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Comparative Analysis of Natural and Synthetic Zeolite Filter Performance in the Purification of Groundwater

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Abstract: Zeolite materials are among the relatively cheap and readily available materials for wastewater treatment. However, the performance of zeolite-based systems can be highly affected by the material properties. In this study, the treatment system based on natural zeolite materials from Chankanai mines in Kazakhstan was compared with a synthetic zeolite treatment system for the purification of groundwater. Water quality indices were also developed from a set of selected water quality parameters to further assess the state of water quality of raw groundwater and the effluents treated with natural and synthetic zeolite. The lowest removal efficiency of natural zeolite (30%) was observed with zinc, while the lowest removal efficiency (36%) of synthetic zeolite was observed with arsenic. With turbidity and beryllium, we observed the maximum removal efficiency (100%) of natural zeolite, whereas with turbidity, we observed the highest removal efficiency (100%) of synthetic zeolite. When the groundwater samples were put through the natural zeolite treatment system, removal efficiency of 50% and above was obtained with 27 (79.4%) out of the 34 water quality parameters examined. On the other hand, when the groundwater samples were put through the synthetic zeolite treatment system, more than 50% removal efficiency was attained with 30 (88.2%) out of the 34 water quality parameters studied. The aggregated water quality index of raw groundwater was 3278.24, falling in the "water unsuitable for drinking" category. The effluent treated with natural zeolite generated 144.82 as a water quality index, falling in the "poor water" quality category. Synthetic zeolite generated 94.79 as a water quality index, falling in the "good water" quality category. Across the board, it was shown that the synthetic zeolite treatment system outperformed the natural zeolite treatment system according to a number of water quality parameters. The findings of this study offer substantial knowledge that can be used to develop more efficient groundwater treatment technologies.

Keywords: groundwater treatment; groundwater water quality; natural zeolite; synthetic zeolite; water quality index

1. Introduction

Even though it is one of the main sources of water supply on Earth, groundwater has been continuously stressed by contamination with anthropogenic and natural causes. Generally, poor waste management is one of the causes of pollution, including inadequate industrial, agricultural, or building practices [1–4]. Pollution can happen naturally as a result of the existence of a tiny and undesired element, contaminant, or impurity in groundwater; in this case, contamination is more appropriate than pollution [5]. On the other hand, groundwater contamination can result from on-site sanitation systems, landfill leachate, wastewater treatment plant effluents, leaking sewers, gas stations, hydraulic fracturing, or excessive fertilizer use in agriculture [6]. Using contaminated groundwater puts the public at risk of illness or poisoning [7]. Moreover, among the contaminants endangering the quality of groundwater are total hardness, calcium, chlorides, manganese, fluorides, sulfates, and nitrates, as well as nitrites. There are two main factors that contribute to a high concentration of fluoride in groundwater: hydrogeology and human activity [8]. Fluoride is transported to rivers through the weathering of fluoride-containing rocks, and it may also percolate into the soil and groundwater aquifers. In addition, human activities such as excessive fertilizer use and improper irrigation management can raise the concentration of fluoride [9].

On the other hand, fuel burning, fertilizer, animal waste, and atmospheric deposition are the main sources of nitrate [10–12]. Even though nitrate is less harmful than nitrite, it can nevertheless have a negative impact on people's health and ecosystems. Chronic nitrate exposure might cause headaches, stomach pain, vomiting, or an elevated heart rate [13]. It is also important to note that an aquifer frequently develops a contamination plume as a result of the pollutant [14]. Pollution is dispersed across a larger area by water movement and dispersion inside the aquifer. Its expanding boundary, frequently referred to as a plume edge, can collide with surface water sources, such as seeps and springs, and groundwater wells, rendering the water dangerous for both people and wildlife to drink [15]. The analysis of groundwater pollution may concentrate on the geology, hydrology, hydrogeology, and hydrology of the location as well as the nature of the contaminants. Pollutants can be transported by a variety of mechanisms, including diffusion [16], adsorption [17], precipitation [18], and degradation [19].

Complex interrelationships exist between groundwater and surface water [20,21]. As an illustration, groundwater supplies many rivers and lakes. This implies that rivers and lakes that depend on groundwater aquifers may be impacted by damage to those aquifers, such as that caused by fracking or excessive extraction. Such interactions include the intrusion of saltwater into coastal aquifers [22]. Applying the precautionary principle, monitoring groundwater quality, zoning land for groundwater protection, correctly situating on-site sanitation systems, and enforcing laws are some prevention approaches. Groundwater remediation, point-of-use water treatment, and, as a last resort, abandonment are all management options where pollution has occurred. The development of quality indicators is one of the potential strategies for tracking the condition of groundwater quality. The groundwater quality index (GWQI) is the most precise method for determining the potability of groundwater, according to Sabino et al. [23]. Horton created the water quality index (WQI) model in 1965 to distinguish between different types of water [24]. It is a single, dimensionless number that is calculated by adding all of the important factors that have a bearing on the quality of water.

Humanity's demands, including the need for clean water, are being met through technology, which is always changing and evolving. The water treatment field is always investigating, testing, and creating new and better methods to treat wastewater and drinking water in ways that are effective and environmentally beneficial. For the treatment of wastewater, gray water, and drinking water, zeolite water filtration media offer a natural, sustainable option [25,26]. Zeolite can be produced by means of the reaction of volcanic rock or ash with alkaline fluids. The mineral zeolite is capable of forming a wide range of aluminosilicates, which are arrangements of the elements oxygen, silica, and aluminum [27]. They are highly predisposed to cation exchange capabilities and are microporous due to their structure and composition. Due to possible impurities, the strength of these exchange capabilities varies from type to type and is considerably weaker in naturally occurring zeolites. Zeolites can be made synthetically, however, by heating a mixture of sodium hydroxide, alumina, and silica. The goal is to catch particles that are too large to pass through using the spaces between the grains. In the arrangement mentioned above, everything is caught at the top, and the bottom levels offer support and space for drainage.

