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Removal of Magnesium Ion from Aqueous Solution by Natural Zeolite as Adsorbent: Kinetic, Equilibrium, Mechanism and Thermodynamic

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ABSTRACT

The adsorption of magnesium ions (Mg^{2+}) from aqueous solutions using natural zeolites has garnered significant attention due to its high cation-exchange capacity and environmental compatibility. Despite extensive research, the combined effects of operational parameters on Mg^{2+} adsorption remain inadequately understood. This study investigated the effects of pH, adsorbent dosage, contact time, and temperature on Mg^{2+} adsorption by natural zeolite. The zeolite was chemically activated with 6N HCl to enhance its adsorption capacity. The optimal conditions for Mg^{2+} removal were found at pH 7 using 20 grams of zeolite and a 10-minute contact time, resulting in a maximum adsorption capacity of 0.191 mg/g. Thermodynamic studies revealed an endothermic adsorption process, with a positive enthalpy change (ΔH) of 44.64 kJ/mol and a positive entropy change (ΔS) of 121.99 J/mol·K, indicating increased randomness at the solid-solution interface. The adsorption kinetics followed a pseudo-first-order model, suggesting physical adsorption mechanisms. These findings provide critical insights for optimizing zeolite-based adsorption systems for water treatment applications.

1. Introduction

The adsorption of magnesium ions (Mg^{2+}) from aqueous solutions using natural zeolites has garnered attention due to the increasing necessity for efficient, cost-effective water treatment methods [1,2]. Natural zeolites, owing to their high cation-exchange capacities and environmental compatibility, provide a promising alternative to conventional adsorbents [3-5]. Previous studies have documented the adsorptive properties of zeolites in removing various contaminants, highlighting their adaptability and effectiveness across different conditions [6-13]. The relevance of this study is further underscored by the need for sustainable technologies that can mitigate heavy metal ion levels in water, which if uncontrolled, can contribute to environmental and health issues such as scale formation and kidney stone development.

The influence of solution conditions such as pH and temperature on the adsorption dynamics offers crucial insights into the design of effective treatment systems. Research indicates that the

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adsorption efficiency of ions like Ni(II) and Cu(II) significantly varies with pH adjustments, which alter the availability of adsorption sites by modulating the concentration of competing H^+ ions [14-16]. Similar observations have been noted for magnesium adsorption, which is considerably influenced by solution pH, thereby affecting the overall process efficiency [17].

The primary challenge addressed in this study is the removal of magnesium ions from water using natural zeolite under varying operational parameters – pH, adsorbent weight, temperature, and initial magnesium concentration. These parameters critically influence the adsorption capacity and efficacy, necessitating a thorough investigation to optimize the adsorption process for practical applications.

Investigations into the adsorption process have demonstrated that adjusting the pH can enhance the availability of adsorption sites on zeolites, leading to improved removal efficiencies for various metal ions [18]. Similarly, modifying the zeolite structure by substituting sodium ions with magnesium has shown to increase the microporous volume, thereby improving the adsorption characteristics [19]. These modifications not only bolster the adsorptive capacity but also extend the utility of natural zeolites across a broader spectrum of concentrations and contaminants.

Despite extensive studies on the adsorptive removal of metal ions using zeolites, there remain gaps in understanding the combined effects of operational parameters on the adsorption of magnesium ions specifically. While individual effects of parameters such as temperature and pH are well-documented, their interactive effects and optimal conditions for magnesium ion removal are less understood. Moreover, the kinetic and thermodynamic aspects of magnesium ion adsorption on modified zeolites are not fully explored, thus limiting the development of predictive models that are crucial for process scaling and design.

This study aims to fill the aforementioned gaps by systematically analyzing the effects of pH, adsorbent weight, temperature, and initial magnesium concentration in the adsorption process. The objective is to elucidate the interdependencies of these variables and their collective impact on the adsorption efficiency, guided by equilibrium, thermodynamic, kinetic, and mechanistic evaluations. By integrating comprehensive process design considerations, this research will contribute novel insights into the optimization of zeolite-based adsorption systems for magnesium ion removal, thereby enhancing both theoretical understanding and practical application scopes.

2. Materials and Method

2.1 Preparation of Zeolites

The natural zeolite used in this study was sourced from local market in Indonesia. The procedure of preparing natural zeolite followed an experiment by Neolaka *et al.,* [20]. The zeolite was sieved to obtain a particle size of 100 mesh (150 µm). For physical activation, the zeolite was washed with demineralized water at a ratio of 2:3 (500 g zeolite in 750 mL demineralized water) and stirred continuously using a magnetic stirrer for 1 hour at 70°C, then let settle overnight. This washing procedure was repeated three times before the washed zeolite dried at 105°C.

For chemical activation, 500 g of physically activated zeolite was sampled to soak in 750 mL of 1% HF solution for 30 minutes, then rinsed with demineralized water, and let dried at 120°C for 3 hours. Subsequently, the sample was immersed in 500 mL of 6 N HCl solution at 50°C for 30 minutes under continuous stirring, then filtrated and washed repeatedly, and dried again at 130°C for 3 hours. Finally, the sample was soaked in 500 mL of 1 N NH4Cl solution at 60°C for 3 hours with stirring, then filtered and washed repeatedly with demineralized water until no Cl^- ions were detected using AgNO3 solution, then it was dried at 130°C for 3 hours. The sample was ready for adsorption and characterisation.

Natural zeolite was analysed by using a Scanning Electron Microscope (EVO 40, Carl Zeiss AG, USA) to obtain information of the surface morphological structure of natural zeolite before and after adsorption.

2.2 Adsorbate and Other Chemicals

This study used all analytical-grade chemicals. The $MgCl_2.6H_2O$ obtained from Sigma Aldrich with 99.9% purity was used as the source of Mg ion. Exactly 100 mg/L of stock solution was prepared by dissolving 100 mg of $MgCl_2.6H_2O$ in 1,000 ml of volumetric flask, then the stock solution was diluted with ultra-pure water to obtain different concentrations of experimental Mg ion (10, 15, 20 and 25 mg/L). The solution pH was adjusted by addition of either 1 M hydrochloric acid or 0.5 M sodium hydroxide solutions, then measured using a digital pH meter (PHTESTR30).

2.3 Adsorption Studies

The adsorption experiments were conducted to evaluate the efficacy of natural zeolite as an adsorbent for magnesium ions (Mg^{2+}) from aqueous solutions. The process was optimized through batch studies, focusing on key operational parameters such as adsorbent dosage, initial concentration, initial pH, and temperature.

