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Zeolite ZSM-5 as a filler for pvc membranes used for the removal of iron and copper from aqueous solutions

Tahani-Achouak Chinar [a*], Mohammed Benbouzid [a] and Said Benfarhi [b]

[a]*Laboratory of Analytical Sciences, Materials and Environment (LSAME), Department of Chemistry . Larbi Ben M'Hidi University. Oum El Bouaghi. 04000. Algeria.*
[b]*Laboratory of Chemistry and Environmental Chemistry (LCCE), Department of Chemistry, Elhadj Lakhdhar University, 05000-Batna, Algeria.*
Corresponding author: email: Tahani91ach@gmail.com

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Abstract

In this study, a polyvinyl chloride (PVC) membrane impregnated with thezeoliteZSM-5 was used to remove Fe^{2+} and Cu^{2+} ions from aqueous solutions. The results obtained by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analyzes indicated that the zeolite produced by the hydrothermal method was a pure porous material. The prepared zeolite was then incorporated into the PVC to obtain composite films which behave as filters. These composite membranes were used for the removal of metal ions contained in aqueous solutions. The filtrates obtained were analyzed by atomic absorption spectroscopy. The results showed the existence of a selective retention of metal ions according to their ionic radii. It increases with the ionic radii (R_{Fe}: 55 µm, R_{Cu}: 73 µm), and which increased in general with the concentration of the ZSM-5zeolite.

Keywords: membrane; filtration; zeolite; hydrothermal; composite; films; filters; retention

1. Introduction

Zeolites are porous materials [1,2]. They belong to the family of aluminosilicates[3] and have been used in the development of mixed matrix membranes.The studies that have used zeolite membranes for the applications of separation or liquid phase depollution are not very numerous, and one of the major challenges is to use and / or develop membranes conferring new properties on processes (or combinations of properties)[3]. The use of zeolithic membranes as filters showed that after a chemical treatment, these materials could acquire very particular properties of selectivity.The principle of this method is to filter a solution through a membrane that retains some molecules and lets others pass. This selection is essentially related to the size of the pores and also to the affinity between molecules or ions and the membrane [4,5].
This membrane treatment method is economical, cost effective and utilizes materials with form selection properties and adsorption characteristics such as zeolites [2-6]. The increasing application of these porous materials is related to their physicochemical characteristics [7,8].
In this work, we study the preparation of the zeolite ZSM-5 and its use in the preparation of polymeric matrix membranes which will be used for the removal of metal ions (Fe^{2+} and Cu^{2+}) contained in solutions [9, 10]. Its structure was characterized by XRD, SEM-EDX and FTIR-ATR. The determination of metals was carried out by atomic absorption spectroscopy.

2. Experimental

2.1. Synthesis of the zeolite ZSM-5

The hydrothermal synthesis of the zeolite ZSM-5 was carried out in aqueous phase and under autogenous pressure, in a stainless-steel reactor lined with an inert Teflon jacket. The following molar compositions of the reactants were used for the synthesis: 0.07 TPABr: 1.00 SiO_2: 0.012 $Al_2(SO_4)_3.18H_2O$: 80H_2O, For the zeolite ZSM-5 prepared in the fluorinated medium, the experimental conditions used were very close to those found in the literature [11]. TPABr (Sigma Aldrich 98%), NH_4F (Sigma Aldrich ≥ 98%) and the aluminum source (Panreac 98 - 105%) were dissolved in water at room temperature with continuous stirring. The silica (Merck 98%) was then added slowly and regularly as a fine powder. A white and translucent gel was formed. The mixture was homogenized by continuous stirring and then transferred to an autoclave reactor lined with an inert Teflon jacket and subjected to a high temperature (393K). The reactor was then removed from the oven and cooled under a stream of cold water and the crystals obtained were then washed, filtered, dried, and then calcined (773K).

2.2. Membranes preparation

The composite films of the polymer / zeolite membranes were prepared by the solvation method .The zeolite ZSM-5 used in the preparation of the membranes was grounded manually and sieved (45 µm) before use. The PVC and the zeolite were dissolved at room temperature separately in tetrahydrofuran (Fluka 99%) under constant stirring. The two solutions were then mixed with continuous stirring for 30 minutes and the mixture was then spread on the glass surface (20 x 20 cm). After evaporation of the solvent, the film formed, was easily removed from the surface of the glass. The percentages by weight of zeolite mixed with the polymer were the following: 2%, 5% and 10% relative to the total weight of the polymer. The thicknesses of the membranes were between 0.03 and 0.04 mm. The prepared membranes were then tested for their effects of depollution of the aqueous solutions containing the metal ions of Fe2+ and Cu2+.