With zeolite filters, the filtering effectiveness may be improved by increasing the number of pores in the treatment medium. Zeolite media feature many pores, which allows them to absorb particles into their pores before capturing them [28]. As a result, they not only catch particles between grains but also absorb them. This is facilitated by the mineral zeolite ability of cation exchange, which involves taking up positive ions from water and exchanging them for other ions. Because of its high pore density and vast surface area, zeolite may collect a lot of contaminants without the need for backwashing [29,30]. The medium can capture and remove particles through the adsorption process. Particles during this process stick to the surface of the medium, which is an active effect, as opposed to passively getting caught between grains. Zeolite also experiences less pressure decrease during treatment because it does not clog up as rapidly. This medium can operate as a water softener, since it can remove or reduce some hard minerals and is more chemically resistant than some other media [28]. Additionally, it should be mentioned that the properties of water to be treated and the source of natural zeolite as well as the level of modification to form synthesized zeolites can have a significant impact on the efficacy of zeolite-based filters. The sole distinction between natural and synthetic zeolite is that the former is produced using energy-intensive chemicals, while the latter is created by processing natural ore bodies. Clinoptilolite zeolites have a silica-to-alumina ratio of 5 to 1, whereas synthetic zeolites have a ratio of 1 to 1. It is also significantly important to note that the amount and type of zeolites used, the size distribution of the zeolite particles, the initial concentration of contaminants (cations/anions), the pH value of the solution, the ionic strength of the solution, the temperature, the pressure, the contact time of the zeolite/solution system, and the presence of other organic compounds and anions all affect how effectively natural and modified zeolites can treat water [31]. Unfortunately, there is presently little available evidence comparing the effectiveness of natural zeolite (particularly that from Central Asia) and synthetic zeolite in the remediation of groundwater.

In the current study, the effectiveness of natural and synthetic zeolites in treating groundwater from Tselinograd District in Akmola Region, 70 km from Kazakhstan's capital, was compared. Natural zeolites were retrieved from the Chankanai mines in Kazakhstan. To assess the quality levels of groundwater and treated effluents, water quality indices were also created based on the chosen water quality parameters.

2. Materials and Methods

2.1. Case Study Description

The groundwater samples utilized in the study were gathered in Kazakhstan's Tselinograd District. The district is situated between latitude 50.9585° N and longitude 70.9230° E. In Akmola Region, groundwater supply makes up around 14% of the total river runoff, although, in exceptionally dry years, this percentage rises significantly. River waters in the area have a higher salt content, and downstream, from 1500 mg/L near Kamenny Quarry to 450 mg/L at the river mouth, total mineralization observed over a number of years declines. The enhanced mineralization of water is principally caused by the hydroclimatic characteristics of the basin, which is characterized by high predominance of evaporation over the amount of precipitation. The ratio of precipitation to evaporation, or the moisture coefficient of the basin area, is roughly 0.5, which indicates the natural disparity between the heat and moisture resources. The territory's aridness causes mineral salts to build up in the soils and throughout the landscape. Ishim River and its tributaries receive an increased supply of these salts from the runoff of melting water within the catchment region [32].

Additionally, the considerable mineralization of groundwater is justified by the dry climate. Depending on the river discharge for each unique year and season, the river hydrochemical makeup varies. However, a recurring pattern can be seen: in the southern stream, calcium cations dominate, whereas anions are dominated by hydrocarbonates. The chloride–hydrocarbon composition is observed downstream of Astana (the latter during the flood period), with calcium ions also predominating among the anions. The hydrocarbonate class of the calcium or sodium group predominates around the Sergeevskoye reservoir and up until the village of Dolmatovo's outlet portion. Indicators of water hardness can range from 2.95 to 3.88 mg/eq. during a spring flood, from 4 to 5.6 mg/eq. during a summer or autumn low-water period, and from 6.0 to 8.4 mg/eq. during winter. The river overall oxygen level has consistently been rated as good. During the freeze-up period, the lowest oxygen content is seen. At saturation, the dissolved oxygen content is typically 88% [32].

2.2. Experimental Techniques, Characteristics of Raw Water, and Characteristics of Filter Materials

Purposive sampling methods were employed to choose 14 boreholes at random for the study, with samples being taken once per week throughout summer. The collected samples were subsequently cleaned utilizing 28.3 cm deep treatment systems of both natural and synthetic zeolites (Figure 1). The containers had a 4.68 cm diameter. The zeolite adsorbents were of 1.5 mm sized particles on average. The depth filter was supplied at a controlled rate of 0.0032 L/s from a 100 L storage drum [26]. Water was gently and repeatedly swirled through the effluent to maintain all of the particles suspended. The porous material was packed with wet packing to stop stacking and air from becoming trapped inside the file. Glass wool served as the support for the adsorbent beds at the bottom of the three vertical columns. Before injecting feed water, the column was originally packed and briefly washed with deionized water. Filtrate samples were taken at predetermined intervals.

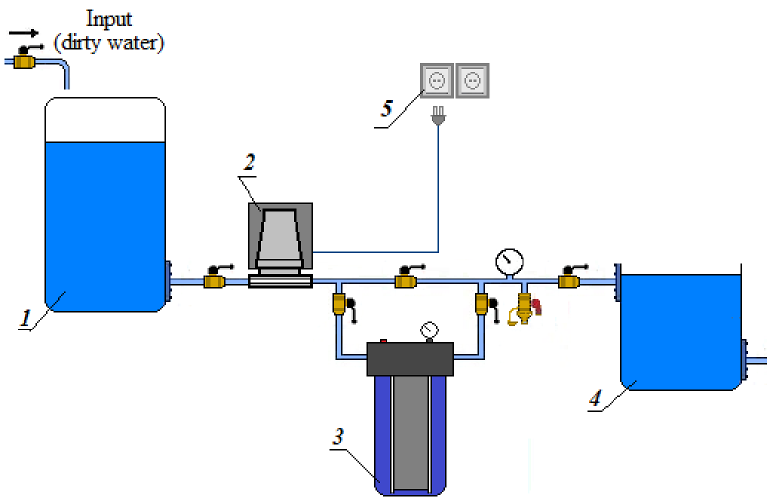

Figure 1. Treatment plant setup: 1—initial water tank; 2—pump; 3—zeolite filter; 4—storage tank; 5—power supply.

