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Influence of Ammonium on the Adsorption and Desorption of Heavy Metals in Natural Zeolites

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Abstract

Natural zeolites have gained attention as low-cost adsorbents for the removal of heavy metals (HMs) from wastewater. However, their performance can be compromised by the presence of competing cations such as ammonium (NH_4^+). This study investigated the competitive adsorption and desorption dynamics of NH_4^+ and six HMs (Cd, Cr, Cu, Ni, Pb, and Zn) on two natural zeolites. Batch and column experiments using synthetic wastewater were conducted to evaluate the effects of different NH_4^+ concentrations, pH, and particle size on HM removal efficiency and desorption effects. Results showed that increasing NH_4^+ concentrations significantly reduce HM adsorption, with total capacity decreasing by ~45% at 100 mg/L NH_4-N in kinetic tests. Adsorption isotherms of the HM mixture for both zeolite types followed a clear sigmoidal trend, which was captured well by the Hill model (R^2 = 0.99), with loading rates up to 56.14 mg/g. Pb consistently exhibited the highest affinity for zeolites, while Cd, Cr, Ni, and Zn were most affected by NH_4^+ competition in the column tests. Desorption tests confirmed that NH_4^+ rapidly re-mobilises adsorbed metals, in particular Cd, Cu, and Zn. Slightly acidic to neutral pH conditions were optimal for minimising HM remobilisation. These findings underscore the need to consider competitive interactions and operational conditions when applying natural zeolites for HM removal, especially in ammonium-rich environments such constructed wetlands, soil filters, or other decentralised applications.

Keywords: competitive adsorption; ammonium; desorption; heavy metals; natural zeolite

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1. Introduction

Heavy metal (HM) contamination affects approximately 40% of the world's rivers and lakes [1]. Although certain HMs are essential to living organisms in trace amounts, their persistence, bioaccumulative nature, and non-biodegradability pose significant risks to both human health and the environment [2]. Particularly concerning are arsenic (As), cadmium (Cd), chromium (Cr), mercury (Hg), nickel (Ni), and lead (Pb), which are recognised as priority pollutants due to their prevalence in drinking water sources and their toxicological impact on the human body [3]. Additionally, metals such as copper (Cu), iron (Fe), manganese (Mn), and zinc (Zn), though essential, can also exert harmful effects when present in elevated concentrations.

Some of these HMs play key roles in various industries. Cd is used in rechargeable batteries and pigments, while Cr is essential for stainless steel production. Cu is widely employed in electrical wiring, electronics, and alloys due to its excellent conductivity and corrosion resistance. Fe is primarily used in steel production, and Mn improves steel

strength and is also used in batteries. Ni is crucial for stainless steel and battery production, while Zn is mainly used for galvanising steel to prevent rust. Pb has historically been used in lead–acid batteries and as a radiation shield [4].

Various methods are used to decrease the levels of HMs in wastewater, such as chemical precipitation, electrochemical techniques, and membrane filtration. However, these methods are often complex to operate, expensive, and consume significant amounts of energy [5]. Zeolites have been extensively studied as an effective, low-cost ion exchange adsorbent, particularly in constructed wetlands (CWs) for the removal of HMs from all water sources [6–9]. Due to their chemical nature, the dominant mechanism for natural zeolites is ion exchange by exchanging alkali and alkaline earth ions [10]. Further reported removal mechanisms comprise electrostatic attraction, intrapore adsorption, surface complexation, and surface precipitation [11]. Depending on the (waste-)water composition, other cationic pollutants can compete for the binding sites on the zeolites. Ammonium (NH_4^+), which originates from the biological degradation of nitrogenous matter, is a common contaminant, especially in wastewater, which also showed high affinity to zeolites in prior studies [12,13]. Due to its cationic nature, the NH_4^+ competes for binding sites with HMs. It is also able to displace already adsorbed HMs, leading to a rerelease. This can result in high effluent concentrations, which can significantly exceed influent concentrations. A study of Zhan et al. [14] investigated the competitive adsorption of NH_4^+ and Zn^{2+} on activated carbon and zeolite and found that zeolite demonstrated effective removal of both contaminants through ion exchange, while preferring NH_4^+ over Zn^{2+} (surface occupation of 87.3% and 12.7%, respectively). Activated carbon selectively removed Zn^{2+} via surface complexation. As the concentration of Zn^{2+} increased, competitive adsorption processes emerged, significantly affecting the breakthrough behaviour of both cations. In another study, the rerelease of Cr, Cu, Pb, and Zn from a CW was investigated, highlighting a strong correlation with their bioavailability and leachability [15]. Zn, in particular, demonstrated high mobility due to its tendency to persist in an exchangeable form. Consequently, significant Zn loss occurred as a result of leaching by low-concentration rainfall runoff. In comparison, smaller amounts of Cu, Cr, and Pb were also mobilised and released from the system. However, limited data is available on the competitive interactions, particularly regarding the displacement of already adsorbed HMs by NH_4^+ ions.

Therefore, this study investigates the competitive interactions between NH_4^+ and six different HMs and their impact on the adsorption and desorption processes on natural zeolites (clinoptilolite). Batch and column tests were conducted using synthetic wastewater. This study also examines how varying pH values and particle sizes influence these interactions. pH plays a crucial role in HM speciation, affecting their adsorption capacity, mobility, and toxicity. Therefore, this study explores the effects of different pH levels on desorption. Kinetic studies were also performed to gain a better understanding of how NH_4^+ mitigates the adsorption of HMs over time. To the best of our knowledge, this is the first paper to address the adsorption and desorption dynamics of ammonium and a mixture of HMs on natural zeolites in the current context.

2. Materials and Methods

2.1. Natural Zeolite Properties

The elemental composition of the prepared samples was determined by X-ray fluorescence (XRF) analysis (Epsilon 4, Malvern Panalytical, Malvern, UK). The XRF system was calibrated against certified reference materials (CRMs) of similar matrix composition to ensure accuracy and reproducibility. Each sample was measured in triplicate to ensure consistency of data and results were averaged. Concentrations were expressed in weight percent (wt%), as this helps to estimate the cation exchange potential and thermal stability

of the selected natural zeolites. BET analysis was also conducted to determine the specific surface area (NovaWin, Quantachrome Instruments Inc., Boynton Beach, FL, USA) (Table 1).

Table 1. Properties of the used natural zeolites for batch and column tests.

Supplier	Zeolite	BET (m^2/g)	SiO_3 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	K_2O (%)
Zeobon GmbH, Dattenberg, Germany	Zeogran K 80	27.41	65.47	11.63	1.43	2.91	3.81
Zeocem Inc., Bystré, Slovakia	ZeoAqua	33.03	66.99	11.81	1.51	2.80	3.81

2.2. Pre-Processing of Adsorbents

In order to obtain the desired fractions of 125–250 µm and 250–500 µm, the natural zeolites were crushed using a swing mill (Emax, Retsch GmbH, Haan, Germany). The particle size was chosen to obtain adequate bed volumes without clogging the columns and to compare the influence of particle size on the remobilisation effects. The crushed material was then sieved using a sieve inset with the required mesh sizes. The smallest fractions < 45 µm were retained for the batch tests and the determination of the zeolite properties. The fractions of 125–250 µm and 250–500 µm were washed until the effluent was clear to remove adherent fine dust. The sieved materials were then dried at 100 ± 2 °C for 24 h to achieve a constant weight and finally stored in Schott bottles without further treatment until use (oven: UE 500, Memmert GmbH, Schwabach, Germany). Particle size was determined using a microscope (VHX 2000, Keyence, Osaka, Japan). The size distribution is given in Figure 1.

