ИЗВЕСТИЯ ВЫСШИХ УЧЕБНЫХ ЗАВЕДЕНИЙ.
Т 66 (3) Серия «**ХИМИЯ И ХИМИЧЕСКАЯ ТЕХНОЛОГИЯ**» 2023
V 66 (3) **ChemChemTech** 2023

DOI: 10.6060/ivkkt.20236603.6722

ПОЛУЧЕНИЕ НОВЫХ МАТЕРИАЛОВ НА ОСНОВЕ КОМБИНАЦИИ СИНТЕТИЧЕСКИХ ЦЕОЛИТОВ И НАНОЧАСТИЦ СЕРЕБРА

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Наносеребро давно известно как высокоэффективное дезинфицирующее средство, способное ограничивать рост и уничтожение многих видов плесени и бактерий. Наносеребро можно синтезировать разными способами, в зависимости от цели и требований использования. Наносеребро можно диспергировать в растворах или наносить на носители для различных применений. Однако в растворе наночастицы серебра часто агрегируют, снижая при этом свою антибактериальную активность. Чтобы повысить антибактериальную активность наносеребра и обеспечить возможность многократного восстановления и повторного использования, а также возможность хорошо диспергироваться в различных материалах, наносеребро часто наносят на носители. В этом исследовании было синтезировано наносеребро на поверхности цеолита с помощью таких методов, как химическое восстановление с помощью $NaBH_4$, N_2H_4 или термическое восстановление при 350 °C. Ионы Ag^+ адсорбируются на цеолите 4А по механизму ионного обмена, а затем восстанавливаются различными методами. Результаты показали, что при восстановлении Ag^+ до Ag^0 химическими реагентами наночастицы серебра распределяются на поверхности цеолита более равномерно, чем при термическом восстановлении. Содержание серебра на поверхности цеолита при восстановлении гидразином примерно в 3 раза выше, чем при восстановлении боргидридом натрия. Цеолит, содержащий наносеребро, обладает способностью обеззараживать кишечную палочку с концентрацией ≥ 5 мг/мл. Образец Ag02/Z, в котором Ag^+ до Ag^0 восстановлен гидразином, обладает наилучшей антибактериальной активностью против E.coli по сравнению с остальными образцами. Диаметр стерильного кольца при концентрации 20 мг/мл составляет 9 мм.

Ключевые слова: цеолит, наносеребро, антибактериальный материал

Для цитирования:
Суан Минь Ву, Тхи Лан Фам, Тхи Ми Хань Ле, Тхи Тху Хоай Фам, Чи Май Нгуен, Дай Лам Чан Получение новых материалов на основе комбинации синтетических цеолитов и наночастиц серебра. *Изв. вузов. Химия и хим. технология*. 2023. Т. 66. Вып. 3. С. 59–65. DOI: 10.6060/ivkkt.20236603.6722.

For citation:
Xuan Minh Vu, Thi Lan Pham, Thi My Hanh Le, Thi Thu Hoai Pham, Chi Mai Nguyen, Dai Lam Tran Obtaining new materials based on a combination of synthetic zeolites and silver nanoparticles. *ChemChemTech* [*Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol*.]. 2023. V. 66. N 3. P. 59–65. DOI: 10.6060/ivkkt.20236603.6722.

