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"Investigating the Properties of Natural Heulandite Zeolite from Qom Mines for the Removal of Methylene Blue and Methyl Orange Dyes from Aqueous Solutions"

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ABSTRACT

This study evaluates the effectiveness of natural adsorbents in removing water pollutants. Natural heulandite zeolite from Qom mines was sampled, prepared, and tested for the removal of methylene blue (MB) and methyl orange (MO) dyes from aqueous solutions. The zeolite was characterized using XRD, XRF, and ICP analyses, confirming its composition as $Ca_{1.23}(Al_2Si_7)O_{18}\cdot 6H_2O$ (or $CaAl_2Si_7O_{18}\cdot 6H_2O$), with heulandite as the primary component. The dye removal efficiency was measured via UV-Vis spectroscopy at wavelengths of 665.0 nm (MB) and 465.0 nm (MO). Results demonstrated removal efficiencies of 100% for MB (a cationic dye) and 43.7% for MO. The near-complete adsorption of MB suggests that heulandite zeolite is highly effective for cationic dye removal, potentially reducing energy consumption in water purification processes.

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1. Introduction

The uncontrolled increase in hazardous pollutants, such as heavy metals and synthetic dyes, in water sources poses a serious threat to public health and ecosystems. Among various water treatment methods, **adsorption** is widely preferred due to its simplicity, cost-effectiveness, and high efficiency [1–3].

Zeolites, aluminosilicate minerals hydrated with alkali or alkaline earth metals (e.g., Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}), are particularly notable for their applications in ion exchange, water purification, and wastewater treatment. Their unique porous structure and chemical properties make them effective for pollutant removal, including disinfection, deodorization, and chemical sieving [4–8].

Recent studies highlight the potential of modified zeolites for dye adsorption:

- Pinedo-Hernández et al. (2019) achieved **87.02% removal** of brilliant blue dye using Fe^{3+}/Fe–Cu nanoparticle-modified clinoptilolite [9].
- Radoor et al. (2021) reported a **maximum adsorption capacity of 4.31 mg/g** for methylene blue (MB) using PDADMAC-modified ZSM-5 zeolite under optimized conditions (pH 10, 30°C) [10].
- Alver et al. (2012) demonstrated **93% removal** of anionic azo dyes using 2-HMDA-modified heulandite [11].
- Briao et al. (2017) achieved an exceptional **1217.3 mg/g adsorption capacity** for crystal violet dye using mesoporous ZSM-5 [12].

Further advancements in zeolite-based adsorption include:

- Imessaoudene et al. (2023) employed a **23 full factorial design** to optimize Congo red dye removal, identifying key factors (adsorbent dose, initial concentration, ionic strength) [13].
- Gadore et al. (2023) reviewed the synthesis and application of zeolite nanocomposites as **adsorbents and photocatalysts** for dye removal [14].

Methylene blue (MB) (Figure 1), a cationic heterocyclic dye widely used in textiles, is particularly concerning due to its toxicity. Exposure can lead to **cyanosis, tachycardia, and shock** in humans and other organisms [15, 16]. Given its persistence and health risks, efficient removal methods are critical.

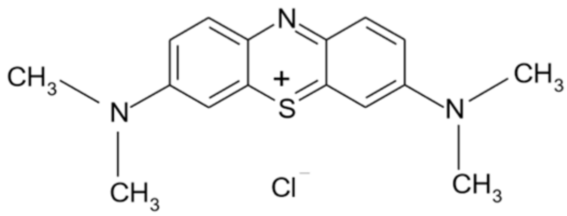

Figure 1. Chemical structure of Methylene Blue Dye.

Methyl orange (Figure 2) is one of the azo and anionic dyes, with excessive application in the textile industry. It is very resistant to light and washing and is not easily degradable. This dye forms strong, non-biodegradable complexes and is not removed by conventional wastewater treatment process. These types of dies can cause severe health hazards to human beings, such as dysfunction of the kidney, reproductive system, liver, brain, and central nervous system, and thus should be treated before discharging into the receiving body of water [17].

