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Gamma Irradiation Route to Large-Scale Production of Ag Nanoparticles and Fixing in Porous Ceramic Candle for Point-Of-Use Water Treatment

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ABSTRACT

The Ag nanoparticles/PVP solution (AgNPs) with concentration of 500 mg/L and AgNPs diameter of 10–15 nm was synthesized on a large scale up to 100 L/batch by gamma irradiation route. Porous ceramic candle (PC) samples were functionalized by treatment with a 3-aminopropyltriethoxysilane (AS) coupling agent and then impregnated in AgNPs solution for fixing AgNPs. The AgNPs content attached in PC (PC/AgNPs) determined by ICP-AES was of about 200–250 mg/kg. The average pore size of PC/AgNPs was about 48.2 Å analyzed by BET method. Owing to strong bonding of silver atoms to the wall of PC treated with AS, the contents of silver released from PC/AgNPs into filtrated water by flow test at a flow rate of about 5 L/h were less than 10 μg/L, it is satisfactory to the WHO guideline (<100 μg/L) for drinking water. Thus, PC/AgNPs candles can be potentially applied for point-of-use drinking water treatment.

Keywords: Silver Nanoparticles, Porous Ceramic, Water Treatment, Gamma Irradiation

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1. INTRODUCTION

Although there are many routes available for the synthesis of nanoparticles, there is an increasing demand to develop high yield, low cost, green chemistry and environmentally friendly procedures. According to previously many reports have verified that the gamma irradiation route to synthesis of colloidal nanoparticles solution provides several advantages and satisfiable to above demands. (Du et al., 2008; Li et al., 2007; Phu et al., 2010) Among of nanoparticles, excellent antibacterial activation and low cytotoxicity to human cells favor silver nanoparticles (AgNPs), making them applicable to fields. (Shen et al., 2011; Bao et al., 2011) The presence of pathogenetic microbes in drinking water is a potential health risk. The removal of bacterial from water is an extremely important process for drinking and sanitation systems especially against concerns on growing outbreaks of waterborne diseases. (Bao et al., 2011) According to WHO, at least one billion people in the worldwide do not have access to clean, potable water sources. (Dankovich and Gray, 2011)

Recently, considerable interest has arisen in the use of AgNPs based on gigantic high antimicrobial and biofouling improvement for water disinfection. (Zodrow et al., 2009) In particular, the formation of by-products into water by conventional treatment techniques and the increasing of resistance of some pathogens to conventional disinfectants have encouraged researchers to explore the AgNPs. (Quang et al., 2011) The reliability and ease of operation of membrane-based water filtration systems such as polyurethane foam, (Jain and Pradeep, 2005) paper sheet filter, (Dankovich and Gray, 2011) porous ceramic filters (Shen et al., 2011; Bielefeldt et al., 2010; Lv et al., 2009) have led to enlarging utilization. Traditional ceramics are often employed in water filtration because of the ease of creating a uniform structure of fine pores. Such ceramic structures can remove many water contaminants by size exclusion through the pores or by adhesion to the pore walls. (Larimer et al., 2010) However, porous ceramics (PC) can only block bacteria and do not have the capability to kill them. (Lv et al., 2009)

Numerous investigations have been carried out on loading AgNPs with the functionalized PC filters as an effectively antimicrobial agent for water treatment. (Jain and Pradeep, 2005; Bielefeldt et al., 2010; Mwabi, 2012) Unfortunately, the AgNPs were commonly inert with PC, (Lv et al., 2009) so that silver releases into water filtrate with overdoses compared to the limit of 0.1 mg/L at maximum, according to the WHO and US-EPA guideline. (Dankovich and Gray, 2011; Mwabi, 2012) Several approaches were studied to improve on loading and holding abilities of AgNPs onto polymer and PC filters, mainly by using a coupler and/or modification by appropriate agents containing functional groups which have affinity with AgNPs. (Shen et al., 2011; Lv et al., 2009) Although up to now, it has still not been reported on production of fixing AgNPs in PC candles.