OBTAINING NEW MATERIALS BASED ON A COMBINATION OF SYNTHETIC ZEOLITES AND SILVER NANOPARTICLES

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Nano silver has long been known as a highly effective disinfectant, capable of limiting the growth and eliminating many types of mold and bacteria. Nano silver can be synthesized by many different methods, depending on the purpose and requirements of use. Nano silver can be dispersed in solution or carried onto carriers for different applications. However, in solution, silver nanoparticles often tend to bind together, reducing antibacterial activity. In order to promote the antibacterial ability of nano silver and be able to recover and reuse many times, as well as to be able to disperse well into different materials, nano silver is often put on the carriers. In this study, nanosilver was synthesized on the surface of a zeolite by simple methods such as chemical reduction with $NaBH_4$, N_2H_4 or thermal reduction at 350 °C. Ag^+ ions are adsorbed onto 4A zeolite by ion exchange mechanism, then reduced by different methods. The materials were morphologically analyzed by XRD, SEM, EDX methods. Results showed that the method of reducing Ag^+ to Ag^0 on zeolite surface by chemical agent produce more evenly distributed silver nano-sized particles than the thermal reduction method. The silver content on the zeolite surface of the hydrazine reduction method is about 3 times higher than that of the sodium borohydride reduction method. The highest content of silver nanocarrying to zeolite. Zeolite bearing nano silver has the ability to disinfect against E.Coli with a concentration of ≥ 5 mg/ml. The Ag02/Z sample reducing Ag^+ to Ag^0 by Hydrazin has the best antibacterial ability against E.coli compared with the remaining samples when the diameter of the sterile ring at the concentration of 20 mg/ml is 9 mm.

Key words: zeolite, nano silver, antibacterial material

INTRODUCTION

Nano silver has long been known as a highly effective disinfectant, capable of limiting the growth and eliminating many types of mold and bacteria. Nano silver can be synthesized by many different methods, depending on the purpose and requirements of use. Synthesis methods of nanosilver can be divided into two main groups, chemical and physical methods. Chemical methods are often used such as chemical reduction [1-5], substitution reaction [6], electrochemistry [7], etc. Physical methods are commonly used such as physical evaporation [8], thermal decomposition [9, 10], electromagnetic microwave radiation [11], and so on. Among the above methods, chemical reduction and thermal decomposition are the methods with the simplest manufacturing process.

Nano silver can be dispersed in solution or carried onto carriers for different applications. However, in solution, silver nanoparticles often tend to bind together due to Van der Waals forces, reducing antibacterial activity. In order to promote the antibacterial ability of nano silver and be able to recover and reuse many times, as well as to be able to disperse well into different materials, nano silver is often put on the carriers. One of the commonly used carriers is zeolite, which is a medium capillary material with a uniform capillary system and many other outstanding properties [12-15]. Silver nano-bearing zeolite is mainly made by impregnation, ion exchange between cations in the structural framework of zeolite and Ag^+ ions in solution [16-20].

In this study, zeolite bearing nano-silver was fabricated by impregnation, then using different reduction methods to convert silver ions to silver nanoparticles, such as chemical reduction with $NaBH_4$, N_2H_4 and physical reduction (decomposition by heat). The material was then subjected to structural analysis to evaluate the ability to form silver nanoparticles on zeolite and evaluate its antibacterial activity.

MATERIALS AND METHODS

Material

$AgNO_3$, Zeolite 4A, $NaBH_4$, made in China, are used directly in the experiments without further purification.

Fabrication of nanosilver- bearing zeolite

Nanosilver-bearing zeolite is produced by different methods with and without chemical reductants. Before reducing Ag^+ to nanosilver Ag^0, zeolite must adsorb Ag^+ on its surface, through direct ion exchanging or indirect through NH_4^+ ions. The synthesis of nanosilver-bearing zeolite is carried out specifically as follows:

- Reduction by sodium borohydride:

Neutralize 1kg Zeolite (pH~ 10.6) to pH = 6 in 1.3 L of distilled water using 2M nitric acid HNO_3 solution. Add 17.5 g silver nitrate $AgNO_3$ and stir at 60 °C in 2 h, leave to settle overnight, filter through blue-band filter paper to collect Ag^+/Z deposit. Then, Ag^+/Z was washed three times with distilled water and dried in an oven at 100 °C to completely dry, finally obtaining Ag^+/Z powder.