The natural zeolite called clinoptilolite is made up of microporous silica and alumina tetrahedra [25]. Sodium concentrations in clinoptilolite are often higher than potassium concentrations. However, there are some sources that are rich in potassium and low in sodium [25]. The natural zeolite materials used in the investigation are summarized in Table 1 along with their material attributes. Information about the parameters was supplied by the vendor (Himiya i Tehnologiya, TOO, Almaty, Kazakhstan). Natural zeolite had high concentrations of SiO_2 and Al_2O_3, as can be observed in Table 1.

Table 1. Material properties of natural zeolite.

Parameter	Concentration (%)
CaO	0.1 to 6.4
MgO	0 to 2.1
MnO_2	0.1 to 0.2
Fe_2O_3	1.4 to 5.8
TiO_2	0.1 to 0.7
Al_2O_3	14.0 to 15.0
SiO_2	60.0 to 74.0
Na_2O	0.6 to 5.5
K_2O	0.7 to 4.0
P_2O_5	0.1 to 0.2
H_2O	0 to 4.1

It is crucial to remember that synthetic zeolites are crystalline aluminosilicates produced through a thermal process [33]. By adjusting the process temperature and the chemical composition of the constituent ingredients, it is possible to precisely regulate the structure and surface characteristics of the adsorbent [33]. Table 2 provides a summary of the physicochemical characteristics of the synthetic zeolite filter materials used in the experiment. Information about the parameters was supplied by the vendor (Himiya i Tehnologiya, TOO, Almaty, Kazakhstan).

Table 2. Characteristics of the synthetic zeolite materials.

Parameter	Concentration/Value
Fe_2O_3	0.1
Na_2O	0.1
Al_2O_3	4.2
BET general surface (m^2/g)	315
Water vapor	No more than 0.1
Zeolite external surface (m^2/g)	70
Zeolite overall pore volume (cm^3/g)	0.235
SiO_2/Al_2O_3	40

2.3. Water Quality Parameters and Analytical Procedures

The study covered the following water quality parameters: total hardness, colors, turbidity, pH, general mineralization, permanganate oxidability, dry residue, calcium, chlorides, sulfates, polyphosphates, fluorides, silicic acid (Si), nitrates, nitrites, cadmium, lead, cyanides, barium, zinc, manganese, nickel, iron, arsenic, hydrargyrum, copper, aluminum, chrome, bohrium, beryllium, molybdenum, selenium, strontium, HCG pesticide DDT and its metabolites, phenol, and oils. Additionally, some of the analytical techniques employed in the study are highlighted in this section. For instance, the groundwater sample calcium contents were determined using the Ethylenediaminetetraacetic Acid method [34] using Na2EDTA 0.05 M, Acetylacetone, and Tris (hydroxymethyl). The pH levels in the samples were measured using a lab pH meter (Corning–Pyrex, Frederick, MD, USA). On the other hand, the levels of chlorides, polyphosphates, nitrites, and nitrates in the water samples were measured using a colorimeter (Hach DR900; Berlin, Germany) and a spectrophotometer (Hach DR3900; HACH/LANGE, Berlin, Germany) together with standard reagents and test kits. The measurements of turbidity were conducted using Great Lakes National Program Office (GLNPO) of the US Environmental Protection Agency in Washington D.C.'s Standard Operating Procedure for Turbidity. The overall mineralization was measured using flame atomic absorption spectrometry [35]. In order to determine permanganate oxidizability [36], potassium permanganate was used in a hot, acidic medium to detect oxidation. The process involved heating a sample for a predetermined amount of time (10 min) in a boiling water bath with potassium permanganate and sulfuric acid. Moreover, utilizing Ca-ISE and EGTA as titrants allowed us to determine sulfate. Sulfate was precipitated by adding excess $BaCl_2$ to the water sample. The Ba ions that had not responded were re-titrated with EGTA titrant. On the other hand, an inductively coupled plasma mass spectrometer was used to measure the cadmium levels in the water samples. In general, Standard Methods for the Examination of Water and Wastewater of the American Public Health Association (APHA) were used to analyze the water samples [37]. Before being brought to the lab for examination, the samples were all kept at 4 °C (for preservation) and examined on the same day as collection to preserve the sample original state.

2.4. The Applied Statistical Methods

2.4.1. Analysis of Variance

Single-factor analysis of variance (ANOVA) was also employed in this investigation to determine whether the variances in the data on water quality were statistically significant. It is important to note that the approach evaluates the degree of variation in each group of water quality data using samples from each group. The discrepancy between the *p*-values and alpha (0.05) values was used to assess the significance level. It is also important to keep in mind that even if the null hypothesis is true, the alpha number represents the chances of rejecting it. The null hypothesis is accepted if the *p*-value exceeds the alpha value. The *p*-value, on the other hand, shows the chance of obtaining a result that is more extreme than the one obtained from the experiment [38,39].

2.4.2. *t*-Test Analysis

The *t*-test served as yet another crucial statistical method in the investigation. This was additionally used to check for statistically significant differences between the means of the two groups for each parameter as determined using the two treatment procedures. How much the variations in the data differ from one another is indicated by the T-value. Accordingly, the greater the value of T is, the more evidence there is that the null hypothesis is incorrect (based on two-sample assuming equal variances) [40].

2.4.3. Calculation of Water Quality Indices

The WQIs were developed using a total of 15 water quality measures, including total hardness, colors, turbidity, calcium, chlorides, sulfates, fluorides, nitrates, cadmium, lead, cyanides, zinc, manganese, nickel, and arsenic. Using the WQI methodology, the 15 parameters that were chosen to gauge the level of water quality were compiled into a single index. This made it easier to obtain a complete picture of how effective both treatment methods, based on synthetic and natural zeolite, were overall. Equations (1)–(4) describe the sequential process for creating the WQIs.

The first stage was to give each parameter a weight (w_i) on a scale of 0 to 6, with 0 representing the least impact and 6 representing the greatest impact on groundwater water quality. The method of weighting was based on how the intended usage was believed to be impacted by the water quality measurements. The factors in this study were weighted using National Sanitation Foundation of the United States Water Quality Index as a reference [41]. The relative weight (W_i) was then determined by dividing each weight by the total of all weights, as given in Equation (1) [42].

$$W_i = \frac{w_i}{\sum_{i=1}^{n} w_i} \quad (1)$$

where n is the number of parameters being researched, W_i is the assigned relative weight, and w_i (note, lowercase w) is the weight of each individual parameter.

