Removal of Fe\(^{2+}\) and Mn\(^{2+}\) from Water by Using Mining Rock Wastes and Their Synthesized Zeolites

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To cite this article:

Received: August 13, 2022; Accepted: January 25, 2023; Published: February 4, 2023

Abstract: The process of using mining rock waste as raw material to synthesis zeolite species is a viable alternative. Such process is minimizing serious impact of mining wastes on the environment and solving environmental problems such as water purification. In the present study, faujasite (NaX) and sodalite – cancrinite (sod-can) zeolites were successfully synthesized by hydrothermal crystallization using green siltstone, mudstone and black shale of mining rock wastes from Abu Tartur phosphate mine, western desert, Egypt. The raw materials as well as synthesized zeolites were characterized by means of X-ray Diffraction (XRD), Fourier Transform Infrared (FTIR), X-ray Fluorescence (XRF), Scanning Electron Microscopy (SEM), Thermogravimetry (TG), Differential Thermal Analysis (DTA) and Brunauer–Emmett–Teller (BET). Raw material (black shale) and synthesized zeolites (Na-X) faujasite were examined as heavy metal (Fe and Mn) adsorbent from aqueous solution. The results show that Na-X faujasite is very faster and higher in the up taking of Fe\(^{2+}\) and Mn\(^{2+}\) ions relative to the black shale absorbent or even the synthesized sodalite-cancrinite. Fe\(^{2+}\) and Mn\(^{2+}\) adsorption onto black shale absorbent and synthesized faujasite followed Langmuir isotherm, however, Freundlich isotherm model is accepted in the case of sodalite-cancrinite adsorbent. The adsorption kinetics of Fe\(^{2+}\) and Mn\(^{2+}\) onto the studied samples follow pseudo-second order model indicating chemical interaction (chemisorption) adsorption process.

Keywords: Waste Rocks, Zeolite, Heavy Metals, Adsorption, Sodalite-Cancernite, Isotherm

1. Introduction

"The synthesis of crystalline aluminosilicate zeolites can be carried out from clay minerals, such as kaolinite" [1-3], halloysite [4], illite, smectite, inter-stratified illite - smectite [5], montmorillonite [6] and bentonite [7, 3].

"Zeolites are widely used for different applications. Several properties account for their commercial use: they are good adsorbents, excellent solid catalysts and show a very high selectivity. They are utilized in the recovery of our environment, such as removal of heavy metals from the environment, e.g. cobalt, zinc, copper and manganese ions" [8].

This paper concerns with the evaluation and applications of both mining rock wastes and their synthesized products as absorbents for removal of heavy metals ions Fe\(^{2+}\) and Mn\(^{2+}\) from artificial or natural polluted effluents as a potential remediation alternative for the purification of polluted waters. In order to achieve the above aims, the following processes must be performed:

1. Study the transformation of geological materials (Green siltstone, mudstone and black shale waste) to zeolite, via alkaline fusion prior to hydrothermal reaction.
2. Study the characterization of both the raw materials and their synthesized zeolite products by, X-ray
Fluorescence (XRF), X-Ray Diffraction (XRD) Analysis, Fourier Transform Infrared Spectroscopy (FT-IR), Scanning Electron Microscope (SEM), Thermal analysis (TGA, DTA and DrTGA) and the surface area of Brunauer-Emmett-Teller (BET).

3) To examine the effectiveness of the raw materials and their synthetic zeolites as sorbents in removing heavy metals (Fe$^{2+}$ and Mn$^{2+}$) from artificial polluted water.

4) To understanding the conditions under which zeolites form in the natural environment, by using the knowledge and techniques gained during the study of the hydrothermal synthesis of zeolites.

2. Materials and Methods

The rock waste materials of (illite rich) green siltstone, mudstone (Quseir Formation, Hindaw Member) and black shale (smectite-rich) belonging to Duwi Formation from Abu Tartur phosphate mine are used as sources of aluminosilicate. These materials were calcinated to temperatures up to 900°C to obtain a more reactive phase under chemical treatments, with the loss of structural water. Only a small part of AlO$_6$ octahedra is maintained, while the rest are transformed into much more reactive tetra- and penta-coordinated units. Calcinated clays were used as starting materials for the synthesis of zeolite types with other reagents used in the activation of the raw materials were sodium hydroxide (NaOH) as pellets (99.99%, Aldrich Chemical Company, Inc.) and distilled water.

The standard solutions of Fe$^{2+}$ and Mn$^{2+}$are prepared by dissolving a known weight of FeSO$_4$·7H$_2$O and MnSO$_4$·H$_2$O respectively in deionized water. The Fe$^{2+}$ and Mn$^{2+}$ concentrations are determined using Atomic Absorption Spectrophotometer (AAS) Perkin Elmer at Geology Department, Assiut University. The results are expressed as ppm for Fe$^{2+}$ and Mn$^{2+}$.

3. Batch Adsorption Experiments

To perform the adsorption isotherm experiments, several solutions with different concentrations of Fe$^{2+}$ and Mn$^{2+}$ (50–300 ppm) are prepared by dilution of the stock synthetic standard solution. In individual Erlenmeyer Flasks (50 mL), 0.1 g of sorbent was weighted and added to 25 mL of solution with different Fe$^{2+}$ and Mn$^{2+}$ concentrations. The solution was well stirred to ensure that equilibrium was reached. The supernatants are filtered to remove suspended solids. The filtrates were placed in polyethylene bottles to determine directly the remaining concentrations of Fe$^{2+}$ and Mn$^{2+}$ using Atomic Absorption Spectrophotometer (AAS).

4. Preparation of Zeolites

Zeolite synthesis is conventionally developed by hydrothermal crystallization under alkaline conditions, which has been reported by several researchers and technical articles.

In general, the conversion of the raw materials into zeolitic materials was carried by two ways:

1) Conventional hydrothermal synthesis.

2) Alkaline fusion prior to hydrothermal synthesis.

According to Rios [9], "the direct treatment of the raw materials using alkaline solutions could be quite time consuming, energy intensive and/or environmentally unfriendly, which can be overcome by using the alkaline fusion approach".

Alkaline fusion followed by hydrothermal reaction

Alkaline fusion followed by hydrothermal treatment method was used for synthesis zeolite from rock waste of Abu Tartur phosphate mine, Egypt. Alkaline fusion plays an important role in enhancing the hydrothermal conditions for synthesis zeolites, as well as larger amounts of aluminosilicates can be dissolved.