The effect of adsorbent dosage on the adsorption process was investigated over a range of 5-20 gram where 250 ml of Mg ion solution operated in a condition of 15 mg/L initial Mg ion concentration, pH 7.0, 25°C temperature, and 100-rpm shaker speed). The initial Mg ion concentration was measured by varying the Mg ion concentration from 10 to 25 mg/L (250 ml of Mg ion solution; 20 mg of adsorption mass; pH 7.0; 25°C; 100-rpm shaker speed). pH solution effects were assessed at 3, 7 and 9 (250 ml of Mg ion solution; 20 mg of adsorption mass; 15ppm of Mg ion initial concentration; 25 °C; 100-rpm shaker speed). The temperature varied from 20 to 40^{O}C (250 ml of Mg ion solution; 20 mg of adsorption mass; 15ppm of Mg ion initial concentration; pH 7.0; 100-rpm shaker speed).

The Mg ion was analyzed using the Calmagite method. The Mg^{2+} ions left after adsorption was measured using Hanna Instrument HI83300 and two reagents, HI93752A-Mg and HI93752B-Mg.

The adsorption capacity of the natural zeolite at time t (q_t) was calculated by the following mass balance relationship:

$$q = \frac{(C_O - C_t).V}{m} \tag{1}$$

where C_O is the initial Mg ion concentration (mg/L), C_t is the concentration of Mg ion concentration at any time t (mg/L), V is the volume of solution (L) and m is the mass of natural zeolite (g).

2.4 Isotherm Study

Equilibrium adsorption studies were conducted by mixing 250 ml of Mg ion solutions at various concentrations (10, 15, 20, and 25 mg/L) with 15 mg of natural zeolite in 250 ml of Mg^{2+} ion solution for 180 min which was more than sufficient to equilibrium time. The method is presented in Section 3.

3. Theory

3.1 Adsorption Kinetic and Mechanism

The mechanism of adsorption and the transient behaviour of the dye adsorption process were investigated by analyzing the adsorption kinetics using pseudo-first-order and pseudo-second-order models.

3.1.1 Pseudo-first and pseudo-second-order models

The linearized forms of the pseudo-first-order and pseudo-second-order models are expressed as per Eq. (5) and Eq. (6), respectively:

$$\log(q_e - q_t) = \log q_e - \frac{k_F}{2.303} t \qquad (2)$$

where q_t (mg/g) is the amount of Mg ion adsorbed at time t, q_e (mg/g) is the adsorption capacity at equilibrium. The adsorption rate constant k_F (min^{-1}) and q_e (mg/g) were calculated from the slope and intercept of the linear plot of $\log(q_e - q_t)$ against (t).

$$\frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{k_S q_e^2} \qquad (3)$$

The pseudo-second-order rate constant k_S (g/mg.min) and q_e (mg/g) can be calculated from the slope and intercept of the linear plot (t/qt) against (t).

3.2 Adsorption Isotherm

Freundlich and Langmuir models were used to explain the Mg ion-natural zeolite interaction and to determine the adsorption capacity.

3.2.1 Freundlich isotherm

Freundlich model was developed to explain how adsorption takes place on heterogeneous surfaces [4]. In this study, Freundlich model was selected to explain Mg ion and natural zeolite interaction relationship:

$$\ln q_e = \frac{1}{n} \ln C_e + \ln k_F \qquad (4)$$

where q_e (mg/g) is the amount of Mg ion adsorbed at equilibrium time, C_e is equilibrium concentration of Mg ion in solution (mg/L). The Freundlich adsorption parameter, k_F and the heterogeneity factor (1/n) can be calculated from slope and intercept of the linear plot of ln q_e against ln C_e. Also, if n value > 1, this indicates a favourable adsorption system.

3.2.2 Langmuir isotherm

Langmuir isotherm model was developed to explain how adsorption takes place on homogeneous surfaces. The linearised form of Langmuir model can be written as per Eq. (5):

$$\frac{C_e}{q_e} = \frac{1}{k_L q_e} + \frac{C_e}{q_m} \tag{5}$$

The maximum adsorption capacity q_m (mg/g) and Langmuir constant related to adsorption energy k_L (L/mg) were calculated from the slope and intercept of the linearised forms of the plots where (C_e/q_e vs. $1/q_e$).

3.3 Thermodynamic Study

Thermodynamic studies have been investigated based on the equilibrium data. Gibb's free energy (ΔG^O), enthalpy change (ΔH^O), and change in entropy (ΔS^O) were calculated in the following equations, respectively:

$$\log \frac{q_e}{C_e} = \frac{\Delta S^0}{2.303R} + \frac{-\Delta H^0}{2.303RT} \tag{6}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{7}$$

The linear form of the plot $\log(q_e/C_e)$ vs. $1/T$ presents Van't Hoff equation where q_e is the solid phase concentration at equilibrium (mg/L), C_e is equilibrium concentration in solution (mg/L), T is temperature in K, and R is the gas constant (8.314 J/mol K). The enthalpy change (ΔH^0) and entropy change (ΔS^0) were calculated from the slope and intercept of the linear Van't Hoff plot $\log q_e/C_e$ vs. $1/T$.

4. Results and Discussion

4.1 Effect of Adsorbent (Natural Zeolite) Dosage on Mg Ion Adsorption

Figure 1 illustrates the impact of varying dosages of natural zeolite on the adsorption of magnesium ions from an aqueous solution under controlled conditions. As depicted, increasing the adsorbent weight from 5 grams to 20 grams resulted in a significant enhancement in the removal efficiency of magnesium ions. At 5 grams, the magnesium concentration decreased steadily from an initial 15 mg/L to approximately 6 mg/L over 60 minutes. In contrast, with 20 grams of adsorbent, the magnesium concentration rapidly declined to below 2 mg/L within the same timeframe. The equilibrium time for all dosages was remarkably rapid, occurring within the first 10 minutes, and therefore, suggesting a fast adsorption process. This is indicative of the high efficacy of natural zeolite in capturing magnesium ions from solution, likely due to its high cation-exchange capacity and surface area which facilitate quick ion exchange and adsorption. These findings share similar trend with Ayar *et al.,* [21] and Mihajlović *et al.,* [22] who suggested that while natural zeolite is a promising adsorbent, the treatment process may need to be optimized for higher initial concentrations, potentially through adjustments in adsorbent dosage or the incorporation of pre-treatment steps.

