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Removal of lead ions using a cellulose acetate/ zeolite composite membrane and their analyzes by inverse voltammetry

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Abstract

Zeolitic faujasite Y type was prepared from the crystallization of the gel resulting from the combination of the solutions of silica and alumina. Its structure was characterized by XRD, SEM, BET, ATR-FTIR, and elementary analysis. The composite membranes were prepared from a biodegradable polymer "cellulose acetate" serving as a matrix and different percentages of the synthesized faujasite Y. The filtrates obtained were analyzed by inverse voltammetry. The results showed that the retention of lead ions increased with increasing faujasite Y concentrations, and indicated an adsorption capacity of more than 50 % for the lead ions.

Keywords: zeolite; membrane; voltammetry; retention; adsorption; capacity.

1. Introduction

Zeolites are microporous crystalline solids [1-2], with a structure based on a rigid anionic framework with well-defined channels and cavities. The perfectly controlled porosity and the presence of negative charge due to the presence of aluminum in the frame confers to these materials remarkable properties that allow them to find applications in many different fields and new applications are constantly being considered.The negative charge is neutralized by positive charge cations of typically alkaline or alkaline earth cations located inside the pores of materials. Compensation cationsare often exchanged and can be replaced by a large variety of alkaline cations,transition metals, organic and inorganic cations[3].

Zeolites are widely used as catalysts in the petroleum industry, water softeners in the field of detergency, molecular sieves in the purification and separation of gases, without forgetting their applications in ionic exchangein the anti-pollution treatments [4-6]. They have been used in the development of membranes and membrane processes and for the applications of liquid phase depollution [7-10].

The purpose of this work is to investigate one of the zeolite applications where prepared composite membranes [11;12] based on polymer matrix and zeolite are studied for their abilities to remove lead ions from aqueous solutions.

In this work, we study the preparation of zeolite of the faujasite Y type and its use in the preparation of polymeric matrix membranes which will be used for the removal of lead ions contained in aqueous solutions

2. Experimental

2.1. Preparation of the Faujasite Y

The composition used for the preparation of the faujasite Y is: 5 NaO_2;1 Al_2O_3;10 SiO_2;120 H_2O. It is prepared by the process of gelling and crystallization of the gel resulting from the combination of the silica source (silicon oxide « Merck 98% ») and alumina (aluminum hydroxide « Riedel-de Haen 65% »), dissolved in alkaline solution (NaOH « Aldrich 98% »). The gel obtained is mechanically stirred for 3 hours in a polypropylene container. The resulting hydrogel was transferred to an ultrasonic bath (25 ± 1°C.) for 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 for 24 hours then calcined for 6 hours at 600°C.

2.2. Preparation of the membranes

The polymer and the zeolite are dissolved separately in a proper solvent under constant mechanical stirring and at room temperature. The two solutions are mixed and stirred for 30 minutes. The resulting mixture is then spread on a glass surface (20 × 20 cm). After evaporation of the solvent, a film is formed which can easily be removed from the glass surface. The polymer used is cellulose acetate and the solvent is the acetone (BiochemChemopharma 99.78%). The % weight of the faujasite powder (45 µm) mixed with the polymer are the following: 2%, 5% and 10% based on the total weight of the polymer. The thickness of the prepared membranes varied between 0.03 and 0.04 mm.

The lead metal sorption capacity of the membrane was examined from the concentration of lead ion in the filtrates which were analyzed by the inverse voltammetry method.

2.3. The inverse voltammetry

- *Prelectrolysis (accumulation) :*

For the lead analysis the electroplating phase is carried out in stirred solution with a potential sufficiently lower than the oxidation-reduction potential of lead to reduce the Pb^{2+}cations present in solution.