Calculating a quality rating scale (q_i) for each selected water quality parameter was another important step in the WQI development process. This was accomplished by multiplying the result by 100 after dividing the concentration of each parameter by its corresponding suggested guideline in accordance with Kazakhstan standards [42].

$$q_i = \frac{C_i}{S_i} \times 100 \tag{2}$$

where the quality rating is q_i, while the concentration of each parameter is C_i, and for each measure, S_i is the suggested guideline according to the government of Kazakhstan.

The sub-index (SI) for each parameter needed to be calculated in order to calculate the general WQI, as indicated in Equation (3).

$$SI_i = W_i \times q_i \tag{3}$$

Finally, the total of all the sub-indices from each of the investigated parameters was used to generate the overall WQI.

$$WQI = \sum_{i=1}^{n} SI_i \tag{4}$$

where SI_i refers to a parameter's i^{th} sub-index, q_i considers the quality rating based on the concentration of the i^{th} parameter, W_i is referred to as relative weight (with capital W), and n is the number of chemical parameters. Table 3 lists all the allocated weights and relative weights.

Table 3. Weights and relative weights of the studied parameters.

Parameter	Weight (w_i)	Relative Weight (W_i)	Guideline	Unit
Total hardness	4	0.06	7	$mmol/dm^3$
Colors	4	0.06	20	mg/dm^3
Turbidity	4	0.06	1.5	mg/dm^3
Calcium	4	0.06	7	mg/dm^3
Chlorides	5	0.07	350	mg/dm^3
Sulfates	5	0.07	500	mg/dm^3
Fluorides	5	0.07	1.2–1.5	mg/dm^3
Nitrates	5	0.07	45	mg/dm^3
Cadmium	4	0.06	0.001	mg/dm^3
Lead	4	0.06	0.03	mg/dm^3
Cyanides	4	0.06	0.035	mg/dm^3
Zinc	4	0.06	5	mg/dm^3
Manganese	5	0.07	0.1	mg/dm^3
Nickel	5	0.07	0.1	mg/dm^3
Arsenic	6	0.09	0.05	mg/dm^3
Total	68	1.00		

The status value categories of "excellent water," "good water," "poor water," "very bad water," and "water unsuitable for drinking" were used to define the estimated WQIs (Table 4) [43,44].

Table 4. Categories of the water quality indices.

Class	WQI Value
Excellent water	<50
Good quality groundwater	50–100
Poor quality groundwater	100–200
Poor quality groundwater	200–300
Groundwater unsuitable for drinking	>300

3. Results

3.1. Raw Groundwater Characterization

Investigating the quality of groundwater in the case study served as the study's first crucial component. Therefore, a large number of factors affecting water quality were taken into account. Table 5 lists the general characteristics of groundwater in terms of the minimum and maximum concentration values, arithmetic mean, and standard deviation (SD). The concentration values of a few of the examined water quality metrics are highlighted in this section. The average total hardness concentration in raw groundwater was found to be 18.63 mg/dm^3, which is around 2.7 times the acceptable level for drinking water. The average overall mineralization concentration found in the sample was 1691.67 mg/dm^3, which is 1.7 mg/dm^3 more than the suggested guideline. In the study, the average dry residue concentration was 867.48 mg/dm^3, which is 0.9 times higher than the suggested standard. The average calcium concentration in untreated groundwater was 63.03 mg/dm^3, which is nine times higher than the advised standard for drinking water quality. The average amount of chlorides in raw groundwater was 170 mg/dm^3 or about half of the acceptable level for drinking water. The average sulfate concentration in untreated groundwater was 165.09 mg/dm^3, which is 0.3 times higher than the suggested standard for drinking water quality. The average amount of manganese in raw groundwater was 45.6 mg/dm^3, which is 456 times greater than the acceptable standard for the quality of drinking water. It is also important to note that sediments and rocks both contain naturally occurring pollutants with a high potential to affect the state of groundwater quality [45]. Metals such as iron and manganese are dissolved as groundwater passes through sediments, and the resulting water may have significant amounts of these dissolved metals [46]. The quality of groundwater can be impacted by industrial discharges, habitation, agriculture, groundwater pumping, and waste disposal. Groundwater contamination of the aquifer might result from leaking fuel tanks, spills of harmful chemicals, or gasoline. The water table may get contaminated by pesticides and fertilizers that have been applied to crops and lawns [47].

3.2. Removal Efficiency Analysis

In general, the natural zeolite treatment plant had removal efficiency that ranged from 30 to 100%, while synthetic zeolite had removal efficiency that ranged from 36 to 100% (Table 6). With zinc, we observed the lowest removal effectiveness (30%) of natural zeolite, whereas with arsenic, we observed the lowest removal efficiency (36%) of synthetic zeolite. With turbidity and beryllium, we observed the maximum removal efficiency (100%) of natural zeolite, whereas with turbidity, we recorded the highest removal efficiency (100%) of synthetic zeolite. When the groundwater samples were put through the natural zeolite treatment system, removal efficiency of 50% and above was obtained with 27 (79.4%) out of the 34 water quality parameters examined. On the other hand, when the groundwater samples were put through the synthetic zeolite treatment system, about 50% and above removal efficiency was attained with 30 (88.2%) out of the 34 water quality indicators studied. By utilizing the depth of a particular medium, depth filters can effectively remove a wide range of contaminants, including particles, submicron particles, colloidal material, and soluble material [48]. Something that it is important to note is that before the water sample can reach the opposite side of the depth filter, it must pass through the filter medium. It makes sense to believe that pollutants bigger than the pore size of the filter could be easily removed by means of mechanical filtration. This process is also known as size exclusion, sieving, or straining. Adsorption, which draws pollutants using either electrokinetics or surface affinity, is another purification method that works with depth filters. These submicron particles, colloidal material, and soluble pollutants can all be removed thanks to the electrokinetic action found in charge-modified depth-filter media [49].

Table 5. Summary of the recorded concentrations in raw groundwater.