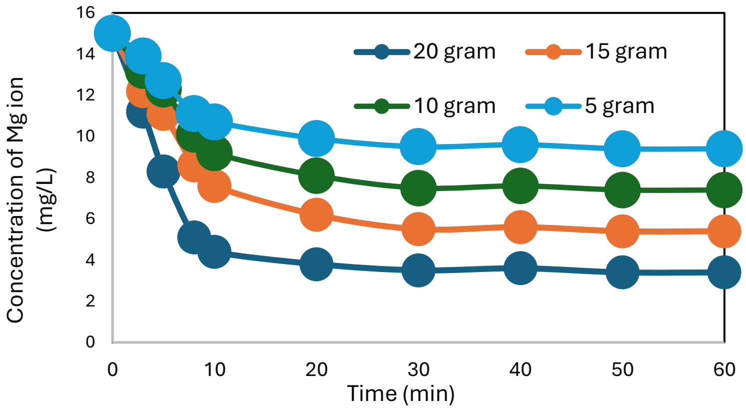


Fig. 1. Effect of adsorbent dosages onto Natural Zeolite of adsorbent (Volume of Mg Ion Solution = 250 ml; Initial Mg Ion Concentration = 15 mg/L; pH = 7.0; Temperature = 25 °C; Shaker Speed = 100 rpm)

A rapid decrease in magnesium ion concentration observed in this study has confirmed previous findings which documented the efficiency of natural zeolites in adsorbing various metal ions due to their structural and chemical properties [23,24]. The initial rapid adsorption phase typically corresponds to the external surface adsorption or physisorption, followed by a slower intraparticle diffusion phase, as noted in similar adsorption studies [21,25]. Notably, the adsorption efficiency increases markedly with higher dosages of zeolite, which is consistent with the literature suggesting that increased adsorbent mass enhances the availability of adsorption sites [22].

However, this study extends existing knowledge by quantifying the equilibrium time across different adsorbent weights, offering practical insights into the operational dynamics of using natural zeolite in water treatment systems. The stability of post-equilibrium Mg ion concentration highlights the potential of natural zeolite to maintain adsorption efficacy over prolonged periods, which is advantageous for continuous treatment applications.

The findings from this study underscore the practical and scientific relevance of employing natural zeolite as an efficient adsorbent for magnesium ion removal from aqueous solutions. The rapid attainment of adsorption equilibrium suggests that natural zeolite can be effectively utilized in treatment systems requiring quick response times, such as in emergency water purification scenarios or in industrial applications where rapid water treatment is essential.

Scientifically, these data provide a basis for further investigation into the kinetics and mechanisms of ion adsorption by natural zeolite, particularly in relation to how adsorbent dosage influences the speed and efficiency of the process. Practically, the ability of natural zeolite to achieve low residual concentrations of Mg ions offers significant environmental benefits, potentially reducing the ecological impact of magnesium-laden effluents.

These results have implications for the design of adsorption systems, indicating that higher dosages of natural zeolite can be more effective in achieving lower concentrations of contaminants, thus informing dosage guidelines for large-scale water treatment operations. The study also contributes to the broader field of sustainable water treatment technologies, highlighting the utility of natural materials in environmental remediation efforts.

4.2 Effect of Initial Mg Ion Concentration

Figure 2 illustrates the effect of varying initial Mg ion concentrations (10, 15, 20, and 25 mg/L) on the adsorption efficiency of natural zeolite. The adsorption profiles indicate a rapid decrease in Mg concentration within the first 10 to 20 minutes, followed by a plateau, signifying equilibrium. Notably, lower initial concentrations (10 and 15 mg/L) reached equilibrium faster (10 minutes) than higher concentrations (20 and 25 mg/L) which required 20 minutes. It suggests that at lower concentrations, the ratio of magnesium ions to available adsorption sites on the zeolite is lower, allowing a quicker saturation of the adsorbent. At higher initial Mg concentrations, the longer time to reach equilibrium can be attributed to the increased driving force for adsorption which requires more time to overcome mass transfer limitations and fully utilize the available adsorption sites [26,27].

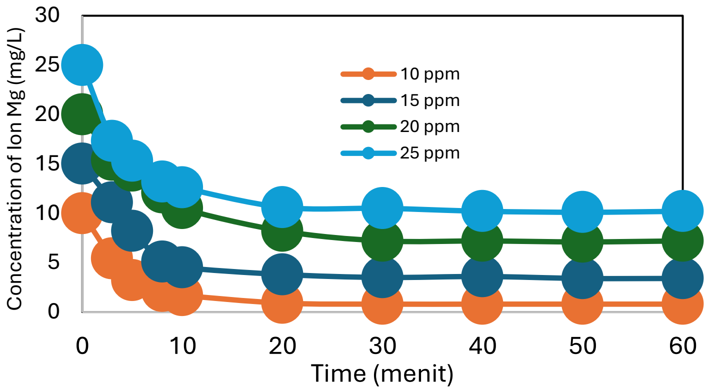


Fig. 2. Effect of Initial Concentration of Mg Ions onto Natural Zeolite of adsorbent (Volume of Mg Ion Solution = 250 ml; Mass of adsorption = 20 mg; pH = 7.0; Temperature = 25 °C; Shaker Speed = 100 rpm)

The adsorption capacity of natural zeolite shows a dependency on the initial concentration of Mg ions. Despite a longer time to reach equilibrium at higher concentrations, the final Mg ion concentrations remain higher than Mg with lower initial concentrations despite a longer time to reach equilibrium. This indicates that while the adsorbent can effectively reduce magnesium levels, its capacity is challenged as the initial ion concentration increases, leading to higher residual concentrations post-equilibrium.

These results demonstrate the importance of considering initial ion concentration in the design and operation of adsorption systems using natural zeolite. For applications requiring lower residual Mg concentrations, it may be necessary to either operate at lower initial concentrations or increase the adsorbent dosage. This study has presented the adsorption behavior of natural zeolite, offering practical guidance for its application in water treatment and environmental remediation. Additionally, the need for optimizing operational parameters such as contact time and adsorbent quantity to enhance the efficiency of magnesium removal from aqueous solutions has been highlighted. Understanding these dynamics is crucial for engineering robust and effective water treatment systems that can adapt to varying feed water qualities, ensuring consistent compliance with environmental standards and public health requirements.

4.3 Effect of Initial Solution pH on Mg Ion Adsorption

Figure 3 provides a comparative analysis of magnesium ion adsorption by natural zeolite across different pH levels (3, 7, and 9) under uniform experimental conditions. The data illustrated a marked influence of pH on the adsorption efficiency. At pH 7, Mg concentration decreased sharply to approximately 2 mg/L within 10 minutes, achieving rapid equilibrium. Conversely, at pH 3 and pH 9, the decrease in Mg ion concentration was less pronounced, stabilizing around 4 mg/L and 6 mg/L respectively, with a longer equilibrium time of 20 minutes. These observations underscore the sensitivity of zeolite's adsorption capacity to the solution pH, reflecting the complex interplay between hydrogen ion concentration and the availability of adsorption sites on the zeolite surface.