The surface of the working electrode is small, the duration of accumulation is less than that acquired for a complete electrolysis, and the current preserve during this phase maintains a substantially constant intensity. On the mercury's surface, a reaction occurs which forms an amalgam.

$$Pb^{2+} + 2é + Hg \longrightarrow Pb(Hg) \qquad (1)$$

The working conditions must be strictly monitored if reproducible measurements are to be made (time and accumulation potential, stirring speed, the volume of the sample). A waiting time separates this step from the next one which is the homogenization of the concentration of the metal accumulated in the film. The control solution is no longer agitated but the electrolysis potential remains applied.

- *Redissolution :*

In this step the metal goes from mercury to the solution and returns to the initial state. To do this, the potential of the electrode is displaced so as to cause oxidation of the amalgam. This step is defined by the potential scan, which is the speed at which the voltammogram is saved. The intensity of the current is proportional to the concentration of the amalgamated metal and it is self -representative of the initial concentration of the metal present in the solution.

$$Pb(Hg) \longrightarrow Pb^{2+} + 2é + Hg \qquad (2)$$

2.4. Characterization Techniques

The qualitative elementary analyzes of faujasite have been obtained 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 Kα1 radiation (λ = 1.5406 Å) 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 N_2 for the measurement of the surface areawas carried out by an automatic apparatus MicroActivefor TriStar II Plus at the temperature of liquid nitrogen (77K).

To analyze the filtrates containing traces of the lead ions, an autolab of (PGZSTAT 30) was used with :

- ✓ A reference electrode (Ag/AgCl/KCl 3M).
- ✓ A platiniumauxillaryelectrode .
- ✓ Working electrode ; vitreous carbon 3mm^2.

3. Results

3.1. Characterization of the Faujasite

The powder diffractogram (Figure 1) showing the characteristics of the faujasite phase without other identifiable phases. These results arecompatible with those reported in the literature [13] after indexing the DRX (hkl) models corresponding to the phase of faujasite Y.

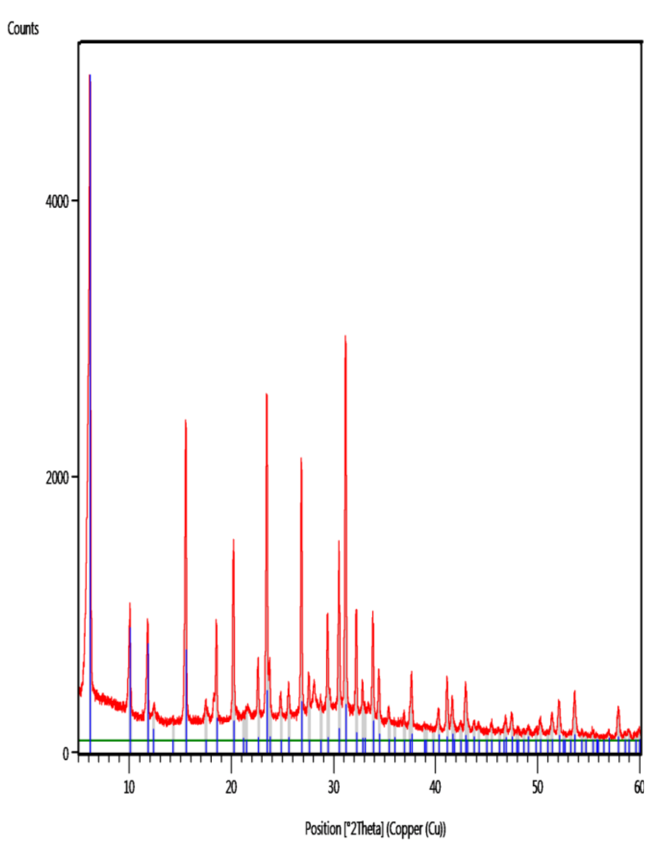

Figure 1: DRX of the faujasite Y.

Figure 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 with a size less than 50 nm.

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) , we notice large cavities of irregular shape.