Reduce Ag^+ to Ag^0 by sodium borohydride with the reaction below:

$$2Ag^+ + 2NaBH_4 \rightarrow 2Ag^0 + H_2 + B_2H_6 + 2Na^+ \quad (1)$$

Ag^+/Z powder was added to 0.1M $NaBH_4$ solution, gently stirred for 30 min, then settled, filtered with blue-band filter paper and washed three times with distilled water. The product is then completely dried at 100 °C, denoted Ag01/Z.

- Reduction by hydrazin

The synthesis of Ag^+/Z is similar to the above, just replacing sodium borohydride with hydrazine. The reaction goes as follows:

$$4Ag^+ + N_2H_4 + 4OH^- \rightarrow 4Ag^0 + N_2 + 4H_2O \quad (2)$$

Ag^+/Z powder was added to 50 ml of 25% hydrazine solution, stirred for 4 h at 70 °C, then let stand overnight for the powder to settle at room temperature. The product was filtered with blue-band filter paper, washed 3 times with distilled water and dried at 100 °C until constant weight. The sample is denoted as Ag02/Z.

- Thermal decomposition:

The method is based on the same principle as above but differs in the process of exchanging Ag^+ ions on the zeolite surface and the reduction process does not use chemicals but uses heat. The principle behind the process is as follows:

Adsorption of NH_4^+ ions on zeolite surface:

$$NaZ + NH_4NO_3 \rightarrow NH_4Z + NaNO_3 \quad (3)$$

Exchange Ag^+ ions with NH_4^+ ions on zeolite surface:

$$Ag^+ + NH_4Z \rightarrow AgZ + NH_4^+ \quad (4)$$

Then calcined at high temperature so that Ag^+ changes back to Ag^0.

The specific manufacturing process is as follows: The zeolite powder is added to NH_4NO_3 solution with a solid-liquid mass ratio of 1:20, then magnetically stirred and heated at 80 °C for 4 h. Then, the mixture was filtered through blue-band filter paper and dried at 80 °C for 12 h. Repeat the above steps three times to obtain NH_4^+ adsorbed zeolite, denoted as NH_4Z. To adsorb Ag^+ ions onto zeolite, we continue to add NH_4Z to 0.1 M $AgNO_3$ solution, gently shake at 100 v/p for 2 h, then filter it through blue-band filter paper and wash it 3 times with distilled water, then dry at 100 °C. Repeat the above steps 3 times to obtain Ag^+/Z. Heating Ag^+/Z at 350 °C for 4 h, obtaining the material denoted Ag03/Z.

Structural analysis

The zeolite powder and zeolite bearing nanosilver were morphologically analyzed and structurally characterized by modern physicochemical methods. Fe-SEM field emission scanning electron microscopy and energy dispersive X-ray spectroscopy were performed on the Hitachi S4800 instrument (Japan).

Test for antibacterial activity by agar perforation method

Prepare bacterial culture medium (MHA). Then, the MHA medium was autoclaved and poured into petri dishes with a volume of about 15 ml to create agar surfaces.

Preparation of test strains: Inoculate the test strains of bacteria into sterilized bacterial growth medium (TSB). Incubate at 37 °C for 6-8 h for bacterial strains to activate and proliferate. Determine the bacterial cell density by optical densitometry at 625 nm, the bacterial density must reach ~ 106 CFU/ml. This bacterial density will be fixed to proceed to use for the antibacterial activity test of the test sample.

Preparation of test substances: Using a pipetteman, accurately aspirate 100 μl of the prepared bacterial solution into a petri dish containing MHA medium, spread the bacteria evenly over the agar surface of MHA medium with a glass spreader.

Wait for the agar surface to be relatively dry, proceed to punch holes of 6mm agar. Use a pipetteman to accurately aspirate 50 µl of the test substances into the agar holes. Operations must be carried out under sterile conditions.

Incubate these petri dishes for 24 h at 37 °C, observe the results based on the size of the antibacterial ring. If the sample has an antibacterial ring, it indicates that the test substance is resistant to the test strain of bacteria.