The synthesis procedures:

1) Dry mixing for 30 min of black shale or green siltstone from the mining rock waste with NaOH (pellets) in the raw material/activator ratio=1:1.2 in weight.

2) The resultant mixture was fused at 600°C for 1 h. The alkaline reagent added to the raw rock material acts as an activator agent during fusion. Some of the inert crystalline phases in the raw materials can be fully reacted.

3) The fused product was ground in agate mortar and then 4.40 g of it was dissolved in distilled water in the case of normal Zeolite, or Mg-chloride solution in the case of Mg-Zeolite (ratio = 1/4.9) under stirring conditions to form the amorphous precursors. "The amount of reagents used for the preparation of the hydrogels were based on previous literatures" [10, 9, 11, 12].

4) Hydrogels were aged under static conditions during 24 h, then transferred to PTFE (polytetrafluoroethylene = Teflon) bottles of 100 ml and/or 150 ml for hydrothermal reactions.

5) The hydrothermal reaction was performed under static conditions, at the temperature required of 80°C to faujasite synthesis, or 150°C to synthetic sodalite-cancerinite for different reaction times (24, 48, 72 h).

6) The reactors were removed from the oven at the scheduled times and were quenched in cold water to stop the reaction.

7) Then, the reaction mixtures were filtered and washed with distilled water to remove excess alkali (pH <11). Finally, the samples were dried in oven at 80°C overnight. The dried samples were weighed and kept in plastic bags for characterization.

A simple scheme of the crystallization of an amorphous aluminosilicate hydrogel to zeolites is given in Figure 1.
Figure 1. Scheme of the crystallization of an amorphous aluminosilicate hydrogel to form zeolites Faujasite and sodalite - cancrinite (modified after Cundy and Cox [13]).

5. Results & Discussion

5.1. Characterization of Raw Materials and Synthetic Products

Generally, the characterizations of the used raw materials and their synthesized zeolites have to provide information on: its structure and morphology, chemical composition, ability to adsorption and retain molecules, and ability to chemically convert those molecules.

5.1.1. X-ray Diffraction (XRD)

Smectite is the predominant clay mineral encountered in the black shale sample from Abu Tartur phosphate mine and is identified by a series a basal at 2θ 5.67°, 17.62°, 19.85°, and their 29.38° and their corresponding d-spaces 15.92, 5.03, 4.47 and 3.04 respectively. Kaolinite is represented by weak peak at 2θ 12.22° and d-space 7.24. Quartz is also recorded in the raw material at 2θ 26.64° peak and d-space 3.35 (Figure 2A). After calcination to 900°C, all clay peaks are disappeared.

An almost complete transformation of the starting clay rich raw materials into faujasite-type zeolite of high purity occurred after hydrothermal reaction at 80°C (Figure 2B). However, relictic quartz of the starting materials still remains in the synthesized products. Complete disappearance of the characteristic peaks of clay minerals, accompanied by gradual decrease in peak intensity of quartz, and the appearance of zeolites was recorded after 48 h and showing an increase in the intensity of characteristic peaks at 48 h (Figure 2B). The broad peaks at around 5.99°, 9.91, 11.64°, 15.35°, 19.99, 23.24°, 28.0°, 30.21, 30.89, 31.92°, 33.52° 2θ are consistent with faujasite framework.

The hydrothermal treatment of smectite – rich shale at 150°C, for 48 h resulted in the co-crystallization of sodalite - cancrinite (Figure 2C). Ríos et al. [11] stated that “a higher NaOH concentration in the synthesis solution can leads to faster dissolution of the original clay minerals, accompanied by more crystalline zeolitic materials”. This can interpret an increase of the relative intensity of the XRD peaks of sodalite - cancrinite (Figure 2C).

As mentioned before, the structural frameworks of both sodalite and cancrinite are similar. A result, many diffraction peaks occur at the same d-spacing of the two zeolite minerals. The main identifying peaks for cancrinite are occurring at d-space ~ 4.67 and 3.24 Å, and angle 19.06° and 27.63°20 respectively. Whereas, the peaks of sodalite – cancrinite occur at 14°, 23.24°, 32.78°, 33.94°, 34.72°, and d-spaces 6.33, 3.83, 2.73, 2.64, 2.58 Å (Figure 2C) respectively, as reported by Zhao et al. [14].
5.1.2. Chemical Characterization

Chemical analyses of mining rock wastes, synthesized zeolites as well as calculated formula are given in Table 1. The initial molar gel composition used in the synthesis of zeolites experiments were calculated using the chemical formula of the raw materials smectite - rich black shale, and illite - rich green siltstones.

For the calculation of the molar gel composition, NaOH and the chemical compositions of raw materials were expressed in terms of molar oxide. According to Rios [9], "the initial reaction gel composition has little resemblance to the chemical stoichiometry of the final zeolitic product and the nature and properties of starting materials used in the reaction mixture are very important parameters that determine the properties of the resulting material". The synthetic zeolitic product depends not only on the chemical composition, temperature, and pressure, but most important, on the nature of the chemical sources needed, as SiO₂, Al₂O₃, OH, Alkali cations, and H₂O.

Lutz [15] reported that the typical composition of synthesis batches of aluminosilicate zeolites based on the initial gel composition are:

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Figure 2. The XRD patterns of black shale absorbent (A) and its synthesized zeolites (B&C).
In the present study, the initial gel compositions calculated are:

\[
\begin{align*}
2.83 \text{SiO}_2 & : 1.6 \text{Al}_2\text{O}_3 & : 5 \text{Na}_2\text{O} & : 85\text{H}_2\text{O} & \text{for (Smeectite - rich black shale)} \\
1.8 & : 1 & : 3.33 \\
3 \text{SiO}_2 & : 1.5 \text{Al}_2\text{O}_3 & : 5 \text{Na}_2\text{O} & : 85\text{H}_2\text{O} & \text{for (Illite - rich siltstone)} \\
2 & : 1 & : 3.33
\end{align*}
\]

Based on the reaction composition diagram according to Breck [1] or Kostinko [16] shown in Figure 3, the initial gel compositions in the present study are consistent to NaA zeolite. Plotting the final composition of the synthetic zeolites on the reaction composition diagram of Breck [1] demonstrate that, sodalite-cancrinite lies in NaA, faujasite lies in the NaA and NaX fields, Mg-faujasite shifted totally to NaX zeolite. This means that the addition of Mg as MgCl₂ to the initial gel composition increasing the \(\text{SiO}_2/\text{Al}_2\text{O}_3\) ratios.