2.3. Characterization techniques.

The quantitative and qualitative elemental analyzes of the zeolite ZSM-5 were carried out by wavelength dispersive analysis using an X, X PHILIPS MagiX fluorescence apparatusat the institute of materials science (IS2M-MPC) in Mulhouse (France).The surface morphology of the zeolite ZSM-5 was observed using the PHILIPS XL FEG microscopeat "CC-MEM" laboratoryin Lorraine (France). A few milligrams of the solid sample are deposited on an adhesive patch fixed on the sample holder and metallized (10 to 20 nm gold) by sputtering or evaporation.The powder diagrams were recorded on a STOE STADI P diffractometer at the center of studies and technological services of the industry of construction materials "CETIM" in Boumerdes (Algeria), equipped with an anticathode copper tube (40 kV, 30 mA), a front monochromator (crystal germanium curve cut according to the family of plans (111)) allowing select the radiation $K_{\alpha 1}$ (λ = 1.5406 Å) and a linear detector PSD (Position Sensitive Detector). The acquisitions are made in Debye-Scherrer mode at room temperature on the milled sample and placed in a Hilgenberg capillary 0.3 mm in diameter.FTIR analyzes of the solid-phase IR absorption spectra were recorded with an ATR-FTIR-type SMART iTR infrared spectrophotometer using the Perkin Elmer 2000 spectrophotometer equipped with a diamond cell and the spectra were obtained by 16 scans with a resolution of 4 cm^{-1}. N_2 adsorption and desorption isotherms for surface measurement were performed with a MicroActive automatic device for TriStar II Plus at the liquid nitrogen temperature (77K).The concentrations of aqueous metal ion solutions were performed using an ANALYTIK JENA atomic absorption spectrophotometer at the physico-chemical analyzes laboratory of Laghouat University (Algeria). The morphology and the pore distribution in the PVC membranes were observed using the FEI and Quanta 250 scanning electron microscopy with a tungsten filament.

3. Results

3.1. Characterization of the zeolite ZSM-5

The powder diffractogram (Fig. 1) reveals the presence of a single pure phase after the indexing of the DRX (hkl) models corresponding to the ZSM-5 phase. These results are consistent with those reported in the literature [12].

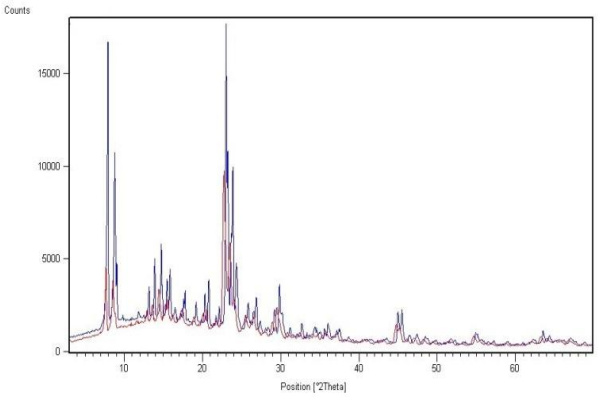


Figure 1. DRX of the zeolite ZSM-5

Figure 2 shows the scanning electron microscopy (SEM) observations made on the zeolite ZSM-5 and showed a fairly regular plate morphology, of hexagonal, elongated and sometimes lozenge-shaped forms. Other crystals are joined face to face to form clusters with a symmetry chipped to the tops.

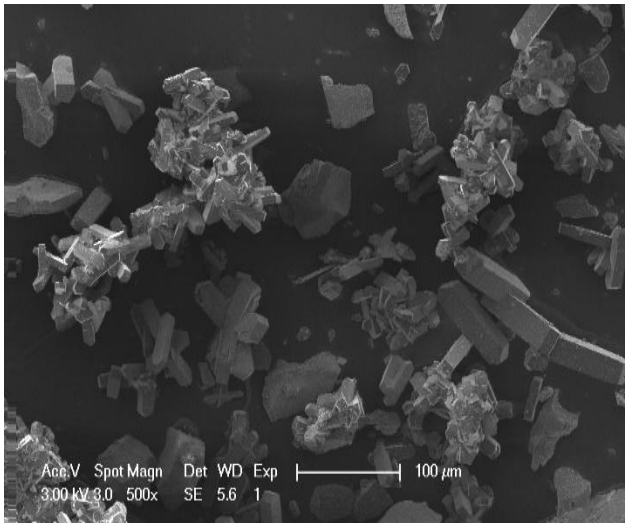


Figure 2. Scanning Electron Microscopy of the zeolite ZSM-5

The EDX spectrum (Fig. 3) of the platelets analyzed shows that they consist of Al, Si and O. The results of the EDX analyze (Table 1) show that the zeolite has the highest percentage in oxygen, followed by silicon and the lowest percentage in aluminum. These results are in agreement with the values found for the zeolite ZSM-5 in the literature [13,14].

