Characterization of the clinoptilolite zeolite and its potential application as the basis of a filtering system for the oil industry

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Abstract. Zeolites are minerals with a wide application in the field of Petrochemicals, mainly as catalysts, in oil refining processes, but their structure and composition also make them good filter materials, for that reason they are used in oil refining processes. Water treatment, when an oil well is exploited, a large amount of water is obtained from the reservoir, known as production water, which is treated and reused in injection processes in the same reservoir, the water from production, contains a high amount of organic compounds, which in many cases prevent an adequate implementation of treatments in the wells, which is why a removal of these organic molecules must be made, in this research, the synthetic zeolite clinoptilolite-Na is used, as a filtration system for organic compounds, using methylene blue as a reference, with which retentions were obtained up to 90%.

1. Introduction
The processes of exploitation of an oil field, bring with them two additional by-products to oil, which are gas and water; this water is known as production water and has in its composition a large number of organic compounds, derived from the hydrocarbon of the reservoir, in addition to metals and salts. The oil industry has this fluid to reinject in the reservoirs in its different treatment or even its disposal in bodies of water, but for both cases, its previous treatment is required, the organic compounds present in its composition, are a problem both for their reinjection and for their disposal in ecosystems. For example, only in Castilla field in Colombia, the production of water is close to 4 million barrels, which is why it is necessary to develop technologies associated with the treatment of water originating in the reservoir. Currently, materials such as polymers, nanoparticles, and zeolites are used.

This research focuses precisely on the synthetic zeolite clinoptilolite. This type of zeolite is part of the heulandite group, is composed of crystalline aluminosilicates, has a porous structure, and has great adsorption capacity, which has even been used in the separation of gas mixtures. In the following investigation, the action of Clinoptilolite is evaluated, as a filtration system for organic compounds present in production waters of the oil industry, carrying out the respective characterization of the material and by means of methylene blue removal tests [1-7].

2. Materials and methods
The zeolite analyzed was obtained through a local company, in the city of Bucaramanga, Colombia. The material was characterized by X-ray diffraction (DR-X), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and a methylene blue retention test was performed to evaluate its ability to filter organic compounds.
2.1. X-ray diffraction characterization
Zeolite were characterized by X-ray powder diffraction (XRD), using Bruker D8 Advance equipment with DaVinci geometry, and the PDF-4 database [8].

2.2. Scanning electron microscopy characterization
The zeolite was placed on metallic stubs with carbon adhesive tape and coated with gold. The Field Emission Gun (FEG) scanning electron microscope QUANTA FEG 650 was used. For analysis, the EDAX APOLO X Detector resolution of 126.1 eV (in. Mn Ka) was used to perform EDS analysis and EDS Genesis Software semi-quantitative information on chemical elements.

2.3. Methylene blue removal test
A methylene blue concentration calibration curve (ppm) vs Absorbance at 610 nm was assembled, for the 0.1 ppm, 0.5 ppm, 1 ppm, 1.5 ppm, and 2 ppm methylene blue solutions; obtaining, by linear regression, the equation that correlates these parameters. The absorbance was measured using the Spectroquant Prove 600 equipment.

Approximately 80 g of zeolite were taken, they were heated to 100 °C for 1 hour, then they were left to cool for 30 minutes in a desiccator with active silica; this was done with the aim of eliminating moisture present. Approximately 5 g of zeolite were taken and they were deposited on a qualitative filter paper; the filter paper-sample system was installed in a funnel, in which 15 mL of a 2 ppm solution of methylene blue was filtered by gravity. It measured the absorbance at 610 nm, and it was compared with the curve obtained in step 1 to know the concentration of methylene blue present in it. To take into account the retention capacity of the filter paper, the same filtration was carried out to a system in the absence of a zeolite sample. This test was performed in triplicate.

