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

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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. In addition, natural polymers such as chitosan [7, 8], alginate [9,10], gum acacia [11], gelatin [12, 13], etc have been also used as stabilizers of colloidal AgNPs solution. 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. studied to deposit AgNPs onto silica by gamma Co-60 irradiation method [21]. The synthetic procedure is described as in Figure 1. The obtained AgNPs/SiO₂ can be used as antimicrobial agent for paints, plastics, ceramic, etc.

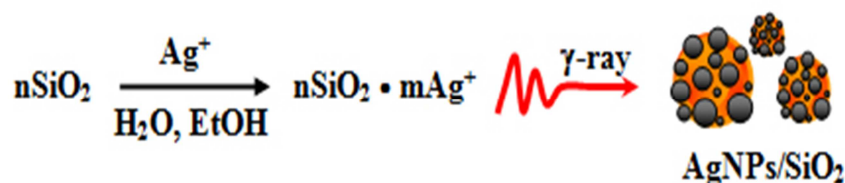


Figure 1. Schematic illustration of the synthesis process of AgNPs deposited onto silica by γ -irradiation.

In this study, the AgNPs were synthesized into the cavities of the zeolite framework using AgNO₃ as silver precursor and hydrazine hydrate (N₂H₄ · H₂O) 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 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 Ag^+ ion in zeolite

1.05 kg of zeolite was suspended into a glass beaker containing 1.3 L water. Then, 1.05 L 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 AgNO_3 was dissolved in 300 ml water and then poured slowly into neutralized zeolite suspension mixture. Stirring was carried out for 2 h at 70 °C for completed Ag^+ exchange.

2.2.2. Reduction of Ag^+ to AgNPs in the zeolite framework

A freshly prepared 50 ml hydrazine 25 % (w/v) solution was added dropwise to the above Ag^+ /zeolite under stirring for 4 h at 70 °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 °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 Bruker, 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 °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 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 schematic illustration of the synthesis of AgNPs into the zeolite framework from Ag^+ /zeolite by chemical reduction was described by Shameli et al. [18].

Figure 2 showed the maximum absorption wavelength (λ_{max}) of AgNPs/zeolite at 427 nm. Shameli et al. also reported the characteristics of their AgNPs/zeolite products with the λ_{max} values in the range of around 394 – 401 nm that correspond to AgNPs smaller than 10 nm [18].

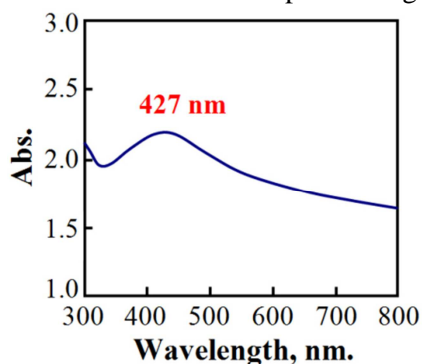


Figure 2. UV-Vis spectrum of 0.5 % AgNPs/zeolite in 2 % PVA solution.

From XRD pattern in Figure 3, 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].

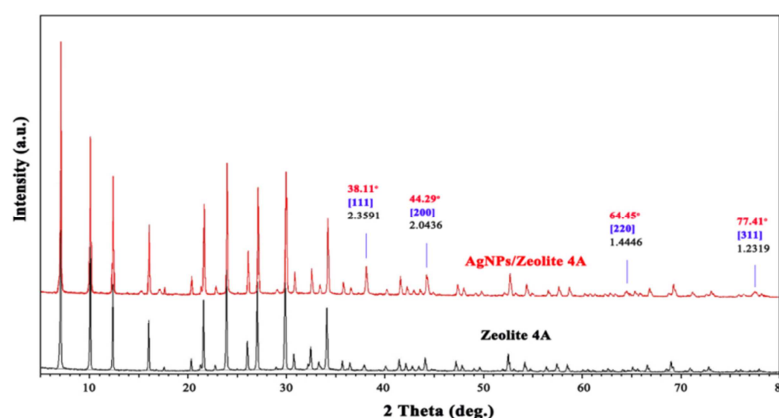


Figure 3. XRD patterns of zeolite 4A and AgNPs/zeolite 4A.

