Adsorption of Nitrite (NO₂⁻) Using Natural Zeolite and Natural Zeolite Modified with Cetyl Trimethylammonium Bromide (CTAB)

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Abstract
Nitrite contamination in water is a critical environmental and public health concern due to its toxicity and persistence. This study investigates the adsorption of nitrite using activated natural zeolite and CTAB-modified zeolite through batch experiments. Natural zeolite was activated with 1M HCl to enhance its surface area, while modification with cetyl trimethylammonium bromide (CTAB) was performed to improve anion adsorption capacity. Adsorption experiments were conducted at different pH levels (2, 4, 6, 8) and contact times (10–90 minutes) using a 100 ppm nitrite solution, with 0.2 g of adsorbent in 50 mL solution. Residual nitrite concentrations were analyzed using UV-Vis spectrophotometry. The results showed that the optimum pH for activated zeolite was 4, with a residual nitrite concentration of 0.108 mg/L, whereas CTAB-modified zeolite performed best at pH 2, reducing nitrite to 0.005 mg/L. The optimal adsorption times were 60 minutes for activated zeolite (0.0106 mg/g) and 75 minutes for CTAB-modified zeolite (0.0156 mg/g). Kinetic analysis indicated that activated zeolite followed a pseudo-first-order model ($R^2 = 0.950$), while CTAB-modified zeolite was influenced by intraparticle diffusion ($R^2 = 0.764$). These findings highlight the potential of zeolites as efficient and cost-effective adsorbents for nitrite removal in wastewater treatment.

INTRODUCTION

Nitrite (NO₂⁻) contamination in water and food has become a pressing issue in Indonesia, driven by industrial activities, agriculture, and improper waste disposal, which frequently pollute nearby water sources (Wu et al., 2021). The excessive use of nitrogen-based fertilizers in agriculture further elevates nitrite levels in groundwater, posing significant health risks, particularly in densely populated agricultural regions (Luetic et al., 2023). Nitrite exposure has been linked to severe health complications, including methemoglobinemia, a condition where hemoglobin is converted into methemoglobin, reducing its oxygen-carrying capacity. Infants and children are especially vulnerable due to their underdeveloped enzymatic systems, leading to higher risks of cyanosis and hypoxia. In extreme cases, methemoglobin levels exceeding 70% can be fatal (Kiranmai & Raajitha, 2023; Voga & Zuran, 2016). Additionally, nitrite may react with amines in the human body to form carcinogenic N-nitrosamines, increasing the risk of stomach cancer (Picetti et al., 2022).

Beyond acute effects, nitrite contamination contributes to long-term health issues, such as chronic inflammation and degenerative diseases, through nitrosative stress that damages cellular structures (Karwowska & Kononiuk, 2020). Studies have also linked nitrite exposure to cardiovascular diseases, neurodegenerative disorders, and oxidative stress-related

conditions, further highlighting its health risks (Picetti et al., 2022). Given these concerns, developing effective and environmentally friendly strategies for nitrite removal is crucial.

Several technologies have been implemented to remove nitrite from water, including reverse osmosis, catalytic reduction, biological denitrification, ion exchange, and electrodialysis. However, these methods are often costly, energy-intensive, or generate secondary waste, limiting their widespread application. Adsorption has emerged as a promising alternative due to its cost-effectiveness, simplicity, and eco-friendly nature (Chen et al., 2021). Among common adsorbents, natural zeolites have been widely studied for their ability to remove nitrogenous compounds from water. Natural zeolites, particularly those rich in clinoptilolite, have shown high efficiency in adsorbing ammonium (NH$_4^+$), nitrate (NO$_3^-$), and nitrite (NO$_2^-$), making them attractive for water treatment applications (Abdulredha et al., 2021; Hulyadi, 2017; Senila et al., 2022). In wastewater treatment, clinoptilolite-rich zeolites have been reported to remove NH$_4^+$ (>98%), NO$_3^-$ (70%), and NO$_2^-$ (54%) (Senila et al., 2022). Despite these advantages, the adsorption performance of natural zeolites can be further improved through chemical activation and surface modification.

One common approach to enhance the adsorption capacity of zeolites is acid activation using hydrochloric acid (HCl). Studies have shown that HCl activation increases the surface area and Si/Al ratio of zeolites, improving their adsorption efficiency (Ngapa, 2017; Sumari et al., 2018). The optimal HCl concentration for activation varies, with 1M HCl reported to produce the largest surface area in one study (Sumari et al., 2018). The activation process alters the zeolite's morphology and functional groups, leading to enhanced adsorption of anionic contaminants like nitrite. HCl-activated zeolites have demonstrated improved adsorption performance not only for nitrogenous pollutants but also for substances like methylene blue dye and ammonia (Ngapa, 2017; Suhendar et al., 2023). Despite these improvements, HCl activation primarily enhances physical properties and does not significantly modify the surface charge of zeolites, which can limit their ability to adsorb anionic pollutants like nitrite.

To address this limitation, surface modification with cationic surfactants such as cetyl trimethylammonium bromide (CTAB) has been explored as a complementary approach to acid activation. While HCl activation increases surface area and removes impurities, it does not significantly alter the surface charge, which limits its ability to adsorb negatively charged contaminants such as nitrite (Ngapa, 2017; Sumari et al., 2018). Unlike previous studies that predominantly focused on nitrate adsorption, this study specifically investigates the adsorption of nitrite, a less studied but equally concerning contaminant. Modification with CTAB introduces positively charged functional groups on the zeolite surface, enhancing electrostatic interactions with negatively charged species like NO$_2^-$. Additionally, surfactant-modified zeolites (SMZs) introduce hydrophobic interactions and electrostatic attraction, further improving their capacity to remove anionic pollutants from aqueous solutions (El Hanache et al., 2019; Singh et al., 2019).

Studies have demonstrated that SMZs effectively adsorb various contaminants, including nitrate (NO$_3^-$), pesticides, organic compounds, and metal ions, making them highly versatile for water treatment applications (de Gennaro, 2019; El Hanache et al., 2019; Harutyunyan et al., 2023). The modification process involves intercalation and coating of CTAB onto the zeolite surface, altering its surface charge and enabling simultaneous cationic and anionic exchange capabilities (de Gennaro, 2019; El Hanache et al., 2019).

