

Article

Study on the Performance of Copper(II) Sorption Using Natural and Fe(III)-Modified Natural Zeolite–Sorption Parameters Optimization and Mechanism Elucidation

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Abstract

This study evaluates and compares the sorption performance of natural zeolite (NZ) and Fe(III)-modified zeolite (FeZ) in removing Cu(II) ions from aqueous solutions, with the goal of assessing their potential for environmental remediation. NZ was modified with Fe(NO₃)₃, NaOH and NaNO₃ solutions to improve its sorption properties. The modification led to a slight decrease in crystallinity (XRD), increase in pore volume (BET), functional groups (FTIR) and negative surface charge (zeta potential), thereby improving the affinity of FeZ towards Cu(II). Batch sorption experiments were conducted to optimize key parameters including pH, solid/liquid ratio (S/L), contact time, and initial Cu(II) concentration. The pH₀ and S/L ratio were identified as key factors significantly influencing Cu(II) sorption on both zeolites, with a particularly pronounced effect observed for FeZ. The optimal conditions determined were pH₀ = 3–5 for NZ, pH₀ = 3 for FeZ, S/L = 10 g/L and a contact time of 600 min. Experimental results confirmed that FeZ has almost twice the sorption capacity for Cu(II) compared to NZ (0.271 mmol/g vs. 0.156 mmol/g), as further supported by elemental analysis, SEM-EDS and mapping analysis of saturated samples. The sorption of Cu(II) followed a mechanism of physical nature driven by ion exchange, dominated by intraparticle diffusion as the rate-controlling step. Leaching of copper-saturated zeolites according to the standard leaching method, DIN 38414 S4, demonstrated the ability of both zeolites to fully retain Cu(II) within their structure over a wide pH range, 4.01 ≤ pH₀ ≤ 10.06. These findings highlight the superior performance of FeZ and its potential as an effective material for the remediation of copper-contaminated environments.

Keywords: natural zeolite; Fe(III)-modified natural zeolite; copper; sorption; leaching; optimization; sorption mechanism



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1. Introduction

Copper is an essential biochemical nutrient of vital importance to humans, animals and plants, and is considered fairly harmless [1–3]. It is essential for plants to form chlorophyll, photosynthesis, cell wall metabolism, etc. [4]. Since the human body is unable to synthesize copper, it must be ingested through diet as it is substantial for the synthesis of so-called cuproenzymes such as cytochrome C oxidase and dopamine β-hydroxylase, for bone and tissue development, and supports iron absorption and hemoglobin synthesis [3,5,6]. Due

to the fact that copper deficiency/excess negatively affects human health, various organizations prescribe a minimum daily copper intake in the form of a U-shaped curve [2,7]. The recommendation for an average dietary intake for adults is 0.9 to 1.3 mg Cu/day, since up to 1 mg of copper is excreted daily from the liver into bile and feces [8,9]. Copper deficiency most often occurs in children, and is manifested by failure to thrive, hypothermia, neutropenia and mental illness, and is also known as Menkes syndrome [6,7,10]. In adults, copper deficiency is quite rare, and symptoms include anemia conditions, immunodeficiency, osteoporosis, and neurological disorders [5,6]. However, in some cases, daily copper intake ranges from 1 to even 5 mg/day, most often through the consumption of contaminated food products (vegetables, seeds, and tap water) and the use of vitamin supplements and food additives [10]. Namely, cases of direct copper intoxication by inhalation, ingestion and skin contact have been reported [11]. Furthermore, acute copper intoxication ($>8\text{--}10$ mg Cu/kg of body weight) [12] causes a number of consequences such as acute kidney damage, gastrointestinal bleeding, cardiac arrhythmia, hypotension, hemolytic anemia, hematuria, methemoglobinemia, hepatocellular toxicity, autism and hypothyroidism [2,3,8,10]. In contrast to acute copper intoxication, chronic copper overload with its abnormal increased accumulation in the liver and brain is an autosomal recessive genetic disorder, and refers to hepatolenticular degeneration, the so-called Wilson's disease [2,7,8,10,13]. This disease first results in liver dysfunction, and then neurological disorders that lead to Alzheimer's, Parkinson's and Huntington's disease [7,8,14]. Although copper is essential for the functioning of cellular metabolism, its excessive amounts in the human body lead to serious disorders mentioned above [8]. For this reason, the US Environmental Protection Agency has set health guidelines for the maximum copper level in drinking water up to 1.3 mg Cu/L [15], while the World Health Organization prescribes 2 mg Cu/L [16]. Likewise, Croatian legislation prescribes a maximum permitted level of copper in drinking water up to 2 mg/L [17].

Namely, copper enters the environment less frequently from natural sources (volcanoes, forest fires, rocks weathering and erosion, and vegetation decomposition) than from anthropogenic sources (mining and smelting activities of copper ores, wastewater, and agriculture) [4,18]. In proximity to iron and aluminum, copper is the third most used metal worldwide [5]. It is used for the production of water pipes, electrical wirings, alloys (brass and bronze), electronics devices, copper coins, electroplating, azo dyes, explosives, phytopharmaceuticals, food additives (coloring agent), etc. [2,3,5,10,19]. Due to its extremely high usage, copper is considered one of the major anthropogenic environmental contaminants from the group of heavy metals [5].

Karim's [2] review paper documented the copper concentration distribution in all parts of the environment: air, soil and water. Thus, the average copper concentrations in the air ranging from a few ng/m^3 to $200 \text{ ng}/\text{m}^3$ were found, while in the industrial area they rise even up to $5000 \text{ ng}/\text{m}^3$. The production and processing of copper causes the emission of fumes and dust particles enriched with copper [2]. Likewise, soil contamination with copper is the primary result of excessive use of Cu-based agrochemicals for agricultural crop protection [4,18,20]. Since copper has antifungal properties, Cu-based fungicides such as Bordeaux mixture ($\text{CuSO}_4 + \text{CaO}$) and other Cu-based agrochemicals are used to treat various plant diseases, and algicides to suppress algae growth in swimming pools [4,18,19]. As a consequence of the widespread use of Cu for agricultural purposes, the average Cu concentration in soil worldwide is estimated to be approximately $30 \text{ mg Cu}/\text{kg}$ [18], and values ranging from 2 to $17,000 \text{ mg}/\text{kg}$ have been recorded. Consequently, increased copper concentrations in the soil lead to its accumulation in vegetables used for human consumption [20]. Furthermore, the concentration of copper in water bodies (rivers, lakes) varies from 0.5 to $1000 \text{ }\mu\text{g}/\text{L}$. An interesting fact is the presence of copper in tap water

in the range of 20–75 µg/L [2]. Therefore, the main routes of human copper intoxication are inhalation of polluted air, consumption of contaminated vegetables and nuts, and tap water from copper plumbing. Moreover, a review paper by Liu et al. [5] documented copper content in wastewater in the range of 2.5–10,000 mg/L. Globally, it is estimated that approximately 90% of wastewater produced remains untreated and is discharged directly into the environment [4]. This finding is quite concerning and indicates the need to raise awareness of the need for adequate wastewater treatment in the 21st century, which is in accordance with Sustainable Development Goal 6 on water and sanitation (SDG 6) and the idea of a circular economy [21,22]. For instance, Croatian legislation prescribes a maximum permissible copper level in treated industrial wastewater of 1 mg/L for discharge into the public sewage system, and even more rigorously for discharge into water bodies of 0.5 mg/L [23]. Therefore, remediation of copper-contaminated areas is necessary to mitigate its negative effects on the all environmental compartments.

Various physical, chemical and biological methods for treating copper-contaminated waters have been investigated. Comprehensive review papers by Liu et al. [5], Li et al. [24] and Al-Saydeh et al. [25] reported that chemical precipitation, adsorption/ion exchange, cementation, membrane and electrochemical methods are the most commonly used for copper removal from industrial wastewater. Notwithstanding, the generation of sludge and the need for its further treatment and/or disposal after chemical precipitation, as well as the high energy requirements for electrochemical and membrane methods, put these methods into consideration and the need to find more environmentally friendly ones. In contrast, the advantage of adsorption is simple design and operation, low capital costs, and removal of cationic and anionic contaminants from relatively large volumes at the parts per billion (ppb) level [25]. Since the 1940s, adsorption and ion exchange has gained importance for the treatment of industrial wastewaters with the use of activated carbon and synthetic ion exchangers [26]. Despite this, the high production costs of these materials call into question the cost-effectiveness of the adsorption implementation, whereby the adsorbent cost price often plays a decisive role in its selection [27]. Consequently, in order to increase the profitability of adsorption, it is crucial to find natural, highly selective, easily accessible and non-toxic green low-cost sorbents.

Specifically, Krstić et al. [28] highlighted adsorption as a promising green technology for the treatment of wastewater containing copper ions using environmentally friendly and price affordable natural adsorbents such as zeolites, clays and biosorbents. In the review paper by Irannajad and Haghighi [29], a sequential order of adsorption capacity of mineral adsorbents for heavy metals is given, among which the following stand out: zeolite > clay > diatomite. Accordingly, natural zeolites appear to be a promising option since they meet the previously mentioned conditions of sustainability and economic viability along with environmental friendliness.

Natural zeolites consist of (Si and Al)O₄ tetrahedra connected by all of their oxygen vertices, with generating channels where exchangeable cations (such as Na⁺, K⁺, Ca²⁺ and Mg²⁺) and H₂O molecules balance the negative charge produced by isomorphous substitution of silicon with aluminum. Zeolites are used in many different applications, except as a sorbent for heavy metals, they are also used as chemical sieves and water softeners, due to their structural characteristics and adsorption capabilities [27,30,31]. According to the findings, copper was primarily removed from water solutions using zeolites by ion-exchange process, wherein copper ions from the solution replace ions like Na⁺, K⁺, Ca²⁺, and others that are present in the pores of zeolite crystalline lattices [28].

Modifying natural zeolites to enhance their adsorption capabilities and selectivity to a certain substance or group of compounds has been the subject of numerous investigations in recent decades. The goal of each modification is to overcome the typical traditional prop-

erties of natural zeolites, such as the lack of active sites or the absence of selective active sites. Accordingly, modifications cause changes in surface physicochemical characteristics as a result of the creation of new active sites, changes in the zeolite surface charge, and an increase in porosity, which ultimately affects the increase in sorption efficiency [28,32–34]. Common methods for activating natural zeolites include single or combined chemical (acids, bases, or inorganic salts), thermal, surfactant modification and metal oxide modification. The intended application and economic cost-effectiveness should be taken into account while selecting modification methods [28]. The modification of zeolite with inorganic salts, among which the most researched ones are those with Fe-salts, is primarily intended to create new active sites, remove impurities from zeolite channels and increase the negative charge of the zeolite lattice. Namely, Fe-zeolites include incorporation of iron on the outer and inner zeolite surface in the form of mononuclear and binuclear oxygen-bridges iron species. The integration of Fe into the zeolite framework effectively addresses the aforementioned limitations of traditional aluminosilicate zeolites and expands their use in environmental applications [34]. In recent years, many researchers have investigated the possibility of copper removal using natural zeolites [35–52] as opposed to acid-modified [53], thermally activated [54], and especially iron-modified natural zeolites [55–58]. This fact provides an opportunity for a more systematic investigation of the application of Fe(III)-modified natural zeolites as sorbents for copper binding, which serves as the foundation of this paper.

Hence, the aim of this study is to comparatively investigate the impact of sorption parameters (pH_0 , solid/liquid ratio, contact time, and initial concentration) and their optimization on the amount of sorbed copper onto natural and Fe(III)-modified natural zeolite, as well as on the removal efficiency. In addition, the sorption mechanism will be clarified by applying kinetic and isotherm models as well as SEM-EDS of copper-saturated zeolites. Finally, the leaching experiments of copper-saturated zeolites will provide a judgment on the possibility of their application for in situ and ex situ remediation of copper-contaminated environments.

