A Novel Approach for Efficient Mineral Depollution and Environmental Remediation Using (Natural Zeolite / Polypropylene) Composite Membranes

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Abstract:

Zeolites play a significant role in many industrial processes, including adsorption, exchange, and catalysis, related to their large porous structure and retention properties. The purpose of the study is to value natural zeolites like microrous charge. Here, for selective ion separation, we mixed a biodegradable polymer (polypropylene PP) with varied ratios of zeolite rock deposits. Natural zeolite is extracted from a rock in the Bejaia region of Tinebdar, Algeria. Different physical-chemical techniques, including XRD, MEB, FTIR, and elemental analysis , have been used to confirm the structure and morphology of these deposits. The synthetic membranes are employed as filters to remove Co^{2+}, Ni^{2+}, Cu^{2+}, and Pb^{2+} ions from aqueous solutions. The atomic absorption technique (AAS) was used to examine the filtrates that were collected. The findings indicate the presence of selective retention for the ions under consideration. The retention increases with zeolite concentration, and the highest retention was obtained in the PP polymer-based zeolite, with an ion-selective retention of about 80%.

Keywords: natural zeolites, rock deposits, membranes, filtrates.

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I. Introduction

Zeolites are porous materials with various developed forms.[1,2] They are hydrated alumino-silicate minerals that are used in the development of mixed matrix membranes.[3,4] The polymer matrix membrane is made of polymer interphase that selectively permits the passage of specific chemical species.[5]

Membrane technologies, which have long been used in the industry (agri-food, desalination), are currently being developed for organic and mineral depollution.[6,7] due to the environmental pollution that different ions generate.[8] The idea is to use a membrane to filter a solution by keeping certain molecules in and allowing others to pass. The concept is to filter a solution using a membrane by keeping specific molecules in and allowing others to pass. This selection depends on the size of pores or affinity criteria between molecules or ions and the membrane. Therefore, one of the pollution control methods used in the filtration and removal of polluting substances is the filtering of liquids containing these ions.[9]

Zeolite membranes have not been extensively studied for liquid phase separation or depollution. According to some studies.[10] Desalination of water and the development of membranes on an a-alumina tubular substrate using MFI zeolites may remove salt from water with a high efficiency of about 90%. Some researchers developed a Faujasite zeolite membrane using the water flow growth method, and they used it to eliminate Cr (III) with an estimated 95% removal rate.[11]Another development separated proteins using the same membrane, and they assessed its efficiency to be 82%.[12, 13] Retention of 86% was achieved by the membranes' removal of metal ions.[14–15] Precipitation and coagulation-flocculation are two treatment methods for the on-site displacement of metal ions. These techniques are less efficient in reducing ionic concentrations to standard levels.[16] However, other techniques such as ion exchange, electrochemical treatment, adsorption, filtration, and reverse osmos is allow for good ionic concentration decreases.[16] although they are frequently quite expensive. The need required the design and development of more economical, effective, and selective procedures for the removal of metal ions from aqueous solutions that could be carried out at room temperature.[17] The cost effective and successful mixed matrix membrane treatment method employs adsorption materials such as zeolites.[2,18] The aim of this study is to valorize natural zeolite by using it in the fabrication of biodegradable polymeric matrices-based membranes for the removal of metal ions from aqueous solutions.

2. Characterization techniques

The elemental analysis was carried out by wave length-dispersive analysis using a PHILIPS MagiX X-ray fluorescence spectrometer. The microscope used in the laboratory is a PhilipsXL 30 F G model. The samples are prepared for observation in the following ways: first, a few milligrams of solid are placed on an adhesive pad attached to the sample holder ; next, they are metalized by sputtering 10 to 20 nm of gold on them. A copper anticathode tube (40kV; 30 mA), a front monochromator (a germanium crystal curve cut in accordance with the family of planes (111), allowing selection radiation copper K1(=1,5406),and a linear detector PSD were used to capture the powder diagrams (Position Sensitive Detector). The acquisitions were performed in Debye-Scherrer mode on the ground sample inside a 0.3 mm diameter Hilgenberg capillary at room temperature.

