

Mexican natural zeolites: A low cost alternative to pigment retention

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ABSTRACT

Several materials such as synthetic zeolites, clays and aluminas were studied as sorbent pigments. Majority of materials need pre-treatment to be capable to absorb molecules on the porous structure. These treatments include thermal treatment, washing with several solvents, cation exchange, among others. At the same time, treatment increases the cost to use porous material as sorbent in some industrial process. An alternative of this synthetic materials are natural zeolites. In this work, some Mexican natural zeolites (clinoptilolite, mordenite and eriotnite) have been used as starting material for retain different pigments: basic fuchsine, violet crystal and eriochrom black T. Natural zeolites were characterized by X-ray diffraction, energy-dispersive X-ray spectroscopy, scanning electron microscopy and N₂ adsorption. Pigment adsorption capacity was determined by UV-Vis.

Keywords: mexican zeolites, pigments, basic fuchsine, violet crystal, eriochrom black T.

1 INTRODUCTION

The presence of pigments in water may have different environmental negative effects such as affection to industrial plants economy due to the necessity of more numerous and effective water treatment plants, reflection of sunlight that impedes aquatic organisms to live and grow, low quality of the treated water, non-soluble salts that cause blocking of process tube lines which, in some cases, forces the plant to be stopped for hours or days for reparation [1].

Some process as advanced oxidation, electrochemical coagulation, anaerobic treatment, microorganism degradation, flotation, chemical coagulation, membrane separation, and photo-degradation, were used to remove dyes from wastewater. Nevertheless, these process have some disadvantage as: production of toxic organic intermediates, technical limitations, high operational cost and lack of effective color reduction [2].

Zeolites are microporous crystalline aluminosilicates, which are widely used as sorbents, catalysts and ion-exchange materials [3-6]. A fundamental property of zeolites for these applications is their well-defined porous framework. Composition and framework of zeolite provides a distribution of electron density in such way that both Lewis and Brønsted can be present in zeolites. Thus, the

zeolites have played important roles in the Industry. For instance, the majority of the world's gasoline is obtained from the fluidized catalytic cracking (FCC) of petroleum using zeolite catalysts [7, 8]. The family of zeolites is numerous and at present approximately 200 structures are known. Each zeolite differs in the shape, size and distribution of pores, in the acidity strength, etc., [9-13] making possible the above mentioned applications. Thousands of papers have been devoted to zeolites and the number increases every day. This is comprehensible because, the zeolites physicochemical properties are easily modified by tuning simple parameters as the chemical composition or introducing organic molecules into the zeolite framework [14-20]. In this paper, we present the pigment absorption on mexican zeolites.

2 EXPERIMENTAL SECTION

There Mexican natural zeolites were used in this work: mordenite, clinoptilolite and eriotnite. All zeolites were calcined at 200 ° C for 12 hours. 1 g of each natural zeolite, as previously crushed were placed in 100 mL of a 2M NaCl solution and stirring at room temperature for 24 hours. The solids are separated by centrifugation and washed 3 times with 100 mL of deionized water. This exchange process was conducted for ten times to ensure the presence of sodium ions. Subsequently the zeolites were dried at 100 ° C for 12 hours, and proceeded to characterization.

The pigment adsorption process is performed using a quantity of 0.4 g of zeolite in 100 mL of a solution containing 100 ppm of each pigment. Natural zeolite was pretreated at 150 ° C for 12 h to remove 10-3 torr presnetes water molecules in the pores. The result solid was separated by centrifugation and dried at 323 K for 2 h. The remained solution was kept to determined the quantity of dye not retain into zeolite structure.

Materials were characterized by X-ray diffraction, energy-dispersive X-ray spectroscopy, scanning electron microscopy and N₂ adsorption. EDX, was performed using an EDX instrument (EDAX DX4 SUTW-USA, coupled to a Philips XLS30 ESEM high resolution scanning electron microscopy); the chemical composition was obtained by the average of five measurements for each sample. A powder diffractometer (Philips X'PERT PRO) coupled to a copper anode X-ray tube was used to identify compounds present in each sample. The K α 1 radiation (45 kV, 40 mA, $\lambda = 1.5406 \text{ \AA}$) was selected with a diffracted beam

monochromator and with a step size of 0.01" and a time per step of 0.9 s. The micrographs were acquired in a scanning electronic microscopy model FIB Quanta3D FEJ, with field emission cathode, in high vacuum. All nitrogen adsorption measurements were conducted using a BELSORP-max (BELL Japan Inc.) system at -196 °C. Samples were degassed under dynamic conditions (extra-dry air flow) over 24 h at 100 °C prior to adsorption measurements. BET specific surface areas were calculated from the N₂ adsorption isotherms. Ultraviolet-visible spectroscopy was performed using a Shimadzu Pharm Spec UV-VIS spectrometer.