In this study, we present a facile procedure for synthesis of large scale AgNPs/PVP solution. The domestic commercialized PC product was used for modifying and fixing with AgNPs through coordination bonds by using aminosilane as coupling agent. The influential aminosilane treatments in capacity of AgNPs immobilized in PC were investigated. The silver content released from PC/AgNPs into filtrated water was also investigated by flowing test. The as-prepared PC/AgNPs candles owing to containing antimicrobial AgNPs constituents and acceptable level of silver release, can be potentially further developed towards point-of-use drinking water treatment.

2. EXPERIMENTAL

Materials and chemicals:

$AgNO_3$ is pure grade of China. Polyvinylpyrrolidone (PVP) is a pharmaceutical grade product from BASF, Germany. Absolute ethanol is product of Truong Thinh Co., Vietnam. Aminosilane namely 3-aminopropyltriethoxysilane is a product of Merck, Germany. All aqueous solutions were prepared using distilled water. Commercial porous ceramic (PC) candles supplied by a domestic Ceramic Co., Hai Duong, Vietnam.

Methods:

Synthesis of colloidal silver nanoparticles (AgNPs) solution:

AgNPs/PVP solution was prepared through a modified our method as reported in previous work. (Du et al., 2008) Briefly, PVP and ethanol (EtOH) were dissolved in water to prepare solution with the concentration of 1% (w/v) and 5% (v/v), respectively. $AgNO_3$ was then dissolved in the above prepared solution to obtain final formulation: 5 mM Ag^+/1% PVP/5% EtOH/water to 100 L. The mixture was poured into plastic cans with 25 L/can and tight sealing by a can cap. The irradiation of this solution for the synthesis of AgNPs was carried out on a Co-60 irradiator with dose rate of about 1.2 kGy/h at VINAGAMMA Center, HCM City. Absorption spectra of irradiated AgNPs solution were taken on an UV-Vis spectrophotometer, Jasco V-630. The AgNPs sizes were measured using a transmission electron microscope (TEM), JEM 1010, JEOL, Japan.

Treatment of PC with aminosilane (AS): PC samples of approximately 3.0×2.5×0.8 cm^3 or PC candles with dimensions of 20×4×0.8 cm^3 were cleanly treated in 10% H_2SO_4 at 60^oC for 1 h, washed with water and dried at 110^oC. Then it was impregnated in AS of 0.5–2% (v/v) in

EtOH solution with different time duration. The PC impregnated with AS was dried at rT^o and then heated at 110^{o}C in an oven 2 h for siloxan bonding between PC and AS (PC/AS).

Impregnation PC/AS in AgNPs solution: The as-prepared PC/AS samples were further impregnated in AgNPs solution for 24 h. After that, it was washed in ultrasonic water bath for 15 min. with repetitively three times to remove all unbound AgNPs. Drying AgNPs decorated PC samples (PC/AgNPs) was performed in a forced air oven at 80^{o}C till to dry, subsequently obtained PC/AgNPs with brown-yellow. The content of AgNPs in PC/AgNPs was determined by ICP-AES method on a Perkin-Elmer, Optima 5300 DV. The presence of AgNPs in PC/AgNPs was assessed by energy-dispersive X-ray spectroscopy (EDS) on a JEOL 6610 LA and UV-Vis spectroscopy on a Jasco V-630. The specific surface area, the pore size and pore volume were measured by BET method (Quantachrom Nova 1200) using N_2 as the adsorbate.

Determination of Ag release: The PC/AgNPs candle was connected to tap water with adjusted flow rate of ~5 L/h. The filtrated water was collected for determination of the Ag content by neutron activation analysis at the Nuclear Research Institute, Dalat.