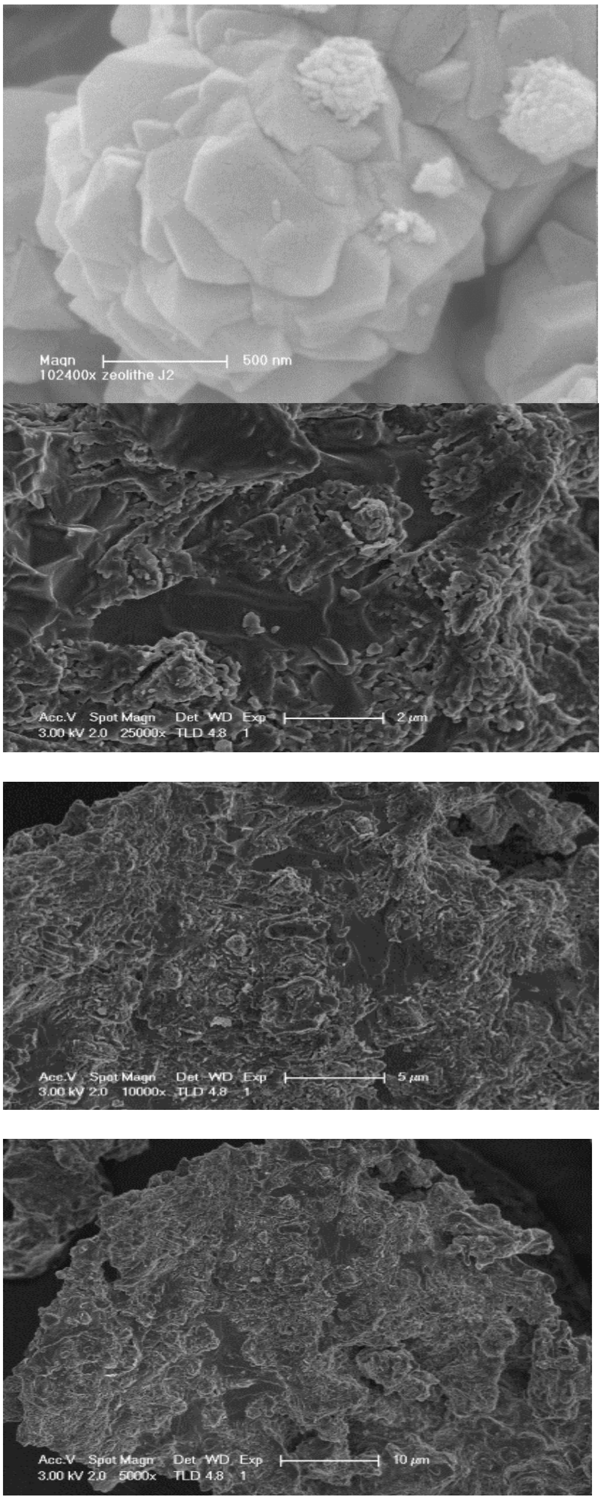

Figure 2: SEM of the faujasite Y.