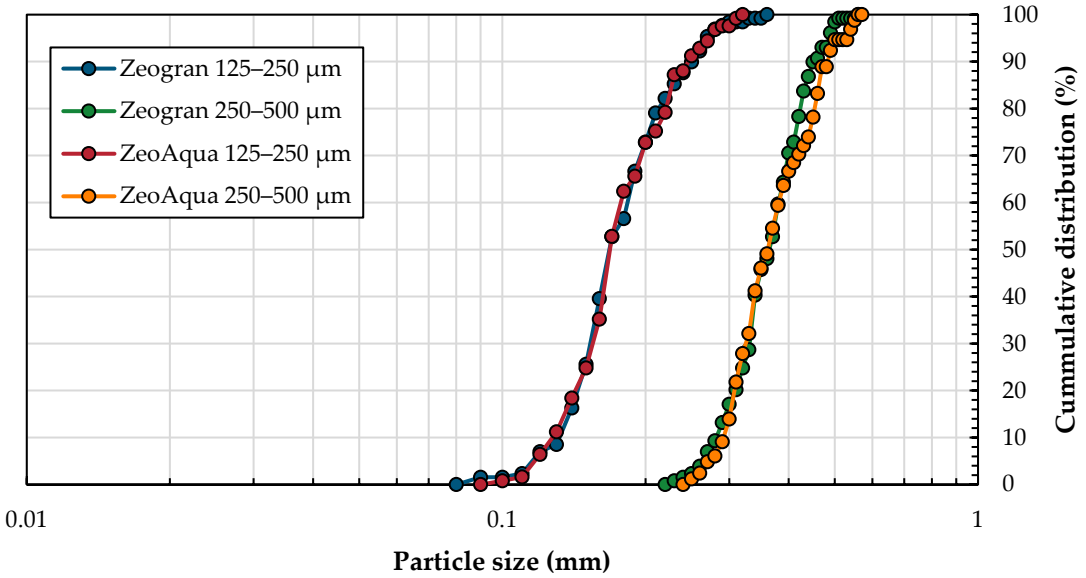


Figure 1. Particle size distribution of the two tested natural zeolites.

2.3. Analytical Devices and Chemicals

The HM stock solutions were prepared using cadmium nitrate tetrahydrate, 98.5% min (Thermo Fisher Scientific Inc., Waltham, MA, USA), copper(II) nitrate trihydrate GPR RECTAPUR (VWR International, Radnor, PA, USA), chromium(III) nitrate nonahydrate, 99% (Acros Organics BV, Geel, Belgium), nickel(II) nitrate hexahydrate, 98% (Alfa Aesar, Haverhill, MA, USA), lead(II) nitrate AnalaR Normapur (VWR International, Radnor, PA, USA), and zinc hexahydrate, 98%, extra pure (Acros Organics BV, Geel, Belgium). For the NH_4^+ stock solutions, ammonium chloride (NH_4Cl) (EMSURE ACS, Reag. Ph. Eur.,

Supelco, Merck GmbH, Darmstadt, Germany) was used. Ammoniacal nitrogen (NH_4-N) was analysed via photometry (WTW photoLab S12, Xylem Inc., Washington, DC, USA) using cell tests (Test kits, ammonium, Spectroquant, Supelco, Merck GmbH, Darmstadt, Germany). Adjustments of the pH were conducted with 1 M sodium hydroxide (NaOH) (VWR International, Radnor, PA, USA) and 1 M nitric acid (HNO_3) (VWR International, Radnor, PA, USA). The pH was measured by a Portavo 907 multimeter using an SE101-MS pH probe (Knick, Elektronische Messgeräte GmbH & Co. KG, Berlin, Germany).

For the heavy metal analysis, the samples were directly acidified to a pH < 2 with HNO_3 and stored at 4 °C until analysis using inductively coupled plasma–optical emission spectrometry (ICP-OES) (Optima 8300, PerkinElmer Inc., Waltham, MA, USA, for desorption tests; Spectrogreen, Spectro Analytical Instruments GmbH, Kleve, Germany, for adsorption tests) according to DIN EN ISO 11885:2009-09 [16]. All batch test samples were separated from the adsorbents using 0.45 µm syringe cellulose membrane filters (VWR International, Radnor, PA, USA).

2.4. Competitive Adsorption Batch Tests

To evaluate competition for bindings sites between the HMs and NH_4^+ on the natural zeolites, batch tests were conducted. The HM concentrations of the six selected HMs were set to 10 mg/L each. Three test runs were carried out with NH_4-N concentrations of 0 mg/L, 10 mg/L, and 100 mg/L. The adsorbent dose was set to 10, 25, 50, 125, 250, 500, 1000, 2500, and 5000 mg/L, with a particle diameter of < 45 µm. The pH in each sample was adjusted to ≤ 4 using HNO_3 to maintain the HMs in a dissolved state. Samples were shaken for 24 h on a lab shaker (Universal Shaker SM 30, Edmund Bühler, Bodelshausen, Germany) with 180 rounds per minute (RPM) and subsequently separated by filtration with 0.45 µm syringe cellulose membrane filters (VWR International, Radnor, PA, USA).

Adsorption Kinetics

Three test runs were carried out similarly to the competitive adsorption batch tests, with a concentration of 10 mg/L of each heavy metal and NH_4-N concentrations of 0 mg/L, 10 mg/L, and 100 mg/L. An amount of 1000 mg/L of natural zeolite with a particle diameter of < 45 µm was added to the sampling bottles and the pH was set to ≤ 4 using HNO_3. Samples were taken after 1, 5, 10, 20, 30, 60, 120, and 180 min. The procedure for shaking and filtration of the samples was identical to that employed in the adsorption batch tests. Subsequently, the adsorption kinetics data were analysed using the pseudo-second-order model (PSO) to determine the rate constants and equilibrium adsorption capacity according to Equation (1) [17].

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (1)$$

The amount of adsorbate adsorbed at a given time is denoted by q_t (mg/g), while q_e (mg/g) represents the amount adsorbed at equilibrium. The rate constant for pseudo-second-order adsorption is denoted as k_2 (g/mg × min).

2.5. Rapid Small-Scale Column Adsorption and Desorption Tests

Custom-made glass columns with an inner diameter of 10 mm (Goetec-Labortechnik GmbH, Bickenbach, Germany) were filled with the preloaded zeolites and backing support layers, consisting of two filter plates (100 µm), glass wool, and glass beads to create a proper flow regime and prevent an outwash of the adsorbents. The columns were calculated according to the constant diffusivity model with Equation (2) [18]. Synthetic wastewater

was fed continuously in down-flow mode using a peristaltic pump (Masterflex L/S, Cole-Parmer, Vernon Hills, IL, USA). The experimental setup was derived from Ofiera et al. [19].

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \left[\frac{R_{SC}}{R_{LC}}\right]^2 = \frac{t_{SC}}{t_{LC}} \quad (2)$$

$EBCT_{SC}$ is the empty bed contact time in the small-scale system (min), $EBCT_{LC}$ is the empty bed contact time in the large-scale system (min), R_{SC} is the adsorbent particle size for the small-scale system, R_{LC} is the adsorbent particle size for the large-scale system, t_{SC} the running time for the small-scale system, and t_{LC} is the running time for the large-scale system.

Prior to the desorption test, the natural zeolites were loaded with a pH-adjusted (≤ 4) stock solution containing 100 mg/L of each HM and shaken for 24 h to ensure sufficient capacity utilisation. The loaded natural zeolites where then rinsed three times with distilled water and methanol to remove non-adsorbed HMs. The EBCT in adsorption tests was set to 30 min and to 45 min in desorption tests to prevent clogging of the columns.