3. RESULTS AND DISCUSSION

3.1. Synthesis of colloidal AgNPs solution:

The method using radiation of gamma ray and electron beam provides several advantages compared to other methods, especially the pure AgNPs can be produced without contamination of excessive reductant and Ag^+ residue; and large scale production can be carried out at a comparatively reasonable cost. (Du et al., 2008; Li et al., 2007; Phu et al., 2010) The mechanism of the γCo-60 irradiation method for synthesis of AgNPs/PVP solution was

described in the previous papers. (Du et al., 2008; Li et al., 2007; Phu et al., 2010) Briefly, the complex Ag^+/PVP was reduced to AgNPs/PVP solution by hydrated electron (e^-_{aq}) and hydrogen atom ($H^\bullet$) which was generated by γ-radiolysis of aqueous solution. (Li et al., 2007) In addition, the hydroxyl radical ($^\bullet OH$) reacts with alcohol (e.g. ethanol, isopropanol,..) yielding hydroxyalkyl radical which is able to reduce Ag^+ ions absorbed on clusters to Ag^o. (Du et al., 2008; Li et al., 2007)

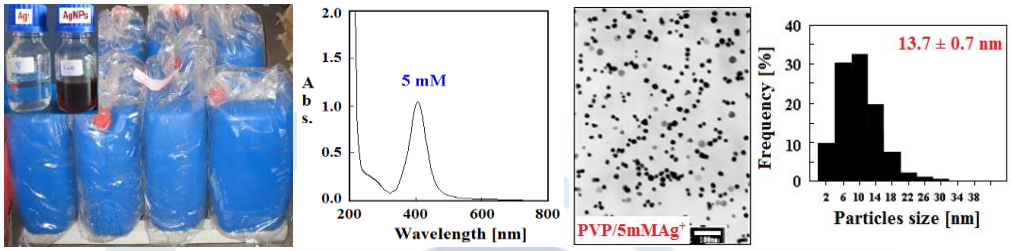

Figure 1. The AgNPs/PVP solution, UV-Vis spectrum and AgNPs particles size values

In Fig.1, the irradiated Ag^+/PVP solution showed red-brown and the maximum absorbed wavelength ~400–410 nm, which are characterizations of the colloidal AgNPs. (Du et al., 2008; Li et al., 2007; Phu et al., 2010) The TEM image showed the AgNPs were mainly sphere-shape and the size distribution was gauss pattern. The average particles size of AgNPs/PVP as-prepared was of 13.7 nm, which is larger than that (~9.5 nm) as synthesized by Du et al. (2008) (Du et al., 2008) The reason can be explained by difference of adsorbing dose rate between small and large volume, the higher the dose rate the smaller the particle size could be produced. (Li et al., 2007) However, according to results reported by Phu et al. (Phu et al., 2010) and Quang et al. (Quang et al., 2011) the AgNPs size ~10–15 nm exhibited highly antimicrobial activity so as-prepared AgNPs/PVP on large scale can be used for fixing onto the wall of porous ceramic (PC) to create antimicrobial PC filters.

3.2. Optimization of concentration and treatment time of PC with AS

Table 1. Effect of treatment conditions of AS on silver content (mg/kg) in PC/AgNPs

AS concentration (%), during 90 min.						AS treatment time (min.), 2% AS					
0	**0.5**	**1**	**2**	**3**	**5**	**30**	**60**	**90**	**120**	**150**	**180**
7.5	94.5	192	228	234	255	200	205	228	226	222	231

The results in Table 1 indicated that the appropriate concentration of AS was of ~2% and the suitable immersion time was of 90–120 min. for maximum fixing AgNPs in PC/AgNPs of ca. 200–250 mg/kg. As we known, this is fist time reported the optimization of treatment conditions of PC with AS. The mechanism of fixing AgNPs in modified PC by AS was in detail explained by Lv et al.(Lv et al., 2009). Briefly, the siloxan (-**Si**-**O**-**Si**-RNH_2) bonds were formed during the PC immerged in AS solution and the PC/AS heated into an oven. After that, the coordination bonds (-R-**NH_2**-**Ag**-AgNPs) of the –NH_2 groups with the Ag atoms were formed during the shocking PC/AS in AgNPs solution.(Lv et al., 2009) also studied to fix AgNPs in PC water treatment, but they only prepared samples of 1×1×0.5 cm^3.