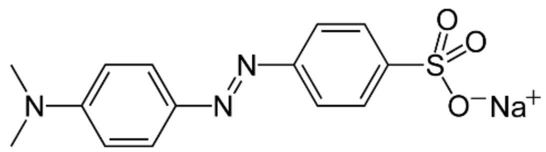

Figure 2. Chemical structure of Methyl Orange Dye.

In this study, **natural heulandite zeolite** from Qom mines was employed as an adsorbent for the removal of **methylene blue (MB)** and **methyl orange (MO)** dyes from aqueous solutions. Zeolites are highly effective adsorbents due to their **large surface area**, **microporous structure**, and **negatively charged framework**, which facilitates the adsorption of positively charged compounds and ions. These properties make heulandite particularly suitable for cationic dyes like MB and MO.

The zeolite was characterized using **XRF, XRD, and ICP** to confirm its composition and structure. The dye removal efficiency was evaluated via **UV-Vis spectroscopy**, where dye concentrations were quantified using calibration curves derived from standard solutions. The removal efficiency was then calculated based on the reduction in dye concentration post-treatment.

This approach demonstrates the potential of natural heulandite zeolite as a **low-cost, energy-efficient** adsorbent for water purification, offering a sustainable alternative to conventional treatment methods.

2. Experimental Section

2.1. Zeolite Preparation

Natural Heulandite zeolite rock was collected from the Manzariyeh region in Qom province. It was powdered and sieved to 200 mesh (Figure 3) to use in dye removal experiments.

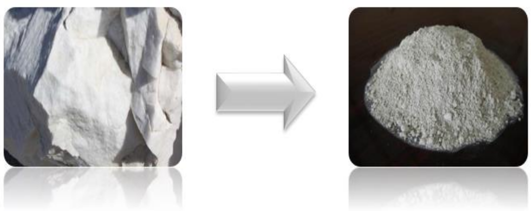

Figure 3. Preparation of Natural Zeolite.

2.2. Preparation of Methylene Blue and Methyl Orange Solutions

Stock solutions of methylene blue (MB) and methyl orange (MO) were prepared at 100 mg/L in distilled water. Serial dilutions were then performed to obtain concentrations of 20.0, 10.0, and 2.5 mg/L for each dye**.**

2.3. Dye Removal Procedure

1. Adsorption Step:

- A total of 25 mL of each dye concentration was mixed with 40 mg of natural heulandite zeolite in glass vials.
- The mixtures were agitated on an orbital shaker for 24 hours at room temperature to ensure equilibrium adsorption.

2. Settling and Filtration:

- After agitation, the suspensions were allowed to settle for 72 hours (3 days).
- The supernatant was filtered through Whatman No. 1 filter paper to separate the zeolite particles.

3. Analysis:

- The filtrate was analyzed using a UV-Vis spectrophotometer to determine residual dye concentrations.

2.4. Equipment

- Zeolite characterization: X-ray fluorescence (XRF), X-ray diffraction (XRD), and inductively coupled plasma (ICP) spectroscopy.
- Dye concentration measurement: PerkinElmer Lambda 35 UV-Vis spectrophotometer (wavelength range: 190–1100 nm).

3. Results and Discussion

3.1. Zeolite Identification

3.1.1. X-Ray Diffraction (XRD) Analysis

The XRD pattern of the mineral sample (Figure 4) was recorded over a **2θ range of 4–70°**, covering the diagnostic peaks for zeolite identification. Key findings:

- **Primary phases**: The sample predominantly contained **heulandite-type zeolite** (two variants), with minor impurities of **calcite, feldspar, and quartz**.
- **Heulandite composition**:
    - **Variant 1**: Ca1.23(Al2Si7)O18·6H2OCa1.23 (Al2Si7)O18·6H2O (peaks at **2θ = 10–40°**).
    - **Variant 2**: CaAl2Si7O18·6H2OCaAl2Si7 O18·6H2O (peaks at **2θ = 10–60°**).
- **Phase dominance**: The higher intensity of heulandite peaks compared to other phases confirms it as the **major component** of the sample.

