

Organic Depollution on Mixed Matrix Membranes Containing a Zeolithe of Faujasite Y Type of Synthesis as a Microporous Charge

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ABSTRACT

The faujasite Y is a zeolite of large-pores with remarkable properties. It knew broad applications and was used in many industrial processes. In this study, it is prepared by crystallization of the gel resulting from the combination of the silica solution and that of the alumina. Its structure was characterized by XRD, SEM, BET, ATR-FTIR, and by elementary analysis. It is used in organic depollution for removing of methylene blue by the technique of membrane treatment. The membranes are made from a biodegradable polymer, cellulose acetate and another non-biodegradable polyvinyl chloride, serving as a matrix and containing different percentages of faujasite Y. The composite films obtained behave like filters and were used for removing of the methylene blue of the aqueous solutions. The filtrates obtained are analyzed by UV. The obtained results show the existence of a selective retention for the selected polymers. Retention in general increases with increasing faujasite Y concentration.

KEY WORDS: Zeolite, Faujasite Y, Pore, Gel; Cleaning Up, Membrane, Polymer, Biodegradable, Composite.

1. INTRODUCTION

Zeolites are porous materials with many elaborate forms (Barrer, 1978; Dyer, 1988). They belong to the family of hydrated aluminosilicate minerals (Jacobs, 2001) and have been used in the development of membranes of a mixed matrix. The polymer matrix membrane is a membrane made of a polymer interphase and provided with selective permeability to certain chemical species. Membrane processes, which have been used for a few years in industry (food processing, desalination, etc.), tend to develop at present in organic and mineral depollution (Erdem, 2008; Petrus, 2003) and the principle consists in filtering a solution through a membrane that stops certain molecules and lets others pass. This selection can be explained either by Pores size's pores, or by criteria of affinity between molecules or ions and the membrane. Therefore, the filtration of liquids containing these ions is one of the depollution methods used in the filtration and elimination of pollutants (Kaya and Oren, 2006). The studies that have used zeolite membranes for the applications of separation or liquid phase depollution are not very numerous. Faujasite Y zeolites were used for the development of membranes on an alumina tubular substrate and used for desalination of water, so they were able to obtain a salt with a high rate of retention and which is estimated at 90 % (Zhu, 2015). Another group of researchers used a technique of growth of flow out of water to synthesize the membrane of faujasite zeolite and to use it in in Cr (III) removal. The elimination rate is estimated at 95% (Covarrubias, 2008). In another development, the similar type of membrane was applied for protein separation and the efficacy of this technique was evaluated at 82% (Kumar, 2015). Removal of metal ions by the membranes resulted in retentions about 86% (Jansen, 2001).

Among the available processing techniques for the displacement of metal ions on site: precipitation, coagulation-flocculation, only these techniques are less effective in reducing ionic concentrations to standard levels however, other techniques such as: Ion exchange, electrochemical treatment, adsorption, filtration and reverse osmosis provide good reductions in ionic concentrations (Basumatary, 2016), but which in most cases are very expensive. Necessity requires the development and development of more economical and efficient processes for removal of metal ions contained in aqueous solutions and which can be conducted at ambient temperatures while ensuring better selectivity (Qin, 2002).

The membrane treatment method is economical, profitable and uses materials that have adsorption characteristics such as zeolites (Dyer, 1988; Nibou, 2010). The increasing application of porous materials is due to their physico-chemical characteristics (Nibou, 2010; Amokrane, 2007).

The purpose of this work is to test one of the applications of zeolite, according to the synthesis of membranes (Leclerc, 1993; Basumatary, 2016) based on polymers reinforced by the zeolite, in order to use them for the organic depollution, because the membranes of the zeolites are promoters because of their unique characteristics such as high separation factor; when also find in the faujasite Y (Qin, 2002; Nibou, 2010).

In this work, we study the preparation of zeolite of the faujasite Y type and its role in the preparation of biodegradable and non-biodegradable polymer matrix membranes which will be used for elimination of the traces as methylene blue contained in aqueous solutions. (Kusakabe, 1997; Huang, 2012; Zhu, 2009; Wang, 2013).