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).

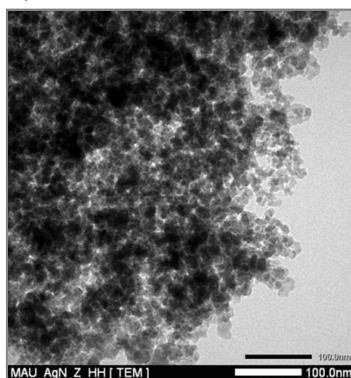


Figure 4. TEM image of AgNPs/zeolite.

Figure 4 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 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 4 were in the range of 10 - 30 nm, smaller than 30 nm.

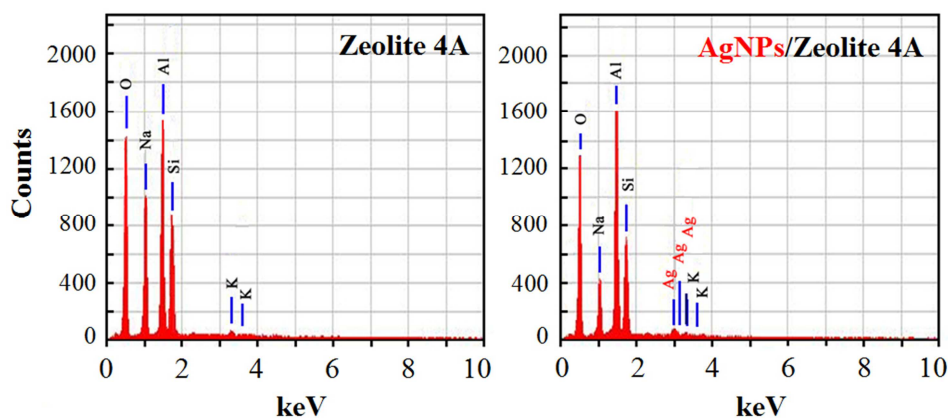


Figure 5. EDX spectra of zeolite 4A and AgNPs/zeolite 4A.

Results of energy dispersive X-ray (EDX) spectra in Figure 5 showed that the composition of zeolite consists of four main elements, particularly silicon, aluminum, oxygen, sodium and a small amount of potassium, but without any trace of silver. After exchange with Ag^+ and conversion of 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.

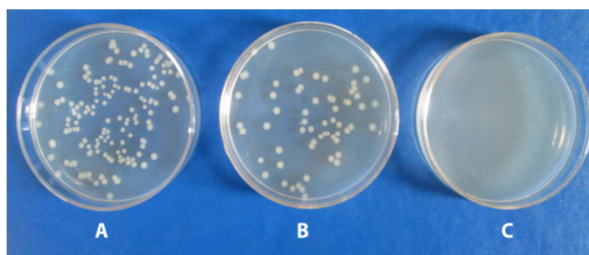


Figure 6. *E. coli* colonies forming on LB agar: A) control, B) PCCF, and C) PCCF/AgNPs.

The surviving number of *E. coli* in the tested medium was of 15×10^5 ; 5.8×10^5 and 0 CFU/ml for control, PCCF and PCCF/AgNPs samples, respectively as shown in figure 6. The *in vitro* test results indicated that PCCF/AgNPs exhibited highly bactericidal activity against *E. coli*.

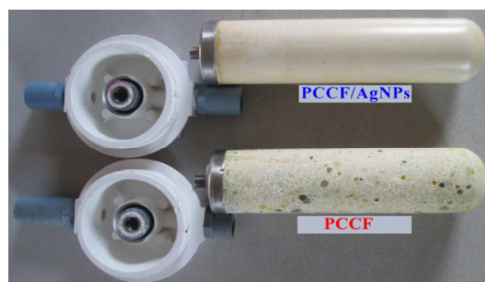


Figure 7. The outside appearance of PCCF and PCCF/AgNPs after using for water treatment.

Figure 7 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 $\sim 1.2\%$ (w/w) were successfully synthesized by two steps: exchange of Ag^+ and reduction of 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.

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TÓM TẮT

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

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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 (λ_{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.

Từ khóa: zeolite, bạc nano, khử hóa học, sứ xốp.