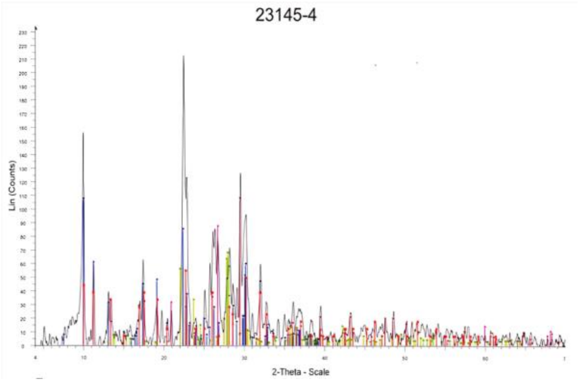

Figure 4. XRD Pattern of Natural Zeolite.

3.1.2. X-Ray Fluorescence (XRF) Analysis

XRF spectroscopy was employed to determine the **elemental composition** of the natural heulandite zeolite sample. This technique provides both **qualitative** (element identification) and **semi-quantitative** (relative abundance) data, particularly suited for mineralogical analysis.

Methodology:

- **Sample Preparation**: The zeolite sample was homogenized and finely ground to ensure analytical consistency.
- **Analysis Principle**:
    - **Qualitative**: Identified elements based on characteristic X-ray emission wavelengths.
    - **Quantitative**: Determined relative concentrations using peak intensities of these emissions.

Key Findings:

1. Oxide Composition:

- Elements were primarily detected as their oxides (Table 1), consistent with typical mineralogical reporting.
- **Silica** **(SiO_2)** and **alumina** **(Al_2O_3)** dominated the composition, confirming the aluminosilicate framework of heulandite.

2. Si/Al Ratio Implications:

- A **higher Si/Al ratio** correlates with:
    - Increased **hydrophobicity**, enhancing affinity for organic pollutants (e.g., dyes).
    - Preference for **monovalent ions** (e.g., Na^+, K^+) over divalent ions (e.g., Ca^{2+}, Mg^{2+}) in ion-exchange processes, relevant to water treatment applications.

3. Complementarity with XRD:

- Combined XRF and XRD data (Section 3.1.1) validate the sample's zeolitic properties and predict its adsorption behavior.

Table 1. Percentage of Compounds in Heulandite Zeolite Using XRF Analysis.

Composition	Weight percentage	Composition	Weight percentage	Composition	Weight percentage
Na_2O	5.75	Cl	0.26	SrO	0.30
SO_3	0.15	Fe_2O_3	0.88	ZnO	N.D
TiO_2	0.11	CuO	N.D	SiO_2	55.4
MnO	N.D[b]	La&Lu	1.0<	CaO	5.36
L.O.I[a]	15.6	Al_2O_3	14.52	Cr_2O_3	N.D
MgO	1.01	K_2O	0.66	PbO	N.D

a. Loss on Ignition
b. Not Detected

As shown in Table 1, SiO_2 and Al_2O_3 have abundances of 55.4% and 14.52%, respectively, indicating the presence of a zeolite type in this mineral sample. After alumina and silica, the alkali and alkaline earth metal oxides Na_2O and CaO have the highest values at 5.75% and 5.36%, respectively. Given the high amount of calcium and the results of the XRD analysis, it can be concluded that zeolite is a calcium type. Since the amount of salt in the soil of the sample region is high, NaCl impurities can be the reason for the high amount of sodium in this sample. It is noteworthy to mention that the Si/Al ratio in Heulandite zeolites is less than 4, and the results of the XRF in Table 1 also prove that [18].