2. EXPERIMENTAL PROCESS

Preparation of the Faujasite Y: The used composition of the faujasite Y is: 5 NaO₂; 1 Al₂O₃; 10 SiO₂; 120 H₂O, it is prepared by the process of gelling and crystallizing of the gel resulting from the combination of the source of silica (silicon oxide « Merck 98% ») and that of alumina (aluminum hydroxide « Riedel-de Haen 65% »), dissolved with an alkaline solution (NaOH « Aldrich 98% »). The gel obtained is mechanically stirred for 3 hours in a polypropylene container. The hydrogel obtained was put in an ultrasonic bath (25 + 1°C.) for duration of 3 hours (ultrasonic frequency: 40 kHz). The product recovered by filtration was then washed with demineralized water (pH = 5.59) and dried at 100°C during 24 hours then calcined for 6 hours at 600°C.

Preparation of Membranes: The method employed to prepare composite films of membranes polymer/zeolite is the solvation pathway. The polymer and the zeolite are dissolved separately in a proper solvent under constant mechanical stirring and at ambient temperature. The two solutions are then mixed with stirring for 30 minutes. The mixture is then spread on a glass surface (20 × 20 cm). After evaporation of solvent, a film is formed which can easily be removed from the glass surface. The two polymers used are polyvinyl chloride and cellulose acetate and their respective solvents are tetrahydrofuran (Fluka 99%) and acetone (Biochem Chemopharma 99.78%). The mass percentages out of faujasite mixed with the polymers are the following: 10%, 25% and 50% based on total weight polymer's. The faujasite used in the preparation of membranes was manually ground and sieved using a 45 µm mesh sieve and the thickness of the membranes thus prepared for removing of organic pollutants is between 0.03 and 0.04 mm.

The membranes prepared are then tested for their depollution effects of aqueous solutions containing methylene blue (BM).

Characterization Techniques: The qualitative elementary analyzes of faujasite have been applied by dispersive analysis in wavelength using an apparatus of x-ray fluorescence X PHILIPS MagiX. Surface morphology of zeolite was observed by PHILIPS XL FEG microscope. Few milligrams of the solid sample are deposited on an adhesive patch fixed on the sample holder and then metalized (10 to 20 nm of gold) by cathodic sputtering.

The powder diagrams were recorded on a STOE STADI P diffractometer equipped with an anticathode copper tube (40 kV, 30 mA), a front monochromator (crystal curve of germanium cut according to the family of planes (111)) allowing to select copper K α 1 radiation ($\lambda = 1.5406 \text{ \AA}$) and a linear detector PSD (Position Sensitive Detector). The acquisitions are done in Debye-Scherrer mode at ambient temperature on the ground sample and placed in a Hilgenberg capillary 0, 3 mm in diameter.

ATR-FTIR spectroscopy using a Perkin Elmer spectrum 2000 equipped with diamond cell, spectrum was obtained by 16 scans experiment with a 4 cm⁻¹ resolution.

The adsorption and desorption isotherms of N₂ for the measurement of the surface area carried out by an automatic apparatus Micro active for TriStar II Plus at temperature of liquid nitrogen (77K).

To analyze the filtrates containing traces of the methylene blue dye, the UV-Visible spectrophotometer of SHIMADSU UV-1650C of double beam (Japan) was used.

The morphology and the distribution of the pores of membranes observed using scanning electronic microscopy of the FEI brand and of the Qanta 250 type with a tungsten filament.

3. RESULTS AND DISCUSSIONS

Characterization of the Faujasite: The powder diffractogram (Fig.1) showing the characteristics of Faujasite phase without other identifiable phases. These results are compatible to those reported in literature (Traey, 2001) after indexing the DRX (hkl) models corresponding to the phase of faujasite Y.

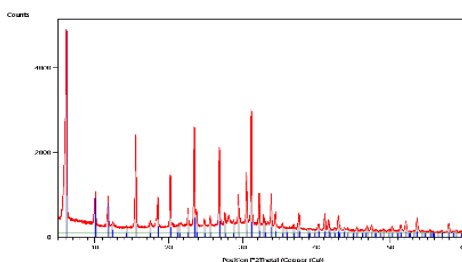


Figure.1. DRX of the faujasite Y

Fig.2, shows that faujasite Y presents two types of crystals because two morphologies can be observed: heaps of crystals of octahedral shape, the individual size of which is of the order of half a micron and heaps of very small crystals whose size is less than 50 nm.