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

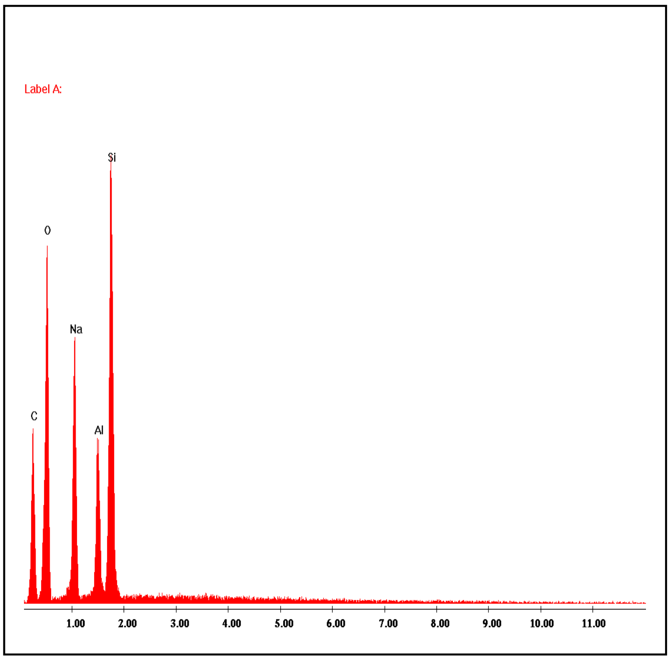

Figure 3: Spectrum of elements present on the outer surface of faujasite Y by EDX (rays energy dispersion).

The results of analyzes by EDX (table 1) show that faujasite Y has a high percentage of oxygen (44.47%), followed by silicon (29.22%) and aluminum (9.76%).
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 [14-15].

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**

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

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

Element	Faujasite Y
Al_2O_3	38.21
SiO_2	11.36
Fe_2O_3	0.36
CaO	3.05
MgO	1.19
K_2O	0.31
Na_2O	7.87
SO_3	0.05
Cl	0.02

Figure 4 shows spectrum FT-IR of the 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 .The bands located from 3750 to 3450 cm $^{-1}$ are attributed to the ;
Si-OH, Si-OH-Al and the OH hydroxyl groups [16-17-18].

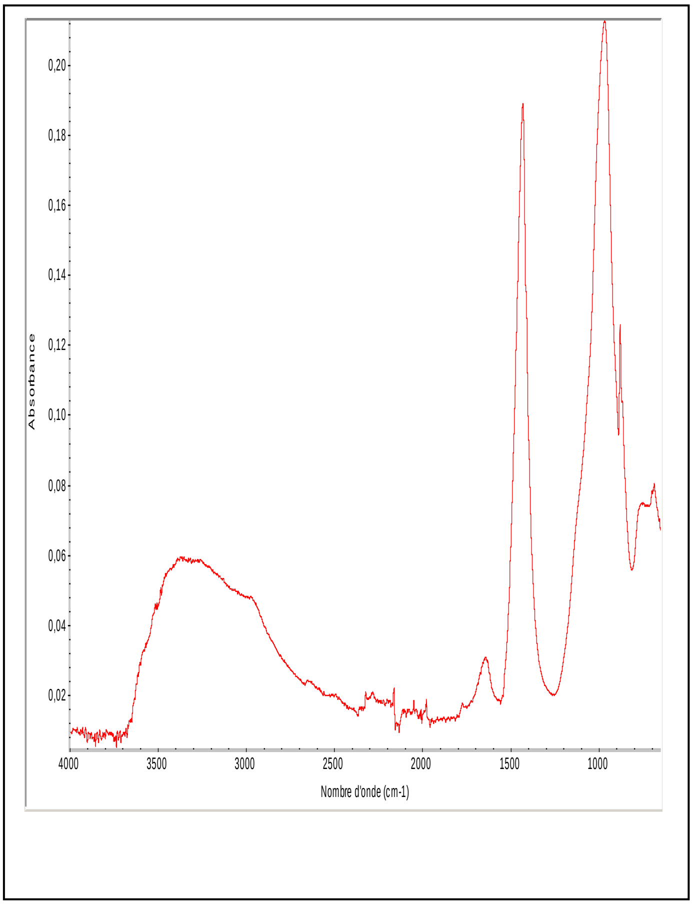

Figure 4 : ATR-FTIR spectrum of the faujasite Y.

The specific surface of the faujasite is estimated from the quantity of nitrogen adsorbed in relation to its pressure at 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 ± 0.0966 m^2 / g, an adsorbed quantity estimated at Qm: 0.11039 mmol / g and an area of a molecular cross-sectional zone equal to: 0.1620 nm^2.