Parameter	Min	Max	Mean	Median	SD	Unit
Total hardness	16.6	20.4	18.63	18.9	1.563	mmol/dm^3
Colors	4.8	8.5	6.47	6.1	1.533	degree
Turbidity	0	2	1	1	0.816	mg/dm^3
pH	7.85	8.45	8.18	8.24	0.249	pH
General mineralization	1465	1896	1691.667	1714	176.662	mg/dm^3
Permanganate oxidability	1.6	4.3	2.767	2.4	1.132	mg/dm^3
Dry residue	786.44	989.68	867.48	826.32	87.929	mg/dm^3
Calcium	48.65	80.32	63.03	60.12	13.092	mg/dm^3
Chlorides	144	195	170	171	20.833	mg/dm^3
Sulfates	138.43	189.98	165.09	166.85	21.082	mg/dm^3
Polyphosphates	0.022	0.044	0.03	0.028	0.009	mg/dm^3
Fluorides	0.2	0.3	0.23	0.2	0.047	mg/dm^3
Silicic acid (Si)	10.8	13.6	12.43	12.9	1.190	mg/dm^3
Nitrates	0.32	0.56	0.453	0.48	0.100	mg/dm^3
Nitrites	0.001	0.006	0.003	0.003	0.002	mg/dm^3
Cadmium	0.001	0.002	0.001	0.001	0.0005	mg/dm^3
Lead	0.02	0.04	0.027	0.02	0.009	mg/dm^3
Cyanides	0.022	0.046	0.034	0.035	0.010	mg/dm^3
Barium	0.1	0.3	0.167	0.1	0.094	mg/dm^3
Zinc	0.01	0.02	0.013	0.01	0.005	mg/dm^3
Manganese	34.8	56.5	45.6	45.5	8.859	mg/dm^3
Nickel	0.01	0.01	0.01	0.01	0	mg/dm^3
Iron	0.02	0.05	0.0367	0.04	0.012	mg/dm^3
Arsenic	0.01	0.03	0.02	0.02	0.008	mg/dm^3
Hydrargyrum	0.0002	0.0004	0.0003	0.0002	9.43×10^{-5}	mg/dm^3
Copper	0.12	0.22	0.173	0.18	0.041	mg/dm^3
Aluminum	0.02	0.03	0.023	0.02	0.005	mg/dm^3
Chromium	0.03	0.06	0.047	0.05	0.012	mg/dm^3
Beryllium	0.00002	0.00005	0.00004	0.00005	1.41×10^{-5}	mg/dm^3
Molybdenum	0.004	0.009	0.007	0.008	0.002	mg/dm^3
Selenium	0.002	0.006	0.004	0.004	0.002	mg/dm^3
Strontium	0.96	1.84	1.473	1.62	0.374	mg/dm^3
HCG pesticide DDT and its metabolites	0.001	0.004	0.002	0.002	0.001	mg/dm^3
Phenol	0.001	0.002	0.002	0.002	0.0005	mg/dm^3
Oils	0.002	0.006	0.004	0.005	0.002	mg/dm^3

3.3. *Analysis of Variance*

In this work, two statistical methods were primarily employed to analyze the state of variance resulting from the concentrations in untreated groundwater and the effluents treated with natural and synthetic zeolite treatment systems.

3.3.1. Summary of ANOVA Results

An overview of the ANOVA outcomes is shown in Table 7. Specifically, the null hypothesis that there are no differences between the means is rejected when the p-value is less than 0.05, indicating that there is a significant difference. The data variances for the water quality data from the analyzed parameters produced a p-value of 0.15, which is larger than 0.05 (alpha value), rendering them statistically insignificant, as is shown in Table 7.

3.3.2. Results of *t*-Test Analysis

To compare the differences between raw groundwater and the effluent treated with natural zeolite, between groundwater and the effluent treated with synthetic zeolite, as well as between the effluent treated with natural zeolite and the effluent treated with synthetic zeolite, t-test analysis was carried out in addition to ANOVA. Figure 2 presents a summary of the findings of the *t*-test study. The differences in concentrations of the analyzed groups of data were not statistically significant, as shown by the fact that all of the *p*-values produced by the *t*-test analysis were higher than 0.005 (alpha value). However, the *p*-values showed the following trend: *p*-value of effluent treated with natural zeolite vs. effluent treated with synthetic zeolite > raw groundwater vs. effluent treated with natural zeolite > raw groundwater vs. effluent treated with synthetic zeolite.

Table 6. Removal efficiency of natural and synthetic zeolite.

Parameter	Natural RE (%)	Synthetic RE (%)
Total hardness	80.20	97.00
Colors	87.63	96.91
Turbidity	100.00	100.00
General mineralization	74.00	92.20
Permanganate oxidability	33.13	67.47
Dry residue	93.48	94.72
Calcium	92.78	98.06
Chlorides	92.56	94.73
Sulfates	91.47	96.10
Polyphosphates	67.02	63.83
Fluorides	61.43	74.29
Silicic acid (Si)	81.90	86.73
Nitrates	73.09	76.18
Nitrites	50.50	63.40
Cadmium	55.00	70.00
Lead	70.00	65.88
Cyanides	47.57	70.87
Barium	66.00	69.40
Zinc	30.00	67.50
Manganese	64.47	67.32
Nickel	56.00	75.50
Iron	54.55	73.64
Arsenic	40.00	36.00
Hydrargyrum	46.75	47.50
Copper	51.31	56.38
Aluminum	65.71	82.86
Chromium	61.43	74.29
Beryllium	100.00	50.00
Molybdenum	71.43	85.71
Selenium	60.00	62.50
Strontium	42.71	44.89
HCG pesticide (a. b.y-isomers) DDT and its metabolites	42.86	47.57
Phenol	60.00	67.26
Oils	80.77	87.69

Table 7. Summary of ANOVA results.

