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Preparing New Ceramic Membranes from Syrian Zeolite Coated with Silver Nanoparticles to Treatment Wells Water

Abdulrazzaq Hammal

Department of Basic Science-Chemistry, College of electrical engineering, University of Aleppo, Aleppo, Syria.
E-mail: hammal1986@gmail.com

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Abstract:

As a result of the exacerbation of the problem of water pollution, research was directed towards studying the treatment using ceramic membranes, which proved to be highly effective in treating all water sources. The research aims to study the possibility of preparing a new type of ceramic membranes from Syrian zeolite that was not previously used in this field. In this research, ceramic membranes were prepared from Syrian raw zeolite in several stages. Zeolite sample was characterized, grinded, mixed with boric acid, pressed to form desks, treated thermally according to experiment program, finally coated with silver nanoparticles .Specifications of prepared membranes were determined according to reference methods, effectiveness of prepared membranes were tested in well water handling, that water sample was filtrated through prepared membranes, and then it type MAC, so removal degree was 100%, While removal degree was 97% for bacterial strains on Agar with type PCA, 93% on Agar with type PDA which were conformed to Syrian standard /45 /2007.

Keywords: Ceramic, Filtration, Membranes, Nanoparticle, Wells Water, Zeolite.

Introduction:

Ceramic membranes refer to the prepared membranes from porous ceramics as aluminum oxide, silicon dioxide, clay or substrates like titanium dioxide and zirconium dioxide. Ceramic membranes have wide applications mostly in separation techniques as solid-liquid and solid-gas. Ceramic membranes with the largest pore size have been prepared at bottom as support, and pore size decreases slowly towards the surface where the real separation occurs, these structures are amenable to modifications depending upon the selection of preparation methods: from inner structures to top surface of membranes. Ceramic membranes have several shapes: tubular, multi-channel monolith membrane etc [1-7].

Ceramic membranes can be prepared by several methods including slip casting, tape casting, extrusion and, powder pressing which change the particle suspension to a membrane forerunner to form symmetric and composite ceramic membranes [8-11]

Many researches have established the effectiveness of these membranes in water treatment, as they are characterized by excessive chemical stability and mechanical stability and can resist different temperatures, but their preparation needs excessive attention and effort [12-16].

Because water pollution is prevalent in all places, research is directed towards natural raw materials as raw materials for producing this type of membranes such as raw zeolite, which has great chemical effectiveness and ion exchange and adsorption makes it usable in purifying drinking water, in organic chemical industries, and in increasing the effectiveness of agricultural fertilizers. It can also be used to conserve soil moisture, and to make fodder. Zeolitic metals distinct in their crystalline structure (Fig. 1), where the tetrahedrons that make up them are aligned and interconnected in a certain way to form tetrahedral star rings, which interconnect to form structures contain relatively large voids that connect with each other to form tubes and channels give characteristic porous structure [17,18].

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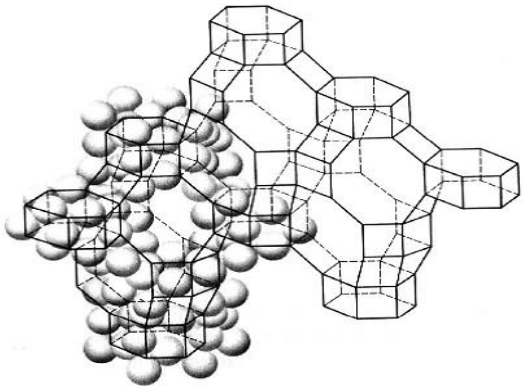

Figure 1. Structure of zeolite

The aim of this research is to prepare ceramic membranes from Syrian zeolite coated with silver nanoparticles to treat wells water, because there is no previous study that prepares ceramic membranes from Syrian zeolite, and a new method was employed by grafting with nano silver for these membranes.

Materials and Methods:

Raw Zeolite

Raw zeolite was brought from Mekhelat-south of Syria, the samples were grinded to **63**-100 µm grain size by laboratory mill. Zeolite properties was determined as:

-Chemical Composition by X-ray (X-ray fluorescence XRF)

An amount of 10 g of grinned zeolite was mixed with 3g of H_3BO_3 and pressed in a metal mold almost 150 KN to form a disc with 30 mm diameter and 5 mm thickness.

-Mineral Phases

X-ray diffraction (XRD) with conditions: nickel filter, wavelength (λ = 1.5405°A), radiation Cu $K_{\alpha 1}$, (2θ: 10-70 A°) was used to determine phases.