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![Reaction composition diagram of aluminosilicate zeolites of the present study. A, X, and Y fields possible gel composition; points-final zeolite composition after Breck [1].](image)

**Table 1. Chemical analysis of raw materials and the final synthetic products (zeolites).**

<table>
<thead>
<tr>
<th>Oxides</th>
<th>Sample No.</th>
<th>Green siltstone &amp; mudstone</th>
<th>Black shale</th>
<th>SOD-CAN</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>Raw FAU</td>
<td>Mg. FAU</td>
<td>Raw FAU</td>
<td>Mg. FAU</td>
</tr>
<tr>
<td>SiO₂</td>
<td>52.61</td>
<td>42.91</td>
<td>37.99</td>
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<td>Al₃O₃</td>
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<td>6.93</td>
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<td>0.23</td>
<td>nd</td>
<td>0.24</td>
</tr>
<tr>
<td>MnO</td>
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<td>1.09</td>
<td>0.55</td>
<td>nd</td>
</tr>
<tr>
<td>CaO</td>
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<td>8.42</td>
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</tr>
<tr>
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<tr>
<td>K₂O</td>
<td>-</td>
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<td>0.14</td>
<td>nd</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.72</td>
<td>0.72</td>
<td>nd</td>
<td>0.39</td>
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<tr>
<td>Na₂O/Al₂O₃</td>
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<td>20.23</td>
<td>23.94</td>
<td>13.85</td>
</tr>
<tr>
<td>SiO₂/Al₂O₃</td>
<td>4.19</td>
<td>3.3</td>
<td>4.74</td>
<td>3.75</td>
</tr>
<tr>
<td>Na₂O/SiO₂</td>
<td>0.007</td>
<td>0.2</td>
<td>0.15</td>
<td>0.001</td>
</tr>
<tr>
<td>Oxides</td>
<td>Sample No.</td>
<td>Green siltstone &amp; mudstone</td>
<td>Black shale</td>
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<td>-----------------------------</td>
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</tr>
<tr>
<td>Raw FAU</td>
<td>Mg. FAU</td>
<td>Raw FAU</td>
<td>Mg. FAU</td>
<td>SOD-CAN</td>
</tr>
<tr>
<td>Chemical formula calculated for green siltstone and mudstone (illite)</td>
<td>Na$<em>0.04$K$</em>{3.55}$Ca$<em>{0.04}$, (Mg$</em>{0.11}$Fe$<em>{0.29}$Al$</em>{0.60}$Si$<em>{3.14}$)O$</em>{39.2}$, 2(OH)$_{0.68}$H$_2$O</td>
<td>Na$<em>{2.0}$K$</em>{0.1}$Mg$<em>{1.0}$Fe$</em>{1.0}$ (Al$<em>{0.86}$Si$</em>{3.14}$)O$_{46}$XH$_2$O</td>
<td>Na$<em>5.1$K$</em>{2.9}$Ca$<em>{0.04}$ (Mg$</em>{1.0}$Al$<em>{0.44}$Si$</em>{3.14}$)O$<em>{39.2}$ (OH)$</em>{0.7}$ (H$_2$O)</td>
<td>Na$<em>{4.5}$K$</em>{0.1}$ (Fe$<em>{0.26}$Mg$</em>{1.74}$) (Al$<em>{0.56}$Si$</em>{6.26}$)O$_{24}$</td>
</tr>
<tr>
<td>Chemical formula calculated for FAU using green silt and mudstones</td>
<td>(Na$<em>{5.1}$K$</em>{2.9}$Fe$<em>{1.0}$) (Fe$</em>{1.0}$Al$<em>{0.44}$Si$</em>{3.14}$)O$<em>{39.2}$ (OH)$</em>{0.7}$ (H$_2$O)</td>
<td>(Na$<em>5.1$K$</em>{2.9}$Ca$<em>{0.04}$ (Fe$</em>{1.0}$Mg$<em>{0.44}$) (Al$</em>{0.56}$Si$<em>{6.26}$)O$</em>{24}$</td>
<td>(Na$<em>5.1$K$</em>{2.9}$Fe$<em>{1.0}$) (Fe$</em>{1.0}$Al$<em>{0.44}$Si$</em>{3.14}$)O$<em>{39.2}$ (OH)$</em>{0.7}$ (H$_2$O)</td>
<td></td>
</tr>
<tr>
<td>Chemical formula calculated for Mg. FAU using green silt and mudstones raw materials</td>
<td>Na$<em>{0.04}$K$</em>{3.55}$Ca$<em>{0.04}$, (Mg$</em>{0.11}$Fe$<em>{0.29}$Al$</em>{0.60}$Si$<em>{3.14}$)O$</em>{39.2}$, 2(OH)$_{0.68}$H$_2$O</td>
<td>Na$<em>{1.0}$K$</em>{0.1}$Mg$<em>{1.0}$Fe$</em>{1.0}$ (Al$<em>{0.86}$Si$</em>{3.14}$)O$_{46}$XH$_2$O</td>
<td>Na$<em>5.1$K$</em>{2.9}$Ca$<em>{0.04}$ (Fe$</em>{1.0}$Mg$<em>{0.44}$) (Al$</em>{0.56}$Si$<em>{6.26}$)O$</em>{24}$</td>
<td></td>
</tr>
<tr>
<td>Chemical formula calculated for black shale raw materials</td>
<td>Na$<em>{0.003}$K$</em>{0.01}$Fe$<em>{0.25}$Mg$</em>{0.01}$Al$<em>{0.85}$Si$</em>{3.14}$O$<em>{39.2}$ (OH)$</em>{0.7}$ (H$_2$O)</td>
<td>(Na$<em>5.1$K$</em>{2.9}$Ca$<em>{0.04}$ (Fe$</em>{1.0}$Mg$<em>{0.44}$) (Al$</em>{0.56}$Si$<em>{6.26}$)O$</em>{24}$</td>
<td>(Na$<em>5.1$K$</em>{2.9}$Fe$<em>{1.0}$) (Fe$</em>{1.0}$Al$<em>{0.44}$Si$</em>{3.14}$)O$<em>{39.2}$ (OH)$</em>{0.7}$ (H$_2$O)</td>
<td></td>
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<tr>
<td>Chemical formula calculated for Mg. FAU using black shale raw materials</td>
<td>(Na$<em>{5.1}$K$</em>{2.9}$Ca$<em>{0.04}$ (Fe$</em>{1.0}$Mg$<em>{0.44}$) (Al$</em>{0.56}$Si$<em>{6.26}$)O$</em>{24}$</td>
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<td>(Na$<em>5.1$K$</em>{2.9}$Fe$<em>{1.0}$) (Fe$</em>{1.0}$Al$<em>{0.44}$Si$</em>{3.14}$)O$<em>{39.2}$ (OH)$</em>{0.7}$ (H$_2$O)</td>
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<tr>
<td>Chemical formula calculated for SOD-CAN using black shale raw materials</td>
<td>(Na$<em>{5.1}$K$</em>{2.9}$Fe$<em>{1.0}$) (Fe$</em>{1.0}$Al$<em>{0.44}$Si$</em>{3.14}$)O$<em>{39.2}$ (OH)$</em>{0.7}$ (H$_2$O)</td>
<td>(Na$<em>5.1$K$</em>{2.9}$Ca$<em>{0.04}$ (Fe$</em>{1.0}$Mg$<em>{0.44}$) (Al$</em>{0.56}$Si$<em>{6.26}$)O$</em>{24}$</td>
<td>(Na$<em>5.1$K$</em>{2.9}$Fe$<em>{1.0}$) (Fe$</em>{1.0}$Al$<em>{0.44}$Si$</em>{3.14}$)O$<em>{39.2}$ (OH)$</em>{0.7}$ (H$_2$O)</td>
<td></td>
</tr>
</tbody>
</table>