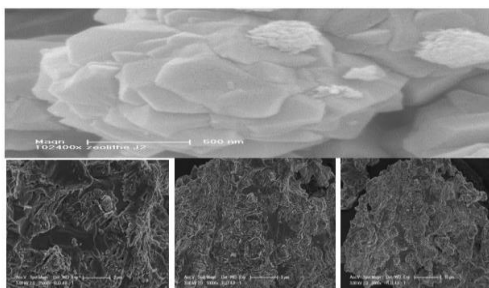


Figure.2. SEM of the faujasite Y

Scanning electron microscope observations also show the presence of structure spotted of aggregates of Y-faujasite grains of heterogeneous dimension, the interstices between the grains form pores. For a higher magnification (from 2 μm to 10 μm) (Fig.2), we notice large cavities of irregular shape.

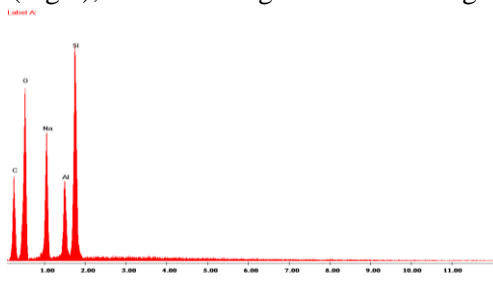


Figure.3. Spectrum of elements present on the outer surface of faujasite Y by EDX (rays energy dispersion)

Some platelets were also noticed, and spectrum EDX (Fig.3) shows that these constitute Al, Si, Na, C and O.

The results of analyzes by EDX are given in table.1, show that faujasite Y has a high percentage of oxygen, about 44.47%, followed by silicon 29.22% and aluminum with 9.76%.

Table.1. Mass Percentage of faujasite, using energy dispersion of X-ray (EDX).

Elements	Weights %	Atomic %
O	44.47	56.71
Na	16.55	14.69
Al	9.76	7.23
Si	29.22	21.37
Total	100.00	100.00

The Si / Al molar ratio is 2.99 and the Al / Na molar ratio is 0.59. This analysis is consistent with a Y-type faujasite (Mohamed and Ezzat, 2015; Wolfgang Lutz and Zeolite, 2014).

These results confirm those found by chemical analysis by fluorescence which was quantitatively treated with the FLS-QCX software which also revealed the presence of these elements in the form of oxides and which are given in table.2.

Table.2. Chemical analyzes of faujasite (Weight %).

Element	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	SO ₃	Cl
Faujasite Y	38.21	11.36	0.36	3.05	1.19	0.31	7.87	0.05	0.02

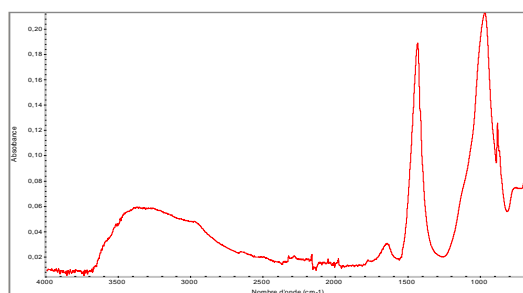


Figure.4. ATR-FTIR spectrum of the faujasite Y

Fig.4, shows spectrum FT-IR of the zeolite elaborated faujasite Y. The bands lying between 500 and 1500 cm^{-1} are due to the vibrations Si-O-Al, Si-O-Si, Si-O, Si-Al (Breck, 1974). The bands located from 3750 to 3450 cm^{-1} are attributed to the Si-OH, Si-OH-Al and the OH hydroxyl groups bonds OH (Nibou, 1999).

The surface specific of faujasite is estimated from the quantity of nitrogen adsorbed in relation to its pressure at the boiling point of liquid nitrogen and normal atmospheric pressure. The information is interpreted according to

the model of BET theory and gave a value of a specific area estimated at $10.7694 \pm 0.0966 \text{ m}^2/\text{g}$, an adsorbed quantity estimated at $Q_m: 0.11039 \text{ mmol/g}$ and an area of a molecular cross-sectional zone equal to: 0.1620 nm^2 . The experimental results of this analysis are mentioned in table.3.