3 RESULTS AND DISCUSSION

In Table 1 the elemental composition of the zeolite prior to treatment is shown with NaCl as determined by EDX. One can observe the presence of different compensation cations. For encapsulating dyes relizar and comparing the physicochemical properties of zeolites diferntes, were exchanged with sodium for ten cycles, the results are presented in Table 2.

In Table 2, the elemental analysis of the subsequent treatment with NaCl zeolites appears to determine the ion exchange capacity and the presence of sodium ion therein. It is observed that the ion exchange was achieved present, only in the case of zeolite eriotnita where part of calcium ion is present. Subsequent characterization analyzes were performed with the sodium zeolites.

Element	Clinoptilolite	Mordenite	Erotnite
C	50.29	11.23	10.76
O	41.82	65.31	62.81
Na	0.00	0.92	1.40
Mg	0.15	0.59	0.59
Al	1.35	2.84	4.60
Si	5.52	17.94	17.81
K	0.41	0.15	0.95
Ca	0.27	0.67	0.73
Fe	0.15	0.34	0.34
Cu	0.04	0.00	0.00
Si/Al	4.09	6.32	3.87

Table 1: Elemental composition and Si/Al ratio of natural zeolites.

Element	Clinoptilolite	Mordenite	Erotnite
C	48.69	13.56	9.45
O	44.18	50.35	60.26
Na	1.02	2.67	3.96
Al	1.04	4.48	5.63
Si	5.07	28.94	20.65
Ca	0.00	0.00	0.05
Si/Al	4.88	6.46	3.67

Table 2: Elemental composition and Si/Al ratio of natural zeolites after cation exchange.

Figure 1 compare the diffraction pattern of the zeolite clinoptilolite reported in the Database of Zeolite Structure (DZS) [21] with natural clinoptilolite, the presence of peaks characteristic of this structure is observed. In addition, characteristic peaks of quartz and 26.65° 20.04 are present. The fund does not line corresponds to an amorphous material. Calculating the percentage of the compounds identified in the samples was performed assuming that the sum of the areas under the diffraction peaks of each compound is proportional to the percentage of the compound. This assumption is valid since the elemental composition of the samples was the same in all cases (aluminosilicate), then, the absorption coefficient is the same [22]. Thus was obtained 82.00, 6.94, 11.06 % clinoptilolite, quartz and amorphous material respectively.

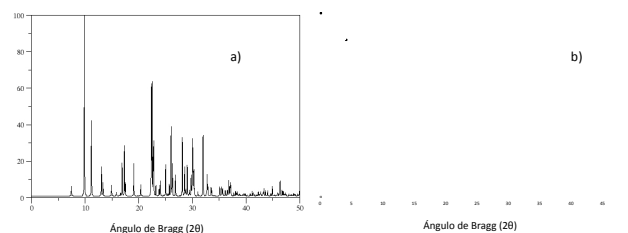


Figure 1. DRX of of a) mordenite reported in Database of Zeolite Structure (DZS) and b) natural clinoptilolite.

The pattern of X-ray diffraction of the mordenite zeolite is presented in Figure 2 show that peaks exist in the same positions as the theoretical pattern, however there is a nonlinear characteristic of amorphous solid background. No additional peaks due to other crystalline compounds are observed, is likely to eliminate cation exchange treatment other crystalline compounds. The percentage of zeolite mordenite and amorphous material of these being 95.77 and 4.23% respectively was determined.

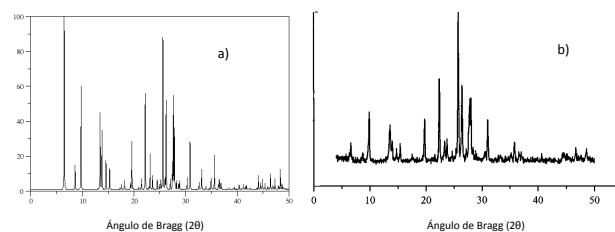


Figure 2: DRX of a) mordenite reported DZS and b) natural mordenite.

Figure 3 compares the diffraction pattern of the zeolite erionite in DBZS reported [21] pattern, the presence of peaks characteristic of this structure is observed. As zeolite clinoptilolite, quartz characteristic peaks at 20.10 and 26.68° occur. The fund does not line corresponds to an amorphous material. Eriotnita the percentage of zeolite and

amorphous material quartz these being 60.37, 15.87 and 23.76% respectively was determined.

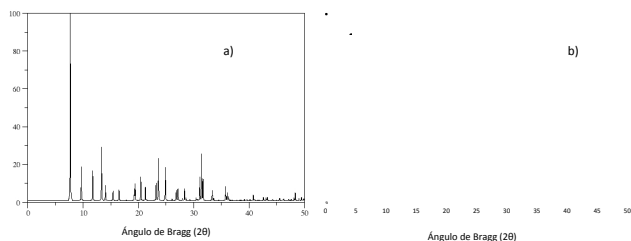


Figure 3: DRX of of a) mordenite reported in DZS and b) natural eriotnrite.