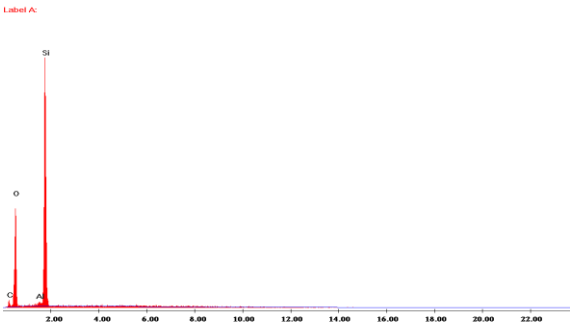


Figure 3. Spectrum of the elements present on the external surface of ZSM-5 by EDX (Energy dispersive X ray)

Table 1: Percentage mass of ZSM-5, using X-ray energy scattering (EDX)

Elements	Weights %	Atomic %
O	60.68	73.03
Al	0.72	0.51
Si	38.60	26.46
Total	100.00	100.00

The ZSM-5 surface area was estimated from the BET equation. The total sorbed volumes, were calculated from the amount of nitrogen adsorbed at a relative pressure p/p_0.The experimental results of these analyses are given in Table 2 and they show a very porous material (density 2 g / cm^3).

Table 2: Results of the BET analyses of ZSM-5

Relative Pressure (P/Po)	Quantity Adsorbed (mmol/g)	1/[Q(Po/P - 1)]
0.003084268	3.19357	0.00097
0.006001635	3.25252	0.00186
0.012424637	3.30889	0.00380
0.025959730	3.37253	0.00790

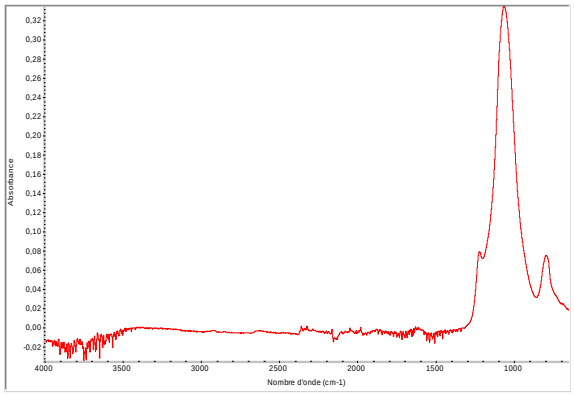
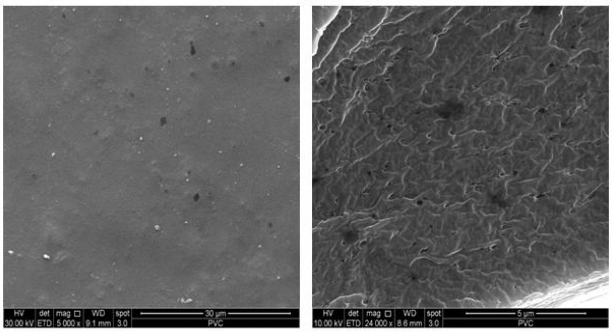


Figure 4. ATR-FTIR Spectrum of of the ZSM-5 zeolite

Several image acquisitions were made on the surface of the membranes. They clearly show a homogeneous surface which is apparently very smooth (Fig. 5). The ATR-FTIR spectrum (Fig. 4) of the ZSM-5 zeolite revealed the presence of absorption bands characterizing the O-H bonds located between 3375-3775cm^{-1}. A band with an average intensity between 1600-1700 cm^{-1}, this band is centered at 1631 cm^{-1} and is attributed to the deformation vibrations of the OH bond of the water constituent and to the deformation vibrations of the bonds of water molecules adsorbed between the sheets. The intense absorption band between 900-1300 cm^{-1} is centered at 1225 cm^{-1} and it characterizes the valence vibrations of the Si-O bond. The angular vibrations of the Al-O-H group is a band of low intensity and appeared at about 1065 cm^{-1}. The 795 cm^{-1} band was assigned to Si-O (symmetrical elongation) [15]. In general, the bands are due to T-O-T, T-O, T-T [16] or T-OH, T-OH-T vibrations (where T is Si or Al) [10, 16].



(a) (b)

Figure 5. SEM analysis of the PVC membrane;(a): superficial view, (b); fractional cross-sectional view.

3.2. Elimination of iron and copper ions by the membranes

3.2.1. Preparation of stock solutions containing metallic ions

The stock solutions were prepared with an initial concentration of 5 mg / l and from these stock solutions of lower concentrations were prepared to plot the calibration curves for iron (Fe^{2+}) and copper (Cu^{2+}) ions. The linear regression of the calibration curves indicated correlation factors of 0.98 to 0.99.

3.2.2. Membrane treatment

The stock solutions (initial concentration = 5 mg / l) containing the metal ions of Fe^{2+} and Cu^{2+} were filtered through the PVC / ZSM-5 composite membranes and the filtrates obtained were analyzed by SAA to determine the ability of the composite membrane to remove metal ions. The results obtained from the final concentrations of the filtrates as well as the percentages of retention are given in Table 3.