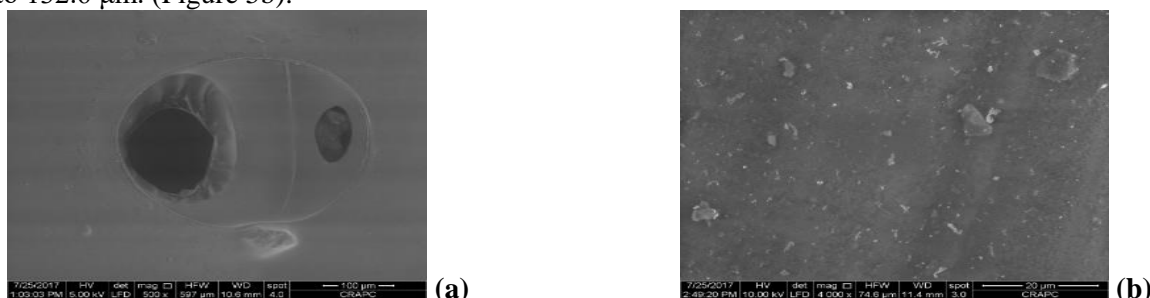
Table.3. Results of the BET analysis

Relative Pressure (P/Po)	Quantity Adsorbed (mmol/g)	1/[Q(Po/P - 1)]
0.006181837	0.05493	0.11324
0.012217748	0.06631	0.18653
0.027038055	0.054900317	0.34457
0.061413899	0.074863799	0.60746
0.099772002	0.112319882	0.66485
0.124793806	0.149664715	0.78255
0.162407906	0.175027112	0.99897
0.181275622	0.11435	1.10650
	0.11752	1.21332
	0.12299	1.43111
	0.12573	1.54215
	0.12825	1.65425
	0.12954	1.70923

Characterization of Membranes:

SEM analysis of Membranes: Analysis by Scanning electron microscope shows that the distribution of the pores in the state of the matrix membrane elaborated in polyvinyl chloride (PVC) is clear whose predominant shape is circular, and their sizes are larger than that prepared from cellulose acetate(AC), whom we could not determine their sizes of pores until after the increase in the accelerating tension (accelerated the primary electron beam): from 5 kV to 10 kV (the porosity in this case is hidden because surface of membrane is Smooth), where:

- PVC membranes: on a $100 \mu\text{m}$ scale and for a magnification of 500 times, the pore size varies from $106.4 \mu\text{m}$ to $162.0 \mu\text{m}$. (Figure 5a).
- AC membranes: on a $20 \mu\text{m}$ scale and for a magnification of 4000 times, the pore size varies from $110.2 \mu\text{m}$ to $132.6 \mu\text{m}$. (Figure 5b).

**Figure.5. SEM of blank membranes (a). in PVC (b). in AC**

Several images acquisitions were analyzed on surface of samples in several zones and with several enlargements to underline the surface porosity of the two types of membranes, first blank and without addition of the zeolite, thus a possible estimation on the dye retention parameters on both types of membranes.

The addition of the different percentage of the zeolite (faujasite Y) to the membranes in the state of composite membranes increases the porosity of latter in both cases. (SEM images are mentioned after membrane treatment).

Removal of the dye by the Membranes:

A-Preparation of the Mother Solution of the Dye: The mother solution was prepared with an initial concentration of $2.5 \times 10^{-5} \text{ mole/l}$, and from this stock solution, daughter solutions were prepared to plot the dye calibration curve (methylene blue solutions have a pH of about 6.15) and the table.4, shows the variation of the absorbance according to the concentration;

Table.4. Variation of Absorbance as a Function of Concentration for Different Solutions of Methylene Blue

solutions	Concentrations of daughters solutions (mole/l)	Volume taken from the mother solution in ml	Volume of H ₂ O to adjust to 50 ml	Absorbance of methylene blue
1	0	0	50	0
2	1.5×10^{-5}	30	20	1.103
3	1.75×10^{-5}	35	15	1.368
4	2×10^{-5}	40	10	1.601
5	2.25×10^{-5}	45	5	1.878
6	2.5×10^{-5}	50	0	2.107

The equilibrium (C_e) concentrations of methylene blue are determined from the UV absorption, at the wavelength $\lambda_{Rmax} = 663 \text{ nm}$.