2.6. Data Evaluation

The HM capacities were calculated for each sorbent in the batch experiments by analysing HM concentrations using the following Equation (3). Removal rates were calculated according to the following Equation (4):

$$q_e = \frac{(C_i - C_e) \times V_L}{m_a} \quad (3)$$

$$\text{Removal}(\%) = \frac{C_i - C_e}{C_i} \times 100 \quad (4)$$

where q_e (mg/g) is the adsorbed amount of HM on the respective sorbent, C_i (mg/L) is the initial HM concentration in the solution, C_e (mg/L) is the HM equilibrium concentration in the solution after shaking or at the respective time in the kinetic experiments, V_L is the solution volume, and m_a (g) is the adsorbent dosage.

Hill Adsorption Isotherms

The Hill model provides a compact, phenomenological description of sorption to binding sites that exhibit cooperative behaviour [20,21]. Originally developed for biochemical ligand binding, it is widely used to capture sigmoidal uptake profiles in diverse systems (Equation (5)).

$$q_e = \frac{q_{max} \times C_e^{n_H}}{K_D^{n_H} + C_e^{n_H}} \quad (5)$$

where K_D represents the Hill constant in mg/L and n_H the Hill cooperativity coefficient. Negative cooperativity is represented when $n_H < 1$, whereas $n > 1$ represents positive cooperativity [22].

3. Results and Discussion

3.1. Competitive Adsorption of Ammonium and Heavy Metals

3.1.1. Pseudo-Second-Order Adsorption Kinetics

The competition for binding sites between NH_4^+ and HMs is caused by their cationic nature. The sorption kinetics of the vast majority of HMs on zeolites in multicomponent solutions can be described by the PSO model [23]. Other important factors are the ion size, the hydration enthalpy, the polarizability the prevailing pH conditions, other ions present in the solution, and the temperature (Table 2) [19].

Table 2. Properties of the investigated heavy metals and ammonium [24,25].

Ion	Charge	Hydrated Radius (nm)	Ionic Radius (nm)	Polarizability	Hydration Enthalpy (kJ/mol)
Cd	+2	0.426	0.097	Moderate	−1800
Cr	+3	0.401	0.062	High	−4600
Cu	+2	0.419	0.073	High	−2100
Ni	+2	0.404	0.069	Low	−2105
Pb	+2	0.401	0.119	Very high	−1480
Zn	+2	0.430	0.074	Moderate	−2045
NH_4	+1	0.331	0.148	Low	−300

At 0 mg/L of NH_4-N, both zeolites exhibited the highest adsorption capacities for Pb (5.84 mg/g for Zeogran and 5.86 mg/g for ZeoAqua), followed by Cr and Zn (Figure S1 and Table 3). ZeoAqua demonstrated superior overall performance, with higher q_e and k_2 values for most metals. Adsorption followed pseudo-second-order kinetics, with good model fits ($R^2 > 0.86$ for most metals) and particularly good fits for Pb ($R^2 = 1.00$).

Table 3. Adsorption kinetic parameters according to the PSO model.

Zeolite	Parameters	Cd	Cr	Cu	Ni	Pb	Zn	All HMs
Zeogran (0 mg/L NH_4-N)	qe (mg/g)	0.41	1.33	0.79	0.27	5.84	1.21	9.36
	k_2 (g/mg × min)	0.714	2.573	0.124	0.012	2.162	0.628	0.315
	R^2	0.82	0.90	0.93	0.59	1.00	0.86	0.94
ZeoAqua (0 mg/L NH_4-N)	qe (mg/g)	0.53	0.97	1.20	0.70	5.86	1.49	9.74
	k_2 (g/mg × min)	3.252	7.214	0.107	0.001	12.407	1.199	0.608
	R^2	0.50	0.67	0.90	0.86	1.00	0.78	0.86
Zeogran (10 mg/L NH_4-N)	qe (mg/g)	0.44	0.84	0.75	0.35	3.97	0.25	5.82
	k_2 (g/mg × min)	0.029	1.679	0.022	0.048	0.271	0.058	0.084
	R^2	0.59	0.44	0.89	0.59	0.98	0.52	0.78
ZeoAqua (10 mg/L NH_4-N)	qe (mg/g)	0.42	0.89	0.58	0.28	4.18	0.46	6.34
	k_2 (g/mg × min)	0.084	1.256	0.160	0.162	0.485	0.058	0.127
	R^2	0.69	0.70	0.94	0.57	1.00	0.72	0.86
Zeogran (100 mg/L NH_4-N)	qe (mg/g)	0.37	0.45	0.45	0.37	3.25	0.32	5.11
	k_2 (g/mg × min)	0.055	0.107	0.107	0.060	0.227	0.045	0.102
	R^2	0.69	0.74	0.74	0.82	0.94	0.72	0.77
ZeoAqua (100 mg/L NH_4-N)	qe (mg/g)	0.25	0.84	0.44	0.27	3.61	0.26	5.43
	k_2 (g/mg × min)	0.221	2.721	0.129	0.272	0.327	0.188	0.132
	R^2	0.41	0.56	0.71	0.49	0.99	0.49	0.85

As NH_4^+ concentrations increased, a clear inhibitory effect on heavy metal adsorption was observed. At 100 mg/L NH_4-N, the total adsorption capacity decreased by around 45% for Zeogran and 44% for ZeoAqua, highlighting the competition between NH_4^+ and active sites. Pb adsorption, although reduced, remained dominant. In contrast, metals with higher hydration energies, such as Ni and Cu, exhibited lower adsorption capacities and were more impacted by the presence of ammonium. This trend can be partially explained by the hydration energy of the competing ions. NH_4^+, with its relatively low hydration energy, competes effectively with weakly hydrated HMs, which shed their hydration shells more readily and bind strongly to zeolite surfaces. As NH_4^+ concentrations increase, this competition intensifies, leading to a decline in metal adsorption, particularly for ions with similar ionic radii or hydration characteristics.

In conclusion, ZeoAqua outperformed Zeogran, offering higher capacities and faster kinetics. However, both materials exhibit diminished performance at elevated NH_4^+ levels due to competitive adsorption.

3.1.2. Competitive Heavy Metal Removal in Batch Tests

The adsorption behaviour of Cd, Cr, Cu, Ni, Pb, and Zn as a function of the adsorbent dose is illustrated in Figure 2. The results reveal distinct differences in removal efficiency, which reflect the varying affinities of the tested natural zeolites for each HM. For Cd, removal remained relatively low across the entire adsorbent dose range (10–5000 mg/L). A gradual increase in efficiency was observed at higher doses, with maximum removal values approaching at 5000 mg/L for Zeogran = 24.8% and ZeoAqua = 38.4%. The mitigating effect of NH_4-N led to a removal decrease for Zeogran to 22.8% and 10.1% and for ZeoAqua to 32.4% and 12.3% at 10 mg/L and 100 mg/L NH_4-N, respectively. Zn followed a similar pattern as Cd, but no effect of 10 mg/L NH_4-N compared to the HM-only solution was observed.

