispersion of nanoparticles and their regular dimension, the disperser was used. The nanosilver solution could directly use as a sterilizing reagent or coating sterilizing materials.

In this article, high density nanosilver solution was prepared from silver nitrate in water media in/with present or absent of disperser. Glucose was used as reductant and ammonium hydroxide played as initiate substance. The direct sterilization capability of nanosilver solution and sterilizing material created by nanosilver coated on calcinated laterite was investigated. The materials were nontoxic and applicable for drinking water disinfection.

2. Material and Methods

2.1. Nanosilver Solution Preparation

Working solutions of silver nitrate with concentration of range from 10^{-4} to 10^{-2} M were prepared from stock solution of $10^{-}1$ M in distilled water. Correct volume of working silver solution equal desired concentration for each experiment was taken and putted into glass flash. Then the flash was putted on magnetic stirrer, glucose solution was added so that its concentration about 10 times higher than silver concentration. In the case of experiments using disperser, the correct volume of PVA solution of 10 g/L concentration was added to meet required concentration. The final solution was mixed for about 10 min then ammoniac was added and stirred continuously until all silver ions reduced into silver metal in nanodimensional state. During reduction process the temperature was kept at 30 – 35°C.

2.2. Coating of Nanosilver on Calcinated Laterite

The dried calcinated laterite grains with size of 0.1 – 0.5 mm diameter were poured into nanosilver solution. The volumetric portion of solid and liquid was 1/1. The soaking time was 8 to 24 hours depending on nanosilver concentration in initial solution. Then the liquid phase was drained off. Solid phase was washed out of dissolved ions and dried to get bacterial removing material (BRM). Silver concentration in waste solution was measured to determine quantity of coated silver on carrying body.

2.3. Investigation of Sterilizing Capability of Nanosilver Solution and BRM

In this article, Total coliform (T Colif.) was chosen as indicating bacteria for all bacterial removing investigation. For direct use of nanosilver solution in water sterilization, the silver concentration was surveyed in the range from 2 to 20 µg/L of infected water. The bacteria number was determined in initial water sample and followed the time of sterilizing process.

For investigation of sterilizing capability of BRM, the glass column with 20 mm diameter containing BRM was installed. The influence of BRM column height (10; 20; 30 and 40 mm) on sterilizing capacity was investigated with spiked and real sample in constant water flow rate condition. Influence of water flow rate inner column (2.0; 4.0; 6.0; 8.0; 10.0; 12.0 $ml.cm^2$/min) on bacterial sterilization was also investigated in the condition of constant BRM column height with the same mentioned samples.

3. Result and discussion

3.1. The Influence of Silver Concentration and Disperser on Nanodimensional Silver Product

The experiment implemented as written in section 2.1. with silver concentration increased along the row of 40; 80; 120; 160; 200; 240; 280; 320; 360 and 400 mg/L.

3.1.1. The result in the case without disperser (polyvinylalcohol – PVA)

In water media and silver concentration was not higher than 200 mg/L the color of nanosilver solution appeared normally after 10–15 min mixing and reductive reaction simultaneously occurred immediately in 3–5 min following (Fig. 1).

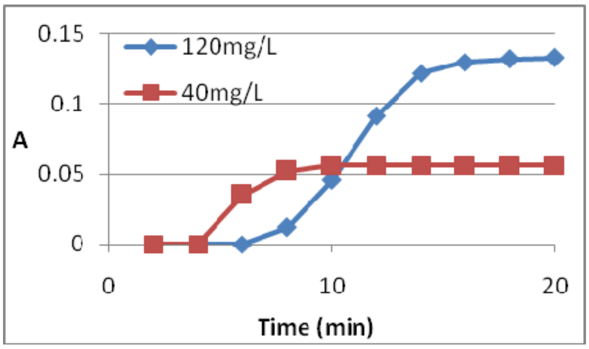


Figure 1. Color appearance vs reduction time

Figure 2. The color changing vs Ag conce

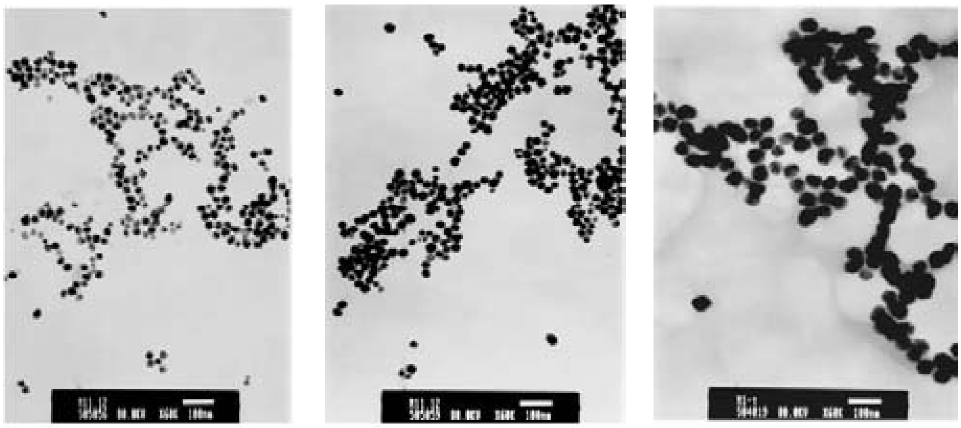
The color of nanosilver solutions changed from yellow to dark-green when silver concentration increased from 40 to 200 mg/L (Fig. 2).