3.1.3. Inductively Coupled Plasma (ICP)

To obtain a more accurate percentage of the elements present in the mineral sample, the Inductively Coupled Plasma method was used. For the sake of simplification, the values of some elements as their oxides are reported in Table 2. The data is related to elements that have a higher concentration in the sample, and it is preferred to use XRF data for these kinds of elements. In this analysis, some elements, such as the ones shown in Table 3, are present in smaller quantities. It is worth noting that the ICP analysis is generally suitable for determining small values down to the ppm level. There are large errors for higher values, and they are not appropriate for conclusions.

Table 2. Percentage of Compounds in Zeolite Using ICP Analysis.

Composition	Weight percentage
Al_2O_3	8.29
CaO	4.4
Fe_2O_3	1.0
K_2O	0.53
MgO	0.69
Na_2O	4.29

Table 3. Amount of Elements in Zeolite Using ICP Analysis.

Element	ppm	Element	ppm	Element	ppm	Element	ppm	Element	ppm
As	8.0	Cu	20.0	Li	6.3	S	375.0	U	1.0
B	3.0	Dy	3.0	Mn	79.0	Sb	0.2	V	21.0
Ba	195.0	Er	1.9	Mo	0.1	Sc	2.7	W	1.0
Be	1.8	Eu	0.1	Nb	7.7	Sm	1.7	Y	20.0
Bi	0.2	Ag	0.1	Nd	6.8	Sn	4.0	Yb	1.9
Cd	0.2	Ga	9.5	Ni	3.6	Sr	196.0	Zn	22.0
Ce	14.0	Gd	0.8	P	131	Ta	19.3	Zr	53.0
Co	0.8	Hf	3.1	Pb	22.0	Th	7.6		
Cr	7.0	La	8.4	Pr	3.1	Ti	587.0		

As can be seen in Table 3, elements such as strontium, titanium, sulfur, barium, phosphorus, and manganese have higher concentrations comparing other elements. Based on the values of the elements in Table 3, it can be deduced that there are no economically valuable elements in this zeolite.

3.2. Efficiency of Dye Removal by Natural Heulandite Zeolite using UV-Vis Spectroscopy

3.2.1 Methylene Blue Removal

To measure the effectiveness of Heulandite zeolite, the concentration of the methylene blue dye in an aqueous solution was measured using UV/Vis spectroscopy at a wavelength of 665 nm, before and after treatment with Heulandite zeolite at different concentrations. Figure 5 shows the UV/VIS calibration curve (linear range) for different concentrations of methylene blue. The results of this analysis are presented in Table 4.

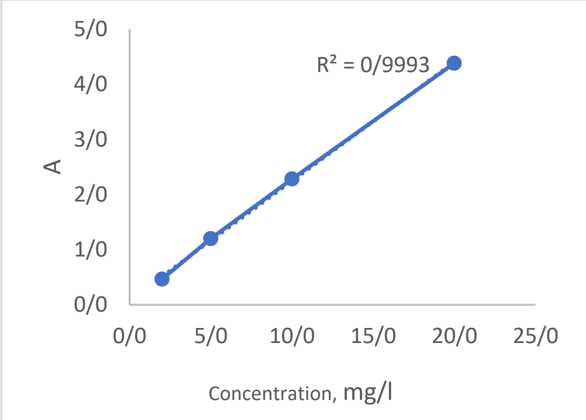

Figure 5. UV/VIS Calibration Curve of Methylene Blue Concentrations.

Table 4. Results of UV/VIS spectroscopic analysis of Methylene Blue treatment with Zeolite.

Concentration of Methylene Blue before treatment (mg/)	Concentration of Methylene Blue after treatment (mg/l)	Absorbent (natural zeolite) (mg)	Removal percentage (%)
2.0	0.0	40.0	100.0
5.0	0.0	40.0	100.0
10.0	0.0	40.0	100.0
20.0	0.0	40.0	100.0

As in Table 4, the investigated zeolite could effectively remove the methylene blue dye in all studied concentrations of 2 to 20 ppm from the aqueous solution.