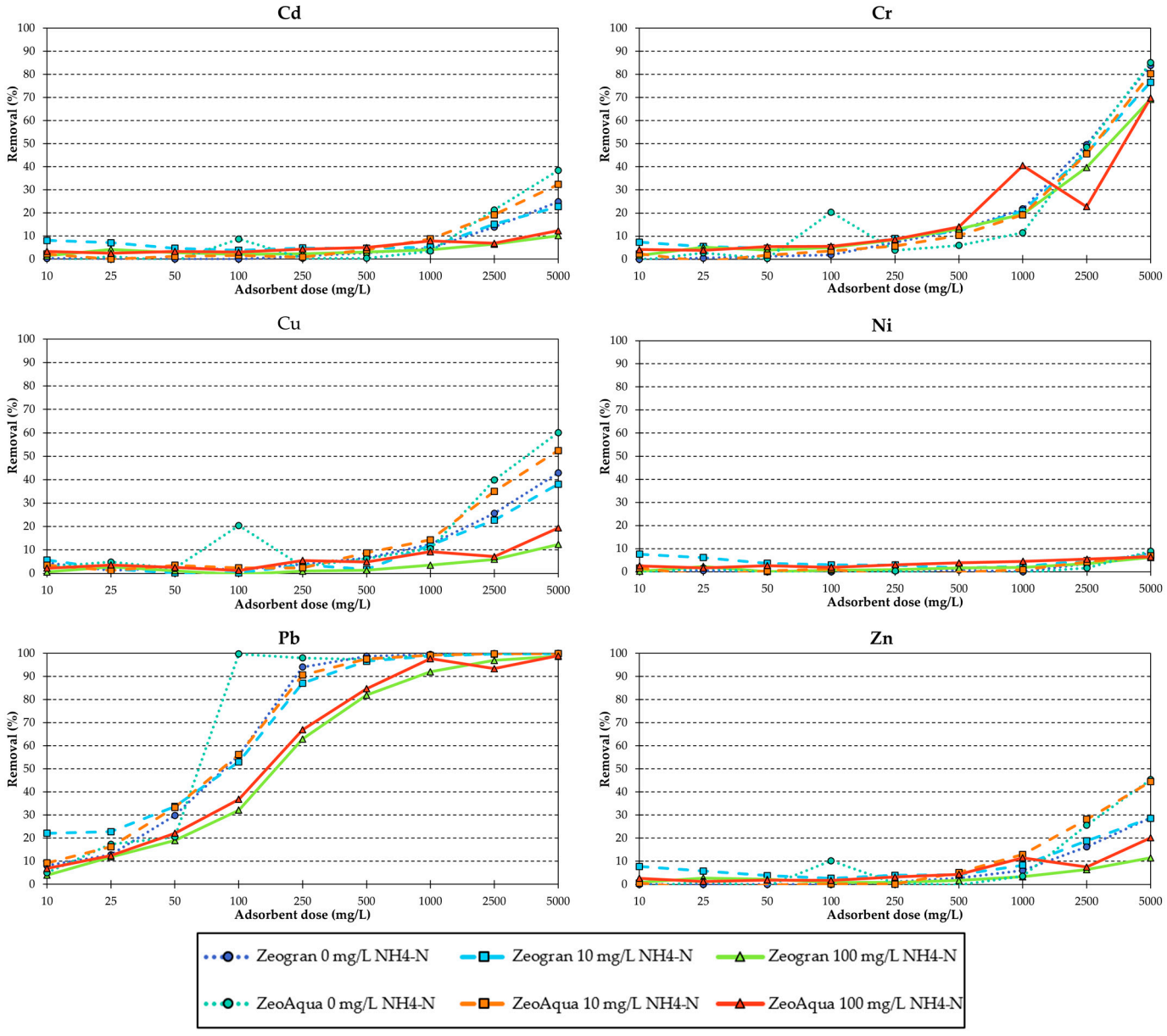


Figure 2. Heavy metal removal in dependence of the adsorbent dose (C_0 = 10 mg/L per HM, particle size = 125–250 µm, contact time = 24 h).

In contrast, Cr exhibited substantially higher removal efficiencies mainly due to its trivalence. While performance was still limited at low doses, a steep increase occurred beyond 500 mg/L, with removal efficiencies above 80% at the highest dose. Cu showed intermediate adsorption behaviour. The removal efficiency was low at doses below 1000 mg/L but increased steadily thereafter, reaching up to ~50% at 5000 mg/L depending on the adsorbent. The influence of NH_4-N concentration was significant at 100 mg/L, reducing the removal from 43.3% to 12.3% for Zeogran and from 60.1% to 19.4% for ZeoAqua. Removal rates for Ni did not exceed ~8% for both zeolites, even under the absence of ammonium. Low Ni removal by natural zeolite is in line with previous studies [26,27]. The low polarizability of Ni^{2+} leads to weak interactions with zeolite. Combined with the relatively high hydration enthalpy of −2105 kJ/mol, Ni is poorly removed.

The opposite was observed for Pb removal, which started at the lowest adsorbent dose of 10 mg/L and was fully completed at 100 mg/L for ZeoAqua. A dose of 10 mg/L NH_4-N showed no significant effect on the removal whereas 100 mg/L NH_4-N postponed the complete removal to 5000 mg/L. Due to its low hydration enthalpy and high polarizability, Pb^{2+} is generally best suited for ion exchange. The adsorption performance of the tested materials followed the order of Pb > Cr > Cu > Zn > Cd > Ni. The observed dose-dependent trends for all HMs highlight the importance of sufficient adsorbent availability to enhance removal, particularly in systems where adsorption sites are limited. This selectivity trend is in accordance with other literature investigating multicomponent HM solution removal. A study by Inglezakis et al. found the selectivity line using clinoptilolite of Pb > Cr > Fe > Cu [28]. Similar results were observed using 4 A zeolite to treat the same HM mix as in this study. After the first treatment cycle the selectivity was Pb > Cu > Cr > Cd > Zn > Ni, changing to Pb > Cr > Cu > Ni ≥ Cd ≥ Zn [2]. Pb removal is generally the highest, whereas Ni retention is difficult. Cd, Cr, Cu, and Zn selectivity differs slightly in prior studies [29,30].

3.1.3. Adsorption Isotherms

The adsorption isotherms of the HM mixture for both zeolite types followed a clear sigmoidal trend, which was captured well by the Hill model (R^2 = 0.9997–0.9999), consistent with a narrow concentration window where uptake increases very rapidly (Figure 3) [21,22]. For Zeogran, the fitted capacities were 56.14 mg/g at 10 mg/L NH_4–N and 31.93 mg/g at 100 mg/L. For ZeoAqua, capacities were 52.85 mg/g at 10 mg/L and 49.03 mg/g at 100 mg/L. Thus, Zeogran outperforms at low background, whereas ZeoAqua performs better at high background.

The Hill slopes were high across all datasets (n_H = 13.87, 9.81, 10.92, 12.38), indicating a sensitive rise in loading rather than the gradual rise expected for a simple Langmuir or Freundlich isotherm. The midpoint concentrations at half capacity (C_{50}) clustered tightly around 44.91, 46.84, 45.88, and 47.27 mg/L. This narrow C_{50} range highlights that most of the adsorption capacity is gained over just a small change in equilibrium concentration (Table 4). Very steep Hill slopes can reflect true cooperativity or apparent cooperativity due to heterogeneity/aggregation.

The slightly higher loading capacity of ZeoAqua in both kinetic and high ammonium isotherm experiments is caused by the different BET surface areas and Al_2O_3 contents. ZeoAqua exhibits a higher BET surface area (33.03 m^2/g) compared to Zeogran K 80 (27.41 m^2/g), suggesting that ZeoAqua provides more active sites for adsorption. A higher surface area typically correlates with a greater ability to adsorb adsorbates such as metal ions [31].