From EDS spectra in Fig. 2 showed that the composition of PC consists of three main elements particularly Si, Al, O and small amount of Na and K, but without any trace of silver. After fixing AgNPs in PC, the peak at 3 keV and 3.2 keV appeared in EDS spectrum confirming the presence of silver in the composition of PC/AgNPs. The EDS spectrum was also used to confirm the presence of AgNPs in another AgNPs fixed materials. (Bao et al., 2011; Dankovich and Gray, 2011; Quang et al., 2011; Larimer et al., 2010)

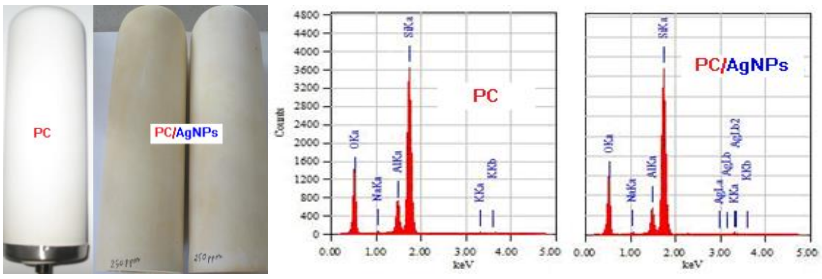

Figure 2. The porous ceramic candle samples and EDS spectra

The observation from Fig. 2 that the PC/AgNPs was yellowish colour after fixed with AgNPs that is also observed by previous studies. (Quang et al., 2011; Lv et al., 2009; Larimer et al., 2010) The λ_{max} of AgNPs fixed onto PC was at ~405 nm with broad peak compared to the original AgNPs (data not shown). Thus, this peak indicated that AgNPs are present in the PC as reported by previous research works. (Jain and Pradeep, 2005; Lv et al., 2009)

The BET is a good tool for characterization of porosity materials. Results in Table 2 showed that the surface area, pore volume and pore size of PC/AgNPs simultaneously decreased in comparison to bare PC. This phenomenon can be attributed by the AS molecules and AgNPs coated on the surface and filled into the tiny pores of PC. (Quang et al., 2011)

Table 2. Characteristics of blank PC and PC/AgNPs candle

Parameters	PC	PC/AgNPs
Silver content (mg/kg)	Not detected	200–250
Specific surface area (m^2/g)	1.83	1.51
Average pore size (A^o)	61.9	48.2
Total pore volume (cm^3/g)	2.8×10^{-3}	1.8×10^{-3}

3.3. Content of silver release from PC/AgNPs candles into filtrated water by flowing test

Table 3. The silver content in the filtrated water released from PC/AgNPs candle

Volume of filtrated water (L)	**20**	**40**	**80**	**100**	**200**	**300**	**400**	**500**
Ag content (μg/L)	9.04	7.49	4.12	2.66	0.64	0.66	0.34	0.92

Results in Table 3 proved that the contents of the silver releasing from PC/AgNPs candle in the filtrated water up to 500 L were less than 10 μg/L, which are far below the WHO guideline (<100 μg/L) for drinking water. Previous studies also studied of silver-impregnated porous ceramic pot filter for low-cost household drinking water treatment. (Shen et al., 2011; Dankovich and Gray , 2011; Bielefeldt et al., 2010; Larimer et al., 2010; Mwabi et al., 2012) However, they did not used coupling agent like AS to fix AgNPs, therefore silver was easily leaching from the pot with overdose and the antimicrobial effect should be decreased with the filtration time. Among the water treatment materials, ceramic filters (disk, candle and pot) proved to be one of the best treatment options for reducing bacteria contaminant in water. (Bielefeldt et al., 2010; Larimer et al., 2010) Therefore, the PC/AgNPs candle prepared in this study with stably fixing 200–250 mg AgNPs/kg is promising to apply for point-of-use drinking water treatment.

4. CONCLUSIONS

The colloidal AgNPs/PVP solution with the particles size of 10 - 15 nm and the AgNPs concentration of 500 mg/L was synthesized by γ-irradiation method. The fixing of AgNPs in PC through coordination bonds using AS as a coupling agent was performed. Results of flow test on silver release indicated that the silver content in filtrated water were less than 10 μg/L, and it is far below the WHO guideline of 100 μg/L at maximum for drinking water. Thus, it is expected that the PC/AgNPs candles with the silver content of 200–250 mg/kg have highly antimicrobial activity for point-of-use drinking water treatment.

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