Because of the negative charges within their network, Zeolites can effectively adsorb positively charged compounds and elements [19]. As the methylene blue dye is a cationic dye, this zeolite was able to remove almost 100% of the dye from the solution.

The reasonable price of this type of zeolite, its availability, and its naturalness along with 100% removal of methylene blue pollutants are among the advantages of this research compared to similar research [20].

3.2.2 Methyl Orange Removal

To measure the effectiveness of Heulandite zeolite, the concentration of methyl orange dye in the aqueous solution was measured using UV/Vis spectroscopy at a wavelength of 464 nm, before and after treatment with the zeolite.

Reduction of the absorption of this dye at 464 nm after treatment with zeolite means that the concentration of the dye is reduced using the studied absorbent. The calibration curve for different concentrations of methyl orange is shown in Figure 6. Data from this experiment is given in Table 5.

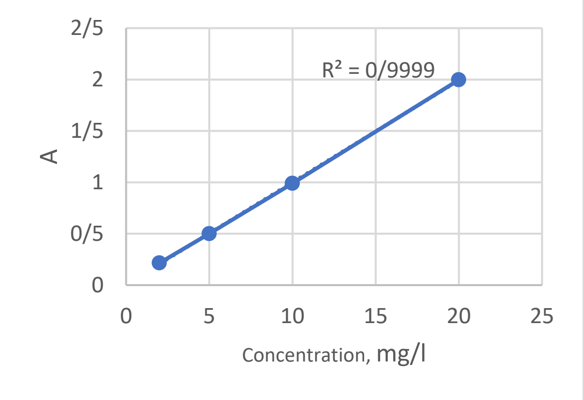

Figure 6. UV/VIS Calibration Curve of Methyl Orange Concentrations.

Table 5. Results of UV/VIS spectroscopic analysis of Methyl Orange treatment with Zeolite.

Concentration of Methyl Orange before treatment (mg/l)	Concentration of Methyl Orange after treatment (mg/l)	Absorbent (natural zeolite) (mg)	Removal percentage (%)
2.0	1.37	40.0	31.5
5.0	3.26	40.0	34.8
10.0	6.1	40.0	39.0
20.0	11.25	40.0	43.75

As can be seen in Table 5, the removal efficiency increases with an increase in the concentration of methyl orange. Considering that methyl orange is an anionic dye, and zeolites are capable of adsorbing positively charged compounds, it can be assumed that dyes are adsorbed by weak forces such as Van der Waals interactions. So, it can be said that the dye removal efficiency is relatively suitable.

4. Conclusion

This study demonstrates that natural heulandite zeolite from Qom mines serves as an effective adsorbent for removing synthetic dyes from contaminated water. Through comprehensive characterization using XRD, XRF, and ICP techniques, the material was identified as a calcium-rich heulandite-type zeolite with a high silicon-to-aluminum ratio. This feature enhances its affinity for cationic pollutants. The adsorption experiments revealed exceptional performance in methylene blue removal, achieving complete elimination from solution, while showing more modest efficiency for methyl orange. These results highlight the material's suitability for treating wastewater containing cationic dyes, where its natural ion-exchange capacity and porous structure prove advantageous.

The superior adsorption of methylene blue compared to methyl orange can be attributed to the zeolite's negatively charged framework, which strongly attracts the positively charged MB molecules. This selectivity suggests potential energy savings in treatment processes targeting cationic contaminants. While the unmodified zeolite shows limited effectiveness for anionic dyes, the findings open possibilities for future research into surface modifications that could broaden its applicability. The demonstrated performance of this locally sourced, natural material offers a promising and sustainable alternative to synthetic adsorbents, particularly for regions with abundant zeolite resources seeking cost-effective water treatment solutions.

Acknowledgments

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