Although research on nitrite (NO$_2^-$) removal using CTAB-modified zeolites remains limited, the proven effectiveness of SMZs in adsorbing other anionic species, particularly nitrate, suggests a strong potential for nitrite removal as well. Prior studies have shown that SMZs exhibit high adsorption capacities for nitrate, and structural modifications such as nanosponge configurations further enhance removal efficiency (El Hanache et al., 2019). Given that nitrite

and nitrate share similar chemical behavior in aqueous systems, it is hypothesized that CTAB-modified zeolites will significantly improve nitrite adsorption through enhanced electrostatic interactions and increased surface hydrophobicity. Furthermore, the low cost and widespread availability of natural zeolites make SMZs a promising solution for large-scale nitrite removal applications (Harutyunyan et al., 2023).

Despite the demonstrated effectiveness of CTAB-modified zeolites for nitrate and other anionic pollutants, their adsorption behavior towards nitrite has not been thoroughly investigated. Nitrite exhibits different chemical behavior compared to nitrate, particularly in varying pH conditions, which may affect its adsorption mechanism. Therefore, further studies are necessary to evaluate how CTAB modification influences nitrite adsorption efficiency and kinetics.

This study aims to evaluate nitrite adsorption using activated natural zeolite and CTAB-modified zeolite, focusing on the effects of pH and contact time on adsorption efficiency. Additionally, adsorption kinetics are analyzed using pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion models to better understand the adsorption mechanisms. The findings are expected to contribute to the development of sustainable and effective water treatment solutions, addressing nitrite contamination while promoting public health and environmental sustainability.
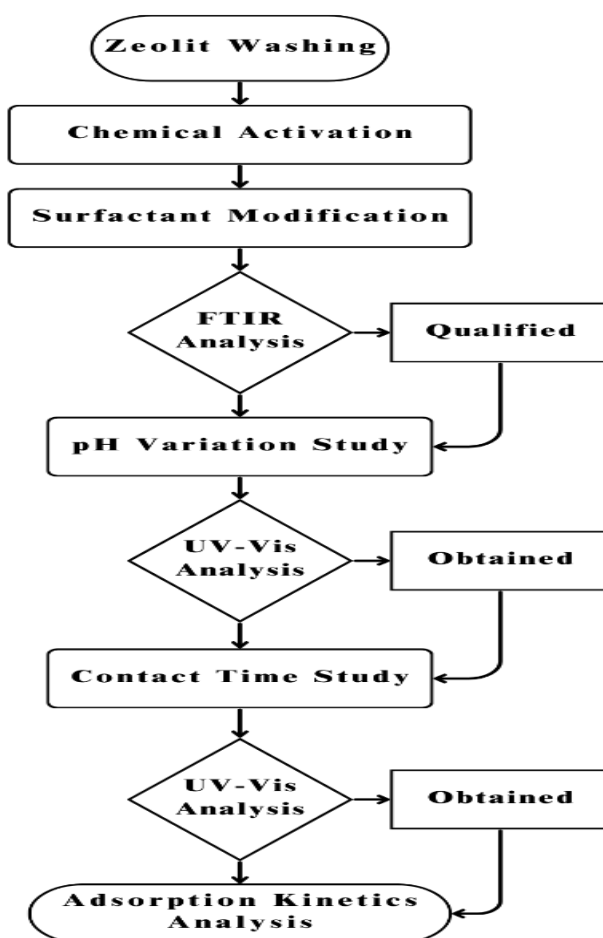
METHOD

Figure 1. Research methodology flowchart

The research method applied in this study is an experimental laboratory-based approach designed to optimize nitrite adsorption using zeolite materials. The methodology is structured to include a series of sequential steps: zeolite preparation, chemical modification, analytical validation, and adsorption performance testing. Specifically, the inclusion of Cetyl Trimethylammonium Bromide (CTAB) modification is critical to improving the adsorption efficiency by enhancing the electrostatic interaction between zeolite and nitrite ions. The CTAB-modified zeolite introduces a positive charge on the zeolite surface, enabling a stronger attraction to negatively charged nitrite ions.

Instruments used in this study include UV-Vis spectrophotometers, hotplate magnetic stirrers, ovens, grinders, sieves, and FTIR spectrometers for characterization. Analytical-grade reagents and solutions, such as NaNO$_2$ for nitrite solutions and CTAB for modification, were used. Experimental outputs, such as adsorption capacity and kinetics, were analyzed using standard kinetic models to evaluate adsorption mechanisms.

Zeolite Washing and Activation

The natural zeolite was ground using a grinder and sieved to 150 mesh. It was then washed with distilled water in a 2:3 ratio (200 g zeolite to 300 mL distilled water) and stirred at 70°C for 1 hour. The washed zeolite was filtered and dried in an oven at 100°C for 1 hour. Chemical activation was performed by soaking the washed zeolite in 1 M HCl solution in a 2:3 ratio for 1 hour, adapting the method described by Akbelen & Ezber (2019), who used a 4-hour activation process. The shorter activation time in this study was selected to optimize efficiency while maintaining adsorption performance. This activation process enhances the SiO$_2$/Al$_2$O$_3$ ratio by partially leaching aluminum from the zeolite framework, improving its adsorption properties (Akbelen & Ezber, 2019). The activated zeolite was then rinsed with distilled water until a neutral pH was achieved and dried at 100°C to ensure complete activation.

Zeolite Modification with CTAB

A 0.1 M CTAB solution was prepared by dissolving 3.64 g of CTAB in 100 mL of distilled water. 10 g of activated zeolite were then introduced into the CTAB solution and stirred continuously for 24 hours at room temperature, following the method described by (Pohan et al., 2016)) and (Sivarama Krishna et al., 2019). After modification, the zeolite was filtered and air-dried for 12 hours. To remove any excess surfactant and unbound CTAB, the material was thoroughly rinsed with distilled water before being further dried in an oven at 100°C. This step ensures the proper attachment of CTAB to the zeolite surface, enhancing its adsorption properties. FTIR analysis was performed to verify the modification by identifying characteristic functional groups associated with CTAB, as outlined in previous studies.