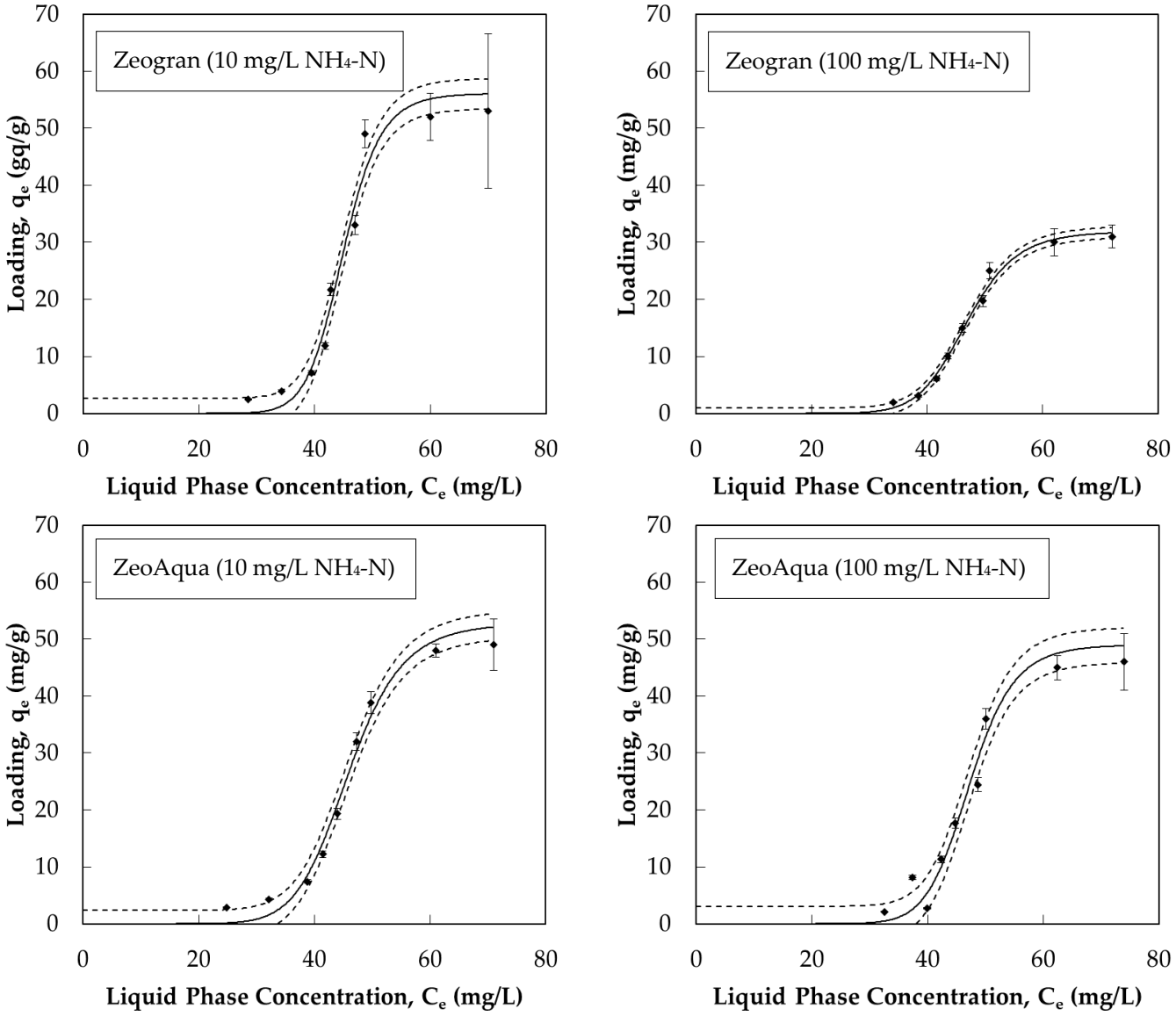


Figure 3. Hill isotherms, standard deviations, and 95% confidence intervals as the sum of the six heavy metals studied for both natural zeolites under different NH_4-N concentrations (C_0 = 10 mg/L per HM, particle size = 125–250 μm, contact time = 24 h).

Table 4. Freundlich and Hill isotherm constants for both natural zeolites under different NH_4-N concentrations.

Isotherm Model	Constants	Zeogran 10 mg/L NH_4-N	ZeoAqua 10 mg/L NH_4-N	Zeogran 100 mg/L NH_4-N	ZeoAqua 100 mg/L NH_4-N
Hill	q_{max} (mg/g)	56.14	52.85	31.93	49.03
	n_H (-)	13.87	9.81	10.92	12.38
	K_D (mg/L)	44.91	45.88	46.84	47.27
	R^2 (-)	0.9999	0.9999	0.9998	0.9997

The Al_2O_3 content plays a vital role in the ion exchange capacity of zeolites. Alumina creates negative charge sites within the zeolite structure, facilitating the exchange of cations such as Na^+, Ca^{2+}, and K^+ [32]. ZeoAqua has a marginally higher Al_2O_3 content (11.81%) compared to Zeogran K 80 (11.63%), which could result in a slightly enhanced ion exchange capacity for ZeoAqua. Overall, these findings indicate that the presence of ammonium

influences the adsorption behaviour of HMs, primarily through competitive interactions with cations such as HMs.

3.2. Heavy Metal Adsorption Column Tests

To assess the influence of NH_4^+ on the adsorption behaviour of HMs, a column test without the addition of ammonium was conducted (Figure 4). The daily overall HM inlet concentration was 0.75 g/d, reaching approximately 2100 BV. This would lead to a theoretical loading of 142 mg/g, far higher than the maximum loading results from the batch tests, assuming complete retention. Fixed-bed operation tends to exploit high driving forces at the inlet and cumulative loading over time, whereas batch systems often operate with declining driving forces and smaller mass balances, leading to lower apparent capacities [20]. Beside adsorption or ion exchange, precipitation as metal hydroxides (e.g., $Pb(OH)_2$) on the zeolite surfaces and formation of Ni-phyllosilicate on the exterior of the zeolite are also possible removal pathways [33,34].

All HMs were retained until 200 BV, where Ni started to break through the fastest. This is consistent with the batch tests, where Ni was not significantly removed, even at a high adsorbent dosage of 5 g/L. Between 500 and 800 BV even a slight desorption of Ni occurred. The retention of Pb differed distinctly, as it was effectively retained up to 14,000 BV, after which it began to break through. However, even at 20,000 BV it was still up to 60%. This high removal is consistent with its low hydration enthalpy (–1480 kJ/mol), large ionic radius (0.119 nm), and very high polarizability, which favour its exchange over other cations on the clinoptilolite framework. These properties allow Pb^{2+} to readily displace exchangeable cations (e.g., Na^+ and Ca^{2+}).

Zn and Cd followed in retention efficiency. Compared to Cu, breakthrough occurred later, and plateau concentrations were lower. These findings deviate slightly from single-ion studies that rank Cu above Zn, highlighting the impact of competitive multicomponent systems [27,35]. At around 10,000 BV Cu also slightly desorbed from ZeoAqua whereas desorption from Zeogran also occurred for Ni, Cd, and Zn.

Cr removal in ZeoAqua was similar but slightly worse than Cd and Zn removal. In Zeogran it was significantly higher compared to these two HMs but showed a similar trend in both zeolites. Cr^{3+} had less competition due to its trivalence. Cr and Pb also build adsorptive hydroxides even under low pH values, which facilitate removal through precipitation [19].

Ni was the least effectively removed HM in both zeolites. Its consistently high C/C_0 values indicate low affinity for zeolite, likely due to its low polarizability, high hydration enthalpy (–2105 kJ/mol), and the small hydrated radius of Ni^{2+}, which may hinder interaction with internal exchange sites. After 500 BV and again after 10,000 BV, it was also desorbed from Zeogran.

A direct comparison of the two natural zeolites reveals notable differences in their selectivity for the tested HMs. Zeogran exhibited superior performance in retaining Pb, with a significantly delayed breakthrough and lower effluent concentrations compared to ZeoAqua. Better retention of Cu was also observed, showing a more gradual breakthrough curve and lower C/C_0 values until 8000 BV, where it started to desorb. In contrast, ZeoAqua demonstrated enhanced retention for Zn and Cd, where breakthrough occurred later and was less steep compared to Zeogran. Interestingly, Ni, despite being generally poorly retained in both systems, was removed more efficiently by ZeoAqua, which maintained a lower C/C_0 plateau. The desorption of Cd, Cu, Ni, and Zn also did not occur in ZeoAqua, but it did in Zeogran after 10,000 BV. Although showing a similar breakthrough curve for Cr, ZeoAqua performed better after 15,000 BV. These results collectively show that Zeogran is more effective for Pb and Cu removal, while ZeoAqua performs better for Zn, Cd, Ni,

and Cr removal. This underscores the need to carefully select, or tailor zeolite materials based on the target contaminant profile in larger-scale applications.