Faujasite (FAU); Magnesium faujasite (Mg. FAU); Sodalite-cancrinite (SOD-CAN).

5.1.3. Thermal Analysis

Thermal stability of synthesized zeolites (faujasite, Mg-faujasite and sodalite-cancrinite) during heat treatment was studied as shown in Figures 4-6. The synthesis products show two and three dehydration steps.

**Figure 4.** Shows thermal analysis curves of faujasite.

**Figure 5.** Shows thermal analysis curves of Mg-faujasite.
According to Covarrubias et al. [17], "the position of DrTGA peaks as well as number of dehydration steps can be attributed to the different compensating cation-water binding energies, and to the different energy associated with the diffusion of the desorbed water through the porous structure of the as-synthesized products". In zeolites, the weight loss percentages reflects the water loss from the zeolite structure, and the amount of desorbed water is related with the number of compensation cations in the framework of the zeolite.

From TGA/DrTGA curves (Figure 4), two weight reductions were observed. The first mass reduction of faujasite occurred in temperature between 23.58°C and 202°C which display the highest mass loss (18.4%). At the same time, it could be seen from the DTA curve (Figure 4) that the strongest endothermic peak was recorded at 128.27°C. The main reason is that the water molecules adsorbed on the faujasite were completely removed. The second mass reduction occurred at temperature between 202 and 500°C. The main reason is the extra framework water molecules were removed [18]. TGA and DrTGA curves of Mg-faujasite (Figure 5) indicate three mass reduction at temperature range from the first 22.96 to 167.31°C, the second peak from 169.92 to 316.87°C, and the third from 318.43 to 492.95°C respectively. DTA curve (Figure 5) indicates that the strongest endothermic peak of the first mass reduction is at 86.65°C, and at 252.1, 270.05°C for the second mass reduction. For the third mass reduction the exothermic peak is observed at 324.25°C. The total mass loss in the Mg-faujasite is up to 23.8%.

Thermogravimetric curves of the synthesized sodalite-cancrinite are shown in Figure 6. Synthesized sodalite-cancrinite shows two dehydration steps. The first dehydration step observed from TGA and DrTGA curves (Figure 6) at temperature between 24.6 and 181.36°C, with endothermic peak observed from DTA curve 90.68°C. The weight loss due to the first step is up to 9.72%. The second dehydration step observed at temperature range from 181.36 and 499.81°C, with endothermic peaks at 354.07°C (Figure 6), and mass loss up to 5.91%. The first weight reduction at endothermic peak 90.86°C indicates that the dehydration of zeolite water. The weight loss at endothermic peak at 354.07°C indicates the extra framework water molecules was removed [18].

5.1.4. Fourier-Transform Infrared (FT-IR)

FT-IR spectroscopy is used to probe the structure of zeolites and monitor reactions in zeolite pores. Specifically, structural information can be obtained from the vibrational frequencies of the zeolite lattice observed in the range between 200 and 1500 cm⁻¹.

According to Flanigen et al. [19] the observed bands can be classified into two types:

1) Internal vibrations of the TO₄ (T=Si or Al) tetrahedra, indicating structure insensitive modes.
2) External vibrations of the zeolite skeleton (as in A, X, Y-type) or pore openings (as, e.g., in mordenite).

The FT-IR spectra of the raw material and synthesized products obtained are illustrated in Figure 7. The vibration bands of smectite- rich black shale are described as follow. The band at 1035 is caused by Si-O-Si lattice vibration. The OH bending vibration 914 cm⁻¹ can be referred to the ‘inner OH bending [20], which are mainly caused by Al-OH groups [21]. Furthermore, bands in the low range of frequency (798, 696 and 527 cm⁻¹) can be attributed to different Si-O and Al-O vibrations [22].
Figure 7. Fourier transform infrared (FTIR) spectra of the raw material and their synthesized products.

Figure 8. SEM images showing a sphere-like aggregates of faujasite (A&B), crystallized cubic and octahedral morphology of Mg-faujasite and the growth of sodalite-cancrinite (C&D) and globular shape of sodalite-cancrinite (E&F).
5.1.5. Scanning Electron Microscope (SEM)

We highlight more examples of the zeolite types obtained using calcinated black shale and green siltstone and mudstone as a starting material. Using alkaline fusion method followed by hydrothermal reaction at 80°C and 150°C, the following morphologies were observed as synthesized zeolite types. Well-developed crystals displaying an octahedral morphology as well as interpenetration-twinning are detected in (Figure 8). The diameter of crystals ranges from 1–3 µm, but also some smaller particles is also detected. The plane view images show that the globular have typical faujasite morphology (Figure 8A & B). Addition of 0.1N MgCl$_2$ to the synthesis mixture before hydrothermal treatment was found to completely inhibit the formation of other zeolite species and enhanced the crystals of faujasite (Figure 8C & D). Note the spherical aggregates of sodalite-cancrinite (Figure 8C & D) growing out onto the surface of faujasite as reported by Ríos et al. [23] and Ríos [9], revealing that sodalite-cancrinite becomes the result of secondary nucleation [24] and not the result of direct solid-state transformation.