2. Materials and Methods

2.1. Zeolite Preparation

The initial sample, natural zeolite (NZ), was sourced from the Zlatokop deposit located in Vranjska Banja, Serbia. The sample was ground, sieved, and a particle size fraction of 0.6–0.8 mm was isolated following the standard procedure (DIN 66165-2) [59]. Subsequently, the sample was rinsed with ultrapure water and dried at 60 °C.

Fe(III)-modified natural zeolite (FeZ) was prepared by treating NZ based on the procedure outlined in a previous study [60]. Briefly, NZ is first mixed with a freshly prepared 1 mol/L solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in acetate buffer at $\text{pH} = 3.6$, followed by the addition of 1 mol/L NaOH solution and finally 4% NaNO_3 . The prepared sample was dried at 40 °C and stored in a desiccator. Physico-chemical characterization of both NZ and FeZ (chemical composition, SEM/EDS, XRD, FTIR, BET surface area, TG/DTG) was detailed in a previous study [60]. XRD analysis showed that NZ primarily consists of clinoptilolite (80%), with quartz, feldspar, and carbonates as secondary minerals. Modification resulted in slight crystallinity loss (XRD), broader hydroxyl bands (FTIR), a small increase in surface area, a significant increase in pore volume (BET), and higher mass loss (TG/DTG). FTIR analyses are shown in Figures S1 and S2 and are explained in detail in the Supplementary Materials. Zeta potential in a wide pH range (2–12) revealed that both zeolites have a negative charge, of which FeZ is more negative. In summary, the modification aimed to bind the predominantly present $\text{Fe}_3(\text{OH})_4^{5+}$ species at $\text{pH} = 3.6$ to the negative surface of NZ. The addition of NaOH caused the hydroxylation of Fe species, forming negative Fe oxo- and hydroxo-complexes, which increased the negative charge of FeZ.

2.2. Batch Sorption Experiments

The salt, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ purchased from Kemika was used to prepare a stock solution with an initial concentration of 15.744 mmol/L. Solutions of lower concentrations were prepared by diluting the stock solution. Ultrapure water was used to prepare all solutions, and a 0.1 or 1 mol/L HNO_3 solution was used to adjust the pH. All experiments were performed in an incubator shaker at 25 °C, 230 rpm, and for 24 h. Cu(II) concentrations before and after equilibrium were determined using a Flame Atomic Absorption Spectrophotometer, AAS, model PinAAcle 900F, (Perkin Elmer Inc., Waltham, MA, USA).

2.2.1. Impact of pH

The impact of pH_0 on the Cu(II) sorption onto NZ and FeZ was examined in the pH_0 range $2.25 \leq \text{pH}_0 \leq 5.01$ and at two initial concentrations of 4.017 mmol Cu/L and 8.137 mmol Cu/L. A mass of 1.0 g of NZ or FeZ was mixed with 100 mL of Cu(II) solution (solid/liquid ratio = 10 g/L). After the equilibrium was established, the equilibrium pH_e was measured, as well as the amount of released exchangeable cations (Na, K, Ca and Mg) by ion chromatography (Metrohm 761 Compact IC, Metrohm Ltd., Herisau, Switzerland).

2.2.2. Impact of Solid/Liquid Ratio

The impact of the solid/liquid ratio (S/L) was examined at $\text{pH}_0 = 4.83$ for NZ and $\text{pH}_0 = 2.98$ for FeZ, and at an initial concentration of 4.017 mmol Cu/L. The specified pH_0 values were determined as optimal based on the experiment described in Section 2.2.1. Experiments for both zeolites were carried out at $\text{S/L} = 2\text{--}18$ g/L ($m = 0.2; 0.6; 1.0; 1.4$ and 1.8 g). After equilibrium was established, the equilibrium pH_e was measured.

2.2.3. Impact of Contact Time

The impact of contact time on the Cu(II) sorption onto NZ and FeZ was carried out at a previously determined optimal pH_0 ($\text{pH}_0 = 4.83$ for NZ and $\text{pH}_0 = 2.98$ for FeZ) and at $\text{S/L} = 10$ g/L based on the conducted experiment described in Section 2.2.2. A mass of 20 g of NZ or FeZ was mixed with 2 L of Cu(II) solution with an initial concentration of 10.061 mmol/L at 550 rpm. Liquid samples were collected at selected time intervals within 24 h, whereby the total volume of the samples not exceeding 5–6% of the total volume of the suspension. The saturated samples, designated as NZCu and FeZCu, were collected, washed several times in ultrapure water, dried at 40 °C, and used for leaching experiments.

2.2.4. Impact of Initial Concentration

The impact of initial Cu(II) concentration on Cu(II) sorption onto NZ and FeZ was tested in the concentration range 0.508–15.744 mmol Cu/L at the previously determined optimal $\text{S/L} = 10$ g/L and pH_0 ($\text{pH}_0 = 4.83$ for NZ and $\text{pH}_0 = 2.98$ for FeZ). A volume of 100 mL of Cu(II) solution, of different initial concentrations, was mixed with 1.0 g of NZ or FeZ. After the equilibrium was established, in addition to measuring the equilibrium pH_e , the concentrations of released zeolite cations (Na, K, Ca, and Mg) were also measured by ion chromatography. Saturated samples with the highest initial concentration of 15.744 mmol Cu/L were collected, washed several times in ultrapure water, dried at 40 °C, and labeled as NZCu and FeZCu. Then, the chemical composition of the starting samples, NZ and FeZ, and the saturated samples, NZCu and FeZCu, was determined by classical chemical analysis of aluminosilicates [61]. A comparison of the chemical composition of the initial and saturated samples is shown in Table 1.

Table 1. Chemical composition of starting and copper-saturated zeolites.

Sample	Content, wt. %									
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Na ₂ O	K ₂ O	CaO	MgO	TiO ₂	Cu	Loss of Ignition
NZ	65.40	14.00	2.16	1.50	1.10	3.56	0.85	0.32	-	11.09
NZCu	65.98	14.63	2.18	1.09	1.11	2.83	0.37	0.17	0.61	11.03
FeZ	62.80	13.90	3.22	3.68	0.94	2.93	0.80	0.17	-	11.56
FeZCu	64.57	13.03	2.68	1.84	0.97	3.84	0.69	0.161	1.51	10.71

Scanning electron microscopy (SEM) combined with energy-dispersive X-ray analysis (EDS) of copper-saturated samples, NZCu and FeZCu, was performed on a JEOL JSM-6610 microscope (JEOL Ltd., Akishima, Tokyo, Japan). On selected surfaces of the analyzed samples, the semi-quantitative chemical composition was determined, and the distribution of elements on the surface was determined by mapping analysis.

2.3. Leaching Experiments

Leaching of Cu(II) from the collected saturated samples (NZCu and FeZCu) after conducting the experiment described in Section 2.2.3., were subjected to the standard leaching method, DIN 38414 S4 [62]. Ultrapure water with pH pre-adjusted with 0.1 mol/L HNO₃ or 0.1 mol/L KOH in the range of 2.06–12.09 was used as leachant. A mass of 1.0 g of NZCu or FeZCu was mixed with 10 mL of ultrapure water of different pH₀ for 24 h at 25 rpm and at 25 °C. After 24 h, in the filtered suspensions the equilibrium pH_e and the concentration of leached Cu(II) were determined using a Flame Atomic Absorption Spectrophotometer.

2.4. Calculation of Sorption Parameters

The quantity of Cu(II) sorbed onto zeolites at time t (up to 24 h), denoted as q_t (mmol/g), as well as the removal efficiency at time t , denoted as α_t (%), were determined using Equations (1) and (2):

$$q_t = (c_0 - c_t) \cdot \frac{V}{m} \quad (1)$$

$$\alpha_t = \frac{(c_0 - c_t)}{c_0} \cdot 100 \quad (2)$$

Here, c_0 and c_t represent the concentrations of Cu(II) at $t = 0$ and at time t (mmol/L), V is the volume of the solution (L), and m is the mass of the zeolite (g). When $t = 24$ h, q_t and α_t represents the equilibrium quantity of Cu(II) sorbed (q_e) and equilibrium removal efficiency (α_e).

The quantity of Cu(II) leached from the saturated zeolites, q_{leach} (mmol/g), and the percentage of Cu(II) leached, α_{leach} (%), were calculated using Equations (3) and (4):

$$q_{\text{leach}} = c_{\text{leach}} \cdot \frac{V}{m} \quad (3)$$

$$\alpha_{\text{leach}} = \frac{q_{\text{leach}}}{q_e} \cdot 100 \quad (4)$$

Here, c_{leach} represents the concentration of Cu(II) leached from the saturated zeolites (mmol/L).

2.5. Theoretical Background—Kinetic Analysis for Identifying Rate-Controlling Steps

To identify the rate-controlling step, whether it is mass transfer, diffusion, or chemical reaction, various reaction and diffusion kinetic models are used to analyze the experimental data. The most commonly used reaction kinetic models to verify if a chemical reaction is the limiting step are the pseudo-first-order (PFO) model (Lagergren), the pseudo-second-order (PSO) model (Ho), and the Elovich model. The pseudo-first-order non-linear equation is given by the following expression [63,64]:

$$q_t = q_m \cdot (1 - e^{-k_1 \cdot t}) \quad (5)$$

In this equation, q_t represents the quantity of Cu(II) sorbed onto the zeolites at time t (mmol/g), q_m is the amount of Cu(II) sorbed on the zeolite obtained from the model, k_1 is the rate constant of the PFO (1/min), and t is the time (min).

The non-linear form of the pseudo-second-order model is expressed by Equation (6) [63,64]:

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

where k_2 is the rate constant of the PSO [g/(mmol·min)].

The Elovich model describes the chemical sorption of Cu(II) onto a heterogeneous zeolite surface, and the non-linear form is represented by Equation (7) [64]:

$$q_t = \frac{1}{\beta_E} \cdot \ln(1 + \alpha_E \cdot \beta_E \cdot t) \quad (7)$$

where α_E represents the initial chemisorption rate [mmol/(g·min)] and β_E is associated with the surface coverage (g/mmol).

Since zeolites are porous materials, sorption is frequently restricted by mass transfer to the active sites within the zeolite structure. In well-stirred systems, the rate-controlling step is typically linked to film or intra-particle diffusion, as the resistance to mass transfer from the bulk to the particle surface is negligible. To determine whether film or intra-particle diffusion is the slowest step of sorption process, different diffusion kinetic models can be applied. The rate-limiting step in sorption, whether due to film or intraparticle diffusion, can be determined using the linear equation of the Weber–Morris model, as shown below [65]:

$$q_t = k_{WM} \cdot t^{1/2} + I \quad (8)$$

where k_{WM} is the Weber–Morris diffusion constant [mmol/(g·min^{1/2})], and I represents the boundary layer thickness (mmol/g).

If $I = 0$, film diffusion is the sole rate-controlling step; otherwise, both film and intraparticle diffusion contribute to mass transfer. The contribution of film or intraparticle diffusion can be estimated using Equation (9) [65]:

$$RC = \frac{I}{q_e} \cdot 100 \quad (9)$$

where RC denotes the relative coefficient, expressed as a percentage. Smaller RC values indicate that film diffusion contributes less to the overall mass transfer process.

The Weber–Morris diffusion coefficient, k_{WM} (cm²/min) is calculated using the following equation [65]:

$$D_{WM} = \pi \cdot \left(\frac{d_p \cdot k_{WM}}{12 \cdot q_e} \right) \quad (10)$$

where d_p is the zeolite particle diameter (cm).