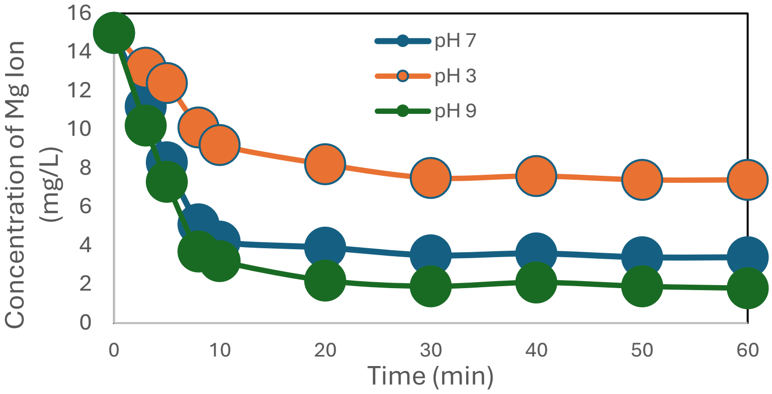


Fig. 3. Effect of pH Solution onto Natural Zeolite of adsorbent (Volume of Mg Ion Solution = 250 ml; Mass of adsorption = 20 mg; Initial Concentration of Mg Ion=15ppm; Temperature = 25 °C; Shaker Speed = 100 rpm)

The dependency of adsorption efficiency on pH is consistent with findings of prior studies documenting similar trends for various adsorbents. For instance, the adsorption of heavy metals is generally optimized at a neutral pH, where competition between metal ions and protons for adsorption sites is minimized [15,17]. The of excess H+ in acidic (pH 3) and OH- in alkaline (pH 9) conditions can inhibit the adsorption process by altering the charge and structure of the adsorbent surface, thereby reducing its affinity for Mg ions [28].

These findings are particularly relevant as they highlight the importance of controlling the pH to maximize the adsorption capacity of zeolites, especially in scenarios where variable pH levels may be encountered, such as in industrial effluents or municipal wastewater treatment.

The demonstrated effect of pH on the adsorption of Mg ions by natural zeolite has significant practical and theoretical implications. Practically, the ability to manipulate adsorption efficiency through pH adjustments provides a valuable control mechanism in water treatment processes, allowing for the optimization of zeolite performance under different operational scenarios. Theoretically, these results contribute to the broader understanding of adsorptive mechanisms at the molecular level, suggesting avenues for future research into the modification of zeolite materials to enhance their performance across a wider range of pH conditions. Additionally, the rapid equilibrium achieved at neutral pH suggests that natural zeolite could be particularly effective in systems where pH can be controlled or is naturally stable, thereby enhancing the applicability of zeolite-based adsorption technologies in water purification.

This study has underscored the importance of pH in the design and operation of adsorption systems using natural zeolites, highlighting the need for careful consideration of solution characteristics to achieve optimal contaminant removal efficiencies.

4.4 Effect of Temperature on Mg Ion Adsorption and Thermodynamic Studies

The effect of temperature on the adsorption capacity of adsorbents is a crucial factor that significantly influences the efficiency of adsorption processes [29,30]. To study the effect of temperature on Mg ion adsorption by natural Zeolite, we carried out experiments at temperatures of 20, 25, 30, and 40°C. Figure 4 illustrates the effect of temperature on the adsorption capacity of natural zeolite for Mg ions. As depicted in the figure, the concentration of Mg ions decreases more rapidly at higher temperatures, indicating an increase in adsorption capacity. Specifically, the equilibrium adsorption capacity rises with temperature, suggesting that the adsorption process is endothermic. This means that higher temperatures enhance the surface activity of natural zeolite, thereby improving its ability to adsorb Mg ions more effectively. This trend was observable from 20°C to 40°C, with equilibrium times decreased significantly as the temperature rising from 20 minutes at 20°C to 10 minutes at 25°C and up. This temperature dependence suggested that higher temperatures facilitate the diffusion of Mg ions onto the adsorption sites of zeolite, enhancing the overall adsorption efficiency. According to Ren *et al.,* [31], adsorption efficiency increases with temperature, suggesting a positive effect of higher temperatures on adsorption process.

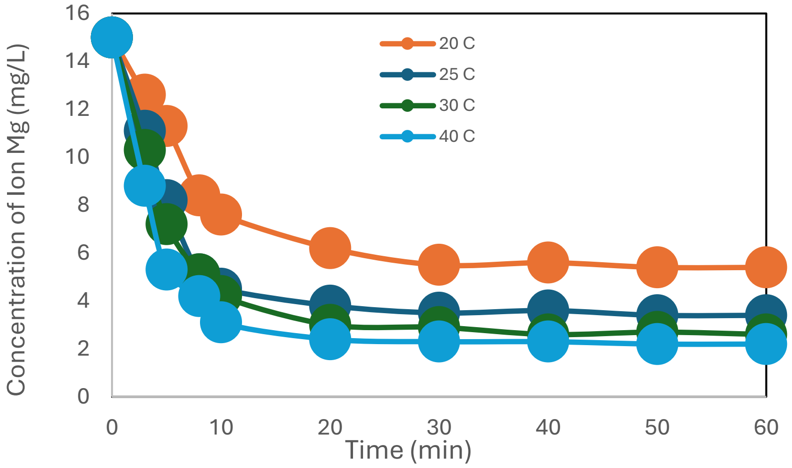


Fig. 4. Effect of Temperature onto Natural Zeolite of adsorbent (Volume of Mg Ion Solution = 250 ml; Mass of adsorption = 20 mg; Initial Concentration of Mg Ion=15ppm; pH = 7.0; Shaker Speed = 100 rpm)

Thermodynamic parameters of an adsorption process aimed to investigate whether the process is favorable. ΔG0, ΔH0, and ΔS0 were obtained from the experiments at different temperatures of 20, 25, 30, and 40^{O}C by the application of Eq. (11), Eq. (12), Eq. (13), and Eq. (14), as well as from the Van ‘t Hoff plots (see Figure 5). The Van ’t Hoff plot in Figure 5 and the derived thermodynamic parameters in Table 1 elucidate the nature of the adsorption process. The plot, displaying a linear relationship with a regression coefficient R^2=0.9494, confirms the reliability of the thermodynamic data. The positive enthalpy change (ΔH) indicates the endothermic nature of magnesium ion adsorption onto natural zeolite, whereas the positive entropy change (ΔS) suggests increased randomness at the solid-solution interface, possibly due to the displacement of water molecules by Mg ions which leads to a more disordered state at the interface.