-Differential Thermal Analysis of Zeolite

The sample was heated gradually by 10°C/min, to temperature 1400°C.

Preparation of Membranes

Membranes were prepared by powder press technique Fig. 2**.** Zeolite was mixed with boric acid as a binder by 5% w/w, in the next stage, the mixture was pressed into a tubular meal to obtain desks with 5 cm diameter and 2-2.5 mm thickness formation press was 100 kg/cm^2. Then treated thermally according to experiment program after several tests by noting several points: the appearance of cracks, the collapse of the sample, the stability of the weight Fig. 3

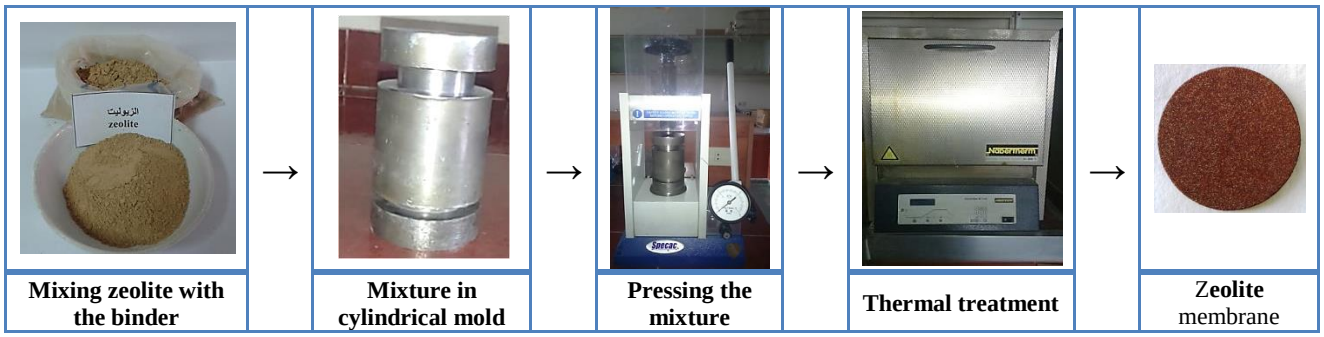

Figure 2. steps of preparing the membranes

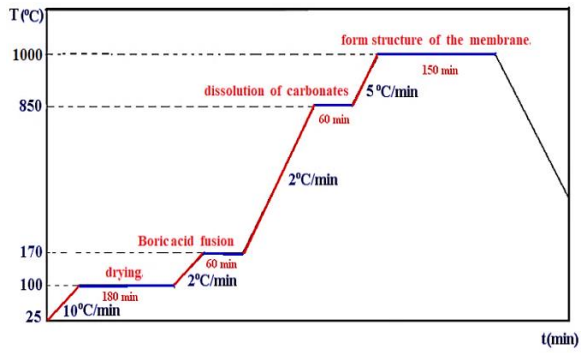

Figure 3. program of thermal treatment of prepared ceramic membrane

Specifications of prepared membranes were determined according to reference methods: apparent porosity, apparent specific gravity, water absorption, and bulk density were measured by (**ASTM C20–00**), to determine permeability Darcy's law method (k=Q.µ.ΔL/A.Δp) where Q: volumetric flow rate, k: membrane permeability, **A**: membrane surface area, **Δp:** pressure difference between the two membrane surfaces, **µ:** dynamic viscosity of the fluid and **ΔL:** thickness of membrane. Chemical stability of the prepared zeolite membranes were measured by immersing zeolite membranes in a NaOH (pH=13.5) and HCl (pH=1.0) separately for 48 hours, then measured the change of weight [19,20].

Coating of Membranes with Nanosilver Particles

To enhance antibacterial properties, prepared membranes were immersed in 100ml of 0.01M silver nitrate solution for 15 minutes, then

5ml of 5% sodium citrate solution (a reducing agent for silver ions) was added to it, after 15 minutes, membranes were treated with UV for 30 minutes, where the color changed to silver as a result of the conversion of silver ions to silver nano particles. Membranes were washed with 3% sodium chloride solution to remove silver ions, then washed with distilled water then dried at 105°C Fig. 4.

Without nano silver With nano silver

Figure 4. prepared ceramic membrane

Treating of Well Water

Well water sample was collected from north Aleppo. Chemical and microbiological analysis was performed to measure its content of different impurities as maintained by reference methods as:

Chemical Analysis

COD: by photometric method, sample was digested by $K_2Cr_2O_7$ and H_2SO_4, color strength was compared with a standard sample.