Preparation of Nitrite Solution

A 1000 ppm nitrite stock solution was prepared by dissolving 0.4928 g of NaNO$_2$ in 100 mL of distilled water, following the standard calibration solution preparation method described by (Sander & Schantz, 2017). A 100 ppm working solution was then obtained by diluting 10 mL of the stock solution in 90 mL of distilled water. The accuracy of the nitrite concentration was verified using UV-Vis spectrophotometry, as outlined in (Yuan et al., 2021) and (Nadhila, 2020), ensuring consistency with established analytical procedures.

pH Variation Study

The pH range (2–8) was selected to encompass the conditions where nitrite adsorption is most effective, as suggested by previous studies. (Arianti & Oktavia, 2021) reported that nitrite adsorption on silica-based adsorbents was optimal around pH 6, while adsorption efficiency declined at more extreme pH levels. Similarly, (Chen et al., 2021)) found that hydrotalcite-based adsorbents effectively removed nitrite in the pH range of 3.36–9.4, but efficiency

decreased at highly acidic or alkaline conditions due to changes in surface charge and competition with OH$^-$ ions. In this study, the pH range was set between 2 and 8 to ensure adsorption was evaluated under conditions relevant to wastewater treatment while preventing excessive structural degradation at extremely low pH and interference from hydroxide ions at high pH. Nitrite solutions (100 ppm) were adjusted to pH 2, 4, 6, and 8 using 0.1 M NaOH. 50 mL of each solution were mixed with 0.2 g of zeolite and stirred for 60 minutes. The solutions were filtered, and the filtrates were analyzed using a UV-Vis spectrophotometer.

Contact Time Study

The effect of contact time on nitrite adsorption was studied at the optimum pH to determine equilibrium time for maximum adsorption efficiency. Adsorption experiments were conducted by varying contact times (10, 15, 30, 45, 60, 75, and 90 minutes) with 0.2 g of zeolite in 50 mL of 100 ppm nitrite solution. Studies have shown that adsorption typically follows a two-phase process: an initial rapid phase due to the high availability of active adsorption sites, followed by a slower phase as the system approaches equilibrium (Rezaei et al., 2019). Rezaei et al. (2019) found that nitrite adsorption on chitosan-based adsorbents reached equilibrium within 60 minutes, whereas (Pohan et al., 2016) reported that zeolite modified with CTAB continued to show increasing adsorption efficiency before stabilizing. Given these findings, adsorption times up to 90 minutes were examined to capture the complete adsorption profile and ensure equilibrium conditions. The filtrates were analyzed using a UV-Vis spectrophotometer to determine the remaining nitrite concentration, and the obtained data were used to evaluate adsorption kinetics, including pseudo-first-order, pseudo-second-order, and intraparticle diffusion models to understand the adsorption mechanism.

Data Analysis and Kinetics

The data from the pH and contact time studies were analyzed to determine adsorption efficiency. Adsorption capacity (q) was calculated, and adsorption kinetics were evaluated using pseudo-first-order and pseudo-second-order models to identify the mechanism of nitrite removal.

RESULTS AND DISCUSSION

Preparation of Natural Zeolite

The preparation of natural zeolite involves physical washing and acid activation to enhance its adsorption performance. The first step is washing the zeolite to remove impurities that may block its pores and reduce adsorption efficiency. This process is followed by acid activation using hydrochloric acid (HCl), which modifies the Si/Al ratio and improves the cation exchange capacity of the zeolite. According to Astuti et al. (2019), HCl activation effectively removes aluminum and other metal oxides, such as Fe_2O_3, Al_2O_3, CaO, K_2O, and TiO_2, increasing the surface area and pore volume. This modification enhances the zeolite's ability to adsorb pollutants while preserving its crystallinity. Additionally, (Zilfa et al., 2020) reported that HCl-activated clinoptilolite zeolite demonstrates superior adsorption performance due to its improved cation exchange properties, which are essential for removing contaminants in aqueous systems.

After activation, the zeolite is rinsed with distilled water until neutral pH is achieved to remove any residual H$^+$ and Cl$^-$ ions that may interfere with adsorption. It is then dried at 100°C to stabilize its structure before use. The effectiveness of HCl activation in modifying zeolite properties aligns with findings by (TERZİ & ÖZDEMİR, 2021), which demonstrated that acid treatment enhances ion exchange capacity and adsorption efficiency. These improvements

make HCl-activated zeolite a promising adsorbent for nitrite (NO₂⁻) removal in water treatment applications.

Figure 2. (a) Natural zeolite and (b) Activated natural zeolite

Figure 2 shows the visual changes in natural zeolite before and after HCl activation. The color change observed after washing and activation indicates the successful removal of impurities and metal oxides that originally coated the zeolite surface. This treatment leads to an increase in pore volume and surface area, which plays a significant role in enhancing adsorption performance.

Activation using HCl facilitates the removal of positively charged cations, while negatively charged anions are retained in the zeolite framework. As a result, HCl-activated zeolite functions as a cation exchanger, which is beneficial for the adsorption of nitrite (NO₂⁻). These findings are consistent with those reported by (Astuti et al., 2019) and (Zilfa et al., 2020), who emphasized that acid activation significantly improves pore accessibility and adsorption properties of natural zeolites.