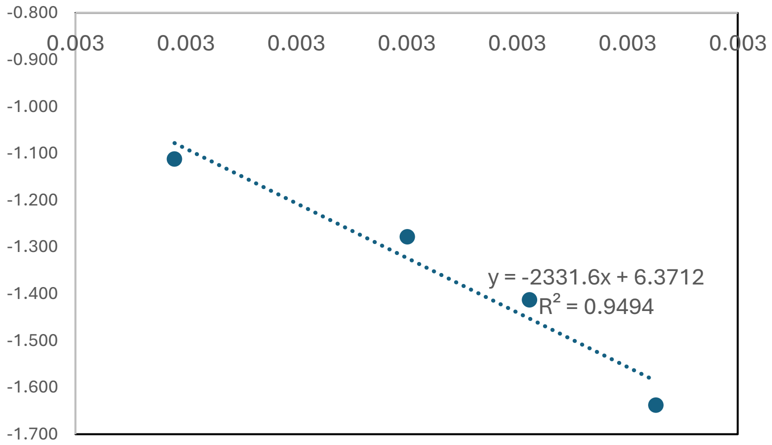


Fig. 5. Adsorption thermodynamics fitting curve

Table 1
Parameters for adsorption of Mg Ion onto Natural Zeolite at different temperatures

Temperature (C)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol)
20	8,900.327	44,643.476	121.990
25	8,290.375	44,643.476	121.990
30	7,680.424	44,643.476	121.990
40	6,460.521	44,643.476	121.990

The Gibbs free energy (ΔG) values are positive across all temperatures studied, suggesting that the adsorption process is non-spontaneous under the experimental conditions. This might be influenced by the external energy provided (e.g., in the form of heat or agitation) to overcome the energy barriers associated with adsorption at these temperatures. The ΔG value that decreases with temperature rising indicates adsorption process driven towards spontaneity and efficiency as the system moves towards equilibrium at elevated temperatures [32].

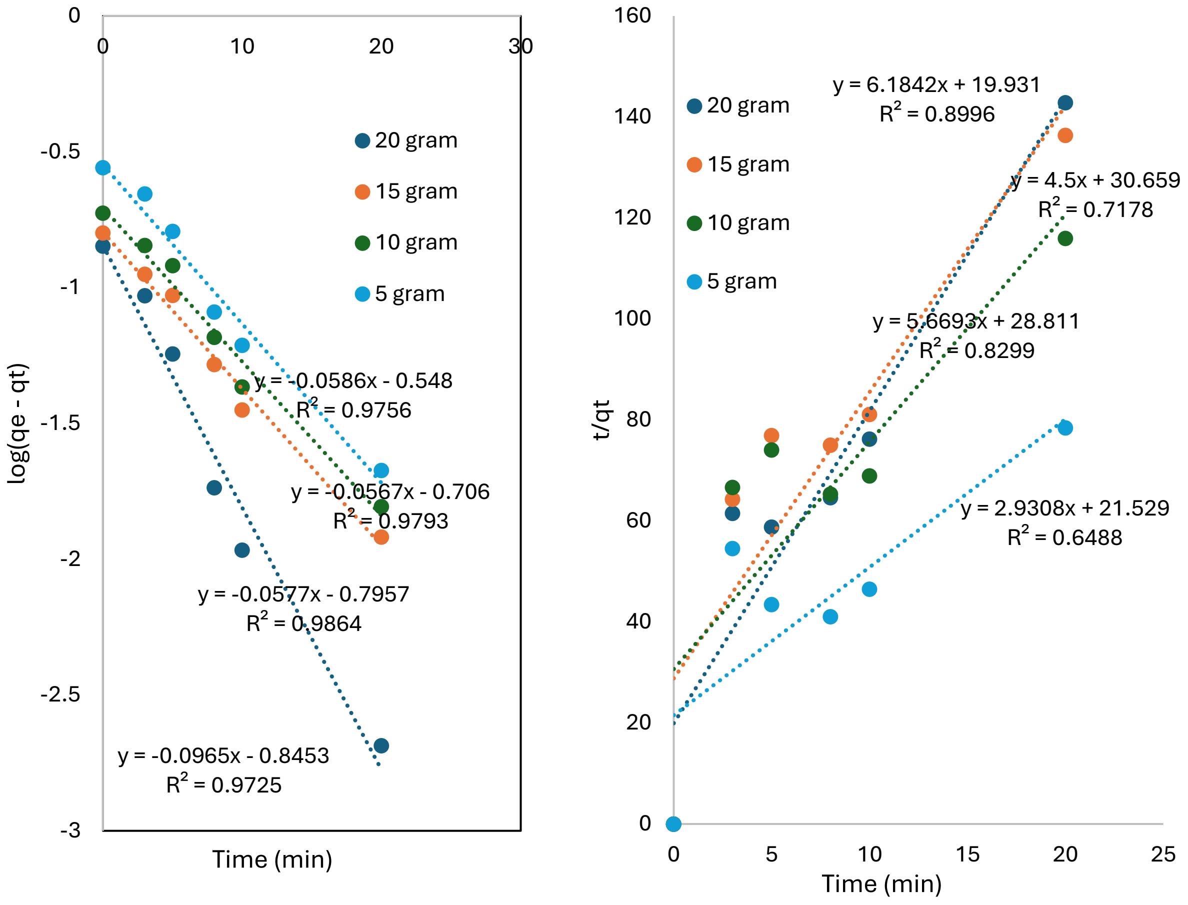
The thermodynamic analysis in this study is crucial for understanding the adsorption behaviour of Mg ions on natural zeolite. The endothermic nature of the reaction suggests that the process can be more efficient at higher operational temperatures, which is beneficial for industrial applications using waste heat to enhance adsorption performance. The positive entropy change supports the theory that the adsorption process increases disorder within the system, which is a common phenomenon in adsorption processes involving ion exchange and complexation.

The non-spontaneous adsorption at the studied temperatures, as indicated by the positive ΔG values, highlights the need for external driving forces for the adsorption process, such as agitation or heating, which are common in industrial settings. This insight is vital for the design and operation of water treatment facilities using natural zeolite, suggesting that process optimization might involve controlling temperature to maximize efficiency.

These findings enhance our understanding of the thermodynamics of magnesium ion adsorption and provide a basis for optimizing and designing more effective adsorption systems using natural zeolites, particularly in terms of temperature management and system energetics.