3.Results and discussion

3.1. Natural zeolite characterization

Figure1 depicts the zeolite sample XRD pattern. After indexing the XRD models, diffraction peaks corresponding to the Sodium Aluminum Silicate Hydroxide Hydrate phase

« $Na_8Al_6(SiO_4)_6(OH)_2(H_2O)_{3.44}$ » with the standar d 04-010-5524 as reported in the literature.[19]

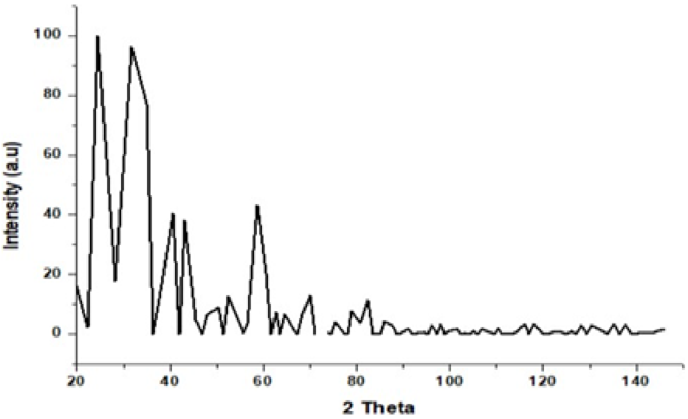
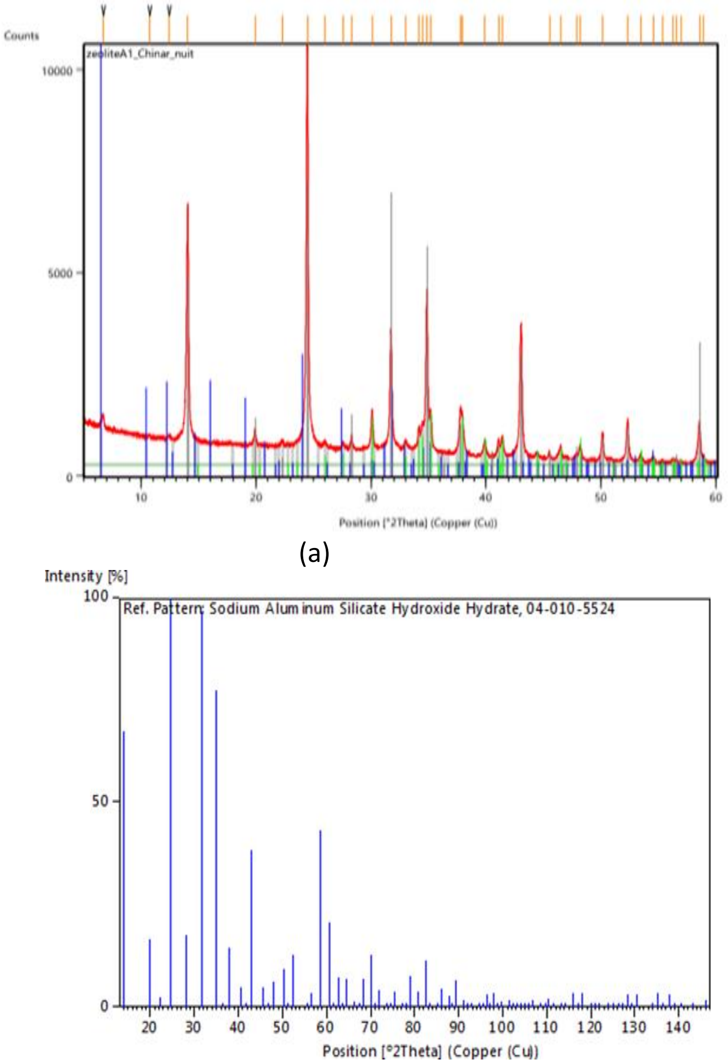


Figure1. Pattern of XRD analysis related to natural zeolite.

The difference powder XRD plot of the zeolite sample (Bejaia region) after the final refinement stage is shown in Figure 2 .The corresponding refined parameters including the unit cell lattice with the atomic position of the pure natural zeolite are represented in Table 1.



(a)

(b)

Figure2.(a) Difference plot of the powder XRD experimental and calculated pattern of zeolite standard 04-010-5524, (b) Standard patentSodiumAluminiumSilicateHydroxydeHydratye,REF04-010-5524.

Table1.Crystal parameters of the natural zeolite

Sample	**Parameters**	**Crystalline System**	**Structure**								
			No.	Name	Elem.	X	Y	Z	Bisosof		Wyck
Zeolite	a=b=c=8,8957 A° α=β = γ = 90°C	Cubic α = β = γ =90 °CP - 43n	1	NA1	Na	0,34900	0,34900	0,34900	0,5000	0,7500	8e
			2	AL1	Al	0,25000	0,00000	0,50000	0,5000	1,0000	6d
			3	SI1	Si	0,25000	0,50000	0,00000	0,5000	1,0000	6c
			4	O1	O	0,06870	0,35450	0,36370	0,5000	1,0000	24i
			5	O2	O	0,12270	0,12270	0,12270	0,5000	1,0000	8e

Figure 3 displays naturally occurring zeolite's spherical crystals. Topas software uses the classical Scherrer equation for crystallite size determination. The crystallite is no larger than 100 nm (three phases: sodalite, sodium carbonate, and faujasite).