RESULTS AND DISCUSSION

Character of nanosilver-bearing zeolite

The elemental composition on the surface of zeolite and zeolite bearing nanosilver was analyzed by X-ray energy dispersive spectroscopy. EDX spectra of zeolite (Z0) and zeolite bearing nanosilver were synthesized by different methods: reduction with $NaBH_4$ (Ag01/Z), reduced by N_2H_4 (Ag02/Z), reduced by heat (Ag03/Z) are shown in Fig. 3.1.

The results of Fig. 1 show that the composition of zeolite consists of 4 main elements: oxygen, sodium, aluminum, and silicon, peaks appear with relatively strong intensity at energy levels of 0.525keV (O), 1.041, respectively. keV (Na), 1.5 keV (Al) and 1.739 keV (Si) and absolutely no trace of the element silver. Meanwhile, the EDX spectrum of Ag/Z has a peak at position 2.98 keV, indicating the presence of silver in the composition of Ag/Z. The peak at the 3 keV position of the Ag03/Z sample is higher than that of Ag02/Z and Ag01/Z, thereby predicting that the Ag content on the surface of the heat-reduced sample is higher than that of the chemical reduction. Mass and atomic percentages are also determined and presented in Table 1 below.

The results are shown in Table 1 shows that the mass % of silver atoms on samples Ag01/Z, Ag02/Z and Ag03/Z are 1.6 %, 4.44% and 7.7%, respectively. Thereby, we can see that the Ag03/Z heat reduction sample has the highest Ag content, but this method will consume more energy than other methods. Of the two chemical reduction methods, the reduction with hydrazine is more efficient than the reduction with $NaBH_4$ with ~3 times higher silver content. To evaluate in more detail, we analyze other methods such as SEM, XRD and investigate the antibacterial activity of the material.

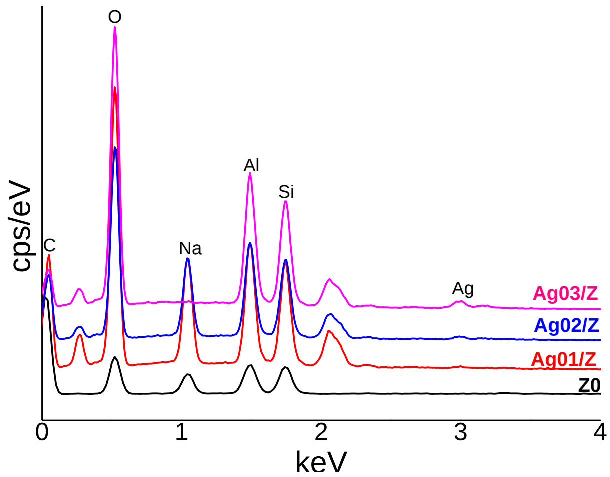

Fig. 1. Energy-dispersive X-ray spectroscopies of Z0, Ag01/Z, Ag02/Z, Ag03/Z samples

Рис. 1. Энергодисперсионная рентгеновская спектроскопии образцов Z0, Ag01/Z, Ag02/Z, Ag03/Z

To better observe the surface structure and size of silver particles formed on the zeolite surface, field emission scanning electron microscopy can be used. Figure 2 shows the surface morphology of zeolite and zeolite bearing nanosilver at 30,000x magnification.

Observing the surface of zeolite in Fig. 2, we can see that silver nanoparticles have formed on the surface of zeolite in all samples Ag01/Z, Ag02/Z, Ag03/Z. In which, the method of reducing Ag^+ to Ag^0 by chemicals such as $NaBH_4$ (Ag01/Z) and N_2H_4 (Ag02/Z)