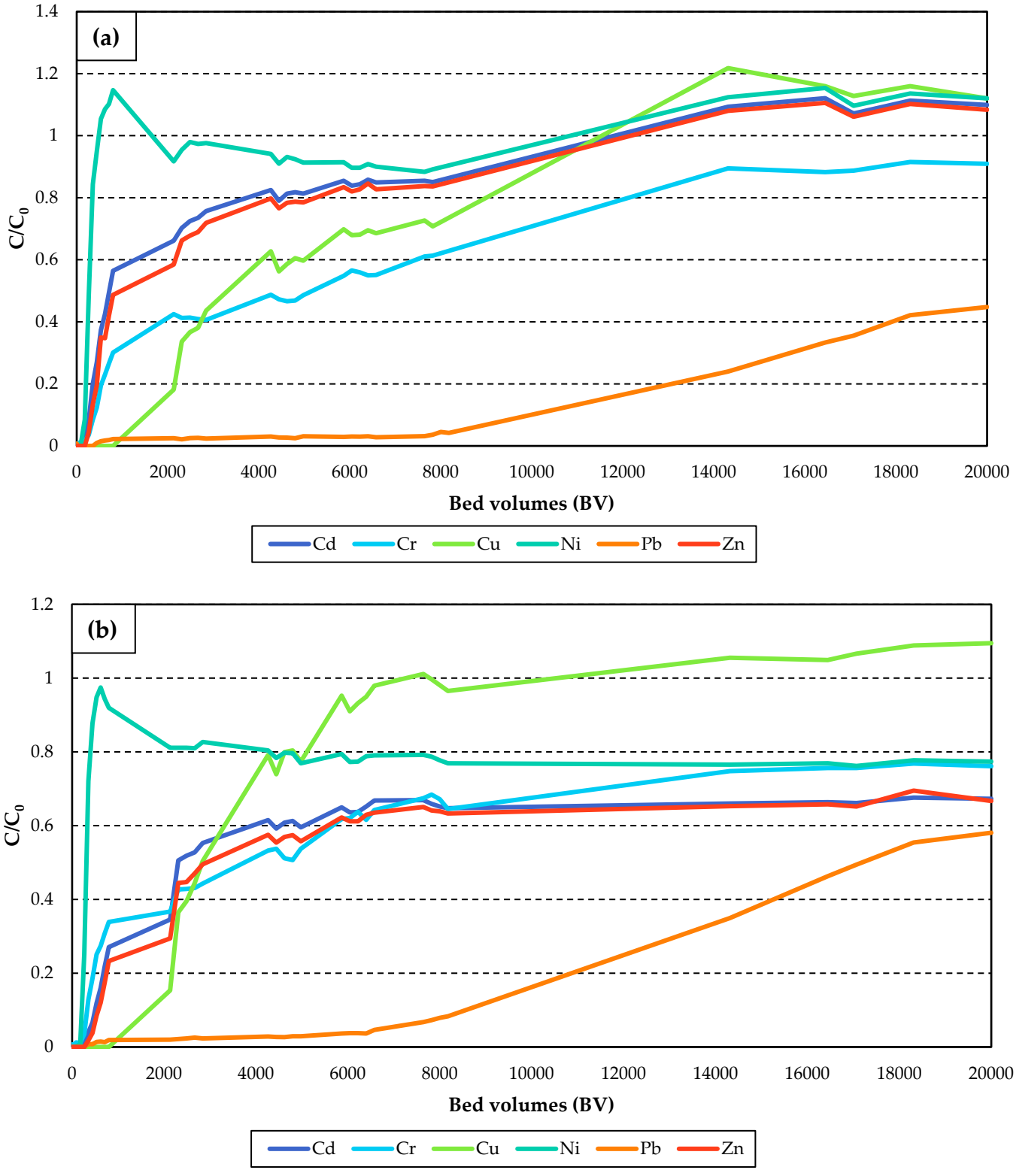


Figure 4. Heavy metal breakthrough curves of Zeogran (**a**) and ZeoAqua (**b**) in the column tests with an EBCT of 30 min (C_0 = 10 mg/L per HM, particle size = 125–250 μm).

Competitive Adsorption Column Tests

Based on the findings of Section 3.2, competitive adsorption tests with ammonium were conducted using the natural zeolite ZeoAqua. Initial HM concentrations were 1 mg/L of each HM. Breakthrough curves for Cd, Cr, Cu, Ni, Pb, and Zn were evaluated using natural zeolites under varying ammonium concentrations (1 and 10 mg/L NH_4-N), with bed volumes plotted against C/C_0 to assess removal performance (Figure 5).

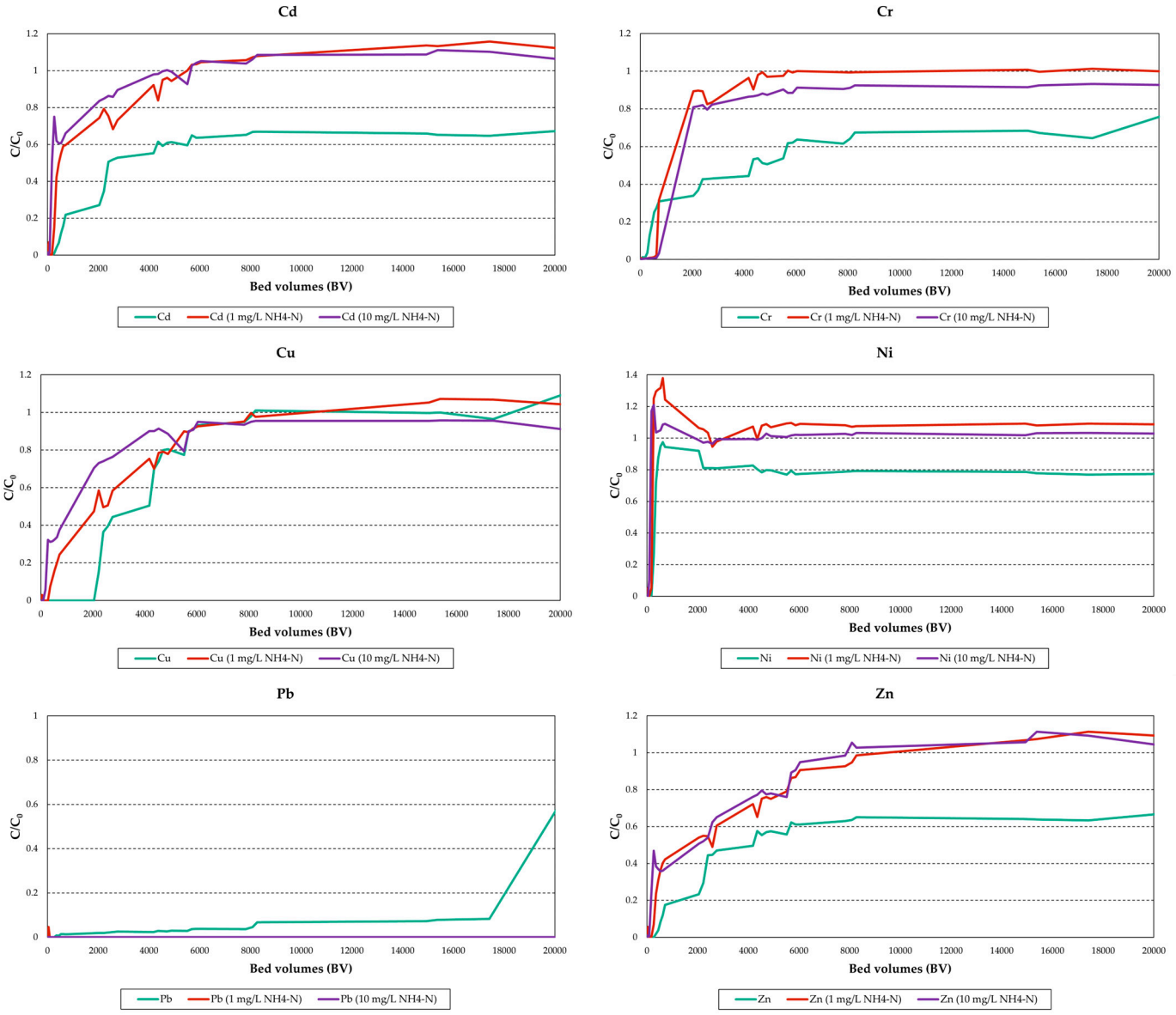


Figure 5. Heavy metal breakthrough curves of ZeoAqua without and under varying NH_4-N concentrations in the column tests (EBCT of 30 min, C_0 = 10 mg/L per HM, particle size = 125–250 µm).