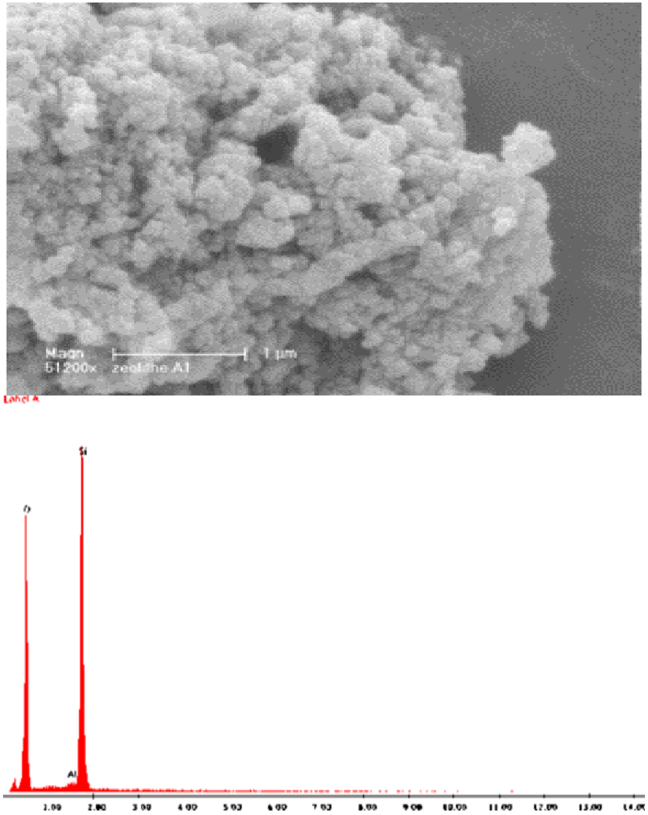


Figure 3.SEM micrograph and EDX analysis elements presented on natural zeolite external surface

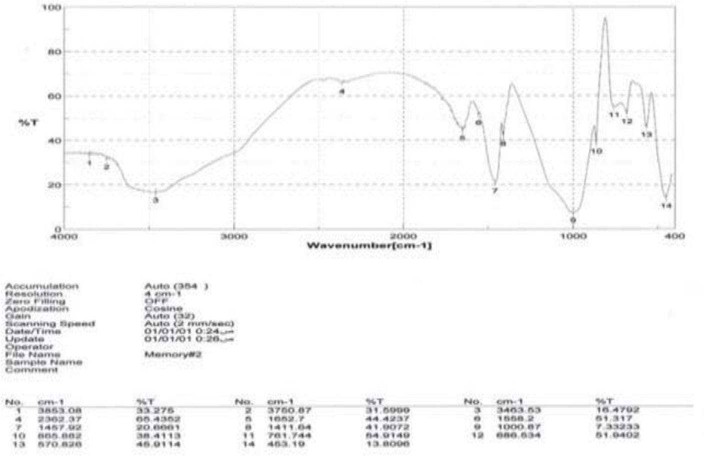
The natural zeolite's EDX elemental analysis revealed that it is mostly made of the elements in the O, Na, Al, and Si Table 2. Al/Na has a molar ratio of 0.85 whereas Si/Al has a molar ratio of 0.96. This is in line with the results of the earlier X-ray diffraction study, which confirmed the existence of the natural zeolite phase, that sodium sodalite as the dominant phase.

Table2.Natural zeolite elementary analysis

	Element	**Conc.(%)**	**Element**	**Conc.(%)**
1	O	43.9	K	0.00806
2	Na	18.4	Ca	0.745
3	Al	18.4	Ti	0.0117
4	Si	18.2	Fe	0.132
5	S	0.0218	Zr	0.00956
6	Cl	0.0582		

The FTIR spectra of natural zeolite are seen in **Figure 3.** The band at 3454 cm^{-1} was attributed to contain zeolitic water. The bands at 1102 and 1008 cm^{-1}, describe Si-O-Al vibrations, and the bands around 680,550 and 456cm-1 indicate the vibrations of the crystallized zeolite. The absorption band located at 456 cm^{-1}couldbeattributedtothe T-O bending vibration of the zeolite interior (where T = Al or Si).The band at 680 cm^{-1} represents typical symmetrical stretches of the primary internal vibrations T-O, where T can be silicon (Si) or aluminum (Al).