Table 1

Elemental composition on zeolite surface

***Таблица 1.* Элементный состав поверхности цеолита**

Element	Z0		Ag01/Z		Ag02/Z		Ag03/Z	
	% mass	% number of atoms	% mass	% number of atoms	% mass	% number of atoms	% mass	% number of atoms
O	55.53	66.76	52.1	63.07	49	60.9	57.17	70.6
Al	14.09	10.04	15.2	10.90	15.41	11.35	15.78	11.56
Si	14.56	9.96	15.3	10.55	15.14	10.72	15.26	10.73
Na	15.83	13.24	12.3	10.36	11.76	10.17	0.13	0.11
N	0	0	3.5	4.84	4.25	6.04	3.96	5.59
Ag	**0**	0	**1.6**	0.29	**4.44**	0.82	**7.7**	1.41
Total	100	100	100	100	100	100	100	100

gives silver particles with nano size < 100 nm. Silver nanoparticles on the surface of the Ag02/Z sample have a thicker density and are distributed quite evenly, which is also consistent with the results of elemental composition analysis by X-ray energy dispersive spectroscopy. Ag03 does not use chemicals, but uses heat at 350 °C to create silver nanoparticles appearing in clusters from 0.2-1 µm, not evenly distributed on the surface, but mainly forming between the slits of the boundary of the zeolite particles. This result shows that, reducing Ag^+ to Ag^0 on zeolite by chemical agent gives silver nanoparticle size smaller and more evenly distributed than thermal reduction method. Therefore, chemically reduced samples were selected to analyze the crystalline phase composition by X-ray diffraction spectroscopy.

The crystalline phase composition of zeolite bearing nanosilver was analyzed by X-ray diffraction and compared with the crystalline phase of the original zeolite. X-ray diffraction patterns of Z0, Ag01/Z, Ag02/Z are shown in Fig. 3.

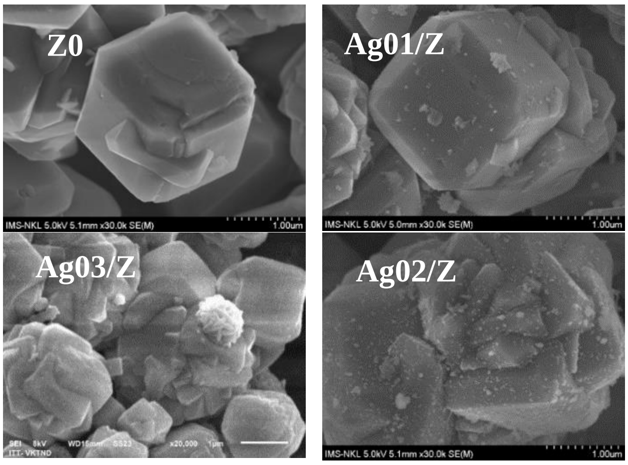

Fig. 2. SEM images of Z0, Ag01/Z, Ag02/Z, Ag03/Z
Рис. 2. СЭМ изображения обарзцов Z0, Ag01/Z, Ag02/Z, Ag03/Z

Through Fig. 3 we see that Z0 zeolite appears characteristic peaks at diffraction angles 2θ: 10,2°; 12.5°; 16.2°; 24.1°; 27.2°; 30° and 34°. With samples Ag01/Z, Ag02/Z, in addition to typical peaks of zeolite, there are also characteristic peaks of silver crystals at diffraction angles of 38°, 44°, and 64.4°, proving that in the composition of Ag01/ Z, Ag02/Z appeared silver crystals. From the size of the semi-spectral width of the silver peak at the 38° diffraction angle, we can calculate the silver crystal grain size based on the Scherrer formula. The results after calculating we calculate that the Ag crystal size of the Ag01/Z sample is 22.4 nm, and that of the Ag02/Z sample is 21.7 nm. Thus, the size of silver particles reduced by chemical method on the nanoscale zeolite surface is in the range of 22 nm.