The two-step sorption kinetics are represented by a double-exponential non-linear model, as shown below [66,67]:

$$q_t = q_m - \frac{B_1}{m_z} \cdot e^{(-k_{B1} \cdot t)} - \frac{B_2}{m_z} \cdot e^{(-k_{B2} \cdot t)} \quad (11)$$

Here, B_1 and B_2 represent the concentrations of the Cu(II) sorbed in the fast and slow steps (mmol/L), while k_{B1} and k_{B2} are the rate constants for the fast and slow steps (1/min), respectively.

The total sorption rate, r [mmol/(g·min)] is the sum of the fast step, r_1 , and the slow step, r_2 [66,67]:

$$r = r_1 + r_2 = \frac{B_1}{m_z} \cdot k_{B1} + \frac{B_2}{m_z} \cdot k_{B2} \quad (12)$$

Furthermore, the percentage of Cu(II) sorbed in the fast (RF) and slow (SF) steps can be calculated as follows [66,67]:

$$RF = \left(\frac{B_1}{B_1 + B_2} \right) \cdot 100 \quad (13)$$

$$SF = \left(\frac{B_2}{B_1 + B_2} \right) \cdot 100 \quad (14)$$

Vermeulen's approximation assumes intraparticle diffusion as the rate-controlling step and is given by Equation (15) [68]:

$$q_t = q_m \cdot \left[1 - e^{\left(\frac{4D_V \cdot \pi^2 \cdot t}{r_p^2} \right)} \right]^{\frac{1}{2}} \quad (15)$$

In this equation, D_V is the intraparticle diffusion coefficient (cm²/min), and r_p refers to the radius of the zeolite particle (cm).

The model parameters were calculated using the mathematical tool MathCad 15. The agreement of the model with the experimental data was determined using the linear and non-linear correlation coefficients, R^2 and r^2 . In addition to this, two error functions were used, non-linear chi-square test (χ^2) and root mean square error (RMSE) as follows [64]:

$$\chi^2 = \sum_{i=1}^n \frac{(q_m - q_e)^2}{q_m} \quad (16)$$

$$RMSE = \sqrt{\sum_{i=1}^n \frac{(q_m - q_e)^2}{n}} \quad (17)$$

3. Results and Discussion

3.1. Determination of Optimal Sorption Parameters

Determining the optimal process parameters (pH₀, solid/liquid ratio, contact time and concentration range) is crucial to maximize both, the amount of metal ions sorbed onto the sorbent as well as the metal removal efficiency from the aqueous phase. Although it is important to fully utilize the capacity of the sorbent, from a practical point of view, removal efficiency is much more important because it reflects the success of the sorption process. Hence, sorption efficiency will be considered as a more critical factor in determining optimal sorption parameters.

3.1.1. Determination of Optimal pH

The pH of the suspension is one of the most important factors in the sorption process, as it directly affects the zeolite surface charge as well as the charge and type of Cu(II) species. Accordingly, based on the hydrolysis constants of Cu(II) in the aqueous medium shown by Equations (18)–(21) [69], the distribution of Cu(II) species as a function of pH was constructed as shown in Figure 1.

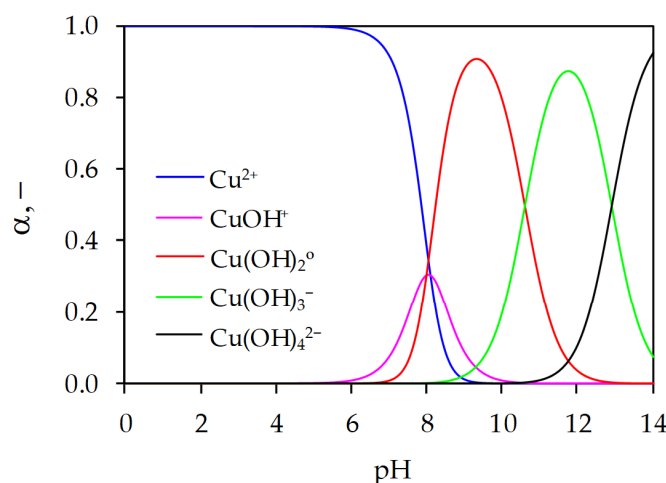
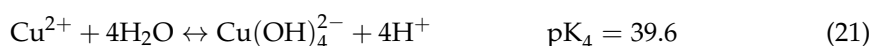


Figure 1. Distribution of Cu(II) species in relation to pH.

Figure 1 illustrates the change in the Cu(II) species distribution in aqueous solution depending on pH. Up to pH = 6, copper is present primarily in the form of Cu^{2+} species with a content of 99%. Above pH = 5, Cu^{2+} starts to convert into hydroxylated species. Thus, in the pH range from 5.2 to 10.7, a small amount of CuOH^+ species appears with a maximum content of 31% at pH = 8. Cu(II) in the form of $\text{Cu}(\text{OH})_2$ starts to precipitate at pH = 6.5 with a maximum content of 90% at pH = 9.5. At pH > 8, anionic Cu(II) species are formed. The $\text{Cu}(\text{OH})_3^-$ species is dominant at pH = 11.8 with a content of 88%. At pH = 10.2, the $\text{Cu}(\text{OH})_4^{2-}$ species appears, which has an increasing trend with increasing pH. Therefore, this suggests that the Cu(II) sorption process needs to be conducted below pH = 6.5 to exclude Cu(II) precipitation.

In order to obtain additional confirmation of the pH value at which Cu(II) precipitation occurs (pH_{ppt}), taking into account the initial Cu(II) concentration, the following expression is used [70]:

$$\text{pH}_{\text{ppt}} = 14 - \log \sqrt{\frac{c_0[\text{Cu(II)}]}{K_{\text{sp}}[\text{Cu}(\text{OH})_2]}} \quad (22)$$

where $c_0[\text{Cu(II)}]$ is the initial Cu(II) concentration and K_{sp} is the solubility product constant of $\text{Cu}(\text{OH})_2$, $K_{\text{sp}} = 2.20 \cdot 10^{-20}$ [71].

The measured pH_e and calculated pH_{ppt} for the two initial Cu(II) concentrations (4.017 mmol/L and 8.137 mmol/L), along with the removal efficiency (α_e) as a function of pH_0 , are presented in Figure 2a,b.

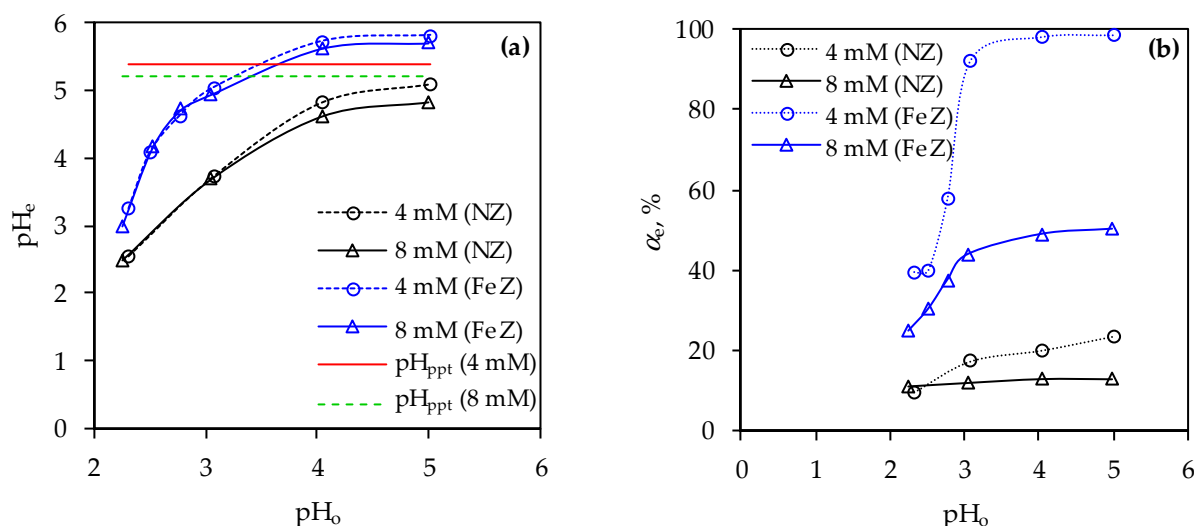


Figure 2. (a) pH_e vs. pH_o after sorption of Cu(II) onto NZ and FeZ. (b) The effect of pH_o on removal efficiency, α_e of Cu(II) onto NZ and FeZ.

In Figure 2a, it is noticeable that for both initial Cu(II) concentrations, $pH_e < pH_{ppt}$ for NZ, which clearly excludes the precipitation of Cu(II) in suspensions for all pH_o . In the case of FeZ, according to the calculated pH_{ppt} , for both initial Cu(II) concentrations at $pH_o \geq 4$, Cu(II) precipitation occurs. The calculated pH_{ppt} value for 4.017 mmol Cu/L is $pH_{ppt} = 5.6$, while $pH_{ppt} = 5.8$ for 8.137 mmol Cu/L. Namely, according to the Cu(II) speciation diagram depending on pH (Figure 1), the proportion of $Cu(OH)_2$ at pH = 5.6 is 0.001%, while at pH = 5.8 it is 0.003%. Although the proportions of the precipitate formed are negligible, in order to reliably claim that no precipitate was formed during the sorption process of Cu(II) on FeZ, an optimal range of pH_o values up to $pH_o = 3$ was selected. The optimal pH_o for Cu(II) sorption on NZ and FeZ will be determined based on the results of Cu(II) removal efficiency depending on pH_o (Figure 2b). Therefore, the optimal pH_o is the value where maximum removal efficiency is achieved without the possibility of precipitation. For both initial concentrations, the optimal pH range is $3 \leq pH_o \leq 5$ for NZ, while for FeZ it is $pH_o = 3$.

Furthermore, for both samples, NZ and FeZ, the removal efficiency increases with increasing pH_o value. Comparing the Cu(II) removal efficiency values for both samples and for both initial concentrations, significantly higher removal efficiency was achieved for FeZ compared to NZ. This indicates that the zeolite modification significantly contributed to the reduction in Cu(II) concentration. Namely, the zeta potential of both samples has negative values in the pH range 2–12, while FeZ having a more pronounced negative charge. This evidence argues that the electrostatic attraction between the positive Cu^{2+} species and the negatively charged surface of NZ and FeZ will be favorable in the acidic pH range where Cu(II) precipitation does not occur. In order to obtain a more complete insight into the effect of pH_o on the sorption of Cu(II) on NZ and FeZ, the interrelationship between in-going Cu(II) ions and out-going exchangeable ions (Na, K, Ca, and Mg) from the zeolite structure was analyzed and shown in Figures 3 and 4 for two initial Cu(II) concentrations.

Interrelationship between in-going Cu(II) ions and out-going exchangeable cations for both initial concentrations and both samples is mostly non-stoichiometric. At extremely acidic pH, where the lowest removal efficiency was recorded, the highest non-stoichiometry is observed for both samples, which is a consequence of the competition between Cu^{2+} and H^+ ions. Non-stoichiometry is more pronounced for FeZ, which is a result of a more pronounced negative charge of the FeZ surface, and thus the more significant influence of the competitive effect. Already at $pH_o \geq 3.05$ for NZ and at $pH_o = 3.05$ for FeZ, the

competitive effect is almost negligible since the non-stoichiometric interrelationship is the least pronounced. Furthermore, for FeZ at $\text{pH} \geq 4.04$, a non-stoichiometric relationship is again observed, but of a reverse character. The non-stoichiometry is reflected in a higher amount of sorbed Cu(II) ions compared to the released exchangeable cations. This is a consequence of Cu(II) precipitation, which additionally contributes to the increase in removal efficiency, which is in accordance with the results shown in Figure 2. These findings suggest and reaffirms that the optimum pH for NZ is in the range of $\text{pH}_0 = 3\text{--}5$, and for FeZ, it is $\text{pH}_0 = 3$.