SUMMARY						
Group	Count	Sum	Average		Variance	
Raw groundwater	34	3046.93	89.62		103,150.48	
Effluent treated with natural zeolite	34	553.82	16.29		5706.09	
Effluent treated with synthetic zeolite	34	213.7691	6.29		561.04	
ANOVA						
Source of variation	SS	df	MS	F	*p*-value	F crit
Between groups	140,765	2	70,382.51	1.93	0.15	3.09
Within groups	3,610,781	99	36,472.53			
Total	3,751,546	101				

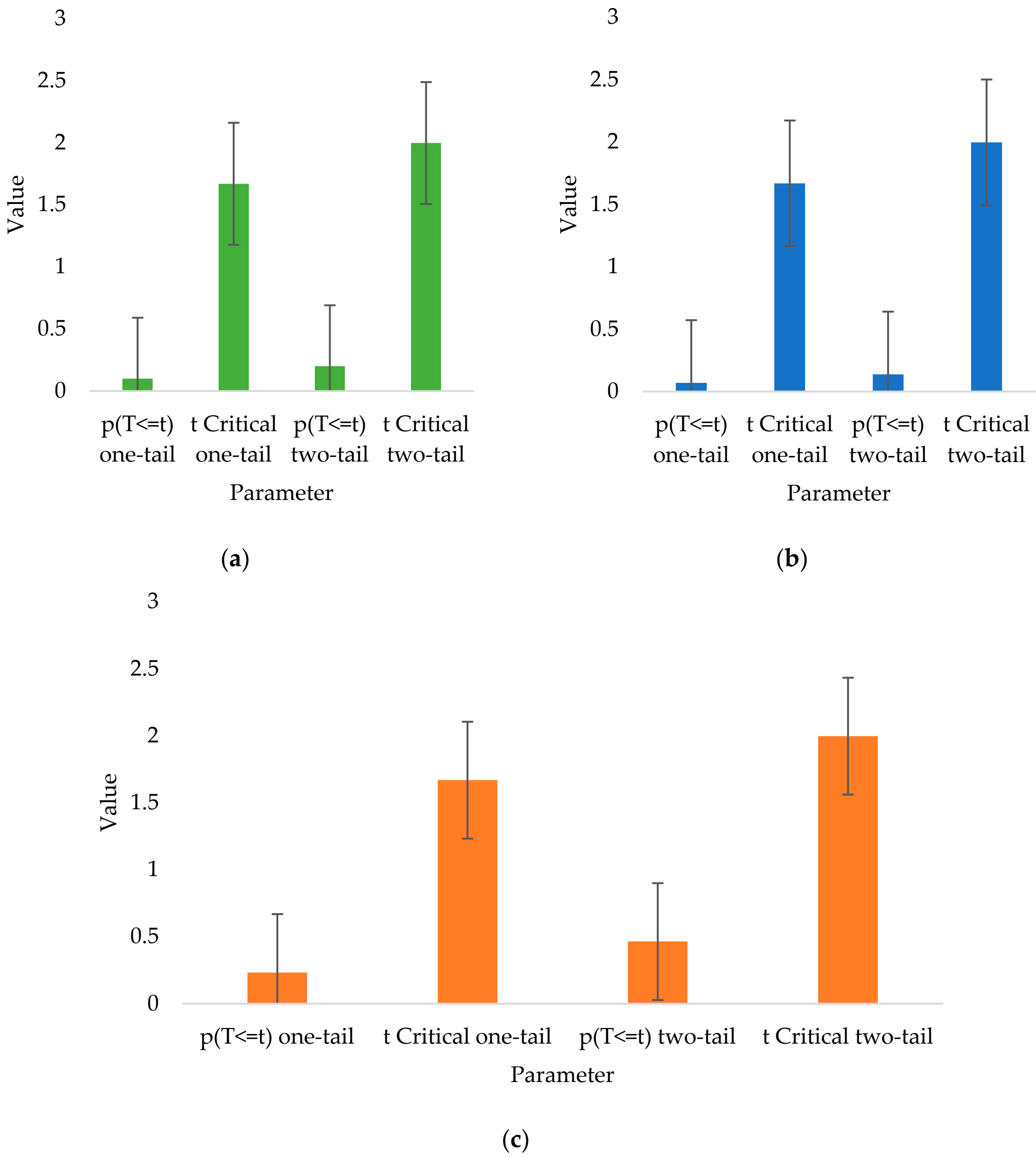

Figure 2. Results of the *t*-test analysis: (**a**) raw groundwater vs. effluent treated with natural zeolite; (**b**) raw groundwater vs. effluent treated with synthetic zeolite; (**c**) effluent treated with natural zeolite vs. effluent treated with synthetic zeolite.

3.4. Water Quality Analysis Based on the Developed WQIs

Water quality indices were also developed in the study to further assess the levels of water quality of raw groundwater and the quality of the effluents treated with natural zeolite and synthetic zeolite. A water quality index gives a single value based on a variety of water quality criteria that indicate the overall water quality at a specific location and time. An index' goal is to simplify complicated data on water quality so that the general public may understand and make use of them [42].

3.4.1. Raw Groundwater WQI

Table 8 provides a summary of the results of the water quality index development based on raw groundwater. In Table 8, it can be seen that manganese presented the highest quality rating (q_i) and sub-index (sl_i) compared with the other parameters involved in the computation of water quality indices. The phenomenon is related to the finding that the case study's groundwater had high amounts of manganese that were beyond the advised limits for drinking water. The average manganese concentration in untreated groundwater was 45.6 mg/dm^3, while the recommended limit for manganese in drinking water is 0.1 mg/dm^3. In comparison with the other water quality indicators used in the development of the water quality indices, the manganese concentration in raw groundwater resulted in a q_i of 45,500 and an sl_i of 3185, which is the highest contribution. A high contribution in terms of quality rating and sub-index can also be seen with calcium and total hardness, with sl_i values of 51.53 and 16.20, respectively. In minimal amounts, manganese is a beneficial mineral, but excessive amounts in drinking water can harm one's health as well as plumbing, appliances, and water fixtures. More frequently than in treated public drinking water, well water supply contains high levels of manganese [50].

Table 8. Summary of the outcomes of the development of the water quality indices using untreated groundwater.

Parameter	q_i	sl_i
Total hardness	270.00	16.20
Colors	0.00	0.00
Turbidity	0.00	0.00
Calcium	858.86	51.53
Chlorides	48.86	3.42
Sulfates	33.37	2.34
Fluorides	16.67	1.17
Nitrates	1.07	0.07
Cadmium	100.00	6.00
Lead	66.67	4.00
Cyanides	100.00	6.00
Zinc	0.20	0.01
Manganese	45,500.00	3185.00
Nickel	10.00	0.70
Arsenic	20.00	1.80

3.4.2. Natural Zeolite-Treated Effluent WQI

Table 9 provides a summary of q_i and sl_i from the water quality index development based on the effluent treated with natural zeolite. Similar to raw groundwater, the effluent treated with natural zeolite had relatively high-quality rating (1800) and sub-index (126) for manganese.