BOD: BOD_5 was measured by pressure feeler technique.

TDS: conductivity/TDS device was used.

Turbidity: by measuring the intensity of light scattered in certain settings.

Metals: atomic absorption technique was used

Microbiological Examination

Culture media were prepared in purified water, treated in an autoclave at temperature of 121°C for 15 minutes, then poured into sterile 9 cm petri dishes, then incubated in incubators.

Full of bacteria, faecal coliforms, Escherichia coli, salmonella and fungi, incubating at temperature 25 °C for 4 days then was applied on fungi plates to give the final effect (colony/100 ml). Culturing was performed on Agar with type PCA. Existence of faecal enteric bacteria was revealed by the colonies growing on Agar with type MC. Escherichia coli appeared green with metallic luster colonies on Agar with type EMB, salmonella was appeared as black colonies on Agar with type SS. Fungi were noticed by growing on agar with type SDA.

Sample of water was filtrated with zeolite membranes. Lastly sample was filtered by zeolite membrane which was coated with silver nanoparticles. Chemical and microbiological specifications of the water sample were measured after the processing to prof the efficacy of the processing.

Results and Discussion:

Characterization of Zeolite

Chemical Composition

Chemical analysis XRF for studied zeolite is shown in Table 1, it is noted that zeolite sample contained a high percent of silicon dioxide SiO_2, which corresponds to the siliceous structure of zeolite, aluminum oxide Al_2O_3 which forms with silicon dioxide SiO_2 the steric structure of various zeolitic metals, sample also was contained iron oxide Fe_2O_3, which can exist unbound (free), and presence of sodium oxides Na_2O and potassium K_2O was noted, which has a special importance in ion exchange.

Table 1. Chemical analysis of zeolite

compound	W%
SiO_2	39.83
Al_2O_3	10.24
Fe_2O_3	11.11
MgO	5.77
CaO	8.34
Na_2O	3.31
K_2O	1.11
SO_3	0.36
L.O.I	17.85

Mineral Phase

Spectrum of XRD showed that studied zeolite mostly contains Analcime, Phillipsite, Chabazite. another peaks produced by presence other secondary metal phases like hematite and calcite Fig. 4, Table 2

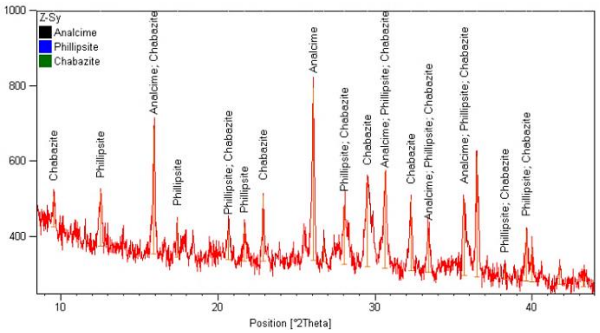

Figure 4. XRD spectrum of studied zeolite

Table 2. Compounds of studied zeolite

Compound	Ref. Code	Chemical Formula
Analcime	01-083-1731	$Na_{14.80}Al_{14.24}Si_{33.76}O_{96}(H_2O)_{16}$
Phillipsite	01-073-1419	$Na_4KAl_5Si_{11}O_{32}(H_2O)_{10}$
Chabazite	00-019-0208	$Ca_2Al_4Si_8O_{24}.12H_2O$

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Deferential Thermal Analysis DTA

Differential thermal curve of raw zeolite showed the presence of several peaks:

1. Endothermic reaction at 90-100 ºC refers to evaporation of moisture water accompanying the zeolite sample.
2. Endothermic reaction at 300-400 ºC which indicates loss of bound water in the form of hydroxyl groups.
3. Endothermic reaction at 650-750 ºC refers to decomposition of carbonates associated with raw zeolite.
4. Exothermic reaction at 800-850 ºC refers to due to recrystallization after the destruction of the zeolite structure Fig. 5.