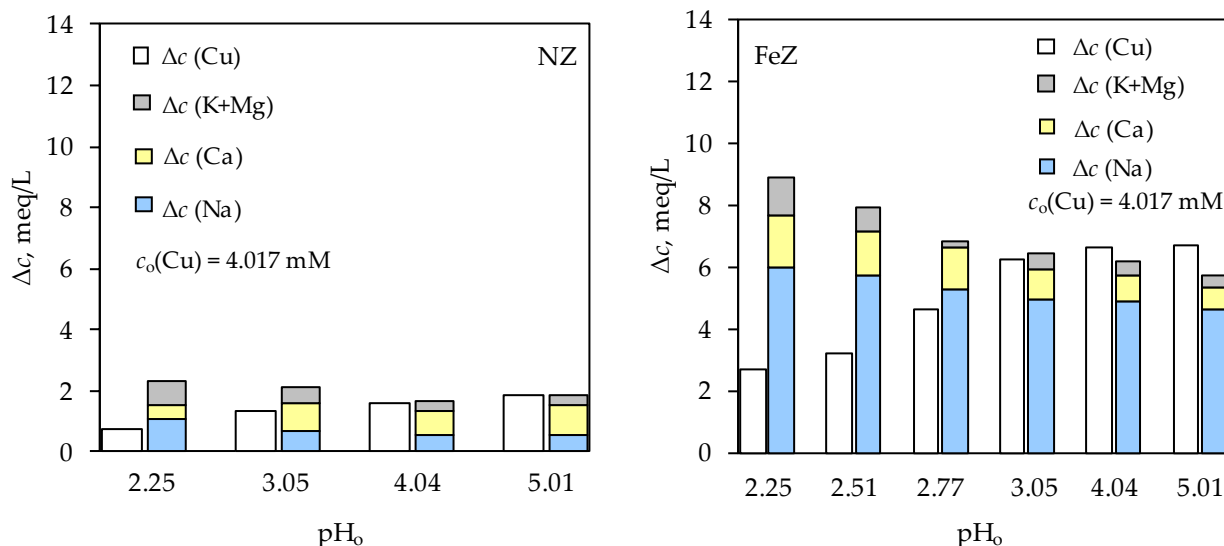


Figure 3. Interrelationship between in-going Cu(II) ions and out-going exchangeable cations as a function of different pH_0 for initial concentration of 4.017 mmol Cu/L for NZ (left) and FeZ (right).

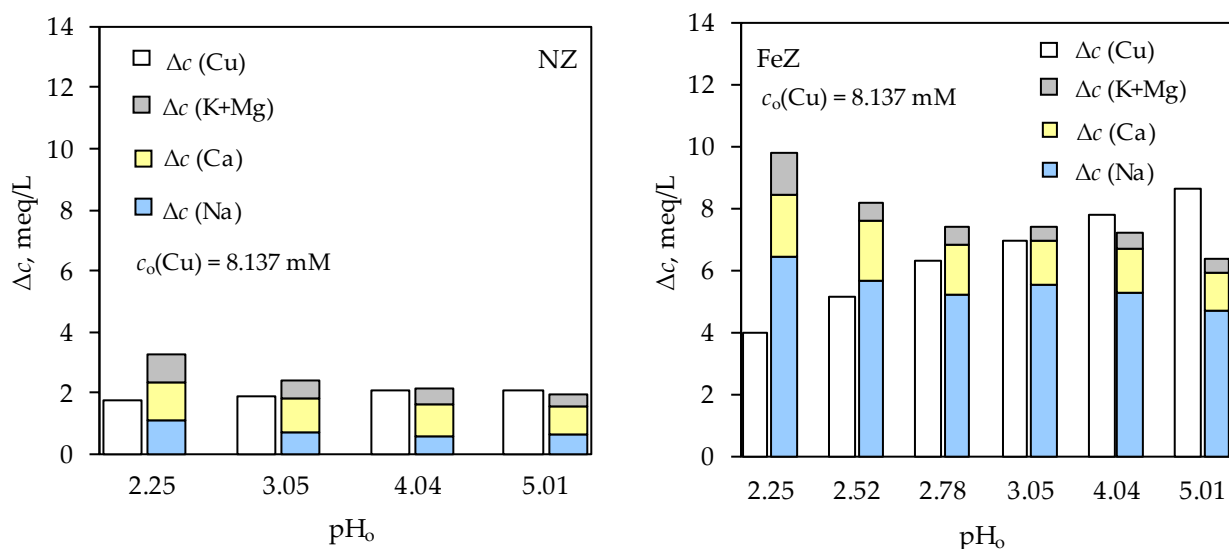


Figure 4. Interrelationship between in-going Cu(II) ions and out-going exchangeable cations as a function of different pH_0 for initial concentration of 8.137 mmol Cu/L for NZ (left) and FeZ (right).

The emphasis on the importance of testing optimal pH is also supported by relatively recent research. Thus, Panayotova [35] reported the optimal pH for Cu(II) removal on Bulgarian natural zeolite in the range 5.5–7.5, which is quite debatable considering the area of copper precipitation according to Figure 1. Forughirad et al. [36] investigated the removal of Cu(II) at $\text{pH} = 7$ and $\text{pH} = 5$ on Azerbaijan natural zeolite clinoptilolite, and found the highest percentage of removed Cu(II) at $\text{pH} = 7$. This is proof that the tests of the

effect of pH on sorption processes must be accompanied by theoretical foundations and knowledge of the speciation of any metal cation depending on pH. Ultimately, this is also the only way to confidently claim that the sorption mechanism is solely responsible for the reduction in metal concentrations, without the possible contribution of precipitation.

3.1.2. Determination of Optimal Solid/Liquid Ratio

The effect of the solid/liquid (S/L) ratio was determined at an initial concentration of 4.017 mmol Cu/L and at $\text{pH}_0 = 4.83$ for NZ and $\text{pH}_0 = 2.98$ for FeZ. The comparison of pH_e with pH_{ppt} and the removal efficiency, α_e of Cu(II) on NZ and FeZ at different S/L ratios is shown in Figure 5.

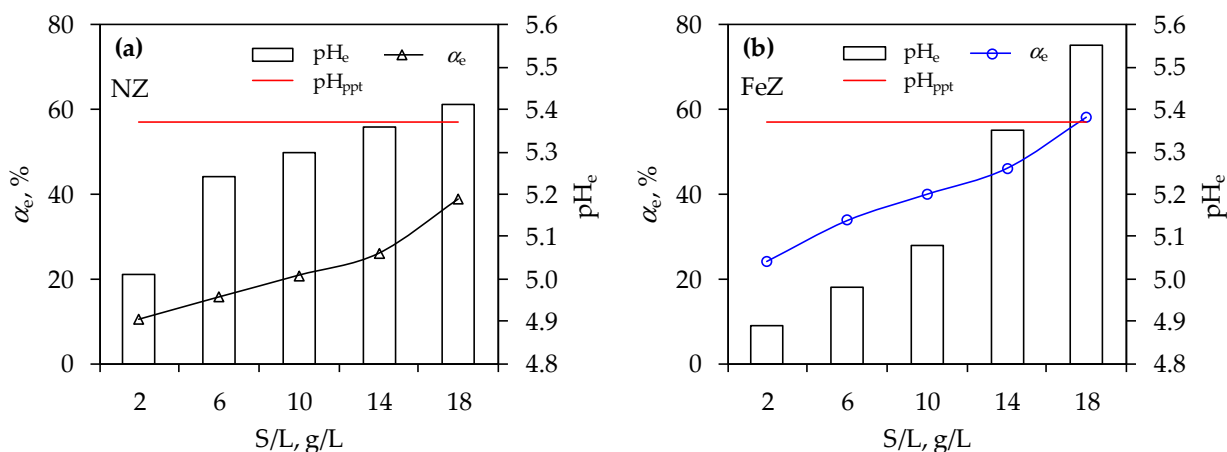


Figure 5. Comparison of pH_e with pH_{ppt} and removal efficiency, α_e at different solid/liquid ratios for (a) NZ and (b) FeZ.

For both zeolite samples, an almost linear increase in removal efficiency is observed with increasing S/L up to S/L = 14 g/L, and then a more abrupt increase in removal efficiency is recorded. Namely, since pH_0 and Cu(II) concentration are constant at all S/L ratios, an increase in the S/L ratio is accompanied by a greater amount of available free active sites on zeolites for Cu(II) sorption, which is reflected in an increase in removal efficiency. On the other hand, although the increase in S/L has a positive effect on the increase in removal efficiency, it also affects the increase in pH_e value (Figure 5). The increase in pH_e is a consequence of both the decrease in the concentration of Cu(II) in the solution and the competition with H^+ ions, which was discussed earlier. However, it can be seen from Figure 5 that $\text{pH}_e > \text{pH}_{\text{ppt}}$ for both samples at S/L = 18 g/L, indicating the occurrence of Cu(II) precipitation, which is consistent with a more abrupt increase in removal efficiency compared to S/L = 14 g/L. Accordingly, in addition to determining optimal pH, determining optimal S/L is essential in order to achieve maximum sorption removal efficiency without the occurrence of Cu(II) precipitation. Keeping the above in mind, for both NZ and FeZ, the optimal S/L is 10 g/L, since at S/L = 14 despite slight increase in α_e , the pH_e is very close to the pH_{ppt} .

3.1.3. Determination of Optimal Contact Time

Determining the impact of contact time is important for balancing the desired efficiency and process cost-effectiveness. Figure 6 depicts time-dependent changes in the amount of Cu(II) sorbed on NZ and FeZ as well as the removal efficiency.

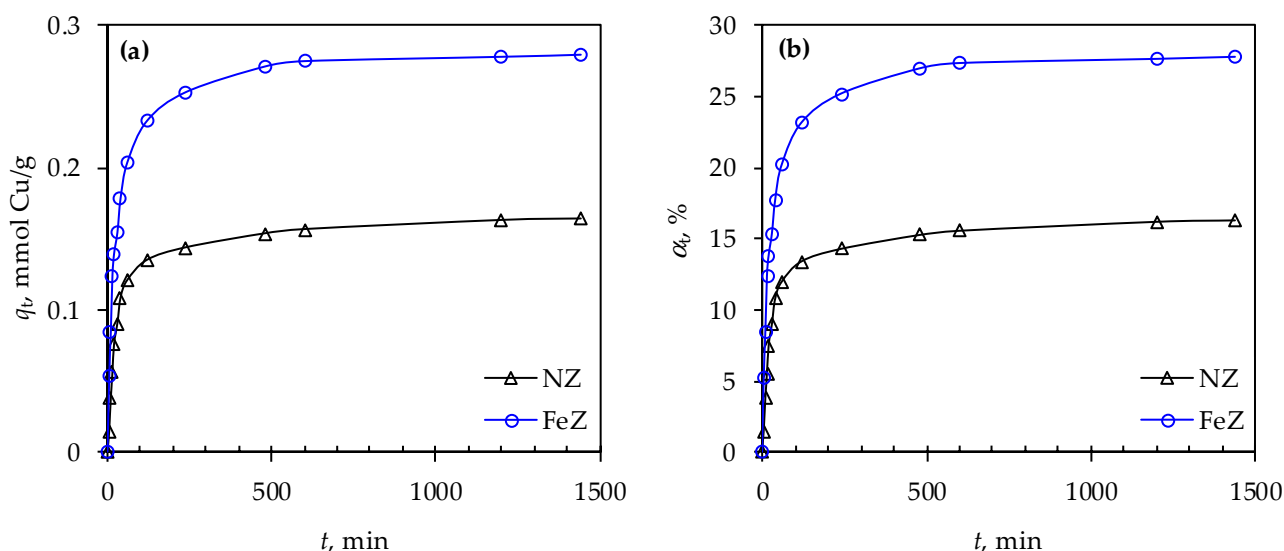


Figure 6. Time-dependent changes in (a) the quantity of Cu(II) sorbed on NZ and FeZ and (b) the removal efficiency.