The linear regression of calibration curve indicates the following correlation factors:

$$A = 81181 * C \text{ avec } R^2 = 0,991 \text{ with } \epsilon = 81181 \text{ L.mol}^{-1}.\text{cm}^{-1}.$$

B- Membrane Treatment: As explained above, we filter a volume of 30 ml of initial deconcentration equal to $2.5 \times 10^{-5} \text{ mol/l}$ of mother solution containing the coloring through the composites membranes; in polyvinyl chloride / faujasite Y and cellulose acetate / faujasite Y separately. The obtained filtrates are analyzed by UV to determine the removal capacity of the dye on the two composites membranes. The procedure is repeated until saturation of the membrane. The filtration is applied with pressure (about 12 bars) at ambient temperature (21°C .) and the absorbance of mother solution is $A = 2.107$.

The obtained results for the final concentrations of filtrates are indicated in the following tables.5 and 6. Figure.6, presents the graphs states that there is filtrates according to number of filtration.

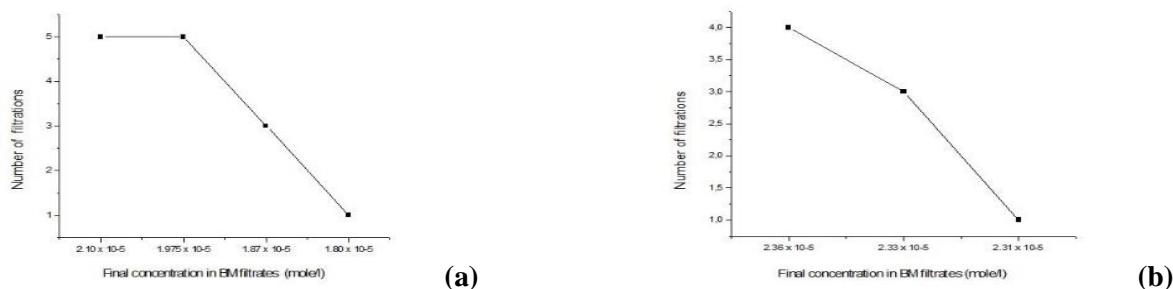


Figure.6. Filtration number graphs on the basis of the final concentrations on the membranes (a). of PVC (b). in AC

We notice with reference to the two preceding graphs a progressive and rapid decrease in the first case, which reaches a final concentration equal to $1.80 \times 10^{-5} \text{ mol/l}$ at the last state of saturation of the membrane, and the same slow decrease is noticed in the second graph.