The surface functional groups of the pure and NaY added cellulose acetate membranes were determined by FTIR-ATR spectrometer and the spectrums in the range of 4000-400 cm^{-1} are illustrated in table 3 [19-20-21-22] and figure 5.

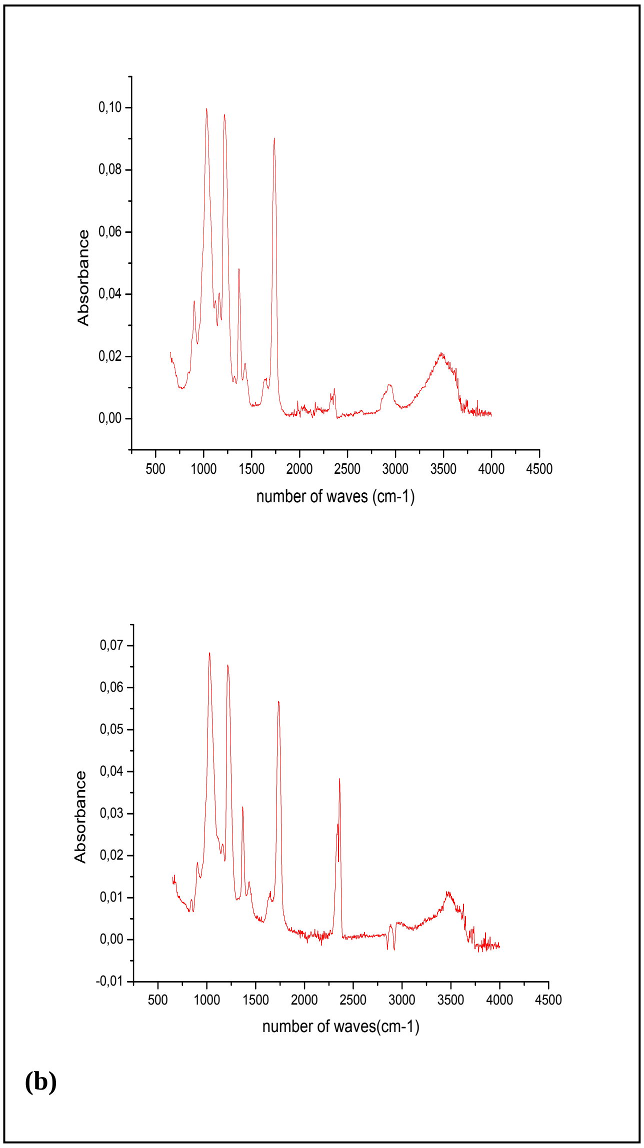

Figure 5 : FTIR- ATR spectrum of membranes : (a): celullose acetate pure,(b):composite cellulose acetate/zeolite NaY (10%).

Table 3 : Attribution of the different vibration bands.

Number of waves (cm^{-1})	Attribution	Nature
1031.03	symetric C-O bond	elongation
1161.30	Antisymmetric C-O-C bond	elongation
1215.98	C-H bonding of CH2 groups	deformation
1367.44	O-H bond in the plane	deformation
1430.57	C-H bond	deformation
2905,10	Skeletal C-H and C-H2	elongation
1657,78	Absorbed H_2O	deformation
1735.13	C = O of a non-conjugated ester	elongation
3545,35	O-H free	elongation

Figure 6 shows a broad band at about 3500 cm^{-1} was assigned to –OH stretching and the peak intensities increased with the amount of particles inside the membrane. This could be attributed to the hydrophilic nature of the zeolite which can adsorb water molecules through hydrogen bonding, hence increasing the hydrophilic characters of the membrane. The presence of NaY-particles on the membrane surface is observed at about 970-1000 cm^{-1} and represents the Si-O-Al species.