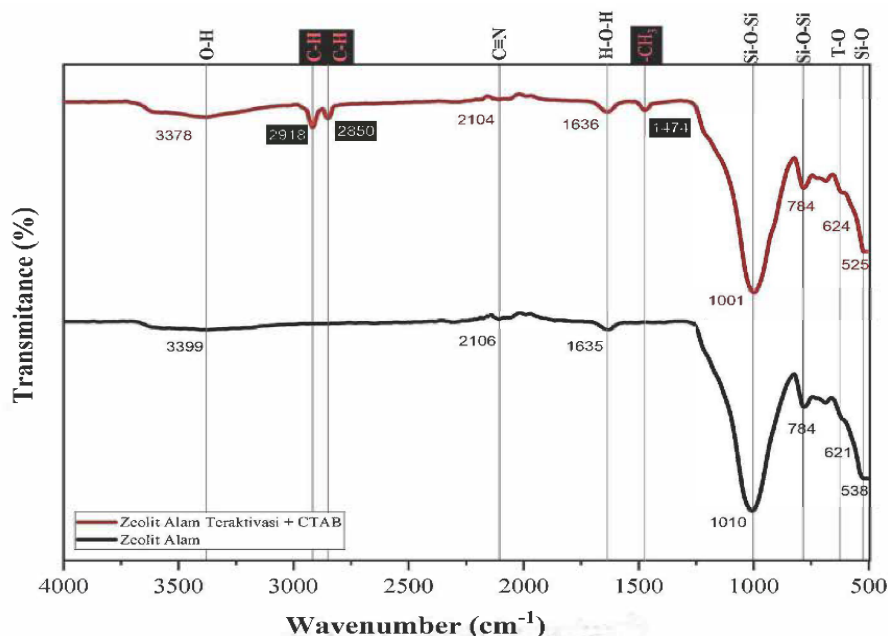**FTIR Analysis of Activated and Modified Zeolite**

Figure 3. FTIR spectrum of activated natural zeolite and ctab-modified natural zeolite

The FTIR spectrum provides essential information about the structural and compositional changes in zeolite after activation and modification with cetyl trimethylammonium bromide (CTAB). These changes are directly associated with the zeolite's enhanced adsorption

properties. As shown in Figure 3, the spectrum of activated natural zeolite reveals distinct peaks characteristic of its silica-alumina framework. The broad band at 3500-3700 cm^{-1} corresponds to the stretching vibrations of hydroxyl groups (-OH), which indicate the presence of adsorbed water or silanol groups on the surface. This hydrophilic property plays a critical role in adsorption processes. The band between 1000-1200 cm^{-1} is attributed to asymmetric stretching vibrations of Si-O and Al-O bonds, while the band at 700-800 cm^{-1} corresponds to symmetric stretching vibrations of the same bonds. Additionally, the band at 400-500 cm^{-1} represents T-O bending vibrations (T = Si or Al), confirming the structural integrity of the zeolite framework, which is essential for its functionality in adsorption (Astuti et al., 2019; Zilfa et al., 2020).

The spectrum further highlights significant peaks specific to activated natural zeolite. The peak at 538 cm^{-1} indicates the deformation of Si-O bonds, while the peak at 621 cm^{-1} reveals aluminum substitution within the framework. Vibrations at 784 cm^{-1} and 1010 cm^{-1} correspond to the symmetric and asymmetric stretching of Si-O-Si bonds, respectively. These structural vibrations are critical for maintaining the zeolite's framework stability. The peak at 1635 cm^{-1}, representing H-O-H bending vibrations, confirms the presence of adsorbed water in the zeolite pores, which influences its adsorption capacity. The peak at 2106 cm^{-1} suggests possible C≡N bonds, likely originating from contaminants during activation, while the broad peak at 3399 cm^{-1} confirms the presence of hydroxyl groups that enhance surface interactions. Similar spectral characteristics have been reported in studies analyzing acid-activated zeolites, where increased Si/Al ratios and the removal of metal impurities contribute to improved adsorption performance (TERZİ & ÖZDEMİR, 2021).

After modification with CTAB, significant spectral changes occur, indicating the successful functionalization of the zeolite surface. New peaks at 1474 cm^{-1}, 2850 cm^{-1}, and 2918 cm^{-1} appear in the spectrum of CTAB-modified zeolite, which are absent in activated zeolite. The peak at 1474 cm^{-1} corresponds to methyl (-CH₃) or methylene (-CH₂) groups, confirming the attachment of CTAB surfactant. These modifications increase the hydrophobicity of the zeolite surface, enhancing its interaction with nonpolar contaminants. The peaks at 2850 cm^{-1} and 2918 cm^{-1} are associated with symmetric and asymmetric stretching vibrations of C-H bonds in the alkyl chains of CTAB. Meanwhile, the persistent O-H stretching band at 3378 cm^{-1} indicates residual water or silanol groups, reflecting the retention of hydrophilic properties essential for balanced adsorption performance. This is consistent with findings from (Harutyunyan et al., 2023) and (El Hanache et al., 2019), where the incorporation of cationic surfactants onto zeolite surfaces resulted in improved adsorption capacities for anionic contaminants.

These spectral changes confirm that CTAB modification successfully alters the surface properties of the zeolite, enhancing electrostatic interactions with nitrite ions. The presence of CTAB functional groups contributes to the increased adsorption efficiency observed in the study, as demonstrated in previous research on surfactant-modified zeolites for anion removal (Harutyunyan et al., 2023). By integrating both acid activation and surfactant modification, the modified zeolite exhibits superior adsorption performance, making it a promising candidate for nitrite removal in water treatment applications.

Effect of pH on Nitrite Adsorption Using Activated and CTAB-Modified Zeolite

The pH of the solution is a key factor influencing the effectiveness of nitrite (NO₂⁻) adsorption by zeolite, both in its activated state and after modification with cetyl trimethylammonium bromide (CTAB). Variations in pH affect the surface charge distribution of the zeolite and the speciation of nitrite ions in the solution. At lower pH values, the surface of the zeolite becomes protonated, resulting in a positive charge that strengthens electrostatic interactions with negatively charged nitrite ions. Conversely, at higher pH values, the surface charge of the