Table 9. Summary of the outcomes of the development of the water quality indices using the effluent treated with natural zeolite.

Parameter	q_i	sl_i
Total hardness	52.71	3.16
Colors	0.00	0.00
Turbidity	0.00	0.00
Calcium	65.00	3.90
Chlorides	3.61	0.25
Sulfates	2.82	0.20
Fluorides	7.50	0.53
Nitrates	0.27	0.02
Cadmium	60.00	3.60
Lead	26.67	1.60
Cyanides	51.43	3.09
Zinc	0.19	0.01
Manganese	1800.00	126.00
Nickel	4.40	0.31
Arsenic	24.00	2.16

3.4.3. Synthetic Zeolite-Treated Effluent WQI

Table 10 provides a summary of q_i and sl_i from the water quality index development based on the effluent treated with synthetic zeolite. Despite the synthetic zeolite contribution to better removal of manganese by means of the treatment system, the manganese sub-index (84) made the highest contribution to the overall water quality index. The sub-index from manganese was equivalent to 88.6% of the aggregated water quality index from the synthetic zeolite treatment system.

Table 10. Summary of the outcomes of the development of the water quality indices using the effluent treated with synthetic zeolite.

Parameter	q_i	sl_i
Total hardness	7.99	0.48
Colors	0.00	0.00
Turbidity	0.00	0.00
Calcium	17.43	1.05
Chlorides	2.56	0.18
Sulfates	1.29	0.09
Fluorides	5.00	0.35
Nitrates	0.24	0.02
Cadmium	40.00	2.40
Lead	30.33	1.82
Cyanides	28.57	1.71
Zinc	0.09	0.01
Manganese	1200	84
Nickel	2.45	0.17
Arsenic	28.00	2.52

3.4.4. Aggregated Water Quality Indices

Table 11 provides a summary of the aggregated water quality indices with their interpretations. According to Table 11, the total water quality index for raw groundwater was 3278.24, which is in the "water not fit for drinking" category. The natural zeolite effluent produced an index of water quality that falls into the "bad water" quality category of 144.82. Artificial zeolite produced a water quality index of 94.79, which falls into the "excellent water" quality category.

Table 11. Summary of the aggregated water quality indices.

Water Type	WQI	Interpretation
Raw groundwater	3278.24	Water unsuitable for drinking
Natural zeolite	144.82	Poor water
Synthetic zeolite	94.79	Good water

4. Discussion

As already said, the first and most important part of the study was examining the quality of groundwater in the case study. Therefore, a wide range of elements impacting water quality were considered. The effluents of the two zeolite-based treatment systems were then scrutinized. It should be emphasized that zeolite is reported to be a non-toxic, crystalline, three-dimensionally porous, hydrated aluminosilicate with natural adsorbent and ion exchange characteristics that eliminates dangerous bacteria as well as scattered insoluble and soluble pollutants from drinking water [51].

Raw groundwater was found to have an average total hardness concentration of 18.63 mg/dm^3, which is around 2.7 times the permissible amount for drinking water. It is critical to emphasize that total hardness, which is measured in milligrams per liter (mg/L), is the sum of calcium and magnesium contents. According to the World Health Organization [52], drinking water with hard minerals has no known negative effects on health. Additionally, very hard water in particular could make a significant additional contribution to the total intake of calcium and magnesium. On the other hand, some studies [53,54] have shown that excessive intake of calcium and magnesium can raise the risk of obesity, coronary artery disease, nephrolithiasis, colorectal cancer, hypertension, and stroke. The pathophysiology of hypertension has been linked to magnesium shortage, and several epidemiological and experimental research studies have found a negative relationship between blood pressure and serum magnesium levels. Nevertheless, in general, hard water can impede the efficacy of soaps and detergents and can lead to deposits of calcium carbonate, calcium sulfate, and magnesium hydroxide ($Mg(OH)_2$) inside pipes and boilers, resulting in reduced water flows and less effective heating [55].

The raw groundwater samples had an average general mineralization content of 1691.67 mg/dm^3, which is 1.7 mg/dm^3 more than the recommended one. However, 74% general mineralization removal efficiency was achieved with natural zeolite, while 92.2% removal efficiency was achieved with synthetic zeolite. As previously said, water in nature becomes mineralized as it filters through various rock layers from the source to the origin. This affects the level of mineralization according to the layers involved. To be more precise, we may say that the groundwater chemical makeup is impacted by the gases and minerals that interact with it as it moves rather slowly through the rocks and sediments of the Earth's crust. Even locally, a wide range of factors contributes to the quality of groundwater. Groundwater absorbs more minerals when it passes through rock pores and crack holes. Water eventually reaches a point of equilibrium or balance, which stops it from dissolving more substances.

By completely evaporating a sample of water, the dry residue is determined by weighing the minerals that remain in the container after the water has evaporated. For daily use, water that has more than 500 mg/L of dry residue is excessively minerally rich. Too many inorganic minerals may accumulate in our intestines as a result of imbalance. A mineral concentration of 50 to 500 mg/L or less is regarded as low and is strongly advised for everyday use [56]. The average dry residue concentration in raw groundwater was 867.48 mg/dm^3, which is relatively higher than the recommended standard. After treatment, 93.5% dry residue removal efficiency was achieved with natural zeolite, and 94.7% was achieved with synthetic zeolite. On the other hand, untreated groundwater had an average calcium concentration of 63.03 mg/dm^3, which is nine times higher than the recommended level for safe drinking water. In groundwater, calcium concentrations typically vary from 10 to 100 mg/L [57]. The principal sources of calcium are limestones and dolomites, which are carbonate rocks that have been dissolved by groundwater carbonic acid. The chemical breakdown of calcic-plagioclase feldspars and pyroxenes may be what causes calcium in groundwater [58]. In addition, the investigated raw groundwater average chloride concentration was 170 mg/dm^3, or approximately half the recommended limit for drinking water. Chloride can enter groundwater via several pathways, such as soil weathering, salt-bearing geological formations, salt spray deposition, salt used for de-icing roads, wastewater discharge, and in coastal areas, salty ocean water intrusion into fresh groundwater sources.