Hydrothermal treatment at higher temperature (150°C) promoted the co-crystallization of the sodalite-cancrinite type structure (Figure 8E & F). A transformation of sodalite into cancrrinite is illustrated in Figure 8. Sodalite shows wedge-shaped blade morphology whereas cancrrinite occurs as lepispheres composed of intergrown thin disks. The phase transformation sodalite to cancrrinite has been reported elsewhere [25, 11, 26, 27].

5.1.6. Surface Area

The Brunauer-Emmett-Teller (BET) adsorption and desorption isotherm of synthetic faujasite and sodalite-cancrinite are shown in Figure 9. According to IUPAC classification, "the shape of N$_2$ gas adsorption/desorption isotherms in the initial phase of P/P$_0$ indicated exhibits a typical type I in all isotherms. However, in the range of intermediate and higher pressures, it can be described as type IV isotherm". This indicates the existence of mesopores in raw material and synthetic zeolites with a maximum N$_2$ uptake of 17 cm$^3$/g for raw material and up to 75 cm$^3$/g for synthetic zeolite.

It is important for the fundamental study and application of porous materials. According to IUPAC classification, hysteresis loops of all faujasite and sodalite-cancrinite (observed in P/P$_0$ range between 0.46 and 0.99) most correspond to the H3 type of Bandura et al. [28], whereas according to de Boer [29] to B type. These types characterize solids with slit-shaped pores (plates or faced/edges particles like cubes) of uniform or non-uniform size or shape [30] which are typically of zeolites.

5.2. Removal of Fe$^{2+}$ and Mn$^{2+}$

Water is the source of life; however, due to pollution and insufficient water source are major problems. Heavy metals pollution of water have a potential to harm life forms and the environment. Therefore, removal of heavy metals from surface water, groundwater and wastewaters is an essential social and environmental subject because of their detrimental effects to water quality and their toxic characteristics for living beings. The presence of iron and manganese in groundwater is a common problem in many countries. The groundwater in the New Valley region in Egypt is characterized by high content of Fe$^{2+}$ and Mn$^{2+}$. According to World Health Organization [31], "a maximum acceptable drinking water concentration for Fe$^{2+}$ and Mn$^{2+}$ are 0.3 and 0.1 mg L$^{-1}$, respectively". Excess Fe and Mn in potable water cause operational and aesthetic problems such as taste, odour and high turbidity and can stain kitchen utensils, bath accessories and laundered clothes [32, 33]. In the other hand, excess ingestion can cause neurotoxicity, lesions in the pancreas, lung inflammation, nausea and headaches [34, 35]. "Several procedures for wastewater treatment, including chemical precipitation, electrodeposition, ion exchange, membrane separation and adsorption, have been developed, although adsorption has been the preferred method for heavy metal removal, because it is considered to be a particularly
The adsorbent employed in this study are mining rock wastes (green siltstone, mudstone, and black shale, and their synthesized zeolites (Na-X faujasite and sodalite-cancrinite).

5.2.1. Optimum Conditions of Fe\(^{2+}\) and Mn\(^{2+}\) Removal

The optimum conditions of removal of Fe\(^{2+}\) and Mn\(^{2+}\) ions onto black shale absorbent and synthesized zeolites are summarized at Figures 10-12 and Table 2.

The removal percentage of Fe\(^{2+}\) and Mn\(^{2+}\) heavy metal ions increase with increasing the sorbent dosage of black shale absorbent and synthesized faujasite. 0.6 g of black shale absorbent uptake up to 34.3% of 200 ppm Mn\(^{2+}\) and 61.5% of 200 ppm Fe\(^{2+}\). The same dosage (0.6g) of faujasite adsorbed about 97.7% Mn\(^{2+}\), and 100% Fe\(^{3+}\). This may attribute to the increases in the surface area and the number of active sites in faujasite relative to black shale absorbent [36]. In the case of sodalite - cancrinite the removal percent of Fe\(^{2+}\) increases with increasing dosage. The maximum removal percent of Fe\(^{2+}\) reached to 75.2% using 0.6g (Figure 10). Vice versa, removal percent of Mn\(^{2+}\) decreases with increasing dosage. The maximum removal of Mn\(^{2+}\) was about 15% of 100ppm (initial concentration) with optimum dosage 0.1 g (Figure 10).

![Figure 10. Effect of sorbent dosage on Fe\(^{2+}\) and Mn\(^{2+}\) removal onto black shale and their synthesized zeolites (faujasite and sodalite-cancrinite).](image)

Adsorption of Fe\(^{2+}\) and Mn\(^{2+}\) ions onto black shale and faujasite absorbents decreased with increasing initial concentration (50-300 ppm). The optimum initial concentration (C\(_i\)) was 50 ppm of Fe\(^{2+}\) and Mn\(^{2+}\) with removal up to 100 and 85% respectively for faujasite absorbent and 70% Fe\(^{2+}\) and 55% Mn\(^{2+}\) for black shale absorbent (Figure 11). Using sodalite- cancrinite, adsorption of Fe\(^{2+}\) and Mn\(^{2+}\) ions increased with increasing initial concentrations. Maximum removal (80% and 20%) of Fe\(^{2+}\) and Mn\(^{2+}\) respectively was achieved at initial concentration (C\(_i\)) 200 ppm (Figure 11).

![Figure 11. Effect of initial concentrations (Ci) on the removal of Fe\(^{2+}\) and Mn\(^{2+}\) onto black shale and their synthesized zeolites (faujasite and sodalite-cancrinite).](image)

In the same manner the effect of initial concentration on the adsorption of Fe\(^{2+}\) and Mn\(^{2+}\) ions decreased with increasing time for black shale and faujasite absorbents but increased for sodalite-cancrinite. For (0.1 gm) black shale, optimum contact time was 15 min and 5 min to remove of Fe\(^{2+}\) and Mn\(^{2+}\) up to 45.2 and 36.04% respectively (Figure 12). 5 min contact time for 0.1 faujasite is enough to uptake up to 68.4% Fe\(^{2+}\) and 41.6% Mn\(^{2+}\). For sodalite-cancrinite (0.1 gm), the equilibrium is reached more slowly, after 30 min, with both Fe\(^{2+}\) and Mn\(^{2+}\) where the removal% was 65 and 25% respectively (Figure 12). Furthermore, increase in contact time has no influence on the adsorption process.