zeolite becomes more negative, leading to electrostatic repulsion with nitrite ions and increased competition with hydroxide ions (OH$^-$) for active adsorption sites (Arianti & Oktavia, 2021; Palit et al., 2023). The effect of pH on nitrite adsorption has also been widely studied in various adsorbent systems, where lower pH values generally enhance adsorption due to the favorable electrostatic interactions between adsorbent surfaces and anionic species (Chen et al., 2021).
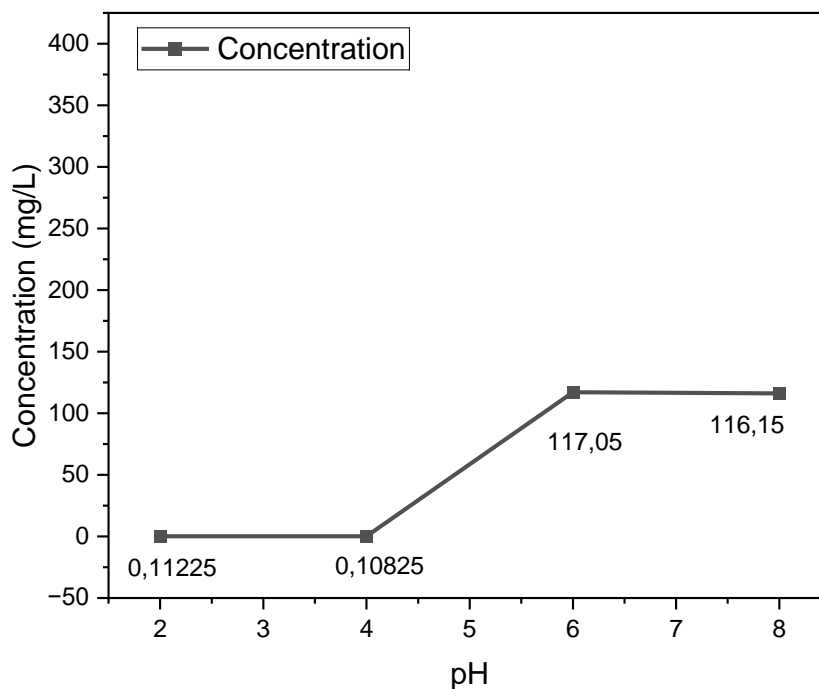

Figure 4. Residual nitrite concentration at different pH values during adsorption using activated natural zeolite

The findings indicate that activated natural zeolite exhibits higher adsorption capacity at lower pH compared to higher pH, as shown in Figure 4. At pH 2, the residual nitrite concentration in the solution is 0.11225 mg/L, while at pH 4, it decreases slightly to 0.10825 mg/L. This efficiency is attributed to the protonated surface of the zeolite, which enhances electrostatic interactions with nitrite ions. The activation process using hydrochloric acid (HCl) also removes impurities and increases the surface area, further supporting improved adsorption performance (Zaharah et al., 2023). The enhancement of adsorption due to acid activation is consistent with previous studies, which report that acid treatment increases the number of active sites, thereby improving anion adsorption efficiency (Astuti et al., 2019; TERZİ & ÖZDEMİR, 2021).

In contrast, at pH 6 and 8, the residual nitrite concentrations rise sharply to 117.05 mg/L and 116.15 mg/L, respectively. This decline is caused by the increasingly negative surface charge of the zeolite, which reduces interactions with nitrite ions. Additionally, hydroxide ions (OH$^-$) at high pH compete with nitrite for active sites, further diminishing adsorption efficiency. Similar trends have been reported in previous studies on nitrite adsorption, where high pH conditions resulted in a significant decrease in adsorption due to electrostatic repulsion (Arianti & Oktavia, 2021). Furthermore, at higher pH levels, the presence of competing anions such as carbonate and hydroxide can negatively impact adsorption capacity, as observed in other anion adsorption studies (Chen et al., 2021).
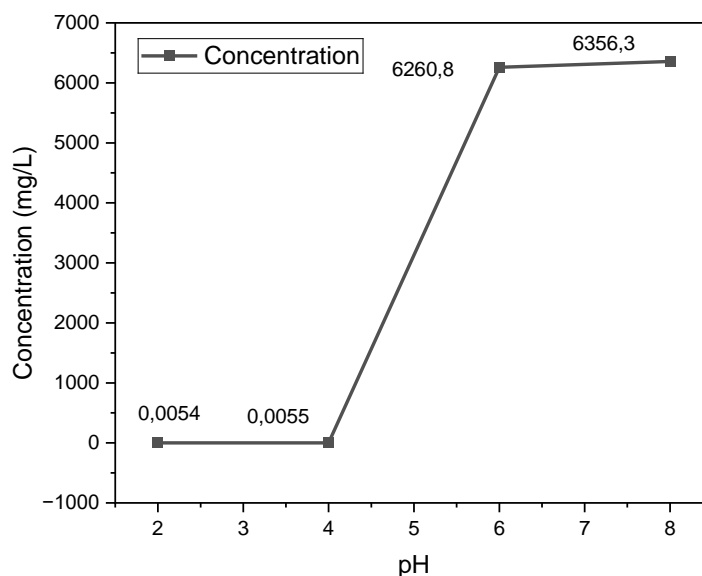
Figure 5. Residual nitrite concentration at different pH values during adsorption using CTAB-
        modified natural zeolite

CTAB-modified zeolite demonstrates superior adsorption capacity at low pH, as depicted in Figure 5. At pH 2, the residual nitrite concentration is only 0.0054 mg/L, and at pH 4, it increases slightly to 0.0055 mg/L. This observation suggests that CTAB modification enhances electrostatic attraction between the positively charged zeolite surface and negatively charged nitrite ions. CTAB, as a cationic surfactant, imparts additional positive charge to the zeolite surface, improving adsorption effectiveness at low pH levels, as also reported by (Adawiah et al., 2020). The role of surfactant-modified zeolites in anion adsorption has been well-documented, showing that CTAB modification enhances the electrostatic interaction between the adsorbent and anionic species (Harutyunyan et al., 2023).

Conversely, at higher pH values (6 and 8), the residual nitrite concentrations significantly increase to 6260.8 mg/L and 6356.3 mg/L, respectively. At high pH, the zeolite surface becomes negatively charged, hindering interactions with nitrite ions. Moreover, under these conditions, nitrite ions in the solution tend to convert into HNO$_2$ species, which have lower affinity for the zeolite surface (Septommy & Badriyah, 2022). This result aligns with previous studies on surfactant-modified adsorbents, where high pH conditions led to reduced adsorption due to unfavorable electrostatic interactions (Pohan et al., 2016; Sivarama Krishna et al., 2019).