Time-dependent changes in q_t indicate rapid sorption of Cu(II) onto NZ and FeZ up to 120 min, followed by slower sorption up to 600 min, after which equilibrium is established. The rapid initial sorption phase is probably attributed to the easily accessible zeolite surface active sites, while the second phase corresponds to the gradual saturation of the less accessible active sites located within the zeolite structure. The minimum contact time to reach equilibrium is 600 min, achieving almost double the amount of sorbed Cu(II) on FeZ compared to NZ (0.279 mmol/g vs. 0.164 mmol/g). In the initial phase, the majority of Cu(II) is sorbed, 13% on NZ and 23% on FeZ, while the maximum removal efficiency was almost double for FeZ compared to NZ (28% vs. 16%).

Figure 7 shows the fitting of kinetic reaction and diffusion models with the experimental kinetic data of Cu(II) sorption on NZ and FeZ, while the calculated parameters of the kinetic models along with the agreement indicators are listed in Table 2.

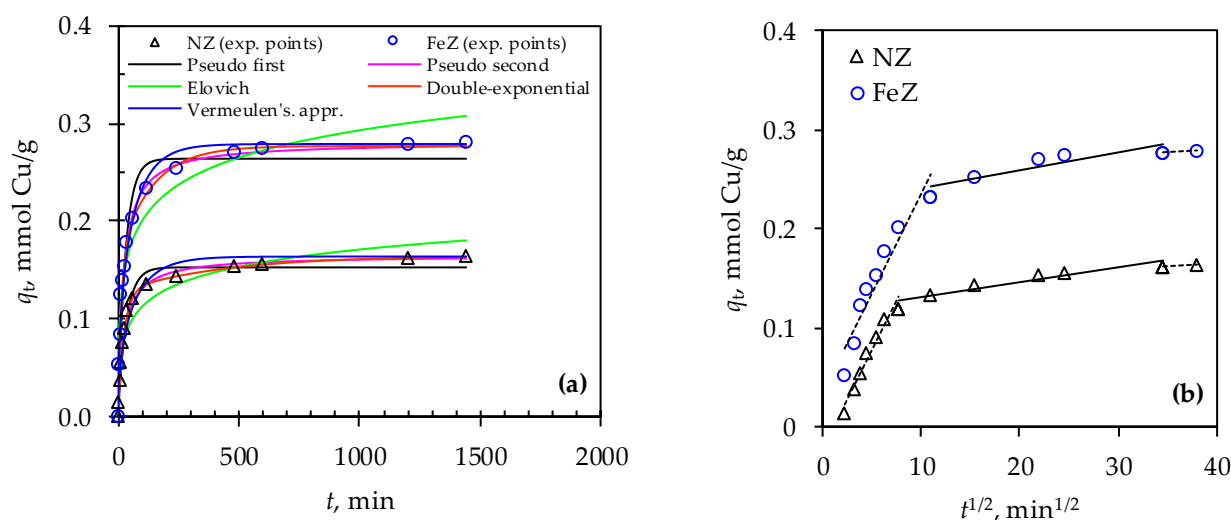


Figure 7. Comparison of experimental data with (a) kinetic model curves (pseudo-first-order, pseudo-second-order, Elovich, Vermeulen's approximation and double-exponential model), and (b) the Weber–Morris model.

Table 2. Calculated kinetic model parameters and agreement indicators for Cu(II) sorption on NZ and FeZ.

Kinetic Model/Parameters	NZ	FeZ
c_o [mmol/L]	10.061	10.061
q_{exp} [mmol/g]	0.164	0.279
Pseudo-first-order model (PFO)		
q_m [mmol/g]	0.153	0.264
k_1 [1/min]	0.029	0.320
r^2	0.987	0.979
$RMSE \times 10^3$	7.339	16.000
$\chi^2 \times 10^4$	7.701	8.838
Pseudo-second-order model (PSO)		
q_m [mmol/g]	0.165	0.281
k_2 [g/(mmol·min)]	0.233	0.161
r^2	0.993	0.998
$RMSE \times 10^3$	5.165	4.993
$\chi^2 \times 10^5$	1.961	2.300
Elovich model		
α_E [mmol/(g·min)]	0.021	0.058
β_E [g/mmol]	39.217	24.814
r^2	0.945	0.966
RMSE	0.015	0.020
$\chi^2 \times 10^3$	1.537	2.638
Weber–Morris intra-particle diffusion model		
k_{WM1} [mmol/(g·min ^{1/2})]	0.019	0.029
$D_{WM1} \times 10^6$ [cm ² /min]	1.545	9.782
I	0.021	0.008
RC [%]	13.060	2.392
R^2	0.965	0.957
k_{WM2} [mmol/(g·min ^{1/2})]	0.002	0.003
$D_{WM2} \times 10^8$ [cm ² /min]	1.019	1.309
R^2	0.993	0.973
Double-exponential model		
q_m [mmol/g]	0.165	0.277
k_{B1} [1/min]	0.041	0.070
B_1 [mmol/L]	1.325	1.594
$k_{B2} \times 10^3$ [1/min]	2.335	7.374
B_2 [mmol/L]	0.373	1.167
$r_1 \times 10^3$ [mmol/(g·min)]	5.443	0.011
$r_2 \times 10^5$ [mmol/(g·min ^{1/2})]	0.871	8.605
$r \times 10^3$ [mmol/(g·min ^{1/2})]	5.520	0.012
RF [%]	78.033	57.733
SF [%]	21.967	42.267
r^2	0.998	0.998
$RMSE \times 10^3$	2.783	4.461
$\chi^2 \times 10^7$	1.329	1.875
Vermeulen's approximation		
q_m [mmol/g]	0.164	0.279
$D_V \times 10^6$ (cm ² /min)	1.288	1.487
r^2	0.976	0.993
RMSE	0.124	0.217
$\chi^2 \times 10^7$	1.201	1.898

The kinetic reaction models were compared based on the fitting parameters (q_{exp} vs. q_{m} , r^2 , RMSE, and χ^2) shown in Table 2. Therefore, the experimental data agree with the kinetic reaction models as follows: PSO > PFO > Elovich model. Since the Elovich model showed the highest disagreement with the experimental results of the three kinetic reaction models considered, chemisorption is certainly not exclusively the slowest limiting step of the sorption process. Furthermore, the deviation of the sorption capacity calculated from the model, q_{m} , and experimentally determined one, q_{exp} , is more significant for PFO than for PSO. This indicates that simple surface sorption of Cu(II) on both zeolites does not take place, but rather more complex interactions such as chemisorption or diffusion. Since the possibility of chemisorption as a limiting step is excluded based on agreement with the Elovich model, it is therefore necessary to fit the experimental data according to diffusion kinetic models.

Accordingly, the kinetic data for NZ and FeZ were fitted to the Weber–Morris model and plotted as a dependence of q_t vs. $t^{1/2}$ as shown in Figure 7b where multicollinearity indicates a more complex kinetic mechanism involving film and intraparticle diffusion. The first linear part corresponds to fast sorption, the second to slower sorption, and the third one to the establishment of equilibrium, which is in line with time-dependent changes in the amount of Cu(II) sorbed on NZ and FeZ (Figure 6a). The values of the parameters $k_{\text{WM1}} > k_{\text{WM2}}$ as well as $D_{\text{WM1}} > D_{\text{WM2}}$ confirm faster sorption in the first phase of the process. In addition, the mentioned parameters are higher in the case of FeZ than NZ, which is reflected in the higher quantity of Cu(II) sorbed on FeZ as well as the higher removal efficiency of Cu(II). Since the value of the calculated relative coefficient (RC) is 13% for NZ and 2% for FeZ, this implies that the proportion of mass transferred by film diffusion is negligible compared to intraparticle diffusion.

The Vermeulen's approximation model considers intraparticle diffusion as the slowest step in mass transfer. According to the values of correlation parameters shown in Table 2, it could be concluded that intraparticle diffusion is the rate controlling step for NZ and FeZ. Nonetheless, in order to confirm the above, the experimental results were also fitted according to the double-exponential model.

The values of the calculated correlation indicators for the double-exponential model are the most satisfactory of all the tested models. This confirms the two-step sorption of Cu(II) on both zeolites. The first sorption phase, which corresponds to mass transfer through the film, is faster ($K_{\text{B1}} > K_{\text{B2}}$) than the second phase, which is attributed to mass transfer by intraparticle diffusion. This is in line with the conclusions drawn from the Weber–Morris model. Since the values, $B_1 > B_2$, as well as $RF > SF$, the majority of Cu(II) was sorbed on both zeolites during the first, faster sorption phase. The values of the kinetic parameters (K_{B1} , K_{B2} , B_1 , and B_2) for both phases of two-step sorption are higher for FeZ, which is attributed to a higher number of active sites on FeZ due to modification. Taking into account all applied models, the sorption of Cu(II) on both zeolites is complex and takes place in active sites located on the outer and inner surfaces of the zeolite grains. From a kinetic perspective, intraparticle diffusion is the slowest mass transfer step.

3.1.4. Determination of Optimal Concentration Range and Sorption Mechanism

The results of the effect of the initial Cu(II) concentration on the quantity of Cu(II) sorbed per gram of NZ and FeZ, as well as the removal efficiency, are shown in Figure 8.

The effect of the initial Cu(II) concentration is manifested by a gradual increase in the amount of Cu(II) sorbed on NZ up to $c_0 = 10$ mmol Cu/L and up to $c_0 = 12$ mmol Cu/L for FeZ. Above the specified concentrations, maximum saturation of zeolite active sites is achieved. The maximum amount of sorbed Cu(II) on FeZ compared to NZ (0.271 mmol/g vs. 0.156 mmol Cu/g) is almost twice as high under optimal Cu(II) sorption conditions.

Furthermore, from the aspect of Cu(II) removal efficiency, the highest removal efficiency is achieved at the lowest initial concentration, while an increase in the initial concentration decreases the removal efficiency. This indicates the need to optimize the two mentioned parameters, i.e., maximizing both sorption capacity and removal efficiency.