According to Hercigonja et al. [37] “at the beginning of the experiment fast adsorption observed possibly because Fe\(^{3+}\) and Mn\(^{2+}\) ions get adsorbed on the sites of the sodalite-cancrinite surface. After the initial period, the adsorption occurred slowly because the Fe\(^{3+}\) and Mn\(^{2+}\) ions had to move through the pores of sorbent”.

Figure 12. Effect of contact time on the removal of Fe\(^{2+}\) and Mn\(^{2+}\) onto black shale and their synthesized zeolites (faujasite and sodalite-cancrinite).
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Figure 12. Effect of contact time on of Fe\(^{2+}\) and Mn\(^{2+}\) removal using black shale and their synthesized zeolites (faujasite and sodalite-cancrinite) sorbents.

Table 2. The optimum conditions of Fe\(^{2+}\) and Mn\(^{2+}\) ions removal using black shale and zeolites (faujasite and sodalite-cancrinite) sorbents.

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Sample</th>
<th>Parameters</th>
<th>Black shale</th>
<th>Optimum conditions</th>
<th>R%</th>
<th>Faujasite</th>
<th>Optimum conditions</th>
<th>R%</th>
<th>Sodalite-cancrinite</th>
<th>Optimum conditions</th>
<th>R%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(^{2+})</td>
<td>1. Adsorbent dosage (0.1-0.6g), initial concentration= 200 ppm and contact time=60 min</td>
<td>0.6 g</td>
<td>61.54</td>
<td>0.6 g</td>
<td>100</td>
<td>0.1 g</td>
<td>75.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2. Contact time (0-30 min), Adsorbent dosage= 0.1g and initial concentration= 100 ppm</td>
<td>15 min</td>
<td>45.2</td>
<td>5 min</td>
<td>68.35</td>
<td>30 min</td>
<td>54.95</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3. Initial concentration (50-300 ppm), Contact time (60 min), Adsorbent dosage (0.1g)</td>
<td>50 ppm</td>
<td>74.9</td>
<td>50 ppm</td>
<td>100</td>
<td>200 ppm</td>
<td>82.85</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn(^{2+})</td>
<td>1. Adsorbent dosage (0.1-0.6g), initial concentration= 200 ppm and contact time=60 min</td>
<td>0.6 g</td>
<td>34.32</td>
<td>0.6 g</td>
<td>97.7</td>
<td>0.1 g</td>
<td>15.75</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2. Contact time (0-30 min), Adsorbent dosage (0.1g) and initial concentration= 100 ppm</td>
<td>5 min</td>
<td>36.04</td>
<td>5 min</td>
<td>41.6</td>
<td>30</td>
<td>24.65</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3. Initial concentration (50-300 ppm), Contact time =60 min, Adsorbent dosage=0.1g</td>
<td>50 ppm</td>
<td>54.7</td>
<td>50 ppm</td>
<td>87.8</td>
<td>200 ppm</td>
<td>20.39</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5.2.2. Isothermal Models

To perform the adsorption isotherm experiments, several solutions with different concentrations of Fe\(^{2+}\) and Mn\(^{2+}\) (50–300 ppm) were prepared by dilution of the stock synthetic solution. The amount of metal adsorbed was calculated according to the following Eq. (1).

\[
q_e = \frac{(C_0 - C_e)}{m} x V (L)
\]

(1)

Where \(q_e\) (mg g\(^{-1}\)) is the amount of metal, \(V\) (L) is the volume of the solution and \(m\) (g) is the weight of the adsorbent. \(C_0\) and \(C_e\) are the concentrations (mg L\(^{-1}\)) at the initial and final time, respectively.

The adsorption isotherm for the adsorptive removal of Fe\(^{2+}\) and Mn\(^{2+}\) ions using black shale and synthesized zeolites sorbents were investigated using the Langmuir and Freundlich isotherm models.

Septhum et al. [38] stated that "The Langmuir isotherm model which proposes a homogeneous surface and adsorption sites of the same energy to the material (i.e., a monolayer adsorption) consistent with a process of chemisorption". The linearized form of the Langmuir isotherm is expressed as:

\[
\frac{C_e}{q_e} = \frac{1}{b q_{\text{max}}} + \frac{C_e}{q_{\text{max}}}
\]

(2)

Where \(q_e\) is the amount of Fe or Mn sorbed at equilibrium in mg/g, \(q_{\text{max}}\) is the maximum sorbed capacity, \(b\) is the sorption constant (L/mg) and \(C_e\) is the equilibrium concentration of Fe or Mn (mg/L). It is possible to calculate the values of \(q_{\text{max}}\) and \(b\) through the graphs of \((C_e/q_e)\) vs. \(C_e\).

A dimensionless constant called an equilibrium parameter \(R_L\) is the essential characteristics of a Langmuir isotherm. \(R_L\) can be defined by [39] as:

\[
R_L = \frac{1}{1 + bC_0}
\]

(3)

Where, \(C_0\) is the highest initial ion concentration (mg/L) and \(b\) is the Langmuir constant that indicates the nature of the adsorption.

\(R_L\) is used to describe the favorable nature of the adsorption process where \(R_L > 1\) is unfavorable, \(R_L = 1\) is linear, \(0 < R_L < 1\) is favorable, and \(R_L = 0\) is irreversible.

Freundlich isotherm is used here to define adsorption processes that occur on heterogeneous surfaces and active sites with different energies based on multilayer adsorption and equilibrium [40, 41]. The linear form of the Freundlich isotherm model is represented by [42, 43] as:

\[
\log q_e = \log K_f + \frac{1}{n} \log C_e
\]

(4)

The plot of \(\log q_e\) against \(\log C_e\) yielded a straight line and \(n\) and \(K_f\) were calculated from the slope and intercept, respectively. \(K_f\) and \(n\) are Freundlich constants and represent the adsorption capacity and adsorption intensity, respectively.
The results of Langmuir and Freundlich isothermal adsorption models for Fe$^{2+}$ and Mn$^{2+}$ onto black shale and synthesized zeolites sorbents (faujasite and sodalite-cancrinite) are given in Figures 13-18 and Table 3.