For Cd, in the absence of NH_4^+, breakthrough was gradual, maintaining C/C_0 below 0.67 even at 20,000 BV, indicating sustained removal capacity. However, the addition of ammonium markedly reduced Cd removal efficiency. At 1 mg/L NH_4-N, breakthrough occurred rapidly, with C/C_0 reaching 0.55 at ~500 BV and slight desorption above 5000 BV. At 10 mg/L NH_4-N, breakthrough was even more rapid (~200 BV), suggesting strong competitive effects with ammonium ions.

Similar trends were observed for Cr, where the no-ammonium condition maintained C/C_0 below 0.6 until ~5800 BV, while both 1 and 10 mg/L NH_4-N treatments exhibited

sharp breakthrough at 1000–1500 BV, reaching C/C_0 values of 0.9–1, indicating near-complete saturation due to ammonium competition. However, the breakthrough started later compared to the HM-only solution. Interestingly, Cr breakthrough occurred earlier under the no-ammonium condition compared to both NH_4^+ treatments. Cr speciation dynamics or minor experimental variability may have contributed to this phenomenon. These results suggest that ammonium presence did not inhibit, and potentially enhanced, Cr removal under the studied conditions.

Cu breakthrough in the absence of ammonium was initially delayed, with C/C_0 remaining near zero up to ~2000 BV and then increasing gradually, reaching 0.8 at ~5000 BV. In contrast, the presence of ammonium accelerated a significant breakthrough. At 1 mg/L NH_4-N, C/C_0 rose steadily from the outset, reaching 0.6 at ~2000 BV. At 10 mg/L NH_4-N, breakthrough was even more rapid, with C/C_0 reaching 0.3 within ~250 BV and rising to 0.7 at 2000 BV. Above 5000 BV, the zeolites are exhausted in all three scenarios.

For Ni, breakthrough was fastest in comparison to the other HMs. At 1 and 10 mg/L NH_4-N, the loading capacity was exhausted at 300 BV and 200 BV, respectively, with subsequent desorption effects up to 2000 BV. Without NH_4^+ exhaustion was observed at 620 BV, with no desorption occurring.

In the case of Pb, removal remained remarkably unaffected by ammonium. Under both NH_4-N concentrations, C/C_0 remained near zero up to 20,000 BV, indicating a strong and selective affinity of Pb for the natural zeolite surface, with minimal competitive inhibition by ammonium. Normally, ammonium ions are known to compete with lead ions for adsorption sites on zeolites, potentially reducing lead uptake. However, the presence of ammonium has been observed to stabilise Pb removal, possibly by altering the zeolite's structure or ion exchange dynamics, leading to improved Pb adsorption efficiency [36].

For Zn, breakthrough was gradual in the absence of ammonium, with C/C_0 stabilising around 0.6. However, the presence of NH_4^+ accelerated breakthrough, with capacity exhaustion at ~8000 BV and slight subsequent desorption. Beside adsorption or ion exchange, Zn^{2+} might be complexed with NH_4^+ as $Zn(NH_3)_n^{2+}$ [37].

The observed variations in breakthrough behaviour can be mostly explained based on ion exchange selectivity and hydration energies of the competing ions [38]. Natural zeolites generally favour ions with lower hydration energies, high polarizability, and smaller hydrated radii due to easier dehydration and stronger electrostatic interactions within the zeolite channels [35]. NH_4^+, with a hydrated radius similar to K^+ and relatively low hydration energy (Table 2), competes effectively with divalent metal cations for exchange sites, displacing weaker binding metals such as Cd, Cu, Ni, and Zn [30]. Pb^{2+} exhibits a higher affinity due to its large ionic radius, lower hydration energy, and ability to form strong inner-sphere complexes, explaining its unaffected removal even in the presence of NH_4^+ [38]. Additionally, the degree of breakthrough acceleration correlated with ammonium concentration, confirming concentration-dependent competition. The possibility of C/C_0 exceeding unity for Ni further suggests desorption phenomena, where ammonium ions displace pre-adsorbed Ni from exchange sites.

Overall, these results indicate that while natural zeolites are highly effective for Pb removal under competitive conditions, their removal performance for Cd, Cr, Ni, and Zn is significantly reduced in the presence of ammonium due to preferential adsorption of NH_4^+ ions. For Cu this observation just applies up until 5000 BC.

3.3. Heavy Metal Desorption Column Tests

Prior to the desorption column tests, the natural zeolites had to be loaded with the selected heavy metals. The following loading rates showed no significant differences in the overall loading, Zeogran 125–250 µm (4.10 mg/g), Zeogran 250–500 µm (4.11 mg/g),

ZeoAqua 125–250 µm (4.02 mg/g), and ZeoAqua 250–500 µm (4.13 mg/g), with a selectivity of Pb > Cr > Cu > Zn > Cd > Ni (Figure 6).

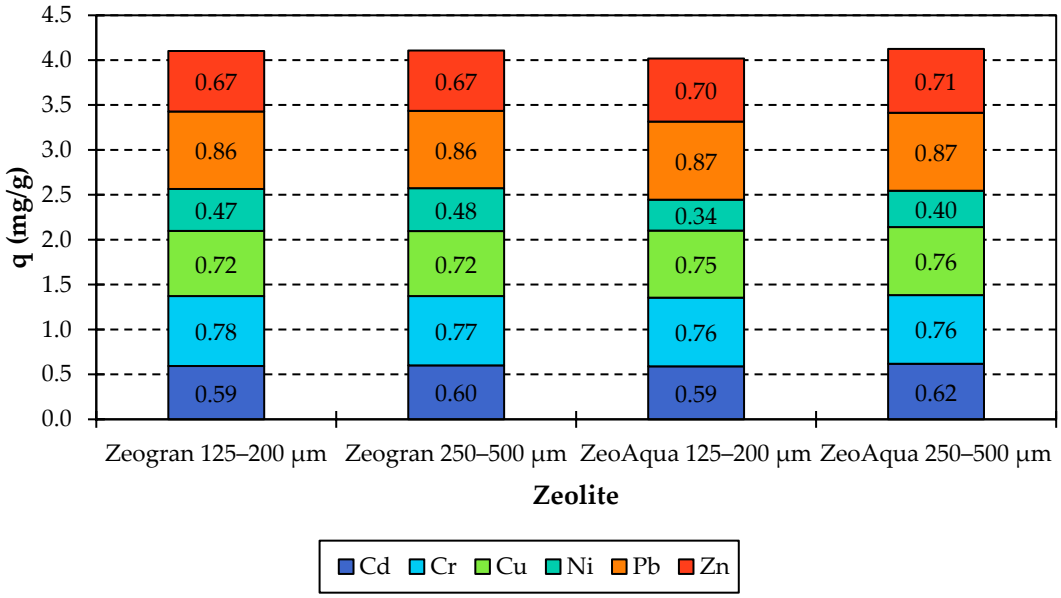


Figure 6. Preloading results for the desorption tests of Zeogran and ZeoAqua with 100 mg/L of each HM (30 g of natural zeolite per sample).