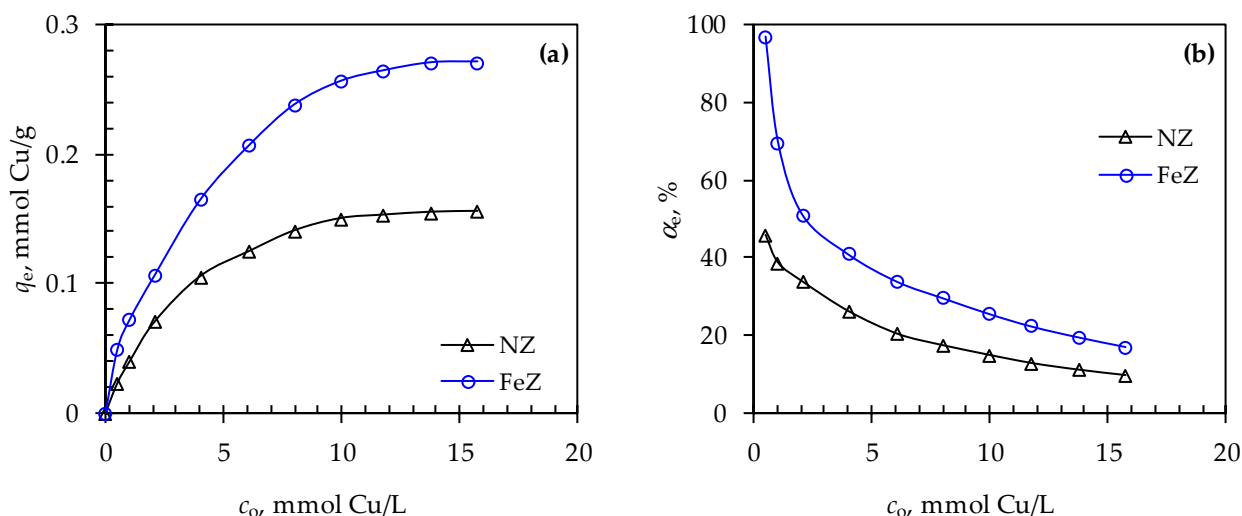


Figure 8. (a) Effect of initial Cu(II) concentration on: quantity of Cu(II) sorbed per gram of NZ and FeZ and (b) Cu(II) removal efficiency.

To place the current research in the context of similar studies, background information from recently conducted research is listed in Table 3 and discussed below.

Table 3. Comparison of sorption capacities of different natural and modified zeolites towards Cu(II).

Zeolite Type	Zeolite Origin	Sorption Capacity, mmol/g	References
Natural zeolite	Bulgarian clinoptilolite	0.150	[37]
	Japanese clinoptilolite	0.074	[38]
	Slovak clinoptilolite	0.037	[40]
	Japanese clinoptilolite	0.064	[42]
	Ukrainian clinoptilolite	0.337	[46]
	Greek clinoptilolite	0.210	[55]
	Slovak clinoptilolite	0.0058	[56]
	Australian heulandite	0.063	[57]
	Chinese clinoptilolite	0.061	[58]
Modified zeolite	Serbian clinoptilolite	0.156	Current study
	Greek clinoptilolite	0.590	[55]
	Slovak clinoptilolite	0.0061	[56]
	Australian heulandite	0.077	[57]
	Chinese clinoptilolite	0.081	[58]
	Serbian clinoptilolite	0.271	Current study

Namely, numerous studies of copper removal have been carried out on natural zeolites from different regions of the world. Zendelska et al. [37] determined the capacity of Bulgarian natural zeolite clinoptilolite to be 0.150 mmol/g at pH = 3.5 and S/L = 50 g/L. Kabwadza-Corner et al. [38] notified the capacity of natural zeolite clinoptilolite from Shimane Prefecture in Japan towards Cu(II) of 0.074 mmol/g at pH = 5 and S/L = 0.2 g/L.

Bakalár et al. [40] obtained the maximum capacity of natural zeolite clinoptilolite from Slovakia towards Cu(II) of 0.037 mmol/g without adjusting the pH. Wilopo et al. [42] determined the Cu(II) capacity of natural zeolite from the Gedangsari deposit, Japan of 0.064 mmol/g at pH = 5. Kyzioł-Komosińska et al. [46] studied the sorption of Cu(II) on Ukrainian natural zeolite clinoptilolite and found a capacity of 0.337 mmol/g at pH = 5 and S/L = 10 g/L. Experimental findings indicate that sorption capacities are primarily related to the geological origin of natural zeolites, wherein each zeolite has unique properties. Furthermore, different experimental conditions yield different outcomes. Notwithstanding, the sorption capacities of different natural zeolites are relatively comparable and consistent with our findings.

Regarding natural zeolites modified with Fe(III) salts, apart to the geological origin, the method of modification also plays a significant role. For example, Doula [55] used Greek natural zeolite clinoptilolite that was modified sequentially with 1 mol/L Fe(NO₃)₃ and 5 mol/L KOH solutions. At S/L = 10 g/L, the sorption capacity of the modified zeolite towards Cu(II) was 2.8 times higher than that of the parent zeolite (0.59 mmol/g vs. 0.21 mmol/g). It is noteworthy that the equilibrium pH ranged from 6.53 to 8.37 after Cu(II) sorption on the Fe-modified zeolite. Lipovský et al. [56] used the same modification procedure as Doula [55] to obtain Fe-clinoptilolite from natural zeolite originating from Nižný Hraboc (Slovakia). The authors did not define pH, but they found a 1.05-fold increase in capacity of the modified zeolite compared to the natural zeolite (0.0061 mmol Cu/g vs. 0.0058 mmol Cu/g). Nguyen et al. [57] also used the same procedure as the previous two studies to obtain iron-coated zeolite using natural zeolite heulandite from the Werris Creek deposit, New South Wales, Australia. The research showed a sorption capacity of 0.063 mmol Cu/g of natural zeolite and 0.077 mmol Cu/g of iron-coated zeolite maintaining pH at 6.5 ± 0.2 . Thus, the modification contributed to the increase in capacity by 1.22 times. On the other hand, Han et al. [58] used 1 mol/L FeCl₃ and 3 mol/L NaOH to produce iron oxide-coated zeolite at 500 °C using natural zeolite clinoptilolite from Xinyang city, China. At S/L = 4 g/L, they found a 1.33-fold higher sorption capacity of the modified sample compared to the starting material (0.081 mmol Cu/g vs. 0.061 mmol Cu/g).

In summary, the modifications contributed to the increase in the capacity of the zeolites, despite differences caused by the origin, type of modification, and experimental conditions. A possible drawback of these studies is that optimization of sorption parameters was not performed, which would be a contribution of the current research. Of the aforementioned studies, Doula [55] achieved the highest increase in capacity, as much as 2.8 times. However, the equilibrium pH values (6.53–8.37) were in the area where copper precipitation is most likely to occur. In this study, the pH was maintained in a range where no precipitation occurred, and the sorption capacity was found to be twice as high. Hence, the almost two-fold increase in the sorption capacity of FeZ is the result of a modification that caused an increase in the negative zeolite surface due to the incorporation of Fe species on the outer and inner surface of the zeolite particle [60]. Since the negative charge is partially compensated by the presence of the exchangeable alkali and alkaline earth cations, the results of interrelationship between in-going Cu(II) ions and out-going exchangeable ions (Na, K, Ca, and Mg) from the NZ and FeZ as a function of the initial Cu(II) concentrations are compared in Figure 9.

For both zeolites, an almost complete stoichiometric interrelationship between the amount of sorbed Cu(II) and released exchangeable cations was observed over the entire concentration range. This implies that ion exchange is the dominant mechanism of Cu(II) sorption on NZ and FeZ, with calcium being the main exchangeable cation for NZ while sodium for FeZ.

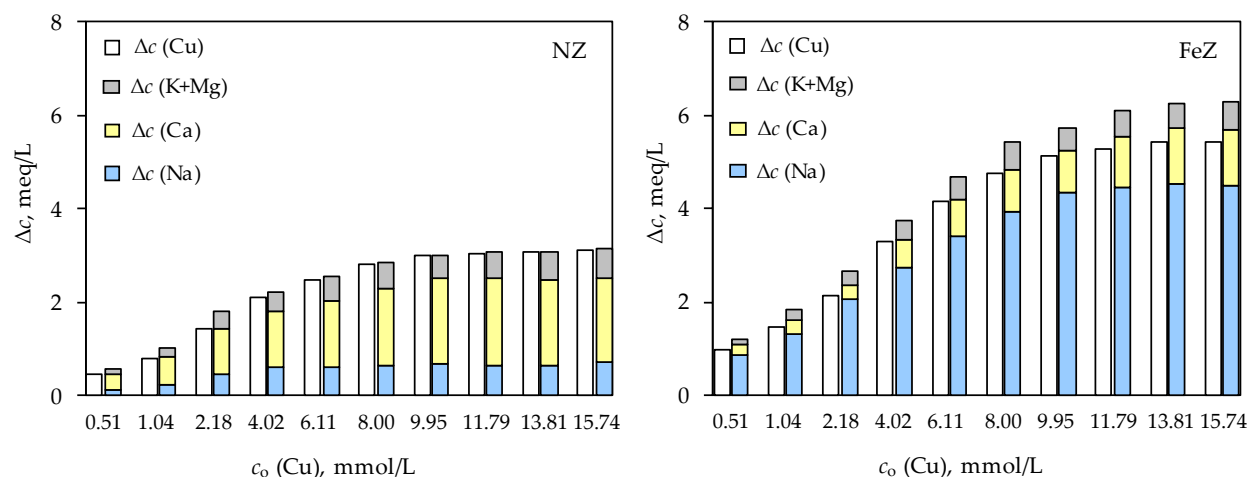


Figure 9. Interrelationship between in-going Cu(II) ions and out-going exchangeable cations as a function of different initial Cu(II) concentration for NZ (**left**) and FeZ (**right**).

It was found that optimal pH is $3 \leq \text{pH}_0 \leq 5$ for NZ, and for FeZ $\text{pH}_0 = 3$. Since the Cu(II) sorption experiment at different c_0 was performed at the optimal pH, which was $\text{pH}_0 = 4.83$ for NZ, and $\text{pH}_0 = 2.98$ for FeZ, the competition effect between H^+ and Cu^{2+} was not observed for NZ and FeZ. Thus, although the initial conditions in terms of pH_0 are different, the quantity of Cu(II) sorbed is higher on FeZ making it a more effective sorbent for Cu(II) ions. According to the above, the main mechanism of Cu(II) sorption on NZ and FeZ is ion exchange. As already mentioned, since both zeolites possess a negative charge in the range $\text{pH}_0 = 2\text{--}12$, the electrostatic attraction between the negatively charged surface and the dominantly present copper in the form of Cu^{2+} at $\text{pH}_0 < 5$ initiates the sorption of Cu(II). However, the ion exchange mechanism dominates as confirmed by the results shown in Figure 9. For the intention to understand the nature (physical or chemical) of Cu(II) sorption on both zeolites, the equilibrium data shown in Figure 8a were fitted in accordance with the Temkin and Dubinin–Radushkevich isotherm models and are explained in detail in the supplementary file (Table S1). These two isotherms clarified that the sorption is of a physical nature on both zeolites.

In order to fully understand the mechanism of Cu(II) sorption on zeolites, based on their chemical composition shown in Table 1, the amount of elements for the starting and copper-saturated zeolites was calculated and is shown in Table 4.

Table 4. Element quantity of starting and copper-saturated zeolites.

Sample	Element Quantity, mmol/g									
	Na	K	Mg	Ca	Si	Al	O	Fe	Ti	Cu
NZ	0.484	0.234	0.211	0.635	10.888	2.746	27.590	0.271	0.040	-
NZCu	0.352	0.236	0.091	0.505	10.981	2.870	27.610	0.273	0.021	0.097
FeZ	1.187	0.200	0.198	0.522	10.452	2.726	27.060	0.403	0.021	-
FeZCu	0.594	0.206	0.171	0.685	10.746	2.556	27.130	0.336	0.020	0.238

The results indicate that the modification caused an increase in iron content and that the dominant exchangeable cation is sodium for FeZ, and calcium for NZ. The amount of calcium decreased slightly for FeZ compared to NZ. This is a consequence of the second phase of modification in an alkaline medium, during which sodium is exchanged with calcium and its precipitation on the surface of the FeZ particle occurs [60]. This is supported by the results of almost unchanged calcium amounts in copper-saturated FeZ, since sodium is the main exchangeable cation. The decrease in the amount of sodium for FeZCu and

calcium for NZCu is a consequence of ion exchange, and this is in accordance with the results shown in Figure 9. The amount of copper is 2.5 times higher for FeZCu compared to NZCu, which is in agreement with the twice higher sorption capacity of FeZ compared to NZ (Figure 8a). This suggests that Cu(II) is sorbed on active sites located on both the outer and inner surface of the zeolite particle.