Effect of Contact Time on Nitrite Adsorption Using Activated and CTAB-Modified Zeolite

Contact time is a crucial parameter in adsorption studies, as it determines the duration required to achieve equilibrium, where no further significant adsorption occurs. The equilibrium time varies depending on the type of adsorbent and adsorbate, as well as the interaction mechanisms involved (Arianti & Oktavia, 2021). Previous studies have reported diverse equilibrium times for nitrite adsorption, ranging from a few minutes to several hours, depending on the nature of the adsorbent. For instance, Fe-HT3.0 zeolite required 6–24 hours to reach equilibrium in nitrite and nitrate adsorption (Ogata et al., 2019). Meanwhile, (Rasuli et al., 2020) found that 30 minutes was sufficient for nitrate adsorption using surfactant-modified zeolites. These variations highlight the role of surface modification in accelerating adsorption rates, as seen in the present study.
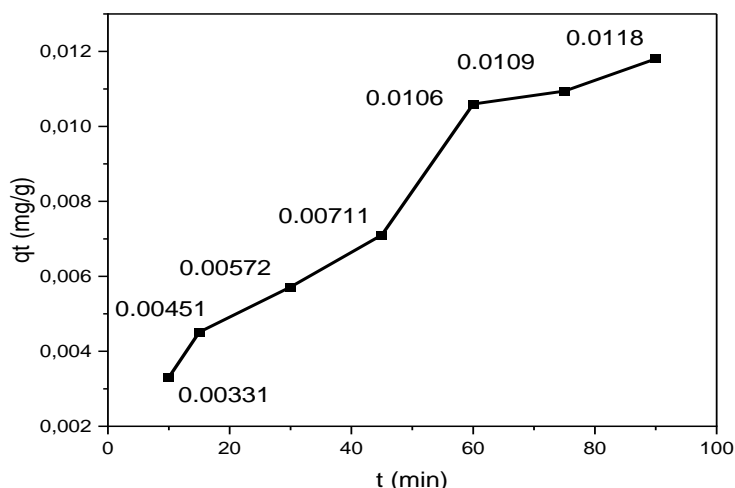
Figure 6. The adsorption capacity (qt) of nitrite ions at different contact times using activated natural zeolite

Figure 6 illustrates the adsorption capacity of activated natural zeolite over time. A rapid increase in nitrite uptake occurred within the first 10 to 60 minutes, with the adsorption capacity rising from 0.00331 mg/g at 10 minutes to 0.0106 mg/g at 60 minutes. After this period, adsorption slowed, reaching 0.01094 mg/g at 75 minutes, suggesting that most active sites were occupied. At 90 minutes, the adsorption plateaued at 0.0118 mg/g, indicating equilibrium had been reached. These results align with (Al Muttaqii et al., 2019), who reported that the adsorption rate initially increased rapidly but gradually stabilized as active sites became saturated. The observed trend suggests that activated zeolite reached equilibrium at approximately 60–75 minutes, consistent with other studies that reported pseudo-second-order kinetics for nitrite adsorption (Arianti & Oktavia, 2021).
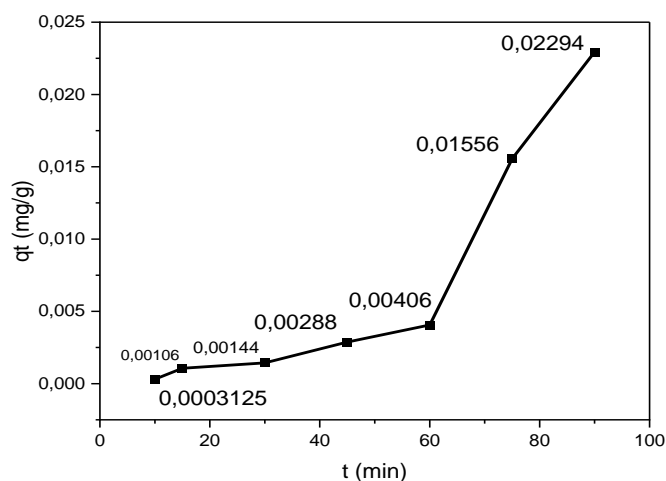

Figure 7. The adsorption capacity (qt) of nitrite ions at different contact times using CTAB-modified natural zeolite

As shown in Figure 7, CTAB-modified zeolite exhibited a similar adsorption pattern but with a higher overall capacity. Within the first 10 minutes, adsorption reached 0.0003125 mg/g, indicating initial nitrite interaction with the modified surface. A rapid increase followed, with

adsorption reaching 0.00406 mg/g at 60 minutes, 0.01556 mg/g at 75 minutes, and 0.02294 mg/g at 90 minutes, where equilibrium was approached. The slower rate beyond 75 minutes suggests that most active sites had been occupied, limiting further adsorption. Compared to activated zeolite, CTAB-modified zeolite consistently showed higher adsorption efficiency, likely due to the increased surface charge and hydrophobicity introduced by surfactant modification (Arnelli et al., 2021; Rasuli et al., 2020).

These findings confirm that CTAB-modified zeolite significantly enhances nitrite adsorption efficiency and reduces equilibrium time compared to activated natural zeolite. The modification process improves electrostatic attraction, leading to more effective interactions with nitrite ions. The results also align with previous studies on surfactant-modified zeolites, which consistently exhibited superior adsorption performance for anionic contaminants (Arianti & Oktavia, 2021; Ogata et al., 2019).