Table 3: Concentrations of metal ion filtrates on the composite membrane
P: Polymer, Z: Zeolite, P/Z: composite membrane

Membrane	Final [conc] in Fe (mg/l)	Percentage retention of Iron (%)	Final [conc] in Cu (mg/l)	Percentage retention of Copper (%)
PVC	4.94	1.12	3.20	36.02
P / Z 2%	4.88	2.32	3.12	37.66
P / Z5%	4.75	4.92	3.03	39.40
P / Z 10%	4.64	7.18	2.97	40.52

From the results obtained, we observe the existence of a selective retention of metal ions (Fe^{2+} and Cu^{2+}) according to their ionic radii. It increases with the ionic radii (R_{Fe}: 55 µm, R_{Cu}: 73 µm), and it appears also that the membrane retention is proportional to the ZSM-5 concentration. This efficiency is related to the ability of zeolites to adsorb pollutants. This selective elimination could be related either to the size of the pores or to the nature of the interactions of the metal ions with the composite material.

4. Conclusion

This paper describes the steps involved in the hydrothermal preparation of the zeolite ZSM-5 and its characterization with different methods of analysis (by XRD, SEM-EDX and FTIR-ATR) and its uses as a decontaminant material to retain metal ions. Removal of the iron and copper ions contained in aqueous solutions was performed on mixed matrix membranes containing zeolite ZSM-5 as a microporous filler. This work demonstrated the ability of these composite membranes to retain metal pollutants (Fe^{2+} and Cu^{2+}ions), and these findings will be used to regenerate this type of membrane and improve their retention for example in future work as prospects.

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References

[1] R.M. Barrer, Zeolites and clay minerals as sorbents and molecular sieves, Ed. Academic Press, London, New York, San Fransisco, 1-28 (1978).
[2] A. Dyer, An Introduction to Zeolite Molecular Sieve, Ed. Copyright by John Wiley and Sons Ltd. (1988) p. 27-51.
[3] A.F. Cronstedt, Akad. Handl. Stockhlm, 18 (1756) 120
[4] S. Kokaoba, Y. Orhan, T. Akyuz, Desalination 214 (2007) 1.
[5] A. Kaya, A.H. Oren, J. Hazard. Mater. B131 (2006) 59.
[6] D. Nibou, H. Mekatel, S. Amokrane, M. Barkat and M. Trari, Adsorption of Zn^{2+} ions onto NaA and NaX zeolites: kinetic, equilibrium and thermodynamic studies, J. Hazard. Mater. 173 (2010) 637-646.
[7] D. Nibou and S. Amokrane, Catalytic performance of the exchanged Y faujasites by Ce^{3+} , La^{3+} ,Co^{2+} , Sr^{2+} , Pb^{2+} , Tl^{+} and NH_4^{+} cations in the disproportionation reaction of ,toluene, Comptes Rendus Chimie, 13 (5) (2010) 527-537.
[8] A.K. Basumatary, R.Vi. Kumar, A. K. Ghoshal, G. Pugazhenthi. Cross flow ultrafiltration of Cr (VI) using MCM-41, MCM-48 and Faujasite (FAU) zeolite-ceramic composite membranes. Chemosphere 153 (2016) 436-446.

[9] K. Kusakabe, T. Kuroda, A. Murata, S. Morooka, Formation of a Y-type zeolite membrane on a porous α-alumina tube for gas separation, Ind. Eng. Chem. Res. 36(1997)649–655.
[10] Z.Z. Wang, I. Kumakiri, K. Tanaka, X.S. Chen, H. Kita, NaY zeolite membranes with high performance prepared by a variable-temperature synthesis, Micropor. Mesopor. Mater. 182 (2013) 250–258.
[11] E. M. Flanigen, J. M. Bennett, R. W. Grose, J. P. Cohen, R. L. Patton, R. M. Kirchner, et J. V. Smith, « Silicalite, a new hydrophobic crystalline silica molecular sieve », Nature, 271(1978) 512-516.
[12] M.M.J. Traecy, J.B. Higging, Collection of simulated X patterns for zeolites, Fourth revised Ed. Elsevier (2001).
[13] N. Lauridant, T.J. Daou, G. Arnold, M. Soulard, H. Nouali, J. Patarin, D. Faye,Micropor. Mesopor. Mater. 152 (2012) 1–8.
[14]] L. Tzanis, H. Nouali, T.J. Daou, M. Soulard, J. Patarin, Mater. Lett. 115 (2014) 229−232.
[15] E. Galan, Applied Clay Science. 10 (1996) 477–90.
[16] Zeolite Characterization and Catalysis, Springer Science and Business Media (2009) 200-206.