In order to gain insight into the distribution of elements on the surface of copper-saturated NZ and FeZ, EDS was performed on four marked surfaces on both zeolites at a magnification of 35 $\times$ as shown in Figure 10. The results of the elemental composition on the four marked surfaces on NZCu and FeZCu given in wt % are listed in Tables 5 and 6.

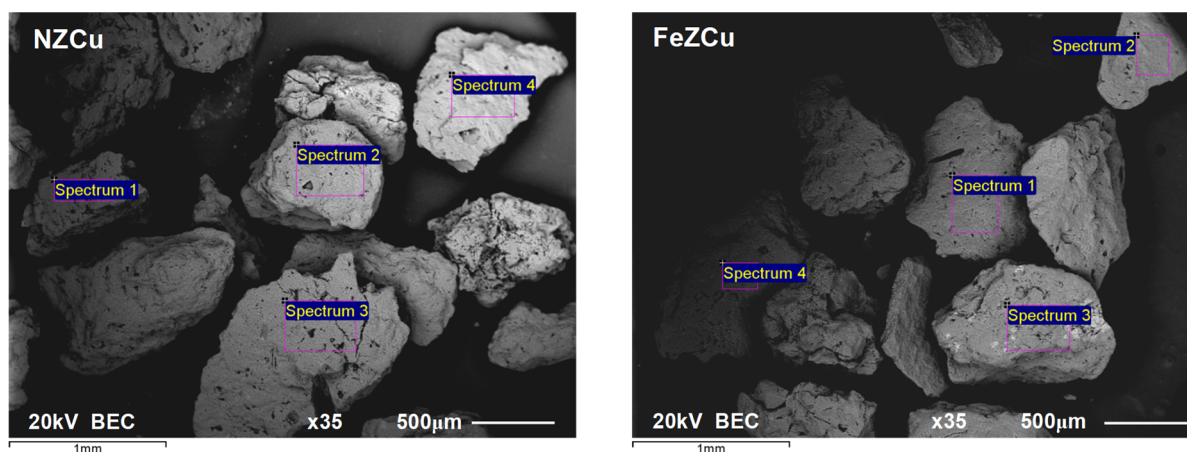


Figure 10. Backscattered electrons mode image (BSE) with four marked surfaces (Spectra, Sp) on NZCu (left) and FeZCu (right) for EDS.

Table 5. Semi-quantitative chemical composition (given in wt. %) of the four analyzed surfaces on the NZCu sample shown in Figure 10 (Spectra, Sp; analyzed with EDS).

Element	Na	K	Mg	Ca	Si	Al	O	Fe	Cu
Sp 1	-	0.76	0.58	1.97	30.12	6.01	58.89	0.71	0.96
Sp 2	0.60	0.94	0.55	2.01	32.03	6.00	55.55	1.28	1.04
Sp 3	-	0.96	0.57	2.07	31.64	5.81	57.02	1.00	0.93
Sp 4	0.53	1.01	0.59	2.26	32.89	6.21	54.80	0.44	1.27
Mean	0.28	0.92	0.57	2.08	31.67	6.01	56.57	0.86	1.05

Table 6. Semi-quantitative chemical composition (given in wt. %) of the four analyzed surfaces on the FeZCu sample shown in Figure 10 (Spectra, Sp; analyzed with EDS).

Element	Na	K	Mg	Ca	Si	Al	O	Fe	Cu
Sp 1	0.65	0.92	0.45	1.16	28.97	5.96	56.47	2.66	2.76
Sp 2	0.78	0.92	0.59	1.17	30.28	7.07	53.05	2.91	3.23
Sp 3	0.89	0.55	0.41	1.07	30.11	5.51	53.78	3.71	3.97
Sp 4	0.96	0.62	0.68	1.20	29.46	6.78	54.92	2.49	2.89
Mean	0.82	0.75	0.53	1.15	29.71	6.33	54.56	2.94	3.21

The results indicate an almost uniform distribution of the analyzed elements on the four marked surfaces (spectra, Sp) for both samples. This reveals an even distribution of active centers, and thus an even binding of copper on the outer surface of both zeolites. The mean value of the copper mass percentage is three times higher on the outer surface of FeZ than on NZ, which once again confirms the more pronounced sorption ability

of the modified sample. For saturated samples, among exchangeable cations, calcium dominates in both samples, which is in line with the chemical analysis results shown in Table 4. Namely, Ca is the dominant exchangeable cation of NZ, and due to its lower sorption capacity towards Cu(II) compared to FeZ, the amount of Ca decreased slightly on the NZCu surface. In the case of FeZ, Na is the main exchangeable cation. The amount of Na decreased significantly on the FeZCu surface due to the exchange with Cu(II), while the ion exchange of Cu(II) with Ca is significantly lower due to the formed Ca precipitate on the FeZ surface as a result of the modification. In order to confirm the uniform distribution of the detected elements (Tables 5 and 6), additional SEM imaging was performed at a magnification of $1000\times$ with EDS and mapping analysis of the detected elements on the surface of NZCu and FeZCu, as shown in Figures 11 and 12.

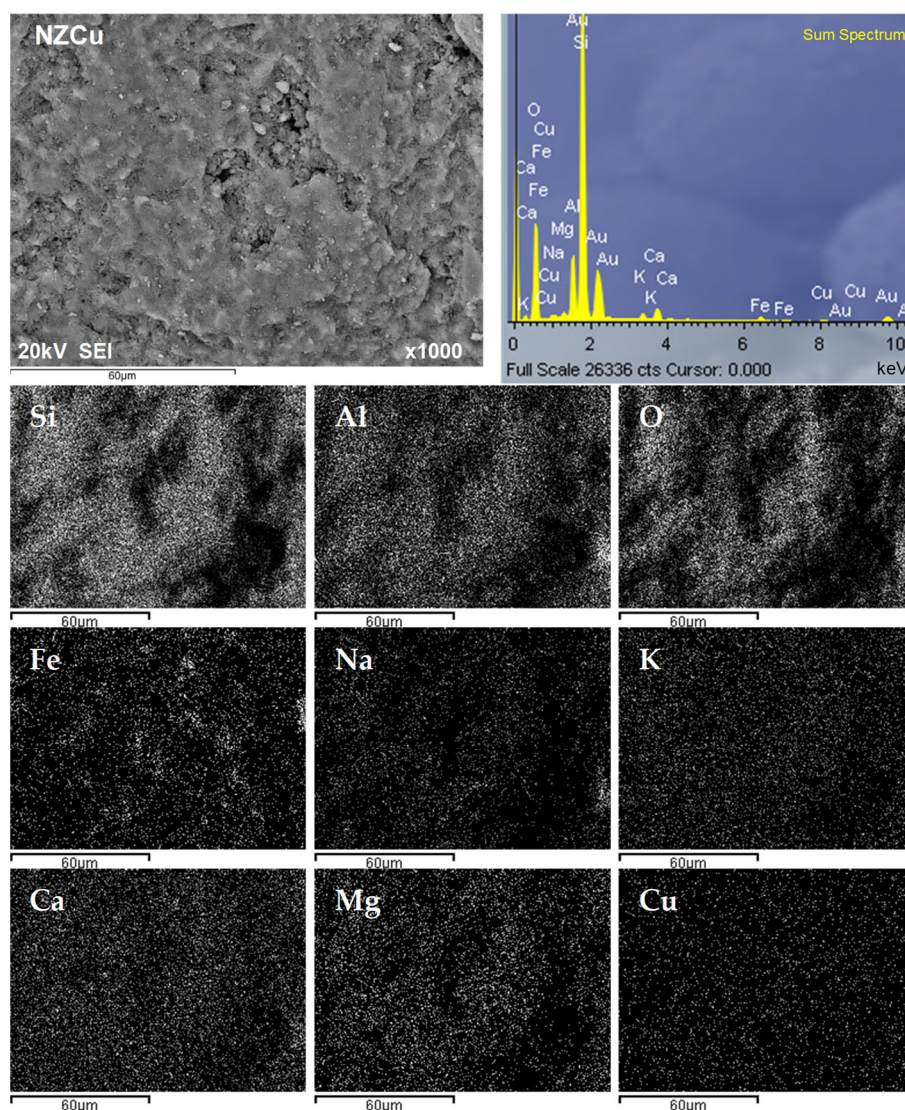


Figure 11. SEM image, EDS of NZCu surface with corresponding mapping analysis.

The results of the mapping analysis confirmed the uniform distribution of the detected elements on the surface of both samples (Figures 11 and 12). This indicates that the exchangeable cations, and thus the active sites, are uniformly distributed on the surface of both samples. In addition, a uniform distribution of copper is observed on both zeolites, with the density of observed dots corresponding to Cu(II) being higher for FeZ compared to NZ. Ultimately, based on the results of monitoring the amount of released exchangeable cations and sorbed Cu^{2+} ions as well as the results of chemical composition and EDS, it

can be concluded that the dominant mechanism is ion exchange initiated by electrostatic attraction between the negatively charged zeolite surface and positive Cu^{2+} ions.

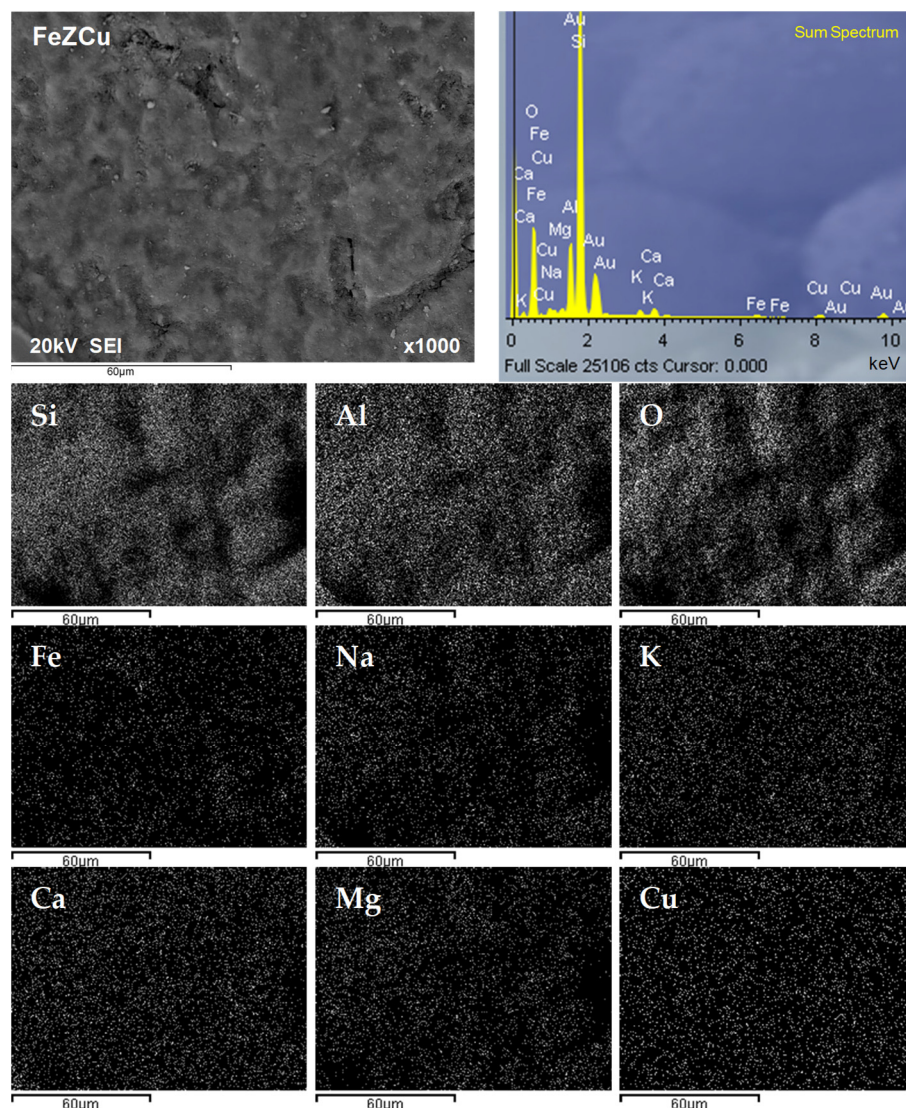
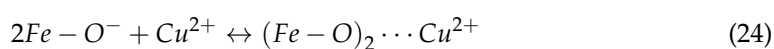
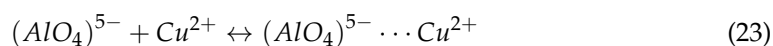
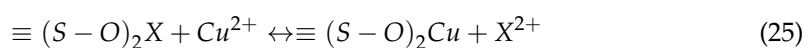