Analysis of Adsorption Kinetics for Nitrite Using Activated and CTAB-Modified Zeolite

Adsorption kinetics is a critical aspect of this study, aiming to understand the mechanisms underlying the adsorption of nitrite ions (NO_2^-) on the surfaces of activated natural zeolite and CTAB-modified natural zeolite. The nitrite adsorption kinetics were analyzed using various models, including pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion models. Each model provides unique insights into the adsorption rate and mechanism, aiding in identifying kinetic parameters and assessing the efficiency of the adsorbent.
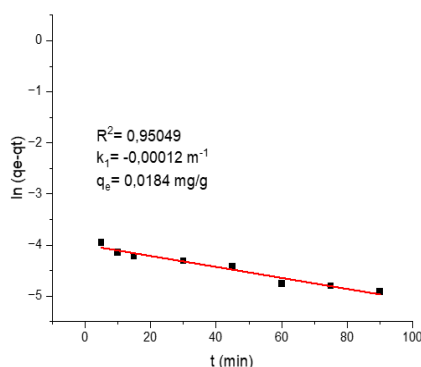

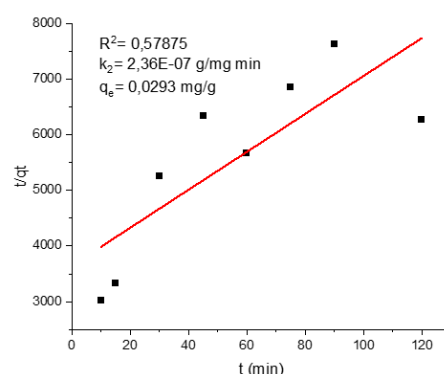Figure 8. Pseudo-first-order kinetic model for nitrite adsorption using activated natural zeolite

Figure 9. Pseudo-second-order kinetic model for nitrite adsorption using activated natural zeolite
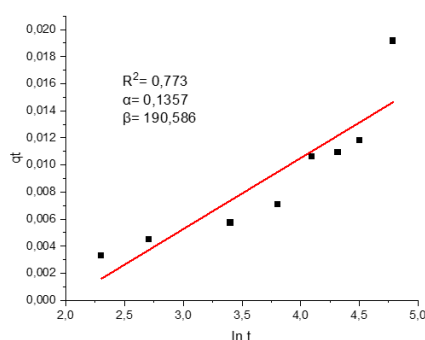

Figure 10. Elovich kinetic model for nitrite adsorption using activated natural zeolite
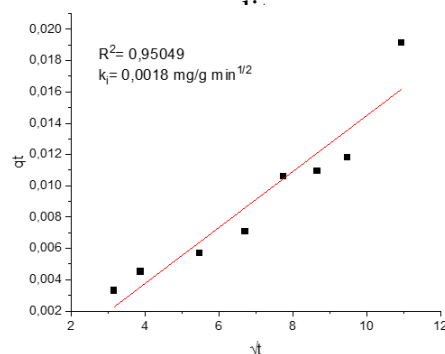

Figure 11. Intraparticle diffusion kinetic model for nitrite adsorption using activated natural zeolite

The analysis revealed that activated natural zeolite exhibited adsorption behavior that fit well with the pseudo-first-order model, as shown in Figure 8. The equilibrium adsorption capacity (Qe) was 0.0184 mg/g, with an R² value of 0.95049, indicating strong agreement with the

experimental data. This model suggests that the adsorption rate is dependent on the concentration of unadsorbed nitrite ions, and the rate decreases as nitrite ions are progressively adsorbed. Studies by (Musah et al., 2022) also reported that pseudo-first-order kinetics are widely applicable for describing physical adsorption processes where no covalent bond formation occurs. These findings align with prior research that demonstrated similar kinetic behavior in nitrite adsorption using modified silica and zeolites (Arianti & Oktavia, 2021; Bețianu et al., 2020).

Conversely, the pseudo-second-order model (Figure 9) yielded a higher Qe value of 0.0293 mg/g but had a lower R² value of 0.57875, indicating poor fit. While this model typically describes chemisorption processes involving strong interactions between adsorbate and adsorbent, it was less suitable for the system studied here. Similar results were observed in studies on nitrate and nitrite adsorption using functionalized adsorbents, where pseudo-second-order kinetics were less applicable (Mohamed Nasser et al., 2024; Tararushkin et al., 2023). For the Elovich model (Figure 10), the initial adsorption rate (α) was 0.1357, and the desorption rate (β) was 190.5857, with an R² value of 0.77332, suggesting moderate agreement with the data. Finally, the intraparticle diffusion model (Figure 11) yielded a diffusion constant (ki) of 0.0018, with an R² value of 0.88602, indicating that intraparticle diffusion plays a significant role in the adsorption process, a trend also observed in the adsorption of organic pollutants onto zeolite-based materials (Bețianu et al., 2020).
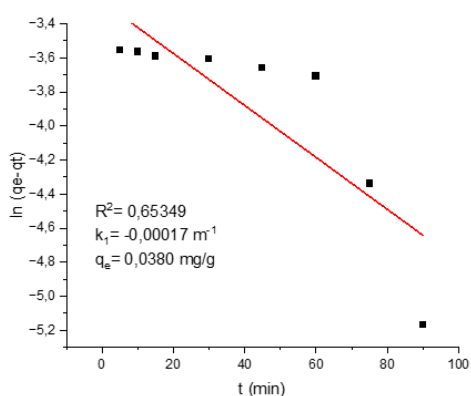

Figure 12. Pseudo-first-order kinetic model for nitrite adsorption using CTAB-modified natural zeolite
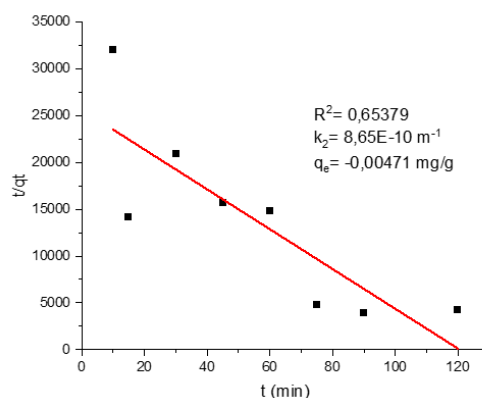
Figure 13. Pseudo-second-order kinetic model for nitrite adsorption using CTAB-modified natural zeolite
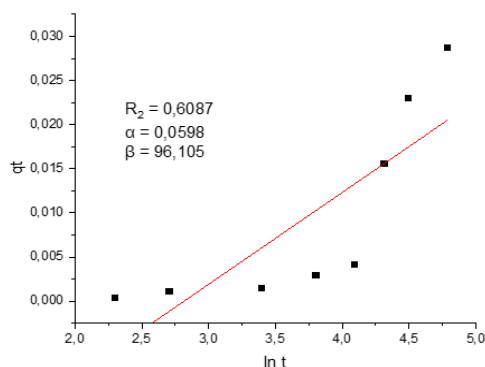

