

## SYNTHESIS OF SILVER NANOPARTICLES DOPED IN THE ZEOLITE FRAMEWORK BY CHEMICAL REDUCTION METHOD

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### ABSTRACT

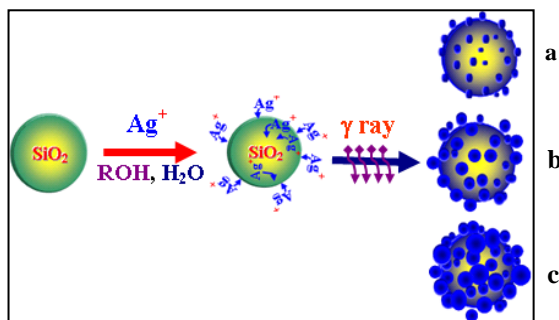
Silver ions ( $\text{Ag}^+$ ) were introduced at first into the porous zeolite 4A lattice by an ion-exchange route. And then silver nanoparticles (AgNPs) were synthesized in the zeolite framework by chemical reduction method using hydrazine hydrate ( $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ ) as reducing agent. The synthesized AgNPs/zeolite product was characterized by ultraviolet-visible spectroscopy (UV-vis), X-ray diffraction (XRD), transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDX). The results showed the maximum absorption wavelength ( $\lambda_{\text{max}}$ ) of AgNPs/zeolite at 427 nm and the average size of the metallic AgNPs doped in the zeolite of about 30 nm. The synthesis process has been considered as suitable one to prepare AgNPs/zeolite with AgNPs content in zeolite of about 1.2% on large scale. The obtained AgNPs/zeolite product has been used for production of porous ceramic water filters with efficiently bacterial disinfection effect for treatment of drinking water.

**Keywords:** zeolite, silver nanoparticles, chemical reduction, porous ceramic

### 1. INTRODUCTION

Synthetic polymers typically polyvinyl alcohol (PVA) [1,2], polyvinyl pyrrolidone (PVP) [3-5] and surfactants such as sodium dodecyl sulfate (SDS) and Tween 80 [6] have been widely used as stabilizers in the bottom-up approach of metallic nanoparticles synthesis typically silver nanoparticles (AgNPs). In addition, natural polymers such as chitosan [7,8], alginate [9,10], gum acacia [11], gelatin [12,13], etc have been also used for capping AgNPs. On the other hand, materials containing AgNPs are regarded as one of the most important nanocomposites especially due to their antimicrobial activities [14-19]. Furthermore, nanocomposite materials of metal particles in particular AgNPs on various solid supports are of great importance

for fundamental research and practical applications [20]. For example, Nguyen et al. described the procedure for depositing AgNPs onto silica by gamma Co-60 irradiation method as shown in Fig. 1 [21]. The obtained AgNPs/ $\text{SiO}_2$  can be used as antimicrobial agent for paints, plastics, ceramic, etc.



**Figure 1.** Schematic illustration of the AgNPs deposited onto silica by  $\gamma$ -irradiation: a) 5 mM, b) 10 mM and c) 20 mM AgNPs

In this study, the AgNPs were synthesized into the cavities of the zeolite framework using  $\text{AgNO}_3$  as silver precursor and hydrazine hydrate ( $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ ) as reducing agent. The obtained AgNPs/zeolite product has been used for production of antimicrobial porous ceramic water filters (PCCF/AgNPs) for treatment of drinking water.

## 2. MATERIALS AND METHODS

### 2.1. Materials

Pure-grade  $\text{AgNO}_3$  (99.8%) and hydrazine hydrate  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  (50%), and industrial grade zeolite 4A were products from China. The Luria-Bertani (LB) medium for bacterial incubation was purchased from Himedia, India. The *Escherichia coli* ATCC 6538 (*E. coli*) was provided by University of Medicine-Pharmacy in Ho Chi Minh City. Polyvinyl alcohol 217 (PVA) was a product of Kuraray, Japan. Distilled water was used in all experiments.