4.5 Adsorption Kinetic Modelling

Figure 6 and Table 2 present a detailed kinetic analysis of magnesium ion adsorption onto natural zeolite using the pseudo-first-order and pseudo-second-order models. The kinetic study demonstrates a better fit for the pseudo-first-order model, as indicated by the high linear correlation coefficients (R^2 values close to 0.999) across various physicochemical conditions such as different adsorbent dosages, pH levels, and temperatures. This suggests that the rate of adsorption of Mg ions onto zeolite is primarily dependent on the number of available adsorption sites, which decreases exponentially with time.



(a) (b)

Fig. 6. Plotting of Kinetic Model (Volume of Mg Ion Solution = 250 ml; Initial Mg Ion Concentration = 15 mg/L; pH = 7.0; Temperature = 25 °C; Shaker Speed = 100 rpm). (a) Pseudo-first-order; (b) Pseudo-second-order

In Figure 6, the higher correlation coefficients obtained for the pseudo-first-order model, compared to the pseudo-second-order model, indicate that the adsorption process aligns more accurately with a physisorption mechanism involving the physical adherence of magnesium ions onto the zeolite surfaces. Theoretical q_e values (amount of Mg ions adsorbed per unit mass of zeolite at equilibrium) calculated from this model are closer to the experimental q_e values, further validating the suitability of the pseudo-first-order model under various experimental conditions. These findings align with the literature that frequently reports similar kinetic behaviours for metal ion adsorption processes where the initial adsorbate concentration and adsorbent surface characteristics dictate the adsorption kinetics [33,34].

The kinetic analysis provides crucial insights into the design and operation of water treatment systems using natural zeolite. Understanding that the adsorption follows a pseudo-first-order kinetic model helps in predicting the time required to reach equilibrium under different conditions, which is essential for optimizing operational parameters in industrial applications. The dependency of kinetic parameters on conditions like adsorbent dosage and temperature can guide the scaling up of adsorption processes to ensure efficiency and cost-effectiveness.

Table 2 highlights the pseudo-first-order rate constant k_1 (min^{-1}) that decreased with the increase of Mg ion concentration, probably due to the lower competition for the sorption sites at lower concentration. Higher Mg ion concentrations led to higher competition for the surface-active sites and hence, attain lower adsorption rates. Moreover, the adsorption capacity (q_e) increases with initial Mg ion concentration. An increase in natural zeolite dose, solution pH, and temperature would increase the adsorption capacity. Similar types of adsorption kinetic parameters were reported for the removal of heavy metal ion [35,36].

Table 2
Pseudo-first kinetic parameters for adsorption of Mg Ion on Natural Zeolite

System Parameters	q_e (mg/g), Experimental	k_1 (min^{-1})	q_e (mg/g), Calculated	R2
Adsorbent Dosage (mg)				
5	0,276	0,135	0,283	0,9756
10	0,188	0,131	0,197	0,9891
15	0,159	0,133	0,160	0,9864
20	0,142	0,222	0,143	0,9725
pH				
3	0,094	0,123	0,096	0,9682
7	0,142	0,222	0,143	0,9725
9	0,163	0,227	0,169	0,9847
Temperature (C)				
20	0,119	0,134	0,122	0,9801
25	0,142	0,222	0,143	0,9725
30	0,153	0,205	0,154	0,9968
40	0,158	0,262	0,159	0,9941
Initial Concentration of Mg Ion				
10	0,115	0,236	0,110	0,9981
15	0,142	0,222	0,143	0,9725
20	0,160	0,126	0,159	0,9959
25	0,182	0,172	0,185	0,9927

The kinetic data above contributes to a deeper understanding of the adsorption mechanism, suggesting that optimizing contact time, adsorbent dosage, and operational temperatures can significantly enhance the removal efficiency of magnesium ions. These results support the development of tailored zeolite-based adsorption systems for various industrial effluents, providing a scientific basis for improving water treatment methodologies.

4.6 Adsorption Equilibrium Isotherm

Figure 7 illustrates the Langmuir adsorption isotherm for magnesium ion adsorption onto natural zeolite. The linear plot with a high correlation coefficient (R^2 = 0.9878) demonstrates that the Langmuir model accurately describes the adsorption process under the specified conditions. The isotherm parameters, including the maximum adsorption capacity (qm = 0.191 mg/g) and the Langmuir constant (Ka = 1.1) were indicative of binding energy, suggesting that natural zeolite has a moderate capacity for adsorbing magnesium ions from aqueous solutions.

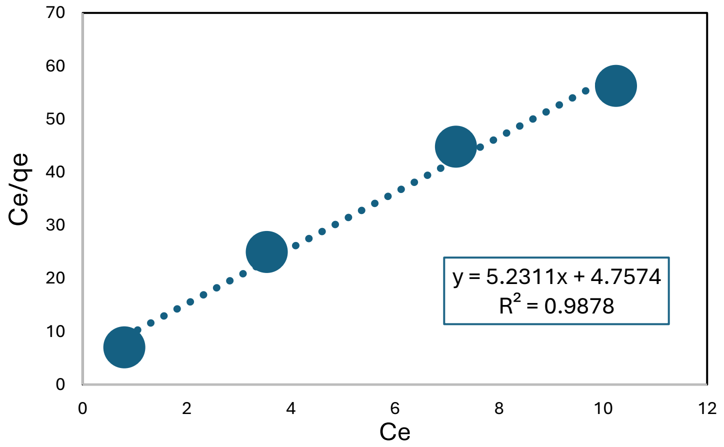


Fig. 7. Langmuir plot: for initial adsorbent dose of Natural Zeolite onto Mg Ion Solution: pH solution = 7.0, volume of Mg Ion solution = 250 ml, initial dose of natural zeolite = 20 mg, temperature = 25˚C, shaker speed = 100 rpm and time (t) = 60 min

The separation factor (RL) calculated from the Langmuir isotherm ranged from 0.08 to 0.03 across the initial magnesium ion concentration range of 10–25 mg/L. These values fall within the range that indicates favorable adsorption (0 < RL < 1). The RL values in this study suggested that under the experimental conditions, the adsorption of Mg ions onto natural zeolite as efficient and advantageous. This favorable adsorption was further supported by the calculated Langmuir constants, which highlighted the affinity and capacity of the zeolite to bind Mg ions effectively.

The Langmuir isotherm analysis provides valuable insights into the adsorptive properties of natural zeolite and its potential applications in water treatment. The moderate maximum adsorption capacity implies that while natural zeolite is effective for magnesium ion removal, its capacity may be limited in scenarios with very high initial ion concentrations unless the adsorbent dosage is adjusted accordingly. The favorable adsorption conditions indicated by the RL values suggest that the zeolite could be particularly useful in systems where moderate reductions of Mg concentration are required.