The adsorption of Fe$^{2+}$ and Mn$^{2+}$ on to the black shale and faujasite absorbents, were better adjusted to the Langmuir model (Figures 13 & 14). This indicates the formation of a monolayer on the surface of the adsorbent. The linearization of the model indicates a maximum capacity ($q_{\text{max}} = 12.59, 9.32 \text{ mg/g}$ for the adsorption of Mn$^{2+}$ and Fe$^{2+}$ respectively onto black shale absorbent, 13.33, 13.07 mg/g onto faujasite and the value for ($b=0.06, 0.47 \text{ L mg}^{-1}$ for Mn$^{2+}$ and Fe$^{2+}$ respectively onto black shale absorbent, 0.10, 1.86 L/mg onto faujasite. Thus, the value $R_L$ was found to be ($0 < R_L < 1$), which indicates a favorable adsorption process.

In the case of sodalite-cancrinite, the adsorption of Fe$^{2+}$ and Mn$^{2+}$ was fitted well with Freundlich isothermal model with $R^2=0.97$ and $n=1.1$ in the case of Fe$^{2+}$ and $R^2=0.99$ and $n=0.81$ in the case of Mn$^{2+}$. $R^2=0.98, 0.95$ for the adsorption of Fe$^{2+}$ and Mn$^{2+}$ respectively onto black shale absorbent, 0.81, 0.91 onto faujasite.

![Figure 13](image1.png)
**Figure 13.** Langmuir isotherm plots for the adsorption of heavy metals (Fe$^{2+}$ and Mn$^{2+}$) onto the black shale absorbent.

![Figure 14](image2.png)
**Figure 14.** Langmuir isotherm plots for the adsorption of heavy metals (Fe$^{2+}$ and Mn$^{2+}$) onto the synthesized faujasite.

![Figure 15](image3.png)
**Figure 15.** Langmuir isotherm plots for the adsorption of heavy metals (Fe$^{2+}$ and Mn$^{2+}$) onto the synthesized sodalite-cancrinite.
Figure 16. Freundlich isotherm plots for the adsorption of heavy metals (Fe$^{2+}$ and Mn$^{2+}$) onto the black shale absorbent.

Figure 17. Freundlich isotherm plots for the adsorption of heavy metals (Fe$^{2+}$ and Mn$^{2+}$) onto the synthesized faujasite.

Figure 18. Freundlich isotherm plots for the adsorption of heavy metals (Fe$^{2+}$ and Mn$^{2+}$) onto the synthesized sodalite-cancrinite.

Table 3. Parameters of the studied isothermal models of black shale absorbent (B.Sh) and their synthesized zeolites [faujasite (FAU) and sodalite-cancrinite (SOD-CAN)].

<table>
<thead>
<tr>
<th>Model</th>
<th>parameters</th>
<th>B.Sh (Mn)</th>
<th>B.Sh (Fe)</th>
<th>FAU (Mn)</th>
<th>FAU (Fe)</th>
<th>Sod-Can (Mn)</th>
<th>Sod-Can (Fe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$R^2$</td>
<td>0.99</td>
<td>0.99</td>
<td>0.98</td>
<td>0.99</td>
<td>0.75</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>$q_{max}$</td>
<td>12.59</td>
<td>9.32</td>
<td>13.33</td>
<td>13.07</td>
<td>-34.01</td>
<td>51.81</td>
</tr>
<tr>
<td></td>
<td>$K_L$</td>
<td>0.06</td>
<td>0.47</td>
<td>0.1</td>
<td>1.86</td>
<td>-0.002</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>$R_L$</td>
<td>0.2 to 0.05</td>
<td>0.008 to 1</td>
<td>0.1 -0.03</td>
<td>1.002</td>
<td>1.1 -3.88</td>
<td>0.11 -1</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.96</td>
<td>0.93</td>
<td>0.91</td>
<td>0.92</td>
<td>0.99</td>
<td>0.97</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$n$</td>
<td>2.08</td>
<td>-1.03</td>
<td>-1.05</td>
<td>-3.29</td>
<td>0.81</td>
<td>1.10</td>
</tr>
<tr>
<td></td>
<td>$K_f$</td>
<td>1.08</td>
<td>584.25</td>
<td>467.95</td>
<td>50.07</td>
<td>0.02</td>
<td>1.08</td>
</tr>
</tbody>
</table>

5.2.3. Adsorption Kinetics

Adsorption kinetics informs the rate of adsorption of metal ions (Fe and Mn) on the adsorbent (black shale and synthesized zeolite). Kinetic experiments were carried out by addition of 0.5 g of adsorbent (black shale absorbent, faujasite or sodalite -cancrinite) to 25 mL of solution with known concentration (100 ppm) of Fe$^{2+}$ and Mn$^{2+}$. The shaking time required for the experiment varied from 5 to 30 min. These tests determine the minimum contact time
required to achieve an adequate efficiency of the adsorbent because this material could be applied at large scales.

Kinetic models of “pseudo-first order” [44], “pseudo-second order” [45], and intraparticle diffusion [46] were applied to explain the adsorption mechanism of Fe$^{2+}$ and Mn$^{2+}$ onto black shale absorbent and synthesized zeolites. The respective linear equations are expressed below:

The pseudo-first order kinetics can be determined based on the following equation:

$$\log (Q_e - Q_t) = \log Q_e - \frac{k_1 t}{2.303} \quad (5)$$

Where $k_1$ (mg/g min) is the rate constant of pseudo-first-order adsorption, and $Q_e$ and $Q_t$ (mg/g) denote the amounts of adsorbed heavy metal anions at equilibrium and at time $t$. The results are shown in Figures 19-21 respectively and Table 4.

The pseudo-second order is defined using the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (6)$$

Where $k_2$ (mg/g min) is the rate constant of the pseudo-second order adsorption. Additionally, the initial adsorption rate $h$ (mg/g min) can be determined using the equation (7) [47]. The results are shown in Figures 22-24 and Table 4.

$$h = k_2 Q_e \quad (7)$$
Figure 22. Pseudo-second order kinetic plots for the heavy metals ions (Fe$^{2+}$ and Mn$^{2+}$) adsorption onto the black shale absorbent.

Figure 23. Pseudo-second order kinetic plots for the heavy metals ions (Fe$^{2+}$ and Mn$^{2+}$) adsorption onto the synthesized faujasite.

Figure 24. Pseudo-second order kinetic plots for the heavy metals ions (Fe$^{2+}$ and Mn$^{2+}$) adsorption onto the synthesized sodalite-cancrinite.