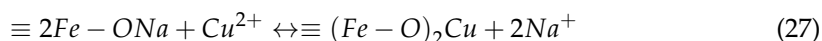
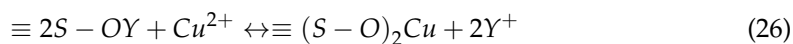
Figure 12. SEM image, EDS of FeZCu surface with corresponding mapping analysis.

Since both zeolites have a negative charge, this indicates a partial compensation of the active sites with alkaline and alkaline earth easily mobile cations and the possession of deprotonated, i.e., negatively charged active sites. As it was previously established that sorption is initiated by electrostatic attraction, an illustration of electrostatic attraction reactions is shown by Equation (23) for NZ and Equations (23) and (24) for FeZ as follows:



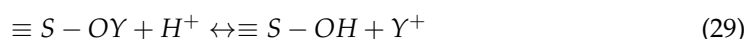
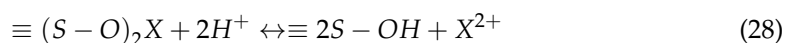
Thus, the enhanced electrostatic attraction in the case of FeZ is due to the possession of $(\text{Fe}-\text{O}^-)$ active sites in addition to those shown by Equation (23) as a result of modification. On the other hand, ion exchange takes place at active sites whose negative charge is compensated by the presence of exchangeable cations. The ion exchange reactions that take place on NZ are illustrated by Equations (25) and (26), and on FeZ by Equations (25)–(27).



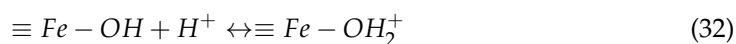
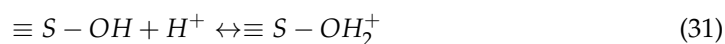


where S denotes a Si or Al atom, X is Ca or Mg, and Y is Na or K.

Furthermore, in acidic media, the competition effect of Cu^{2+} with H^+ ions hinder the sorption efficiency. Competitive reactions that take place on NZ are shown by Equations (28) and (29), and (28)–(30) in the case of FeZ as follows:



The formed hydroxylated neutral active sites shown by reactions (28)–(30) are converted into protonated positive active sites by further protonation reactions in acidic media as follows:



Protonated positively charged active sites affect electrostatic repulsions, which are more pronounced in more acidic media and cause a decrease in the zeolites sorption efficiency. Ultimately, this confirms once again that one of the key sorption parameters is determining the optimal pH.

3.2. Leaching Behavior of Copper-Saturated Zeolites

Leaching properties of copper-saturated zeolites, NZCu and FeZCu were tested according to the standard leaching method DIN 38414 S4 [62] in a wide pH_o range of 2.06–12.09. The results of the percentage of Cu(II) leached from saturated zeolites are shown in Figure 13.

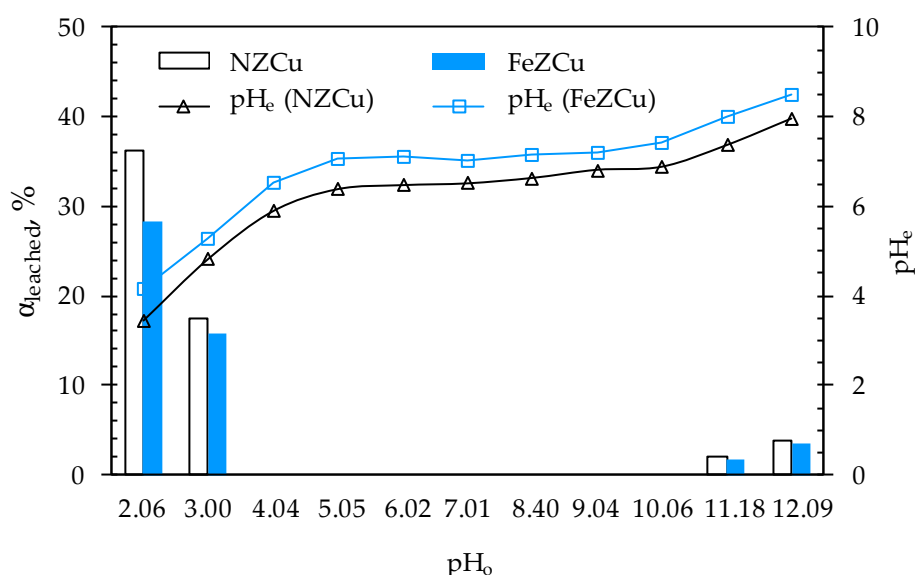


Figure 13. Percentage of leached copper from NZCu and FeZCu, and changes in pH_e as a function of pH_o .

From Figure 13 it is clearly seen that in a wide pH_o range, $4.04 \leq pH_o \leq 10.06$, Cu(II) leaching from both copper-saturated zeolites was not detected. Since in the mentioned pH_o range the pH_e values are around 7, Cu(II) leaching is probably prevented by the formation

of $\text{Cu}(\text{OH})_2$ precipitates on the zeolite surface. This is supported by the fact that $\text{Cu}(\text{II})$ starts to precipitate at $\text{pH}_0 = 6.5$ according to the $\text{Cu}(\text{II})$ speciation diagram depending on pH_0 as shown in Figure 1. In an acidic medium, $\text{pH}_0 \leq 3.00$, $\text{Cu}(\text{II})$ is leached from both zeolites in the amount of 17–36%. Namely, at $\text{pH}_0 < 3.00$, equilibrium pH_e values are below $\text{pH}_e = 6$, which indicates that insoluble $\text{Cu}(\text{OH})_2$ cannot be formed. As it is well known that metal solubility increases in acidic media, the results indicate that the percentage of leached $\text{Cu}(\text{II})$ is higher at lower pH_0 . Moreover, in acidic medium, enhanced protonation of the zeolite structure occurs with the replacement of H^+ ions with sorbed $\text{Cu}(\text{II})$ ions, which is reflected in more pronounced leaching at $\text{pH}_0 = 2.06$. Moreover, in extremely acidic conditions, $\text{pH}_0 = 2.06$, partial dealumination of the zeolite structure cannot be ignored, which additionally contributes to increased leaching. Unlike extremely acidic conditions, in extremely alkaline conditions, $\text{pH}_0 \geq 11.18$, leaching in the range of 1.7–3.8% is observed. Although pH_e values indicate that $\text{Cu}(\text{II})$ leaching should be prevented by the formation of $\text{Cu}(\text{OH})_2$, the highly alkaline conditions caused desilication, i.e., the cracking of Si-O bonds, which resulted in $\text{Cu}(\text{II})$ leaching. Comparing the results of the percentage of $\text{Cu}(\text{II})$ leached from NZCu and FeZCu, a higher percentage of $\text{Cu}(\text{II})$ leached was recorded from NZCu even though twice as much $\text{Cu}(\text{II})$ was sorbed on FeZ. Therefore, in addition to superior sorption efficiency of FeZ, its higher ability to retain $\text{Cu}(\text{II})$ makes it an even more attractive sorbent for $\text{Cu}(\text{II})$ ions. The obtained results imply the possibility of using FeZ for in situ and ex situ remediation of copper-contaminated environments in the pH range $4.04 \leq \text{pH}_0 \leq 10.06$. Moreover, both zeolites show the property of neutralizing the surrounding medium, which is evident from the pH_e range of $\text{pH}_e = 7.5\text{--}8.5$, for all tested pH_0 values.

4. Conclusions

This study provided a comparison of the sorption performance of $\text{Cu}(\text{II})$ on natural and $\text{Fe}(\text{III})$ -modified natural zeolite with optimization of sorption parameters to maximize zeolite utilization while achieving high $\text{Cu}(\text{II})$ removal efficiency. The removal of copper from suspension on both zeolites, especially FeZ, is most influenced by pH, followed by the S/L ratio. Optimization of sorption parameters demonstrated an optimal pH_0 range of 3–5 for NZ, while $\text{pH}_0 = 3$ for FeZ. For both zeolites, the optimal S/L was 10 g/L, the contact time was 600 min, and the concentration range in which $\text{Cu}(\text{II})$ removal was effective was up to 10 mmol/L for NZ and 12 mmol/L for FeZ. The kinetics of $\text{Cu}(\text{II})$ sorption on both zeolites involves a complex two-step mechanism, where intraparticle diffusion dominates as the rate-controlling sorption step with an almost negligible contribution of film diffusion in the initial sorption phase. Almost twice the sorption capacity of FeZ compared to NZ towards $\text{Cu}(\text{II})$ (0.271 mmol/g vs. 0.156 mmol/g) was confirmed experimentally and supported by determining the elemental composition, SEM/EDS and mapping analysis of saturated samples. Under optimal conditions, sorption was found to be driven by the electrostatic attraction of positive Cu^{2+} ions and the negatively charged zeolite structure, while the ion exchange mechanism was dominant. The results of the stoichiometric ratio of sorbed $\text{Cu}(\text{II})$ and released exchangeable cations under optimal sorption conditions confirmed ion exchange as the primary mechanism of $\text{Cu}(\text{II})$ sorption on NZ and FeZ. This was additionally supported by fitting the equilibrium data according to Temkin's and Dubinin–Radushkevich isotherm, which confirmed the physical process of $\text{Cu}(\text{II})$ sorption on both zeolites. Finally, the leaching behavior of saturated NZCu and FeZCu highlight the ability to completely retain $\text{Cu}(\text{II})$ in the structure of both zeolites in a wide pH_0 range, $4.04 \leq \text{pH}_0 \leq 10.06$. Ultimately, both zeolites contributed to $\text{Cu}(\text{II})$ removal, with FeZ standing out as highly promising sorbent for both in situ and ex situ remediation of copper-contaminated environments.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/pr13092672/s1>: Figure S1: XRD spectra of NZ and FeZ; Figure S2: FTIR spectra of NZ and FeZ; Table S1: Isotherm models constants and error analysis for Cu(II) sorption onto NZ and FeZ [72,73].

Author Contributions: Conceptualization, investigation, methodology, formal analysis, writing—original draft preparation M.U.; experimental analysis, formal analysis J.M.; writing—review and editing, M.U., I.N., and J.M. All authors have read and agreed to the published version of the manuscript.

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