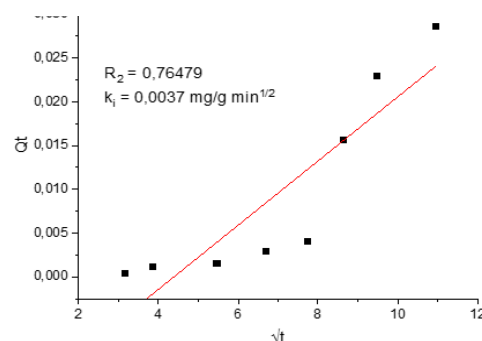Figure 14. Elovich kinetic model for nitrite adsorption using CTAB-modified natural zeolite

Figure 15. Intraparticle diffusion kinetic model for nitrite adsorption using CTAB-modified natural zeolite

For CTAB-modified natural zeolite, the pseudo-first-order model (Figure 12) exhibited moderate correlation, with an R² value of 0.65349. The equilibrium adsorption capacity (Qe) was 0.0380 mg/g, while the adsorption rate constant (k1) was negative (-0.000169525), suggesting a decline in the adsorption rate over time, potentially due to changes on the adsorbent surface or instability during the process. Similarly, the pseudo-second-order model (Figure 13) showed an R² value of 0.65379 but yielded a physically unrealistic negative Qe (-0.0047 mg/g), indicating poor applicability for this system.

The Elovich model (Figure 14) had an R² value of 0.60873, with a high β (96.105) indicating rapid desorption and a low α (0.0598) signifying limited initial adsorption capacity. The intraparticle diffusion model (Figure 15), however, exhibited better correlation (R²=0.76479), with a diffusion constant (ki) of 0.0037, suggesting that intraparticle diffusion is the rate-limiting step for adsorption in this system. These findings are consistent with previous studies that identified intraparticle diffusion as a dominant mechanism for surfactant-modified zeolites and other functionalized adsorbents (Arianti & Oktavia, 2021; Tararushkin et al., 2023).

Overall, for activated natural zeolite, the pseudo-first-order model provided the best fit (R²=0.95049), indicating that the adsorption process is predominantly governed by physical interactions. In contrast, for CTAB-modified zeolite, the intraparticle diffusion model showed the best correlation (R²=0.76479), suggesting that diffusion within the zeolite pores is the controlling factor. These findings align with prior studies by (Musah et al., 2022), which emphasized the importance of intraparticle diffusion in systems involving physical adsorption, and by (Chen et al., 2021), which reported that pseudo-second-order models are not always suitable for nitrite adsorption on modified surfaces. The observed differences in kinetic behavior highlight the role of surface modification in altering the adsorption mechanisms, which is crucial for optimizing zeolite-based adsorbents for nitrite removal in wastewater treatment applications.

Comparative Analysis & Implications

The results of this study demonstrate that CTAB-modified zeolite exhibits superior adsorption capacity for nitrite compared to activated natural zeolite. The enhanced performance is attributed to the introduction of cationic surfactant groups, which improve electrostatic interactions with negatively charged nitrite ions. This finding is consistent with previous studies on surfactant-modified zeolites, which have shown increased adsorption efficiencies for anionic pollutants (Harutyunyan et al., 2023; Tararushkin et al., 2023).

The adsorption kinetics analysis also revealed key differences in the mechanisms governing nitrite uptake. Activated zeolite followed a pseudo-first-order model, suggesting that physical adsorption dominated the process. In contrast, CTAB-modified zeolite was best described by the intraparticle diffusion model, indicating that nitrite ions primarily diffused into the modified zeolite's internal pores. These insights align with research on other surfactant-modified adsorbents, where modifications enhanced pollutant uptake by altering surface charge properties (Arianti & Oktavia, 2021; Bețianu et al., 2020).

In terms of practical applications, the superior adsorption efficiency of CTAB-modified zeolite suggests that it could be a promising material for large-scale wastewater treatment, particularly for nitrite removal from industrial and agricultural effluents. However, the cost and environmental impact of using surfactants must be considered. Future studies should focus on optimizing surfactant loading, regenerability, and long-term stability to enhance the feasibility of implementing CTAB-modified zeolite in real-world scenarios.

CONCLUSION

This study evaluated the adsorption of nitrite using activated natural zeolite and CTAB-modified zeolite. The results indicate that CTAB modification significantly enhances adsorption capacity, particularly at low pH levels, due to improved electrostatic interactions. Adsorption kinetics analysis revealed that activated zeolite follows a pseudo-first-order model, indicating that physical adsorption is the dominant mechanism. In contrast, CTAB-modified zeolite is governed by intraparticle diffusion, suggesting that diffusion within the zeolite's internal pores plays a critical role in nitrite uptake.

Overall, CTAB-modified zeolite demonstrates superior performance compared to its unmodified counterpart, making it a promising candidate for nitrite removal in water treatment applications. These findings contribute to the growing understanding of surfactant-modified zeolites and their enhanced adsorption capabilities for anionic pollutants. Future research should explore the scalability, regenerability, and environmental impact of this method to ensure its feasibility for large-scale wastewater treatment applications, particularly in industrial and agricultural effluents.

RECOMMENDATIONS

Future research should focus on further optimizing CTAB modification techniques to enhance nitrite adsorption efficiency. This includes exploring alternative surfactants and hybrid modification strategies to improve adsorption under varying conditions, such as high pH environments and the presence of competing ions. Additionally, addressing adsorption limitations—such as slower rates at higher pH and limited active site availability—through advanced material characterization and pore structure engineering is crucial for maximizing adsorption capacity.

To ensure practical application, future studies should investigate the scalability, long-term stability, and reusability of CTAB-modified zeolite in real-world wastewater treatment systems. Evaluating its cost-effectiveness and environmental impact will be essential for promoting sustainable and large-scale implementation in industrial and agricultural wastewater treatment.

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