### 2.2. Methods

#### 2.2.1. Exchange of $\text{Ag}^+$ ion in zeolite

1.05 kg of zeolite was suspended into a glass beaker containing 1.3 L water. Then, 1.05 L  $\text{HNO}_3$  2N and water were added into zeolite suspension mixture for neutralization to pH ~6 and for final volume of about 4.2 L. 17.5 g of  $\text{AgNO}_3$  was dissolved in 300ml water and then poured slowly into neutralized zeolite suspension mixture. Stirring was carried out for 2 h at  $70^\circ\text{C}$  for completed  $\text{Ag}^+$  exchange.

#### 2.2.2. Reduction of $\text{Ag}^+$ to AgNPs in the zeolite framework

A freshly prepared 500 ml hydrazine 25% (w/v) solution was added drop by drop into above prepared mixture of  $\text{Ag}^+$ /zeolite for reducing  $\text{Ag}^+$  ions. Stirring was continuing for 4 h at  $70^\circ\text{C}$ . Reduction

reaction was stopped and let standing overnight for AgNPs/zeolite settling down at ambient temperature. Finally, AgNPs/zeolite product was filtered off using cotton fabric and dried at  $110^\circ\text{C}$  till to constant weight.

#### 2.2.3. AgNPs/zeolite characterization

The content of AgNPs in zeolite was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on a Perkin-Elmer, Optima 5300 DV. AgNPs/zeolite product was characterized by x-ray diffraction (XRD) on D8 Advance Brucker, Germany and the AgNPs sizes were measured using a transmission electron microscope (TEM; JEM 1010, JEOL, Tokyo, Japan). UV-vis absorption spectrum of 0.5% AgNPs/zeolite powder in 2% polyvinyl alcohol solution was taken on the Shimadzu, UV-1650 PC spectrophotometer, Japan. The presence of silver in AgNPs/zeolite was also assessed by energy dispersive x-ray spectroscopy (EDX) on a JEOL 6610 LA.

#### 2.2.4. Production of antimicrobial PCCF/AgNPs

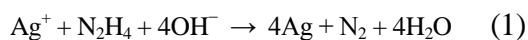
PCCF/AgNPs samples were produced by sintering silica from rice husk with AgNPs/zeolite at  $1050^\circ\text{C}$  at a domestic Ceramic Co., Hai Duong province, Vietnam.

#### 2.3.5. Bactericidal activity of PCCF/AgNPs

*In vitro* test of bactericidal activity of PCCF/AgNPs was carried out following the procedures as described in the reference [21].

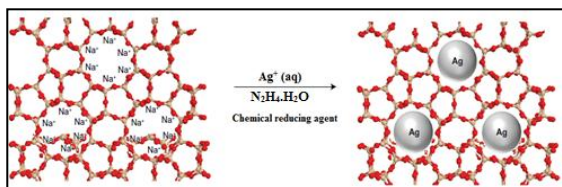
## 3. RESULTS AND DISCUSSION

Reaction of  $\text{Ag}^+$  reduction by hydrazine is shown in eq. (1), in weak basic condition, due to base properties of  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  [22].



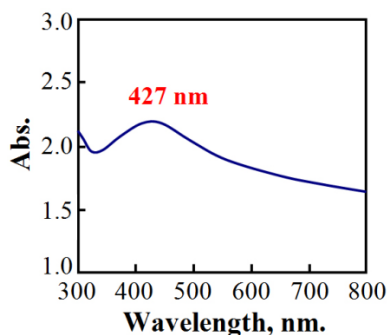
Reaction (1) lowers the pH of the solution and it remains in weak base due to

reducing agent ( $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ ) is added in more three time excess, according to the reaction (1). Dimitrijevic et al. reported that hydrazine hydrate has been considered as preferred reducing agent and used for industrial scale production of silver powder for decades [22]. The synthesis of the silver nanoparticles into the zeolite framework from  $\text{Ag}^+/\text{zeolite}$  by chemical reduction was depicted in figure 2.