When silver concentration was higher than 200 mg/L, solution became turbid. The TEM images showed that nanosilver particles were almost of equal size when they were formed from the same concentration. When nanosilver concentration increased from 40 to 200 mg/L, the dimension of particles increased from 20 nm to near 80 nm together with solution color changing respectively (Fig. 3).

3.1.2. The result in the case with presence of disperser

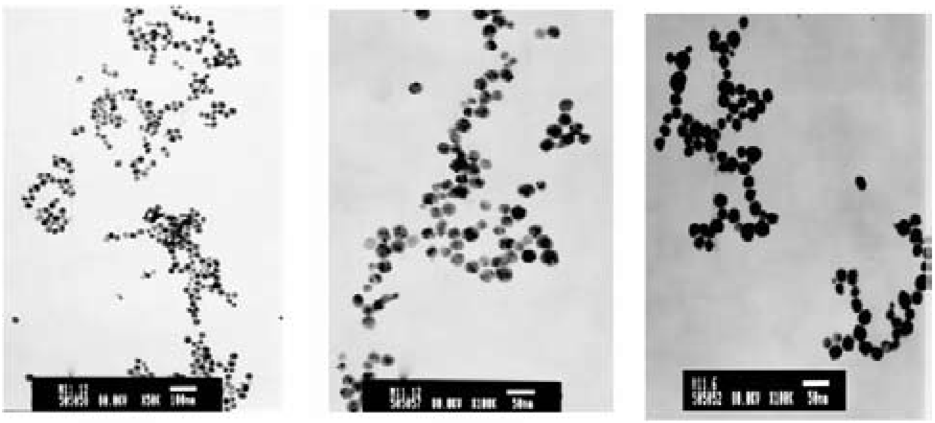
Presence of PVA in solution with optimal concentration separated silver particles each from other so avoided their association to form bigger particles. For this reason the concentration of nanosilver solution could increase to 400 mg/L and in the same silver concentration, particles size was smaller in the comparison with the size of the case without presence of disperser (Fig. 4). The experiment results also showed the color change of the solutions was similar the case without PVA (Fig. 5).

Concentration of disperser PVA also influenced the nanosilver solution structure. At concentration of 2–3 mg/L PVA started showing its effect. In our investigation, optimum PVA concentration was 10–20 mg/L. At higher concentration there appeared phenomenon that each several small silver particles wrapped in PVA



40 mg/L solution   120 mg/L solution   200 mg/L solution

Figure 3. TEM images of nanosilver particles in solution without PVA



40mg/L   160mg/L   360mg/L

Figure 4. TEM images of nanosilver particles in solution with PVA presence

40mg/L   120mg/L   160mg/L   200mg/L   280mg/L   360mg/L   400mg/L

Figure 5. The solution color changing vs silver concentration

envelopes, the nanosilver particles existed unclearly in solution.

3.2. Coating of Nanosilver on Calcinated Laterite

The coating process was according to the flow chart at Fig. 6. The productivity of nanosilver coating on laterite depended on soaking time. For 200 mg/L silver solution almost silver was settled after 20 h (Fig. 7).

Nanosilver particles coated on silica gel were clearly vision in SEM image (Con, 2009); but on laterite surface they were not recognized; because laterite is very complicated matrix and high porous. The confusion of laterite surface structure hid almost silver particles.