Intra-particle linear equation (8) is expressed by:

$$Q_t = C_{ld} + k_{ld}t^{0.5}$$  \hspace{1cm} (8)

Where $k_{ld}$ (mg/g min$^{1/2}$) is the intraparticle diffusion rate constant, the $C$ values determine the boundary layer effect higher values, the greater the effect. The results are shown in Figures 25-27 and Table 4.

Figure 25. Intra-particle model plots for the heavy metals ions (Fe$^{2+}$ and Mn$^{2+}$) adsorption onto the black shale absorbent.
Comparison the correlation coefficients indicates that Fe\textsuperscript{2+} and Mn\textsuperscript{2+} adsorption onto black shale absorbent and synthesized zeolites does not follow a pseudo-first order reaction, because the \( q_{e,\text{cal}} \) values obtained are not satisfactory. The values are also low when compared with the \( q_{e,\exp} \) values. However, the correlation coefficients for the pseudo-second order kinetic model are \( R^2 = 0.98, 0.95 \) for the adsorption of Fe\textsuperscript{2+} and Mn\textsuperscript{2+} respectively onto black shale, 0.81, 0.91 onto faujasite, and 0.90,93 onto sodalite-cancrinite. The \( q_{e,\text{cal}} \) values agreed well with the \( q_{e,\exp} \) data. This model is based on the assumption that the rate-limiting stage can be a chemical adsorption process involving valence.

Additionally, the intra-particle diffusion model presents a non-linear distribution with Fe\textsuperscript{2+} and Mn\textsuperscript{2+} adsorption onto black shale absorbent and their synthetic zeolites (faujasite and sodalite-cancrinite) (Figures 25-27). Therefore, cannot be considered as a determining model in the Fe\textsuperscript{2+} and Mn\textsuperscript{2+} adsorption rate. This is consistent with Obradovic [48] that the Waber - Morris (intra-particle) model is not an appropriate in the case of fast adsorption. Exception is in the adsorption of Fe\textsuperscript{2+} onto sodalite-cancrinite (slow adsorption), intraparticle is appropriate with \( R^2 0.97 \) (Figure 27 and Table 4).

### Table 4. Parameters of the studied kinetics models of black shale absorbent and their synthesized zeolites (faujasite and sodalite-cancrinite).

<table>
<thead>
<tr>
<th>Model</th>
<th>parameters</th>
<th>B.Sh (Mn)</th>
<th>B.Sh (Fe)</th>
<th>FAU (Mn)</th>
<th>FAU (Fe)</th>
<th>Sod-Can (Mn)</th>
<th>Sod-Can (Fe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first order</td>
<td>( R^2 )</td>
<td>0.86</td>
<td>0.49</td>
<td>0.87</td>
<td>0.97</td>
<td>0.90</td>
<td>0.87</td>
</tr>
<tr>
<td></td>
<td>( K_1 )</td>
<td>0.08</td>
<td>0.06</td>
<td>0.12</td>
<td>0.04</td>
<td>-0.11</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>( q_e )</td>
<td>0.83</td>
<td>0.49</td>
<td>0.89</td>
<td>7.10</td>
<td>12.99</td>
<td>7.62</td>
</tr>
<tr>
<td>Pseudo-second order</td>
<td>( R^2 )</td>
<td>0.95</td>
<td>0.98</td>
<td>0.91</td>
<td>0.81</td>
<td>0.98</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td>( K_2 )</td>
<td>-0.07</td>
<td>-0.31</td>
<td>-0.19</td>
<td>-0.07</td>
<td>0.002</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td>( q_e )</td>
<td>242</td>
<td>9.7</td>
<td>3.62</td>
<td>3.58</td>
<td>14.60</td>
<td>19.31</td>
</tr>
<tr>
<td>intra-particle</td>
<td>( R^2 )</td>
<td>0.9</td>
<td>0.9</td>
<td>0.99</td>
<td>0.98</td>
<td>0.91</td>
<td>0.95</td>
</tr>
<tr>
<td>diffusion</td>
<td>( K_{id} )</td>
<td>0.03</td>
<td>0.91</td>
<td>-0.424</td>
<td>-0.467</td>
<td>217</td>
<td>233</td>
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<tr>
<td></td>
<td>( C_{id} )</td>
<td>-0.08</td>
<td>7.63</td>
<td>19.82</td>
<td>26.44</td>
<td>-5.33</td>
<td>0.14</td>
</tr>
</tbody>
</table>

### 6. Conclusion

In the present work, zeolites were synthesized from smectite-rich black shale as well as green siltstone and mudstone rock waste samples using alkali fusion and hydrothermal treatment at temperatures 80°C and 150°C. The synthesized samples are characterized by X-ray diffraction (XRD), X-ray Fluorescence (XRF), Scanning Electron Microscope (SEM), Fourier Transformation Infrared (FTIR) Spectroscopy and Thermal-gravimeter Analysis (TGA), Differential Thermal Analysis (DTA) and Differentiation Thermo-gravimetric Analysis (DrTGA) and the surface area of Brunauer-Emmett-Teller (BET) method. The results
indicated that faujasite zeolite (Na-X) is the major constituent phase with hydrothermal reaction treatment at 80°C for both samples, whereas sodalite-cancrinite is produced at 150°C.

Black shale wastes and their synthesized zeolites (faujasite and sodalite-cancrinite) were tested as effective and low-cost adsorbents for the removal of Fe²⁺ and Mn²⁺ from aqueous solutions. The operational parameters such as initial Fe²⁺ and Mn²⁺ concentrations, contact time and adsorbent dosage affect the adsorption efficiency of the used materials. The reached results show that faujasite is very faster and higher in the up taking of Fe²⁺ and Mn²⁺ ions relative to the black shale absorbent or even the synthesized sodalite-cancrinite. In addition, it is found that the Langmuir model has the best agreement with the adsorption equilibrium data for Fe²⁺ and Mn²⁺ by black shale and synthesized Na-X faujasite, however, Freundlich isotherm model is accepted in the case of sodalite-cancrinite adsorbent. The adsorption kinetics of Fe²⁺ and Mn²⁺ onto the studied samples follow pseudo-second order model indicating chemical interaction (chemisorption) adsorption process. The intraparticle diffusion model was failed as controlling factor in the rate of adsorption onto the black shale and faujasite absorbents due to fast up taking.

Therefore, the Na-X zeolite synthesized from black shale, green siltstone and mudstone rock of rock mining waste can constitute a promising low-cost alternative sorbent used for heavy metals adsorption applications.

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