Moreover, untreated groundwater had an average sulfate concentration of 165.09 mg/dm^3, which is 0.3 times greater than the recommended level for drinking water quality. Mineral dissolution, atmospheric deposition, and other anthropogenic sources are among the sources of sulfate in groundwater. Gypsum has a significant role in the high sulfate concentrations seen in many of the world's aquifers [59]. Sulfate can give a bitter or medicinal flavor to water and have laxative effects at high concentrations. The average concentration of manganese in untreated groundwater was 45.6 mg/dm^3, which is 456 times higher than the allowable limit for drinking water quality. Manganese naturally occurs in low-oxygen or oxygen-free groundwater, typically in deep wells, in regions where groundwater flow is slow, and in regions where groundwater passes through organically rich soil [60]. In the literature, it is reported that the high solubility of manganese under both acidic and neutral conditions makes it one of the hardest elements to extract from groundwater [60]. Long-term consumption of manganese-rich water may impair memory, attention, and motor skills in both children and adults. If young children consume water that contains an excessive amount of manganese, they may experience learning and behavioral issues [61].

In general, the removal efficiency of the synthetic zeolite treatment plant ranged from 36 to 100%, while that of the natural zeolite treatment plant ranged from 30 to 100%. While, with arsenic, we observed the lowest removal effectiveness (36%) of synthetic zeolite, with zinc, we recorded the lowest removal effectiveness (30%) of natural zeolite. The highest removal efficiency (100%) of natural zeolite was observed with turbidity and beryllium, whereas the highest removal efficiency (100%) of synthetic zeolite was observed with turbidity. In total, with 27 (or 79.4%) out of 34 water quality examination criteria, we recorded removal efficiency of 50% or above after the groundwater samples were processed with the natural zeolite treatment system. On the other hand, with 30 (88.2%) out of the 34 water quality water quality indicators investigated, we recorded removal efficiency of 50% and higher when the groundwater samples were passed through the synthetic zeolite treatment system.

Comparing manganese to the other parameters used in the calculation of the water quality indices showed the highest quality rating (q_i) and sub-index (sl_i). However, as already mentioned, the phenomenon is connected to the observation that groundwater, in the case study, is characterized by high levels of manganese that exceed the recommended limits for drinking water. The manganese concentration in raw groundwater contributed the most, with a q_i of 45,500 and an sl_i of 3185, when compared with the other water quality indicators utilized in the development of the water quality indices. The effluent treated with natural zeolite showed comparably high-quality rating (1800) and sub-index (126) for manganese, similar to raw groundwater. Despite the synthetic zeolite contribution to better removal of manganese by means of the treatment system, the total water quality index derived from untreated groundwater was 3278.24, which is considered to be "water not fit for human consumption." The natural zeolite effluent produced a water quality index of 144.82, which is considered to indicate "poor water" quality. Synthetic zeolite produced a water quality index of 94.79, which is considered to indicate "excellent water" quality.

The advantages of synthetic zeolites over natural ones have also been demonstrated in the literature [62]. Generally, natural zeolites are found to be less effective than synthetic zeolites in removing chemicals such as radioactive waste from the environment [63]. In addition, in a study conducted by Król [62], it was observed that in comparison to natural zeolites, synthetic zeolites exhibit a significantly higher ability to adsorb heavy metal ions.

The much bigger pore size of synthetic zeolites compared with natural ones is another benefit. This broadens the variety of possible applications by enabling the sorption of bigger molecules to be achieved. For example, it was found in the study by Bandura et al. [64] that synthetic zeolites made from fly ash are effective mineral sorbents for cleaning up land-based petroleum spills, because they have two times the oil sorption capabilities of natural clinoptilolite. In addition, Parimal Pal [65] reported that synthetic zeolites can eliminate arsenic to a significantly larger extent than natural zeolites. Arsenic removal is impacted by the adsorbent Si/Al ratio and various porous properties. As a result, synthetic zeolites are a promising substitute for natural mineral sorbents for cleaning up land-based petroleum spills. Additionally, when utilized as catalysts, zeolites with smaller pore diameters experience pore blockage, which leads to poisoning and deactivation, whereas zeolites with large, interconnected channels are stable for a significantly longer period of time [66].

5. Conclusions

This study investigated the potential influence of zeolite-based materials on groundwater filtration. It is also crucial to emphasize that the natural zeolite treatment system of Kazakhstan's Chankanai mines was contrasted with a synthetic zeolite treatment system for the purification of groundwater. A number of the examined water quality parameters, such as manganese in untreated groundwater, were found to be somewhat higher than the recommended guidelines, a phenomenon that highlights the importance of treating groundwater before using it for drinking. According to the findings, with zinc, we observed the lowest removal effectiveness (30%) of natural zeolite, whereas with arsenic, we observed the lowest removal efficiency (36%) of synthetic zeolite. This indicates that the performance of synthetic zeolite was relatively higher than that of natural zeolite, as the lowest removal efficacy was recorded when groundwater was treated using the natural zeolite treatment system. However, both treatment systems achieved 100% turbidity removal efficiency. The highest removal efficiency (100%) of natural zeolite was achieved with turbidity and beryllium, whereas the highest removal efficiency (100%) of synthetic zeolite was achieved with turbidity. In total, with 27 (or 79.4%) out of 34 water quality examination criteria, we recorded removal efficiency of 50% or above after the groundwater samples were processed with the natural zeolite treatment system. The total water quality index derived from untreated groundwater was 3278.24, with water quality falling in the " water unsuitable for drinking" category. The natural zeolite effluent produced a water quality index of 144.82, which is considered to indicate "bad water" quality for drinking purposes. Synthetic zeolite produced a water quality index of 94.79, which is considered to be "good water" for drinking purposes. The phenomena suggest that the quality of the effluent from the synthetic zeolite treatment system was generally better than the quality of the effluent from the natural zeolite treatment system, particularly in the removal of manganese. The derived results are useful in the realm of groundwater, particularly in the process of developing more effective treatment techniques. Future research could look into the potential impact of column depth on the performance of both natural and synthetic zeolite.

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