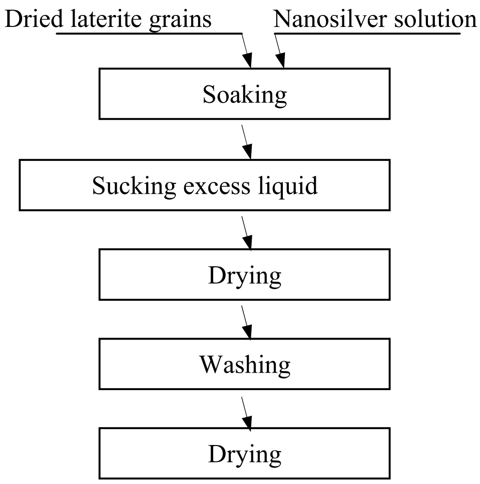


Figure 6. Coating procedure flow chart

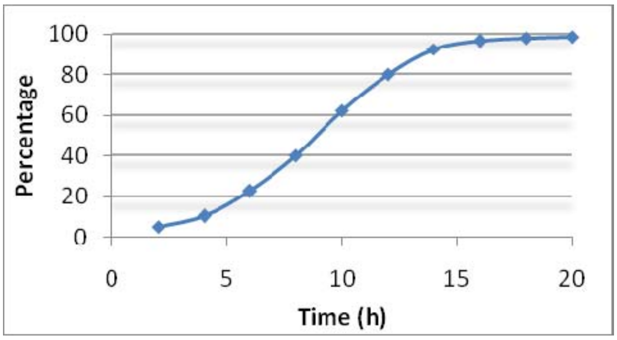


Figure 7. Percentage of nanosilver coated on laterite vs the soaking time

3.3. Investigation of Sterilizing Ability

3.3.1. Sterilizing ability of nanosilver solution in infected water

Bacterial spiked water containing 400 – 500 MNP/100 ml and 120 mg/L nanosilver solution used in this investigation. The experiment realized according to procedure in section 2.3 mentioned above. The results showed that nanosilver concentration lower than 10 µg/L could not exterminate completely bacteria in infected water despite contact time prolonged more than 30 min. With minimum concentration of 10 µg/L nanosilver and 25 - 30 min of contact time almost bacteria were removed (Fig. 8).

3.3.2. Sterilizing ability of BRM

The experiment results presented on Figs. 9-10. There was clear fact that the height of BRM column and flow rate of water current strongly influence on sterilizing ability. The sterilizing ability of column increased together with increase of BRM layer height and decreased when flow rate increased. In latest time, in many published reports, authors used parameter EBCT

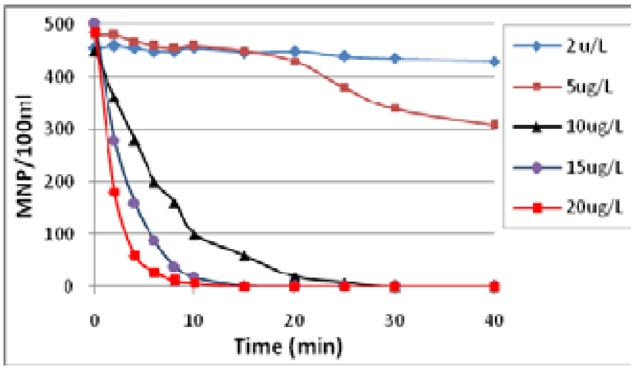


Figure 8. Influence of nanosilver concentration on sterilizing ability

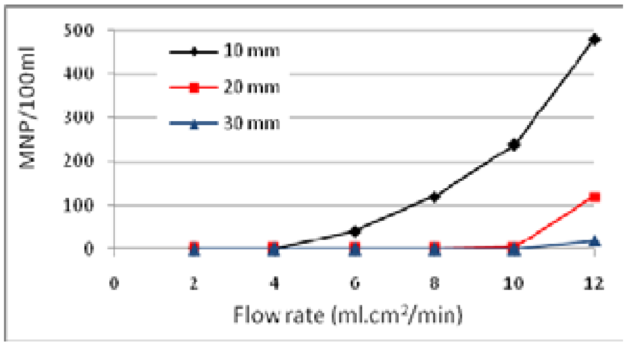


Figure 9. The influence of flow rate on bacteria sterilizing of BRM column

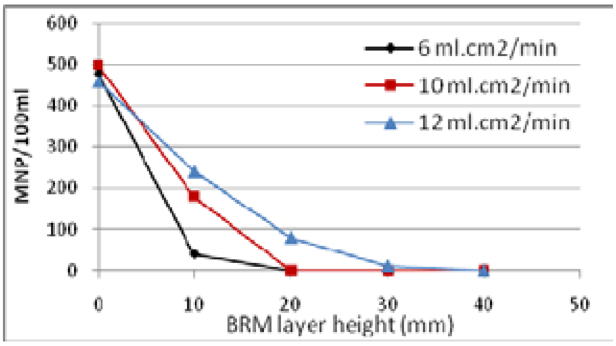


Figure 10. The influence of column height on bacteria sterilizing of BRM column

(empty batch contact time) for characterization of both of column filter parameters above. In the case of our investigation, the minimum EBCT for safely bacterial sterilizing was 15–20 seconds.

The results of experiment implemented with real infected water were similar results experimented in supplied water spiked bacteria lower than 1000 MNP/100ml.

4. Conclusion

The nanosilver solution was prepared at concentration from 40 to 400 mg/L. Although the color of solutions changed, their UV-VIS spectrum had two maxima around 200–210 nm and 400–420 nm. In present of PVA as disperser the concentration of nanosilver in solution could reached 400 mg/L; while absent disperser the nanosilver concentration was limited at 200 mg/L.

Nanosilver can effectively use for supplied water sterilization with minimum concentration of 10 µg/L. By other way, water can sterilize by means of use BRM as column filter. All bacteria in water could safely exterminate when flow through column filter with minimum layer height of BRM 20 mm and maximum flow rate 10 $ml.cm^2$/min or EBCT was guaranteed at least 15 seconds.

Both nanosilver solution and BRM were non toxic and economic, so they have very high potential applying for water sterilizing in water plants as well as at household scale.

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