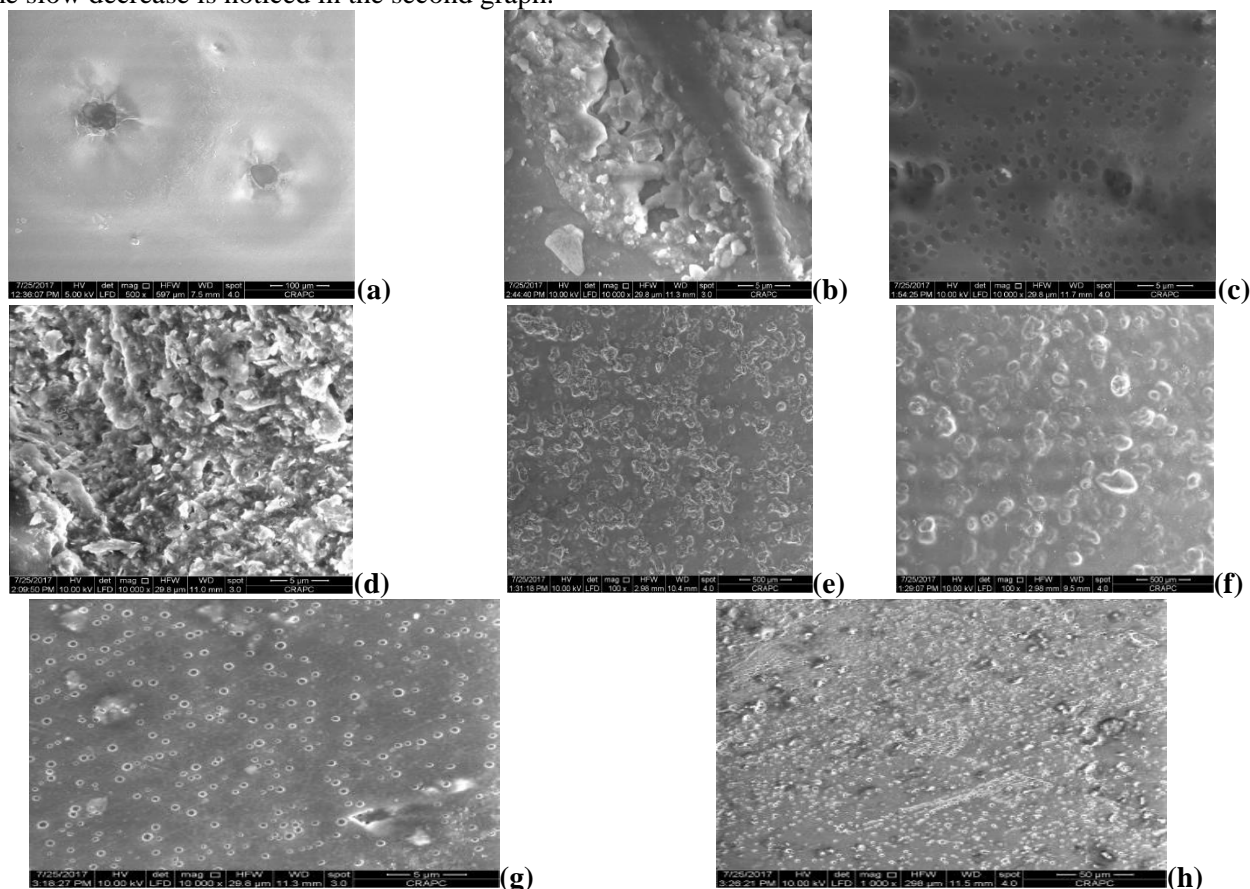


Figure.7. SEM of membranes

The following figures present the SEM cliches of the membranes in the following cases:

- PVC membranes (Figure 7a) and AC (Figure 7b) after membrane treatment.
- Composite membranes of PVC / faujasite Y and AC / faujasite Y before saturation after membrane treatment (25% (Figure 7c) and 10% (Figure 7d), respectively).

- Composite membranes in PVC / faujasite Y and in AC / faujasite Y in the state of saturation before and after membrane treatment (50% (Fig.7e, 7f) and 25% (Fig.7g, 7h), respectively).
- The membranes produced in PVC (7a) and in AC (7b) in the blank after membrane treatment or precisely after adsorption of methylene blue shows that there is a constriction of the pores by comparing the latter with those that are distributed in the membranes that are blanked without membrane treatment (Figure.5 (a) and (b)), which can be explained by the accumulation of this dye in these pores, except that the decrease in pore size in the case where the membranes are made of PVC is more significant compared to those developed in AC since their surface porosity (PVC is higher than that of the AC).
- Composite membranes developed in PVC / faujasite Y and in AC / faujasite Y before their saturations after membrane treatment (25% (7c) and 10% (7d) respectively) allowed us to notice that the addition of certain percentages of zeolite increases the porosity distributed in both cases given the physico-chemical properties of this added porous material which leads to a high elimination of the methylene blue by comparing it with the previous case.
- The composite membranes of PVC / faujasite Y and AC / faujasite Y in the state of saturation before and after membrane treatment (50% (7e, 7f) and 25% (7g, 7h) successively) always states that there is an increase in distribution of the pores, hence an elevation in the percent retention of the pollutant, except that the saturation state of these composite membranes is not the same in the two case: removing of dye in the membranes prepared with PVC is of great interest because of their Physical and chemical properties compared with those prepared using cellulose acetate since the pores of the acetate are rapidly saturated and can only remove a minor amount of dye.