In Figure 4 micrographs presented natural zeolites. Exhibit various morphologies are generally amorphous. The morphology of the zeolite mordenite is irregular with some spherical particles with diameter of 3.5 μm , Figure 4a). Eriotnita morphology zeolite particles has quadrangular prism shaped lengths of 1 to 3 μm and faces 0.3 to 1 μm . Other irregularly shaped particles having diameter of 0.3 μm . In Figure 4c, the characteristic morphology of the zeolite clinoptilolite shown this polyhedra coffins shaped form defined faces with length and 4.3 μm .

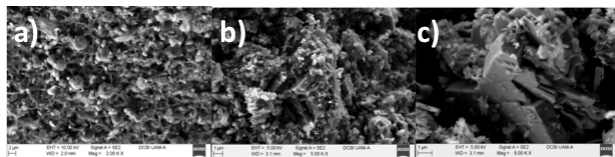


Figure 4. Microscopy of natural zeolites a) mordenite, b) eriotnrite c) clinoptilolite.

Figure 5 shows the adsorption isotherms of natural zeolites are shown. All the isotherms correspond to type I, characteristics of microporous compounds. All isotherms are concave to the axis of the relative pressure also all increase at low pressure. The plateau of each isotherm is practically horizontal, corresponding to microporous solids. Isotherms eriotnita and clinoptilolite, have hysteresis to varying degrees. The isotherm of the zeolite clinoptilolite has the highest hysteresis H3 corresponding to hysteresis characteristic of materials with pores formed by agglomerates parallel plate type. While eriotnita zeolite, exhibit little hysteresis type H1, characteristic of homogeneous sediment [23].

Additionally, an increase in nitrogen adsorption is observed, the result indicates a significant difference in the surface area of each zeolite. The values of surface area calculated with the BET method for clinoptilolite, mordenite and eriotnrite were 274.42, 123.45 and 308.87 m^2g^{-1} , respectively.

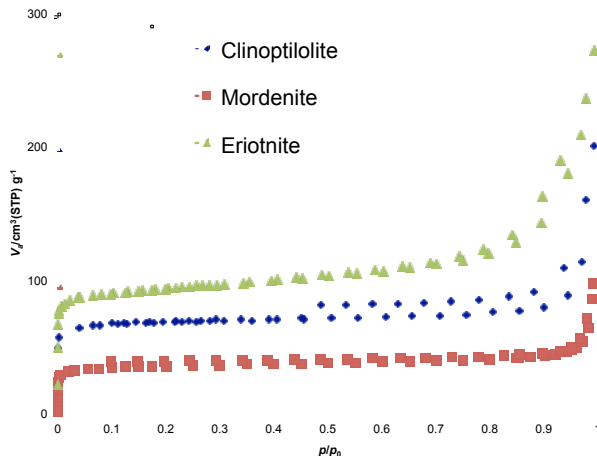


Figure 5. N_2 adsorption isotherms of natural zeolites.

Figure 6 shows the calibration curve of the pigments and the correlation coefficient obtained. This curve was possible to determine the pigment present in catidad remaining difference and calculate the percentage retained on each natural zeolite, the results are shown in Table 3.

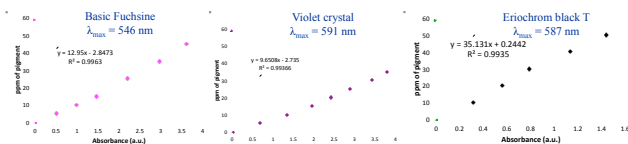


Figure 6. Calibration curves of pigments.

Greater retention of basic fuchsin is achieved with clinoptilolite zeolite, the greatest adsorption of violet crystal pigment is obtained for eriotnrite and finally the greater adsorption for eriochrom black T was obtained for clinoptilolite. Nevertheless, all natural zeolites achieve adsorption greater than 96% for eriochrom black T. Indeed, the physicochemical properties of zeolites as pore size limit the adsorption of some dyes as violet crystal or fuchsin adsorbed in mordenite. The size of the molecule could result in steric impediment resulting in low retention. Still, this is greater than 60% basic fuchsin and violet crystal pigments.






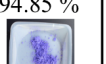
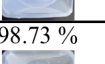
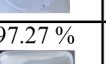
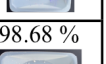
	Clinoptilolite	Mordenite	Eriotnrite
Basic fuchsin	89.60 % 	60.32 % 	87.49 % 
Violet crystal	90.65 % 	70.46 % 	94.85 % 
Eriochrom black T	98.73 % 	97.27 % 	98.68 % 

Table 3. Percent retention of pigments in natural zeolites.

4 CONCLUSIONS

Zeolites structure remained after the adsorption of the pigment. Retention of over 90% was achieved for all zeolites with black eriochrom T. A retention of over 90% crystal violet with mordenite and clinoptilolite was achieved. Thermal stability of 700 °C of natural zeolites.

Natural zeolites may be considered an option in retaining textile dyes, particularly Mexican natural zeolites having low cost and high purities, making them a potential candidate to resolve this problematic.

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