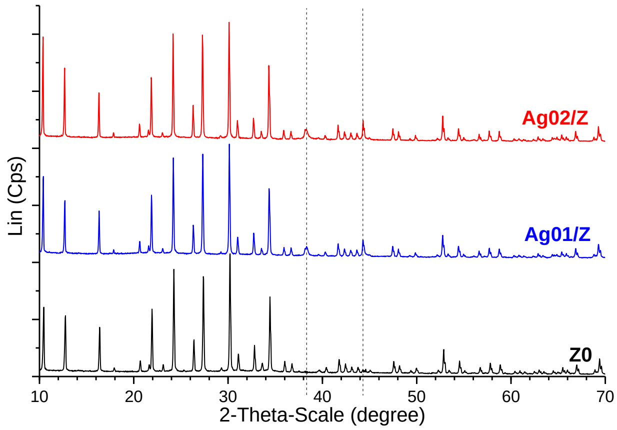

Fig. 3. X-ray diffraction pattern of Z0, Ag01/Z, Ag02/Z
Рис. 3. Рентгенограмма обарзцов Z0, Ag01/Z, Ag02/Z

Table 2

Sterile ring size for *E. coli*
Таблица 2*. Размер стерильного кольца для *E. coli

No.	Sample name	Test concentration (mg/ml)	Diameter of sterile ring (mm) of Gram (-) *Escherichia coli*
1	Z0	20.0	0
		5.0	0
		1.25	0
2	Ag01/Z	20.0	7
		5.0	0
		1.25	0
3	Ag02/Z	20.0	9
		5.0	7
		1.25	0
4	Ag03/Z	20.0	7
		5.0	0
		1.25	0

Thus, from the analysis results of X-ray energy scattering, scanning electron microscopy and X-ray diffraction, we can identify the method of reducing Ag^+ to Ag^0 on zeolite surface by chemical agent produce more evenly distributed silver nano-sized particles than the thermal reduction method. The silver content on the zeolite surface of the hydrazine reduction method is ~3 times higher than that of the sodium borohydride reduction method. To evaluate the bactericidal effect of the material, samples of Ag01/Z, Ag02/Z and Ag03/Z were tested with E. coli and compared with the original zeolite.

Antibacterial activity test results

The antibacterial ability against *E.coli bacteria* of the material was investigated by the agar perforation method. Samples were tested with concentrations 1.25 mg/mL, 5 mg/mL and 20 mg/mL.

The results in Table 2 show that the antibacterial ring has not appeared in all the samples, showing that at the concentration of 1.25 mg/ml zeolite carrying nanosilver has not shown the antibacterial effect. The sterile ring has begun to appear for samples Ag02/Z, and samples Z0, Ag01/Z and Ag03/Z do not appear antibacterial rings. Thus, at a concentration of 5 mg/ml, the sample Ag02/Z has promoted its bactericidal ability, but the sterility ring width is still small, and the samples Z0, Ag01/Z and Ag03/X have not been able to kill bacteria at high concentrations.

Continuing to increase the concentration of substances to 4 times, equivalent to 20 mg/ml, we obtain the sterile ring image shown in Fig. 4.

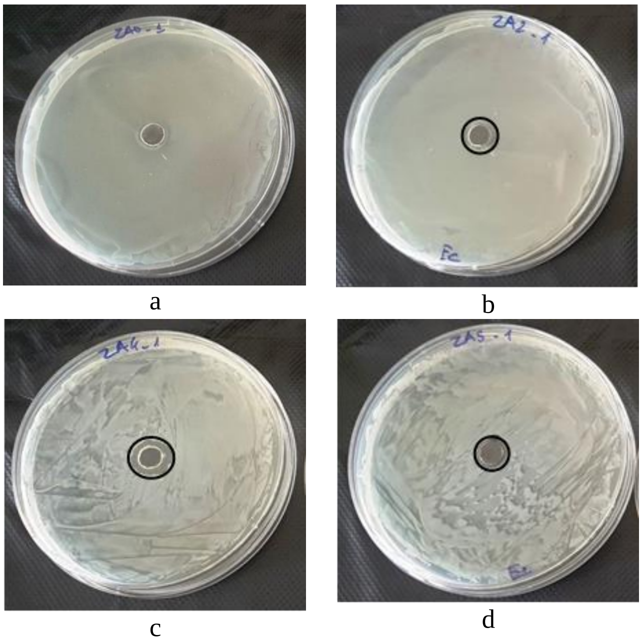

Fig. 4. Test image for *E.coli* sterility determination of samples Z0(a); Ag01/Z (b); Ag02/Z (c); Ag03/Z (d) at a concentration of 20 mg/ml