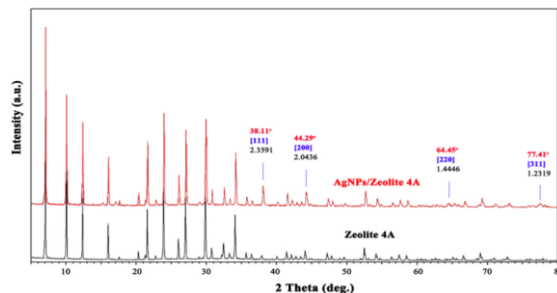
**Figure 2.** Schematic illustration of the synthesis of AgNPs into the zeolite framework by chemical reduction method

Figure 3 showed the maximum absorption wavelength ( $\lambda_{\text{max}}$ ) of AgNPs/zeolite at 427 nm. Shameli et al. also reported the characteristics of their AgNPs/zeolite products with the  $\lambda_{\text{max}}$  values in the range of around 394 – 401 nm that correspond to AgNPs smaller than 10 nm [18].



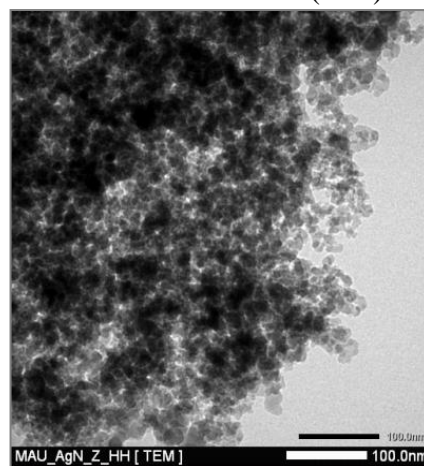
**Figure 3.** UV-vis spectrum of 0.5% AgNPs/zeolite in 2% PVA solution

From XRD pattern in figure 4, the average size of the metallic AgNPs deposited on zeolite was calculated using the peak at  $2\theta = 38.11^\circ$  with full width at half maximum (FWHM) of about 0.277 and based on Debye-Scherrer's formula:  $t = 0.9\lambda/B \times \cos\theta$  as described by Jiang et al. [23].



**Figure 4.** XRD patterns of zeolite 4A and AgNPs/zeolite 4A

As the result of calculation, the size of AgNPs was of about 30 nm. The content of AgNPs deposited on zeolite 4A analyzed by ICP-AES was of about 1.2% (w/w).

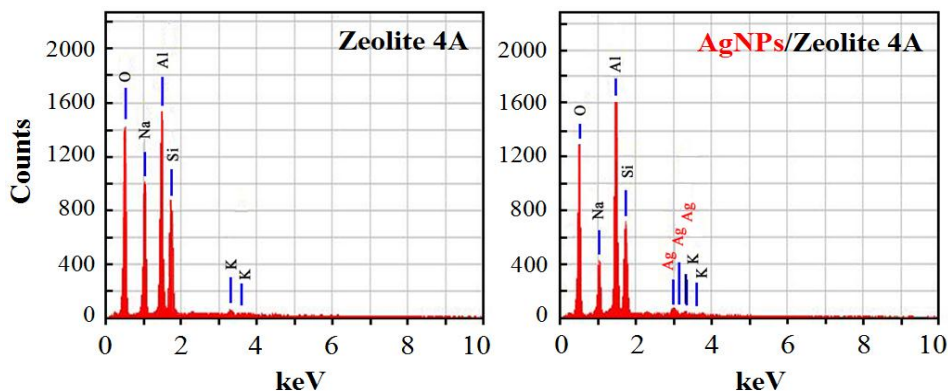


**Figure 5.** TEM image of AgNPs/zeolite

Figure 5 showed the TEM image of AgNPs/zeolite. It can be seen from TEM image that the AgNPs diameters synthesized in the cavities of the zeolite were fairly uniform that was in agreement with the results reported by Shameli et al. [18]. However, the sizes of AgNPs in the zeolite framework obtained by Shameli et al. were smaller (2-4 nm) compared to that of ours (30 nm). This reason may be due to the dilution ratio of zeolite and water during reducing process. Another reason may be due to  $\text{NaBH}_4$ , a stronger reducing agent compared with hydrazine hydrate. Further study should be carried out to clarify this phenomenon. In