The vibration of the four tetrahedra double rings (DR4), which predominates in the secondary building block of the natural zeolite, is related to the next band at 550 cm^{-1} .[20-22]



Accumulation Auto (354)
Resolution 4 cm-1
Zero Filling OFF
Apodization Cosine
Gain Auto (32)
Scanning Speed Auto (2 mm/sec)
Date/Time 01/01/01 0:24.ص
Update 01/01/01 0:26.ص
Operator
File Name Memory#2
Sample Name
Comment

No.	cm-1	%T	No.	cm-1	%T	No.	cm-1	%T
1	3853.08	33.275	2	3750.87	31.5999	3	3463.53	16.4792
4	2362.37	65.4352	5	1652.7	44.4237	6	1558.2	51.317
7	1457.92	20.6661	8	1411.64	41.9072	9	1000.87	7.33233
10	865.882	38.4113	11	761.744	54.9149	12	686.534	51.9402
13	570.826	45.9114	14	453.19	13.8096			

Figure4.FTIR spectrum of natural zeolite

3.2. Membrane performance measurement

Mineral depollution using the membrane treatment approach has been employed to remove metal ions (Co^{2+},$Ni^{2+,}$$Cd^{2+}$,and Pb^{+2}) using zeolite membrane elaborated. The membranes are elaborated using polypropylene, a biodegradable polymer that functions as a matrix and contains zeolite in different proportions. Absorption Atomic Spectroscopy SAA is used to analyze the composite films used as filters and the filtrates produced for mineral depollution. Herein, the sol-gel method is used to prepare composite polymer/zeolite membrane films.

Manually ground, natural zeolite was sieved with a mesh size of 45 µm then incorporated into the polymer at the following mass percentages: 10%, 25%, and 50% of the total polymer weight.

The polymer and the zeolite are separately dissolved in the suitable solvent under constant mechanical stirring and then mixed. The mixture is then spread out over a piece of glass (20x20cm).A film that is easily detachable from the glass surface is formed once the solvent has evaporated. The produced membranes composite (PP/Z) had a thickness of between 0.03and 0.04 mm as determined by Palmer's foot method, and its depollution capabilities were assessed. To achieve this, stock solutions containing the metal ions (Co2+, Ni2+, Cd2+, andPb+2) are filtered through composite membranes in PP/Z, and the filtrates are then analyzed to evaluate the composite membrane's ability to eliminate the metal ions. The stock solutions of initial concentration = 5mg/l are filtered and decrease with the increase in zeolite percentage as listed in the following tables:

Table 3.Concentrations of metallic ions on the PP/Z membranes

The membrane	**Final [conc] of filtrates of Co (mg/l)**	**Final [conc] of filtrates of Ni (mg/l)**	**Final [conc] of filtrates of Cd (mg/l)**	**Final [conc] of filtrates of Pb (mg/l)**
PP	**4.2**	**3.13**	**1.78**	**1.15**
PP/Z 10%	**3.89**	**2.9**	**1.54**	**0.9**
PP/Z 25%	**3.05**	**2.35**	**1.24**	**0.77**
PP/Z 50%	**2.8z**	**2.06**	**1.01**	**0.56**

Table 4.Percentage of removed ions

The membrane	Elimination % of Cobalt	Elimination % o Nickel	Elimination % of Cadmium	Elimination % of Plomb
PP/Z	44%	58.8%	79.8%	88.8%

The results show that this efficiency is correlated to the adsorption capacity of the natural zeolite. We noticed preferential retention for the metal ions that were selected based on the ionic radius: RCo= 65 pm, RNi= 69 pm, RCd= 95 μm, and RPb=119 pm. The selection of pollutants is influenced by the pore size of the zeolite, the criteria of affinity between molecules or ions and the membrane, the pore size of the polymer matrix, and the nature of interaction with the matrix. It was determined that membrane retention is proportional to the zeolite content and that the PP/Z composite membranes are more efficient for removing mineral pollutants (traces of heavy metals). This efficiency is correlated to the adsorption capacity of the natural zeolite. Further research. [23] revealed that the elimination of nickel by zeolite was significantly influenced by the size of the zeolite particle. According to Yi Li et al.[24] theparticle size of the polymer matrix and the way it interacted with the matrix had an impact on the zeolite adsorption process**.**

4. Conclusion

In this study, natural zeolite was used as a micro-porous charge to make mixed matrix PP/Z membranes for the removal of mineral pollutants (Co^{2+}, Ni^{2+}, Cd^{2+}, and Pb^{2+}). The composite with a PP/Z ratio of 50% 1.5:1 had the best elimination at 90%. It was also found that increasing the pollution radius from 65 to 119 p.m. boosted the removal percentage, bringing it up to 44% to 88.8%. To our knowledge, this is the first time that we have used this technique to extract minerals with a retention rate of more than 80%. This kind of natural zeolite rich in sodalite offers perspectives for the development of efficient new membrane structures based on natural zeolite or on natural porous materials.

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Conflict of Interests

The authors declare that there is no conflict of interests.

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