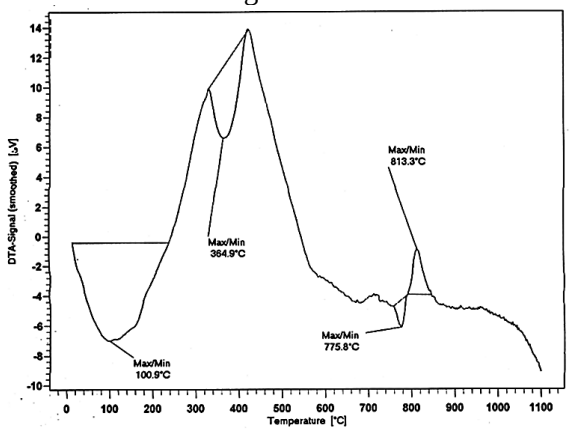


Figure 5. Differential thermal curve of studied zeolite

Characteristics of Prepared Membranes

Spectrum of XRD showed that zeolite membranes mostly contain Diopside, Augite, Anorthite, Pyroxene . In addition, some peaks were produced by the presence other secondary materials Fig. 6, Table 3.

Properties of the prepared membranes were: water absorption 16.05%, apparent porosity 26.68%, bulk density 1.74 g/cm^3, volumetric flow 1.48 x10^{-6} m3/sec, permeability 0.0032 darcy (permeability unit). Zeolite membranes were more stable in acid than in base medium, loss in weight after base processing was 0.015%, while after acid processing was 0.049%.

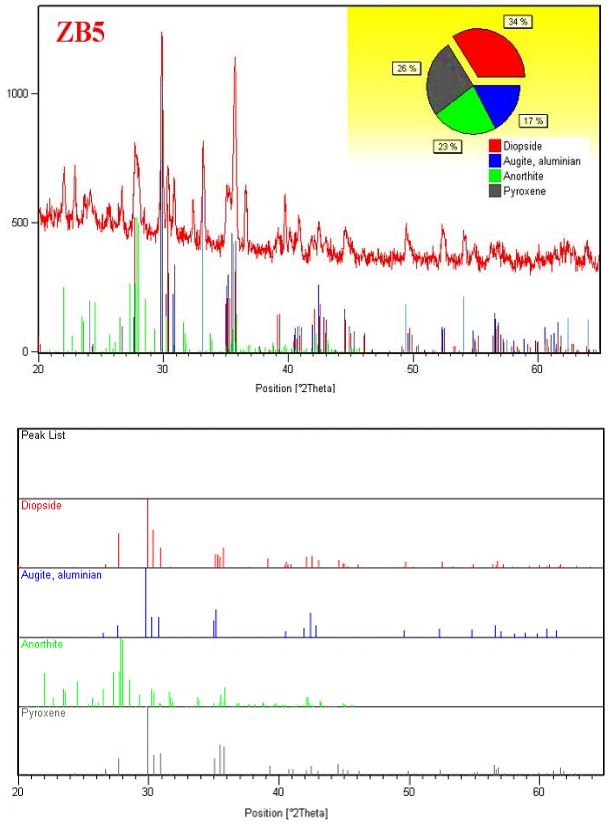


Figure 6. XRD spectrum of prepared membranes.

Table 3. Compounds of prepared membranes

Compound	Ref. Code	Chemical Formula
Diopside	01-075-0945	$CaMgSi_2O_6$
Augite	00-041-1483	$Al_{0.2}Ca_{0.9}Fe_{0.1}MgO_6Si_{1.8}$
Anorthite	01-070-0287	CaAl2Si2O8
Pyroxene	01-078-1392	$Al_{0.60}CaMg_{0.70}O_6Si_{1.70}$

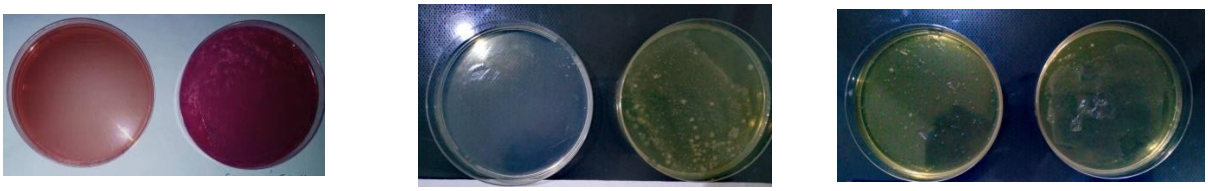
Filtration of Well Water

Water before processing contained different of pollutions (chemical and biological); COD decrease to 96.9%, BOD to 95.45%, turbidity to 90%, TDS to 59.66%, the sample was almost free of heavy metals by atomic absorption analysis

There was important decrease in total bacterial of the handled sample almost 0% on Agar with type MAC, so removal degree was 100%. While removal degree was 97% for bacterial strains on Agar with type PCA, 93% on Agar with type PDA, as shown in Table 4, Fig. 7.