The applicability of the Langmuir model to describe the adsorption process enables the predictive modelling of adsorption behavior, which can be crucial for designing and scaling up water treatment facilities. Understanding the kinetics and equilibrium of the adsorption process enables engineers and scientists to optimize the adsorbent usage and enhance the efficiency and economic viability of water purification systems that utilize natural zeolite.

Figure 8 presents the Freundlich adsorption isotherm for magnesium ion adsorption onto natural zeolite, characterized by a linear correlation coefficient (R^2) of 0.9717. The Freundlich model, which describes adsorption on a heterogeneous surface with multilayer adsorption, fits the experimental data well, indicating that the surface characteristics and adsorption capacities of the zeolite are conducive to Mg ion adsorption under the given conditions. The calculated Freundlich constants are Kf = 0.17 mg/g and n = 5.82 L/mg, suggesting robust adsorption capacity and favorable adsorption conditions.

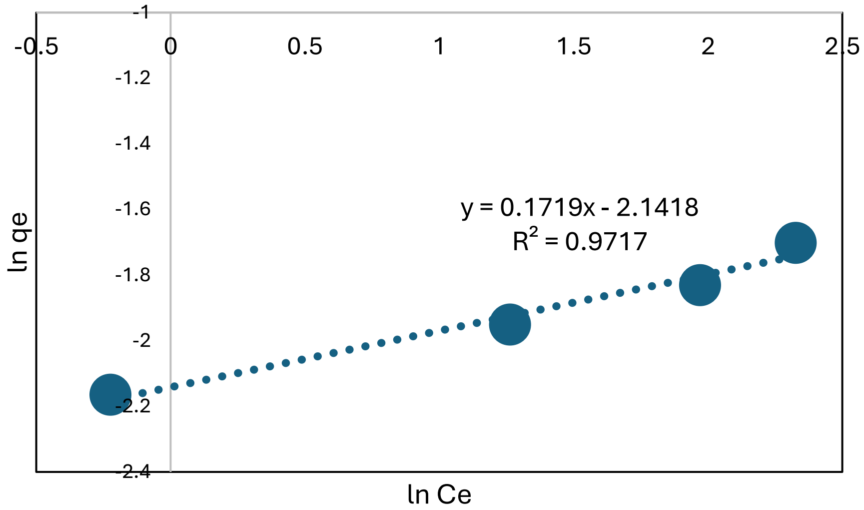


Fig. 8. Freundlich plot: for initial adsorbent dose of Natural Zeolite onto Mg Ion Solution: pH solution = 7.0, volume of Mg Ion solution = 250 ml, initial dose of natural zeolite = 20 mg, temperature = 25˚C, shaker speed = 100 rpm and time (t) = 60 min

The K_f value indicates the adsorption capacity of the natural zeolite, which, while moderate, is adequate for the adsorption of magnesium ions from aqueous solutions at the tested concentrations. The n value, significantly greater than 1, underscores the favorable nature of the adsorption process. According to Freundlich isotherm theory, an n value above 1 indicates a physical adsorption process, characterized by easy adsorbate uptake and desorption, suggesting that the adsorption of magnesium ions onto natural zeolite occurs with minimal resistance and is thus energetically advantageous [4].

The Freundlich isotherm parameters provide critical insights into the nature of magnesium ion adsorption by natural zeolite. The favorable adsorption indicated by the high n value suggest that zeoliteis capable of adsorbing magnesium ions effectively and the process can be efficiently reversed or regenerated an essential feature for sustainable adsorbent use in industrial applications [37,38]. This characteristic makes natural zeolite a promising candidate for water treatment systems where periodic regeneration of the adsorbent is necessary to maintain cost-effectiveness and operational sustainability.

The Freundlich model's applicability to the research allows for the prediction and optimization of adsorption processes at various concentrations and conditions, providing a valuable tool for engineers and scientists in designing more effective water treatment solutions. This understanding helps in tailoring the adsorption system to achieve desired treatment goals while ensuring environmental compliance and resource efficiency.

4.7 Characteristics of Natural Zeolite

Figure 9 presents the X-ray powder diffraction (XRD) patterns of natural zeolite before and after the adsorption process, revealing significant changes in the crystalline phases. The XRD pattern before adsorption shows the presence of clinoptilolite, mordenite, plagioclase, and quartz with respective weights of 66%, 3%, 18%, and 12%. After the adsorption process, the composition adjusts to clinoptilolite 73%, mordenite 3%, plagioclase 14%, and quartz 10%. This shift indicated an increase in the percentage of clinoptilolite, a zeolite phase known for its effective cation-exchange and adsorption properties, thus suggesting its active role in the adsorption of magnesium ions. The decrease in plagioclase and quartz content post-adsorption might be attributed to the replacement of some of the ions in these phases by Mg ions from the solution, or possibly due to structural rearrangements within the zeolite matrix during the adsorption process.