Рис. 4. Тестовое изображение стерильности образцов Z0(a); Ag01/Z (b); Ag02/Z (c); Ag03/Z (d) в концентрации 20 мг/мл для *E.coli*

The image of the agar plate in Fig. 4 shows that the antibacterial ring was present on all the zeolite samples bearing silver, and the normal zeolite sample did not appear one. This proves that at the concentration of 20 mg/ml, all zeolite samples carrying silver nanoparticles reduced by chemical methods and heat treatment have antibacterial ability. However, the diameter of the sterile ring of sample Ag02/Z is larger than that of the other two samples.

Thus, zeolite itself does not have antibacterial ability when at all concentrations it does not show antibacterial ring. All zeolite samples carrying nanosilver showed antibacterial activity at the concentration of 20 mg/mL. Sample Ag02/Z has the best antibacterial activity against *E.coli* compared with the other samples when the diameter of the sterile ring at the concentration of 20 mg/ml is 9 mm, the samples Ag01/Z and Ag03/Z have the highest concentration of 9 mm. The sterile ring is less than 7 mm. At a lower concentration of 5 mg/ml, only the Ag02/Z sample was antibacterial with an antibacterial ring diameter of 7 mm, while the remaining samples did not have a sterile ring.

This result is also consistent with the conclusions drawn from the results of structural analysis of the material. The Ag02/Z material with silver nanoparticles reduced by N_2H_4 has a rather small Ag particle size, uniform distribution on the zeolite surface and a rather large content, which has the best antibacterial ability. Meanwhile, sample Ag03/Z has more silver concentration but uneven distribution, silver particles cluster together with large size, so the bactericidal effect is not high.

CONCLUSION

The zeolite bearing nano silver was synthesized by adsorbing Ag^+ ions on the surface, then reducing Ag^+ to Ag^0 by different methods using chemical reducing agents and thermal decomposition. The results of the structural morphology analysis show that the chemical reduction method for silver particles has nano-size and is more evenly distributed than the thermal reduction method. The content of nanosilver on the zeolite surface of the hydazine reduction method is ~3 times higher than that of the sodium borohydride reduction method.

The zeolite samples bearing nanosilver were tested for resistance against *E.coli* strains by agar perforation method and compared with the original zeolite. The concentrations examined were 1.25 mg/mL, 5 mg/mL and 20 mg/mL. The results show that zeolite has no antibacterial ability; All zeolite samples carrying nano silver showed antibacterial activity at the concentration of 20 mg/ml. The Ag02/Z sample reducing Ag^+ to Ag^0 by Hydrazin has the best antibacterial ability against *E.coli* compared with the remaining samples when the diameter of the sterile ring at the concentration of 20 mg/ml is 9 mm, the largest is 9 mm, and the Ag01/Z samples. The sodium borohydride-reduced Z and the heat-reduced Ag03/Z have a sterile ring of less than 7 mm. At a lower concentration of 5 mg/ml, only the Ag02/Z sample was antibacterial with an antibacterial ring diameter of 7 mm, while the remaining samples did not have a sterile ring.

ACKNOWLEDGEMENTS

This work was supported by The Vietnam Academy of Science and Technology (VAST) under the grant number TĐVLTT.01/21-23.

The authors declare the absence a conflict of interest warranting disclosure in this article.

Эта работа была поддержана Вьетнамской академией наук и технологий (VAST) под номером гранта TĐVLTT.01/21-23.

Авторы заявляют об отсутствии конфликта интересов, требующего раскрытия в данной статье.

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Поступила в редакцию (Received) 12.09.2022
Принята к опубликованию (Accepted) 18.11.2022