Table 4. Specification of well water before and after treatment.

compound	Syrian standard /45 /2007	Before treatment	After treatment
Chemical oxygen demand (COD)	3 mg/L	65	2
Biological oxygen demand (BOD)	2 mg/L	22	1
Turbidity (Turb)	5 NTU	11	1.1
Total dissolved solids (TDS)	1200 mg/l	944	900



(b) (a) (d)

(a) PCA Agar -(b) MAC Agar -(d) PDA Agar

Figure 7. Bacterial examination of handling water

Conclusion:

Ceramic membrane can be prepared from Syrian raw zeolite by powder press method. Prepared zeolite membranes had high effectiveness in the treatment of wells water. Results showed that prepared zeolite membranes had high effectiveness through decreasing chemical and microbial pollutants, COD decreased to 96.9%, BOD to 95.45%, Turbidity to 90%, TDS to 59.66%. There was an important decrease in total bacterial of the handled sample almost 0% on Agar with type MAC, so removal degree was 100%, While removal degree was 97% for bacterial strains on Agar with type PCA, 93% on Agar with type PDA which were conformed to Syrian standard /45 /2007

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Author's Declaration:

- Conflicts of Interest: None.
- I hereby confirm that all the Figures and Tables in the manuscript are mine. Besides, the Figures and images, which are not mine, have been given the permission for re-publication attached with the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee in University of Aleppo, Syria.

References:

1. Hamta A, Ashtiani FZ, Karimi M, Sadeghi Y, MoayedFard S, Ghorabi S. Copolymer Membrane Fabrication for Highly Efficient Oil-in-Water Emulsion Separation. Chemical Engineering & Technology. 2021 May 6. https://doi.org/10.1002/ceat.202000610
2. da Silva Biron D, Santos V dos, Bergmann CP. Tubular ceramic membranes coated with ZnO and applied in the disinfection of water contaminated with Staphylococcus aureus. Ceram Int. 2021 Oct; 47(19): 27082–90.
3. Wang K, Xu X, Ma X, Cheng X, Zhang Y, Ma J. Ceramic membrane bioreactor for low carbon source wastewater treatment: process design performance and membrane fouling. Environ Sci Water Res Technol. 2022; https://doi.org/10.1039/D2EW00361A
4. Mamun Kabir SMd, Mahmud H, Schöenberger H. Recovery of dyes and salts from highly concentrated (dye and salt) mixed water using nano-filtration ceramic membranes. Heliyon. 2022 Nov; 8(11): e11543.
5. Samadi A, Gao L, Kong L, Orooji Y, Zhao S. Waste-derived low-cost ceramic membranes for water treatment: Opportunities, challenges and future directions. RCR Advances. 2022 Oct; 185: 106497.
6. Carter B, DiMarzo L, Pranata J, Barbano DM, Drake M. Determination of the efficiency of removal of whey protein from sweet whey with ceramic microfiltration membranes. J Dairy Sci. 2021 Jul; 104(7): 7534–43.
7. Belgada A, Achiou B, Alami Younssi S, Charik FZ, Ouammou M, Cody JA, et al. Low-cost ceramic microfiltration membrane made from natural phosphate for pretreatment of raw seawater for desalination. J Eur Ceram Soc. 2021 Feb; 41(2): 1613–21.
8. Al-Naemi AN, Abdul-Majeed MA, Al-Furaiji MH, Ghazi IN. Fabrication and Characterization of Nanofibers Membranes using Electrospinning Technology for Oil Removal. Baghdad Sci J. 2021 Dec 1; 18(4): 1338.
9. Xia Y, Lu Y, Kamata K, Gates B, Yin Y. Macroporous Materials Containing Three-Dimensionally Periodic Structures. The Chemistry of Nanostructured Materials. Vol II 2003 Dec; 69–100. https://doi.org/10.1142/7787
10. Silva AO, Hotza D, Machado R, Rezwan K, Wilhelm M. Porous asymmetric microfiltration membranes shaped by combined alumina freeze and tape casting. J Eur Ceram Soc. 2021 Jan;41(1):871–9.
11. Detecting the antibacterial activity of green synthesized silver (Ag) nanoparticles functionalized with ampicillin (Amp). Baghdad Sci J. 2017 Mar 5;14(1).
12. De Falco M, Di Paola L, Marrelli L, Nardella P. Simulation of large-scale membrane reformers by a two-dimensional model. Chem Eng J. 2007 Apr; 128(2-3): 115–25.
13. Belgada A, Charik FZ, Achiou B, Ntambwe Kambuyi T, Alami Younssi S, Beniazza R, et al. Optimization of phosphate/kaolinite microfiltration membrane using Box–Behnken design for treatment of industrial wastewater. J Environ Chem Eng. 2021 Feb; 9(1):104972.