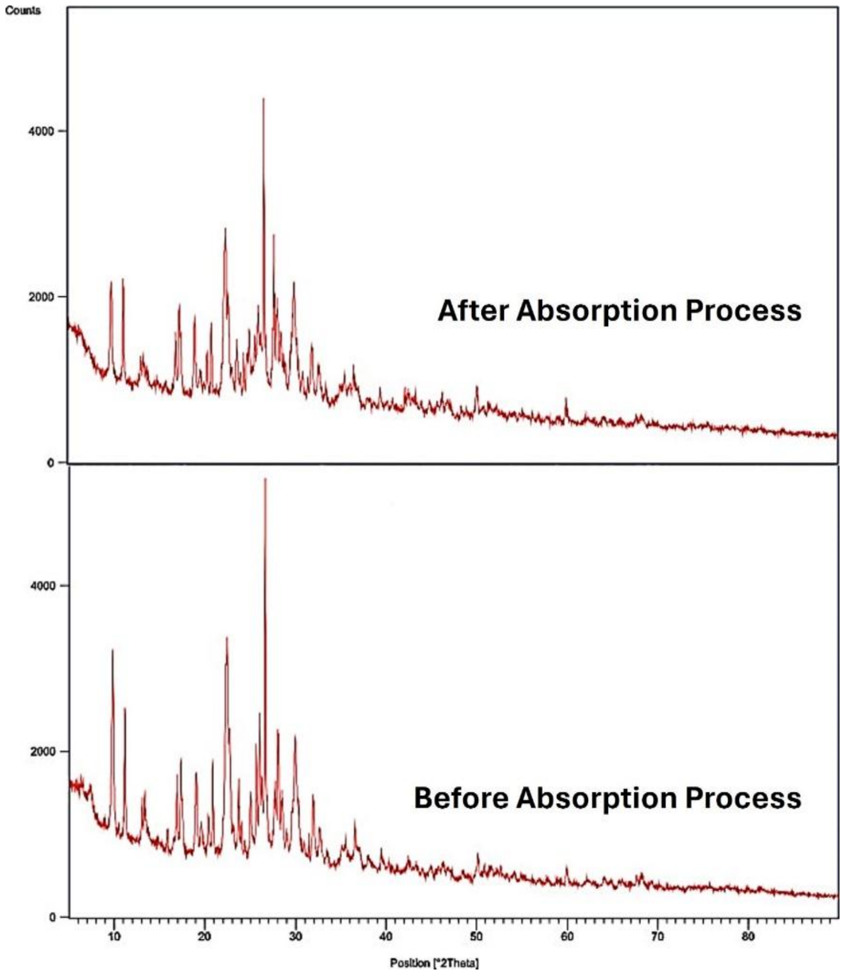
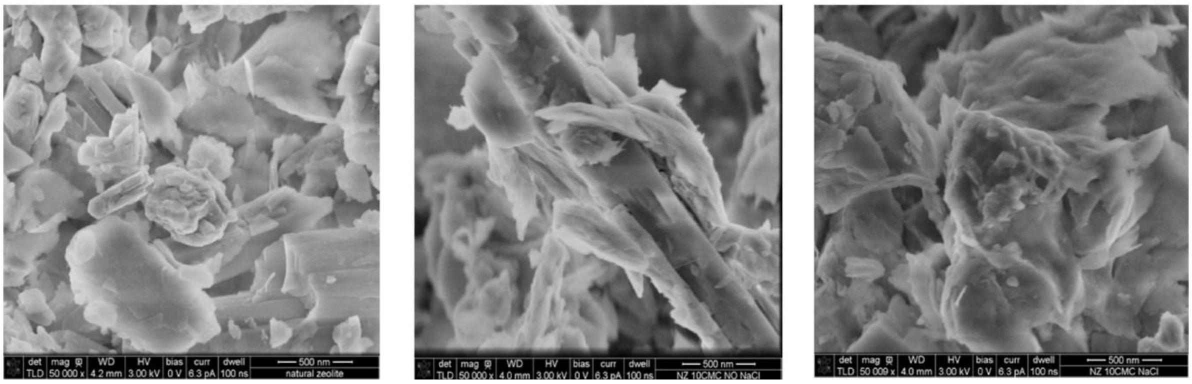


Fig. 9. XRD of Natural Zeolite before and after the adsorption of Mg ion

The mineralogical changes observed in the natural zeolite after the adsorption process as evidenced by the XRD analysis have significant implications for its adsorptive properties. The increase in clinoptilolite content suggests enhanced specificity and efficiency for magnesium ion removal, making natural zeolite a more effective adsorbent after undergoing the adsorption process. These changes can inform future applications and optimizations of the adsorbent, particularly in improving the efficiency and selectivity of ion exchange processes. Additionally, understanding the structural and compositional dynamics of natural zeolite under operational conditions can aid in the development of targeted modifications to the adsorbent to further enhance its performance in water treatment and other environmental applications.

The Scanning Electron Microscopy (SEM) alkaline-treated natural zeolite before adsorption showed a rough and porosity texture, indicating its suitability for adsorption. After Mg Ion adsorption experiment, the pores of alkaline-treated natural zeolite were occupied and attached with tiny white particles. The tiny white particles implied the adsorption of Mg Ion onto the alkaline-treated natural zeolite.

Scanning Electron Microscopy (SEM) images provide a detailed view of the morphological changes in natural zeolite throughout the adsorption process. Figure 10(a) shows the natural zeolite before any treatment, characterized by a rough and porous texture which is ideal for adsorption due to the high surface area and accessibility of adsorption sites. Figure 10(b) presents the zeolite after activation with HCl, which appears to have etched the surface and therefore, increases the roughness and potentially exposes more active sites to adsorption. This treatment likely enhances the ion-exchange capacities of the zeolite. Figure 10(c) illustrates the zeolite after the adsorption process with Mg ions. Notably, the pores of the zeolite are filled and covered with tiny white particles, indicating the presence of adsorbed Mg ions. This visual evidence confirms that Mg ions have been successfully adsorbed onto the zeolite, occupying the available sites and modifying the surface texture.



(a) (b) (c)

Fig. 10. SEM of Natural Zeolite. (a) Natural Zeolite; (b) Natural Zeolite after Activation; (c) Natural Zeolite after Adsorption Process

The SEM analysis effectively demonstrates the impact of chemical activation and subsequent ion adsorption on the structural characteristics of natural zeolite. The activation process with HCl not only prepares the zeolite by enhancing its textural properties but also improves its chemical reactivity towards Mg ions. The evident deposition of Mg ions as tiny white particles within the zeolite's structure post-adsorption highlights the effectiveness of the adsorption process. These morphological changes are critical as they directly correlate with the increased efficiency of the zeolite in removing magnesium from solutions, thus supporting the use of activated natural zeolite in water treatment and pollution control applications. Furthermore, the attachment of magnesium ions to the zeolite framework can be considered a confirmation of the zeolite's capability to serve as an effective adsorbent in environmental remediation technologies. This detailed morphological insight not only helps in understanding the adsorption mechanism but also assists in the optimization and scaling up of the adsorption process for industrial applications.

5. Conclusions

This study investigated the adsorption of magnesium ions (Mg^{2+}) from aqueous solutions using natural zeolite as an adsorbent. It has been demonstrated that natural zeolite, particularly when activated with 6N HCl, exhibits significant potential in removing Mg^{2+} from water under various operational conditions. Optimal adsorption of 0.191 mg/g was achieved at a neutral pH of 7, with a zeolite dosage of 20 grams and a contact time of 10 minutes. Thermodynamic analysis indicated an endothermic adsorption process with positive enthalpy (ΔH = 44.64 kJ/mol) and entropy (ΔS = 121.99 J/mol·K) changes, suggesting that higher temperatures favour the adsorption process. Kinetic studies revealed that the adsorption followed a pseudo-first-order model, indicating that the rate of adsorption is primarily dependent on the number of available adsorption sites. These findings contribute valuable insights into the practical application of natural zeolite for water treatment, highlighting its efficiency, scalability, and influential key operational parameters on its adsorption performance. Future research should focus on further optimizing these parameters and exploring the regeneration and reuse potential of natural zeolite in industrial-scale applications.

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