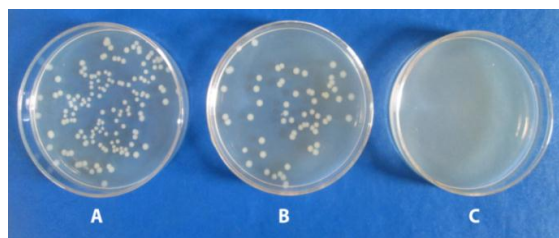
comparison with the AgNPs size of ~30 nm calculated from XRD pattern, the sizes of

AgNPs from TEM image in figure 5 were in the range of 10-30 nm, smaller than 30 nm.



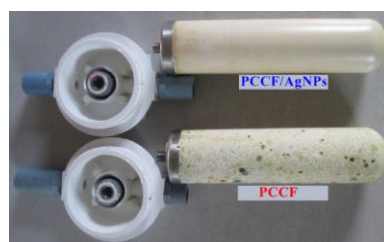
**Figure 6.** EDX spectra of zeolite 4A and AgNPs/zeolite 4A

Results of energy dispersive x-ray (EDX) spectra in figure 6 showed that the composition of zeolite consists of four main elements, particularly silicon, aluminum, oxygen and sodium and a small amount of potassium, but without any trace of silver. After exchange with  $\text{Ag}^+$  and conversion of  $\text{Ag}^+$  into AgNPs, the peak at 3 keV appeared in EDX spectrum confirming the presence of silver in the composition of AgNPs/zeolite. In our previous study [19], the EDX spectrum was also used to confirm the presence of AgNPs in porous ceramic.



**Figure 7.** *E. coli* colonies forming on LB agar: A) control, B) PCCF, and C) PCCF/AgNPs

The surviving number of *E. coli* in the tested medium was of  $15 \times 10^5$ ;  $5.8 \times 10^5$  and 0 CFU/ml for control, PCCF and PCCF/AgNPs samples, respectively as shown in figure 7. The *in vitro* test results indicated that PCCF/AgNPs exhibited highly bactericidal activity against *E. coli*.



**Figure 8.** The outside appearance of PCCF and PCCF/AgNPs after using for water treatment

Figure 8 showed that the outside of the PCCF/AgNPs had almost no growth of microorganisms compared with the bare PCCF one. This observation confirmed again the highly antimicrobial activity of the PCCF/AgNPs.

#### 4. CONCLUSION

AgNPs in the cavities of the zeolite with size of about 30 nm and content of ~1.2% (w/w) were successfully synthesized by two steps: exchange of  $\text{Ag}^+$  and reduction of  $\text{Ag}^+$  exchanged in the zeolite. The synthesis process is fairly suitable to carry out on large scale. The obtained AgNPs/zeolite product has been used for production of porous ceramic water filters with effectively bactericidal activity. Furthermore, AgNPs/zeolite product can be used as antimicrobial agent for other purposes of applications as well.

## CHẾ TẠO BẠC NANO/ZEOLIT BẰNG PHƯƠNG PHÁP KHỬ HÓA HỌC

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### TÓM TẮT

Bạc ion trước tiên được trao đổi vào trong cấu trúc xốp của zeolite 4A. Tiếp theo là khử bạc ion thành bạc nano trong cấu trúc của zeolit sử dụng hydrazin hydrat ( $N_2H_4.H_2O$ ) làm chất khử. Đặc trưng tính chất của bạc nano/zeolit được xác định bằng phổ UV-vis, nhiễu xạ tia x (XRD), chụp ảnh TEM và phổ tán sắc năng lượng tia X (EDX). Kết quả cho thấy bước sóng hấp thụ cực đại ( $\lambda_{max}$ ) của bạc nano/zeolit là 427 nm, kích thước của bạc nano là ~30 nm và hàm lượng bạc nano trong zeolit là ~1,2%. Quy trình chế tạo bạc nano/zeolit khá thuận tiện để phát triển sản xuất. Bạc nano/zeolit đã được ứng dụng để sản xuất ống sứ xốp lọc nước với hoạt tính diệt khuẩn hiệu quả.

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