14. Takht Ravanchi M, Kaghazchi T, Kargari A. Application of membrane separation processes in petrochemical industry: a review. Desalination. 2009 Jan; 235(1-3): 199–244.
15. Jafari B, Rezaei E, Dianat MJ, Abbasi M, Hashemifard SA, Khosravi A, et al. Development of a new composite ceramic membrane from mullite, silicon carbide and activated carbon for treating greywater. Ceram Int. 2021 Dec;47(24): 34667–75.
16. Zhang Z, Ng TCA, Gu Q, Zhang L, Lyu Z, Zhang X, et al. Ultrathin TiO2 microfiltration membranes supported on a holey intermediate layer to raise filtration performance. J Eur Ceram Soc. 2021 Feb; 41(2): 1622–8.
17. Demirci S, Yildrim Y, Sahiner N. A comparison study about antibacterial activity of zeolitic imidazolate frameworks (ZIFs) prepared with various metal ions. Inorganica Chim Acta. 2022 Nov; 542:121110
18. Pambudi FI, Prasetyo N. Theoretical investigation on the structure of mixed-metal zeolitic imidazolate framework and its interaction with CO2. Comput Mater Sci. 2021 Nov; 111033.
19. Mirqasemi MS, Homayoonfal M, Rezakazemi M. Zeolitic imidazolate framework membranes for gas and water purification. Environ. Chem. Lett. 2019 Oct 1; 18(1): 1–52.
20. Ismet. Permeability, Strength and Filtration Performance for Uncoated and Titania-Coated Clay Wastewater Filters. Am J Environ Sci. 2012; 8 (2): 79-94.

تحضير أغشية سيراميكية جديدة من الزيوليت السوري مطعمة بجسيمات الفضة النانوية لمعالجة مياه الآبار

عبدالرزاق حمال

قسم العلوم الأساسية-الكيمياء، كلية الهندسة الكهربائية، جامعة حلب، حلب، سوريا.

الخلاصة:

نتيجة لتفاقم مشكلة تلوث المياه اتجهت الابحاث نحو دراسة المعالجة باستخدام الاغشية السيراميكية التي أثبتت فعالية عالية في معالجة كافة مصادر المياه, يهدف البحث لدراسة امكانية تحضير نوع جديد من الأغشية السيراميكية من الزيوليت السوري غير المستخدم سابقاً في هذا المجال. تم في هذا البحث تحضير أغشية سيراميكية من الزيوليت السوري الخام على عدة مراحل، حيث تم توصيف عينة الزيوليت وطحنها ومزجها بحمض البور, ثم ضغطت لتشكيل أقراص, عولجت حرارياً حسب برنامج حراري تجريبي, تم تغليفها أخيراً بجسيمات الفضة النانوية. تم تحديد مواصفات الأغشية المحضرة وفقاً للطرق المرجعية، تم اختبار فعالية الأغشية المحضرة في معالجة مياه الآبار، رشحت عينة الماء من خلال أغشية محضرة، ثم تم توصيفها بعد المعالجة. أظهرت النتائج أن أغشية الزيوليت المحضرة كانت ذات فاعلية عالية من خلال تقليل الملوثات الكيماوية والميكروبية, حيث انخفض COD إلى 96.9٪ ، BOD إلى 95.45٪ ، العكارة إلى 90٪ ، المواد الصلبة الذائبة إلى 59.66٪ ، كان هناك انخفاض مهم في التعداد العام للبكتيريا بعد المعالجة فكانت بنسبة النمو 0٪ تقريبًا على الوسط من النوع MAC ، لذلك كانت درجة الإزالة 100٪ ، بينما كانت درجة الإزالة 97٪ للسلالات البكتيرية على الوسط PCA، و 93٪ في الوسط من النوع PDA. وهذا يحقق المواصفة القياسية السورية لمياه الشرب رقم 45 لعام 2007

الكلمات المفتاحية: السيراميك، الترشيح, الأغشية، جسيمات نانوية، مياه الآبار، الزيوليت.