All these notes correspond to the experimental values found in (Table.5 and 6), analyzing every time obtained filtrates by UV to know the dye removal capacity.

Table.5. Results of adsorption of the dye on membranes made of polyvinyl chloride.

Membrane	Number of filtrations	Absorbance of methylene blue	Final concentration in BM filtrates (mole/l)
pvc	5	1.774	2.10×10^{-5}
pvc/faujasite 10%	5	1.665	1.975×10^{-5}
pvc/faujasite 25%	3	1.580	1.87×10^{-5}
pvc/faujasite 50%	1	1.522	1.80×10^{-5}

Table.6. Results of adsorption of the dye on the membranes made of cellulose acetate

Membrane	Number of filtrations	Absorbance of methylene blue	Final concentration in BM filtrates (mole/l)
a.c	4	1.989	2.36×10^{-5}
a.c/faujasite 10%	3	1.965	2.33×10^{-5}
a.c/faujasite 25%	1	1.950	2.31×10^{-5}
a.c/faujasite 50%	/	/	/

With reference to the obtained results, we noticed the existence of a selective retention for the polymers used, but the retention is greater with membranes made from polyvinyl chloride than with membranes made with cellulose acetate. It is found that membrane retention is proportional to the faujasite concentration and that the composite membranes are more efficient in removing the organic dye (BM).

This efficiency is related to the capacity of zeolites to adsorb the pollutants.

This selection can also be carried out either by Pores size's pores or by affinity criteria between the molecules or the ions and the membrane;

- The size of the pores of the matrix (PVC and AC).
- The nature of the interaction with the matrix:

* Interaction with chlorine in the state of polyvinyl chloride.

* Interaction with oxygen in the state of cellulose acetate, many OH groups are trapped by inter-chain hydrogen bonds.

Finally, it concluded that organic depollution is better with membranes made out of polyvinyl chloride because of their more interesting physicochemical properties compared to membranes prepared using cellulose acetate. The pores of the acetate are in fact rapidly saturated and have eliminated only a minor amount of the dye.

4. CONCLUSION

In this manuscript, we have described all the steps involved in the preparation of the zeolitic faujasite Y type and its characterization with different methods of analysis and its use as a decontaminating material. Removal of this pollutant was carried out on mixed matrix membranes containing this synthetic faujasite as a microporous charge. This work is the first to use such a technique and has allowed to deepen knowledge on this type of materials whose

characterization suggests prospects for the development of other structures of membranes more specific and more effective.