3. Results and discussion
In order to know the type of zeolite used in the study, an DR-X analysis was carried out. Figure 1 corresponds to the analysis of the crystalline phases of the zeolite, using the PDF-4 database [8], managing to identify the compounds inorganic substances present in the sample (see Table 1). According to this analysis, the working zeolite is a Clinoptilolite-Na, in addition, other common minerals such as quartz, muscovite and albite are present [6-9]. With the certainty that we are working with Clinoptilolite, this type of minerals is mainly constituted by SiO₄ and AlO₄, the load of the mineral is compensated by sodium atoms, Within the clinpolyolite family, zeolites can be found where these sodium atoms are replaced by potassium or magnesium. [9,10], we proceeded to carry out the methylene blue retention evaluations.

Figure 1. X-ray diffraction pattern for zeolite with analysis PDF-4.
Table 1. Crystal phases analysis with PDF 4 database.

| Pattern #   | Compound name                        |
|-------------|--------------------------------------|
| PDF 01-070-7344 | Quartz                              |
| PDF 01-074-2764 | Sodium tecto-alumosilicate, EMT (Na) |
| PDF 01-080-0464 | Clinoptilolite-Na                    |
| PDF 01-070-3666 | Muscovite-3T, syn                    |
| PDF 01-070-3752 | Albite                              |

A morphological analysis of the zeolite was carried out by means of SEM. Figure 2, in addition to a compositional analysis by EDS, Table 2, in these it can be observed that it has a heterogeneous particle size, which can range from 10 microns to more than 100 microns. The EDS confirms the presence of aluminum silicates typical of a zeolite, as well as reveals a large amount of iron, probably as oxides, and it also reveals that the sample contains certain traces of carbon as impurities [1-5].

![SEM image of clinoptilolite used in research.](image)

Table 2. EDS results of the zeolite used.

| Element | % weight |
|---------|----------|
| C       | 1.51     |
| O       | 12.64    |
| Na      | 0.80     |
| Mg      | 1.35     |
| Al      | 3.88     |
| Si      | 15.24    |
| Ca      | 1.21     |
| Fe      | 63.38    |

The first step to evaluate the retention of methylene blue by zeolite is the construction of the curve that relates the concentration of methylene blue, with the absorbance measured at 610 nm, the resulting graph is shown in Figure 3. From these data, the equation that relates the concentration of methylene blue to the absorbance of the solution was proposed, Equation (1).

Methylene blue (ppm) = 0.9556(Abs 610nm) + 0.0262.  \( (1) \)

The results of the methylene blue retention test are shown in Table 3. The test was performed with methylene blue, observing that it only retains 11\% of the initial concentration, which corresponds to 0.22 ppm, on the other hand zeolite, retains about 95\% of the concentration, which corresponds to about 1.92 ppm, the tests with zeolite were carried out in triplicate, according to the results, the material is capable of retaining organic molecules, with aromatic nature, such as many of which are found in the production waters of the oil industry.

In addition to these results obtained in the treatment of water that contains an organic molecule, such as methylene blue, we can add the investigations that have been done with these minerals in the removal of metals [11-13], since it is another of the pollutants that continue the production waters of oil fields,
and affect both the aquifer ecosystems and the health of operations, as well as the normal operation of treatment to the wells, with this mineral, it is possible to think of a removal system both of organic and inorganic pollutants.

![Figure 3. Methylene blue vs. absorbance at 610 nm.](image)

| Table 3. EDS results of the zeolite used. |
|------------------------------------------|
| Sample                  | Initial absorbance | Final absorbance | Methylene blue (ppm) | Methylene blue remotion (ppm) | Methylene blue (% remotion) |
|-------------------------|--------------------|------------------|----------------------|-----------------------------|-----------------------------|
| Filter paper            | 2.073              | 1.84             | 1.78                 | 0.22                        | 11.06                       |
| Clinoptilolite 1        | 2.073              | 0.07             | 0.09                 | 1.91                        | 95.35                       |
| Clinoptilolite 2        | 2.073              | 0.06             | 0.08                 | 1.92                        | 95.82                       |
| Clinoptilolite 3        | 2.073              | 0.07             | 0.09                 | 1.91                        | 95.35                       |

4. Conclusions
According to the X-ray diffraction analysis of the zeolite, the sample used is a clinoptilolite, this material presented very good results as a methylene blue filtering system, retaining about 95% of the initial concentration of the solution. study, for this reason it is postulated as a promising material for the design of filtration systems for production water in the oil industry.

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