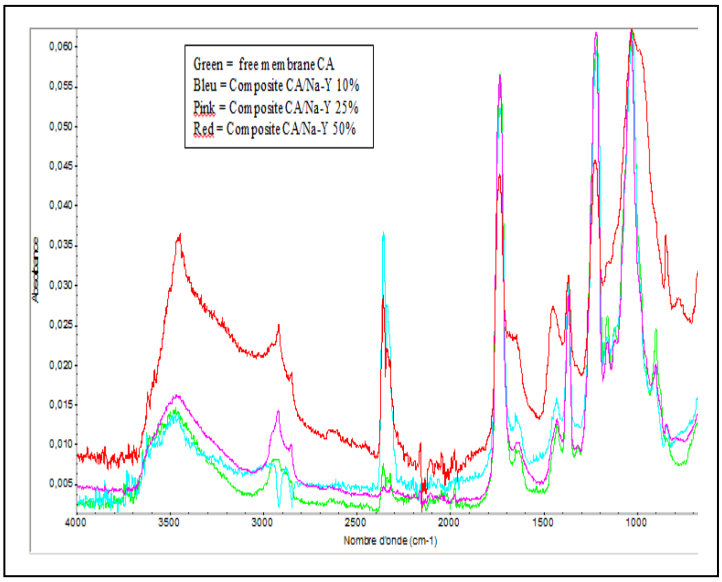

Figure 6 : FTIR- ATR spectrum of composite membranes (CA/Faujasite-Y).

3.2. Removal of lead ions by the composite membranes

A- Preparation of the stock solution

The stock solution was prepared with an initial concentration of 2.95x 10^{-5} mole/l, and was used to prepare a series of more diluted solutions made up to 50 cm^3 in order to plot the calibration curve. Table 4 shows the variation of the concentration with the electrical current intensity. The linear regression of the calibration curve indicated a correlation factor of: R^2=0,99083.

B- Removal of lead ion using the composite membrane

A volume of 10 ml of the stock solution (2.95x 10^{-5} mol/l) containing the lead ions was poured through the composites membranes (cellulose acetate(C.A) / faujasite Y) with different concentrations of faujasite Y. The obtained filtrates were then analyzed to determine the removal capacity of the composite membranes for the lead ions.

The obtained results from the final concentrations of the filtrates are shown in table 5.

The results from table 5 show that the retention of Pb^{++} is proportional to the zeolite concentration and that the composite membranes are more efficient in removing the mineral traces (lead ions). This efficiency is related to the capacity of zeolites in the adsorption of pollutants.

The measurement of metal ions traces, using the inverse voltammetry, allows the detection of several metallic species in a single experiment. It indicated an adsorption capacity of more than 50 % of the lead ions by the composite membrane (retention percentage).

Table 4: Variation of concentration as a function of the electrical current intensity for the solutions of lead ions.

Sample number	**Volume used from the stock solution (ml)**	**Solution concentration (mole/l)**	**Electrical intensity of lead ions (A)**
1	12.5	0.738x10^{-5}	3.104
2	18.0	1.062x10^{-5}	3.514
3	25.0	1.475x10^{-5}	4.594
4	35.0	2.065x10^{-5}	6.355
5	50.0	2.950x10^{-5}	8.777

Table 5: Removal of lead ions using cellulose acetate / faujasite membranes.

Membrane	**Electrical current intensity (A)**	**Pb^{++} concentration in the filtrates (mole / l)**	**Retention of Pb^{++} (%)**
C.A	8.69	2.94 x 10^{-5}	0.34
C.A/faujasite 2%	4.97	1.54x 10^{-5}	46.8
C.A/faujasite 5%	4.73	1.45 x 10^{-5}	50.85
C.A/faujasite 10%	3.82	1.11 x 10^{-5}	62.37

4. Conclusion

The work presented in this study describes the steps involved in the preparation of the zeoliticfaujasite Y type and its characterization with different methods of analysis and its use as a decontaminating material. Removal of lead ions was carried out on composite membranes containing cellulose acetate as a matrix and the synthesized faujasite as a microporous charge and showed a removal capacity higher than 50%.

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