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REFERENCES

- Amokrane S, Ribiai R and Nibou D, Behaviour of Zeolite A, Faujasites X and Y Molecular Sieves, *J. Appl. Sci.*, 7 (14), 2007, 1985-1988.
- Barrer R.M, Zeolites and clay minerals as sorbents and molecular sieves, Ed. Academic Press, London, New York, San Fransisco, 1978, 1-28.
- Basumatary A.K, Vi Kumar R, Ghoshal A.K, Pugazhenth G, Cross flow ultrafiltration of Cr (VI) using MCM-41, MCM-48 and Faujasite (FAU) zeolite-ceramic composite membranes, *Chemosphere*, 153, 2016, 436-446.
- Breck D.W, Zeolite Molecular sieves-Structure chemistry and use, Ed. Wiley Interscience, New York, 1974.
- Covarrubias C, Garcia R, Arriagada R, Yanez J, Ramanan H, Lai Z, Tsapatsis M, Removal of trivalent chromium contaminant from aqueous media using FAU-type zeolite membranes, *J. Membr. Sci.*, 312, 2008, 163-173.
- Dyer A, An Introduction to Zeolite Molecular Sieve, Ed. Copyright by John Wiley and Sons Ltd., 1988, 27-51.
- Erdem E, Karapinar N, Donat R, The removal of heavy metal cations by natural zeolites, *J. Coll. Interface. Sci.*, 280 (2), 2004, 309-314.
- Huang A, Wang N, Caro J, Seeding-free synthesis of dense zeolite FAU membranes on 3-aminopropyl tri ethoxy silane -functionized alumina sup- ports, *J. Membr. Sci.*, 389, 2012, 272-279.
- Jacobs P.A, Flanigen E.M, Jansen J.C, Herman van Bekkum, Introduction to Zeolite Science and Practice, 2nd Ed, 137, 2001.
- Jansen J.C, Introduction to Zeolite Science and Practice, Van Bekkum H, Flanigen E.M, Jacobs P.A and Jansen J.C (Eds.), 2nd Ed., Elsevier, Amsterdam, 2001, 175.
- Kaya A, Oren A.H, Factors affecting adsorption characteristics of Zn²⁺ on two natural zeolites, *J. Hazard. Mater.*, 131 (1), 2006, 59-65.
- Kumar R.V, Basumatary A.K, Ghoshal A.K, Pugazhenth G, Performance assessment of an analcime-C zeolite-ceramic composite membrane by removal of Cr (VI) from aqueous solution. *RSC Adv.*, 5, 2015, 6246-6254.
- Kumar R.V, Moorthy I.G, Pugazhenth G, Modelling and optimization of critical parameters by hybrid RSM-GA for the separation of BSA using a tubular configured MFI-type zeolite microfiltration membrane, *RSC Adv.*, 5, 2015, 87645-87659.
- Kusakabe K, Kuroda T, Murata A, Morooka S, Formation of a Y-type zeolite membrane on a porous α -alumina tube for gas separation, *Ind. Eng. Chem. Res.*, 36, 1997, 649-655.
- Leclerc O, Petit L, Kot C, Les methodes electrolytiques de depollution, *Recents Progres en Genie des Procedes*, 7 (25), 1993, 91-98.
- Mohamed A. Moneim, Ezzat A. Ahmed, Synthesis of Faujasite from Egyptian Clays: Characterizations and Removal of Heavy Metals, *J. Geomaterials*, 5 (2), 2015.
- Nibou D and Amokrane S, Catalytic performance of the exchanged Y faujasites by Ce³⁺, La³⁺, UO₂²⁺, CO²⁺, Sr²⁺, Pb²⁺, Tl⁺ and NH₄⁺ cations in the disproportionation reaction of toluene, *Comptes Rendus Chimie*, 13 (5), 2010, 527-537.
- Nibou D, Mekatel H, Amokrane S, Barkat M and Trari M, Adsorption of Zn²⁺ ions onto NaA and NaX zeolites: kinetic, equilibrium and thermodynamic studies, *J. Hazard. Mater.*, 173, 2010, 637-646.
- Nibou D, PhD thesis, University of Science and Technology Houari Boumediene, Algiers, Algeria, 1999.

Petrus R, Warchol J, Ion exchange equilibria between clinoptilolite and aqueous solutions of $\text{Na}^+/\text{Cu}^{2+}$, $\text{Na}^+/\text{Cd}^{2+}$ and $\text{Na}^+/\text{Pb}^{2+}$, *J. Micro. Meso. Mater.*, 61 (1-3), 2003, 137 -146.

Qin J, Wai M, Oo M, Wong F, A feasibility study on the treatment and recycling of a wastewater from metal plating, *J. Membr. Sci.*, 208, 2002, 213-221

Traacy M.M.J, Higging J.B, Collection of simulated X patterns for zeolites, Fourth revised Ed. Elsevier, 2001.

Wang Z.Z, Kumakiri I, Tanaka K, Chen X.S, Kita H, NaY zeolite membranes with high performance prepared by a variable-temperature synthesis, *Micropor. Mesopor. Mater.*, 182, 2013, 250–258.

Wolfgang Lutz, Zeolite Y, Synthesis, Modification, and Properties-A Case Revisited, *J. Advances in Materials Science and Engineering*, 2014, 2014.

Zeolite Characterization and Catalysis, Springer Science and Business Media, 2009, 200-206.

Zhu B, Myat D.T, Shin J, Na Y, Moon I, Connor G, Maeda S, Morris G, Gray S, Duke M, Application of robust MFI-type zeolite membrane for desalination of saline wastewater, *J. Membr. Sci.*, 475, 2015, 167-174.

Zhu G.Q, Li Y.S, Zhou H, Liu J, Yang W.S, Microwave synthesis of high performance FAU-type zeolite membranes: optimization, characterization and pervaporation dehydration of alcohols, *J. Membr. Sci.*, 337, 2009, 47–54.