3.3.1. Desorption of Heavy Metals by Elevated Ammonium Concentrations

The desorption behaviour of HMs sorbed to zeolite using ammonium as a competing cation was evaluated through two experimental setups (10 mg/L and 100 mg/L NH_4-N), as illustrated in Figure 7. In both experiments, a rapid initial desorption of HMs was observed, followed by a sharp decline and stabilisation of HM concentrations, especially under the high-ammonium conditions. This pattern is indicative of ion exchange mechanisms, where ammonium ions effectively displace HM cations from the zeolite lattice. The gradual increase in NH_4-N concentration over time further supports this exchange process and reflects the progressive saturation of the zeolite with ammonium while simultaneously displacing the adsorbed HMs.

Despite these similarities, the two experiments differed significantly in terms of their operational parameters and outcomes. Under high-NH_4^+ conditions, Cu (3.93 mg/L) exhibited the highest initial desorption before Cd (3.56 mg/L) in ZeoAqua, whereas the opposite occurred in the lower-NH_4^+ experiment at a considerably lower concentration (Cu: 0.23 mg/L; Zn: 0.41 mg/L). At 100 mg/L NH_4-N, the desorption process was mainly over after 1000 BV for both zeolites. Notably, Pb and Zn showed an intermittent spike, particularly around 3300 BV, which was also accompanied by a slight increase in NH_4-N concentration in the effluent. Zn and Cr were also initially desorbed in both approaches to a minor degree whereas Ni was not desorbed at all. Under high-ammonium conditions, NH_4-N saturation was mostly reached at approximately 1000 BV but took up to 20,000 BV at lower concentrations.

The difference in NH_4-N concentration between the two experiments appears to play a central role in both the kinetics and magnitude of metal desorption. While higher NH_4^+ concentrations increase the overall desorption, they may also introduce variability in effluent quality, particularly for HMs like Pb and Zn. Overall, the findings confirm the competitive effects of NH_4^+ and HMs on natural zeolites and indicate fast desorption kinetics within the first 1000 BV for 100 mg/L NH_4-N and 5000 BV for 10 mg/L NH_4-N.

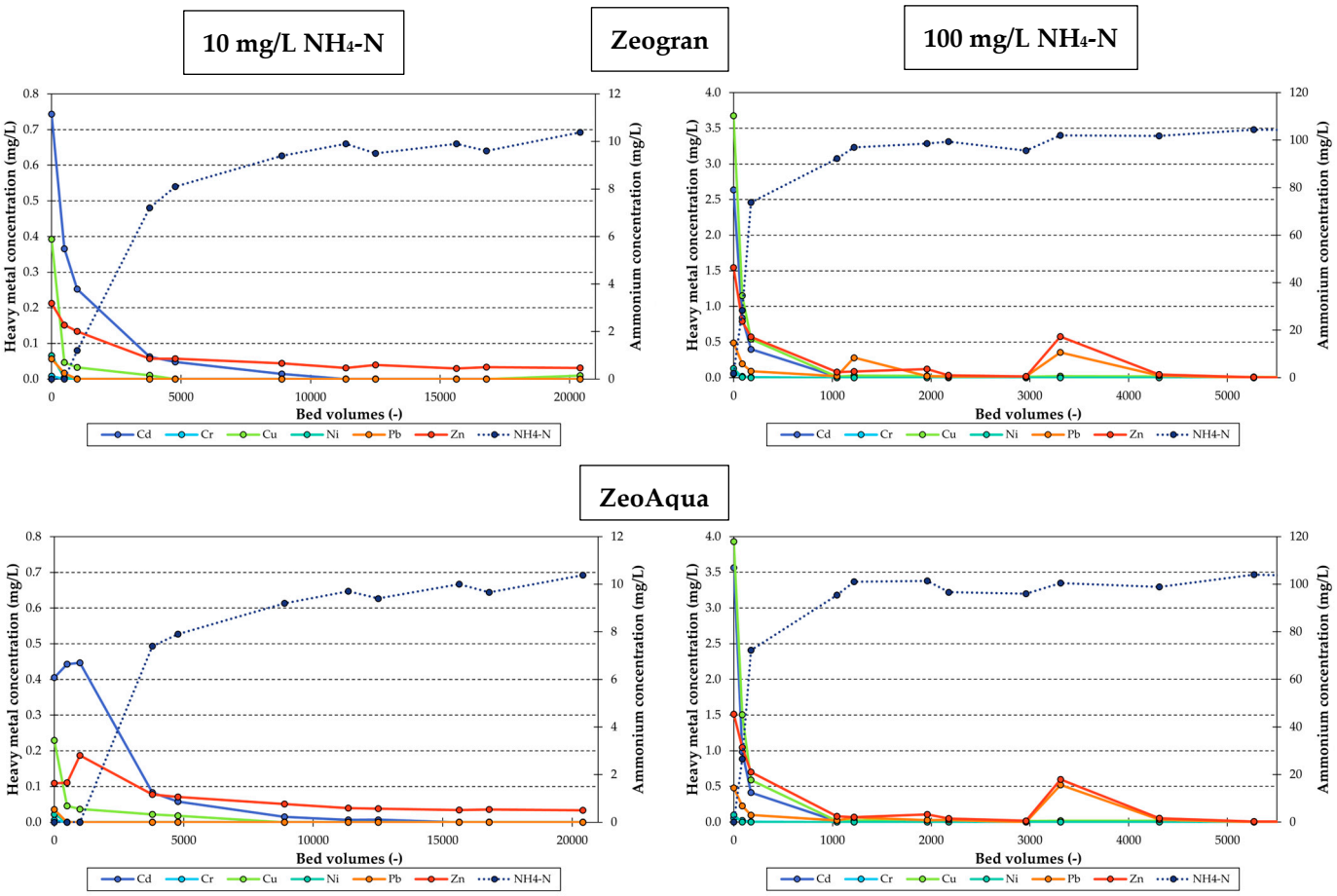


Figure 7. Heavy metal desorption behaviour on preloaded natural zeolites in dependence of the ammonium concentration (left figure: NH_4-N = 10 mg/L, right figure: NH_4-N = 100 mg/L).

3.3.2. Influence of the Particle Size on Heavy Metal Desorption

The desorption behaviour of HMs from adsorbent materials such as natural zeolites is critically affected by particle size. Smaller particles generally have a larger specific surface area and shorter diffusion paths, thereby enhancing adsorption and desorption dynamics [39]. In the context of HM retention on zeolitic materials, these characteristics directly impact the strength and reversibility of the interactions between the metals and the surface. In practical applications, optimising particle size is essential to balance high adsorption efficiency with low desorption potential. Selecting the right particle size distribution can improve the performance of zeolitic adsorbents in heavy metal retention, especially under changing chemical conditions.

The different particle sizes affected both the desorption of HMs as well as the adsorption of NH_4^+. The release of HMs at the smaller particle size of 125–250 µm was significantly lower and stopped after approximately 1000 BV (Figure 8). High initial desorption of HMs with a zeolite particle size of 250–500 µm was observed for Cd followed by Cu and Zn for both zeolites, even though Zeogran desorbed distinctly more Cd (0.74 mg/L) than ZeoAqua (0.41 mg/L). The order of desorption changed from Cd > Zn > Cu > Ni = Cr = Pb at a particle size of 125–250 µm to Cd > Cu > Zn > Pb = Ni > Cr.

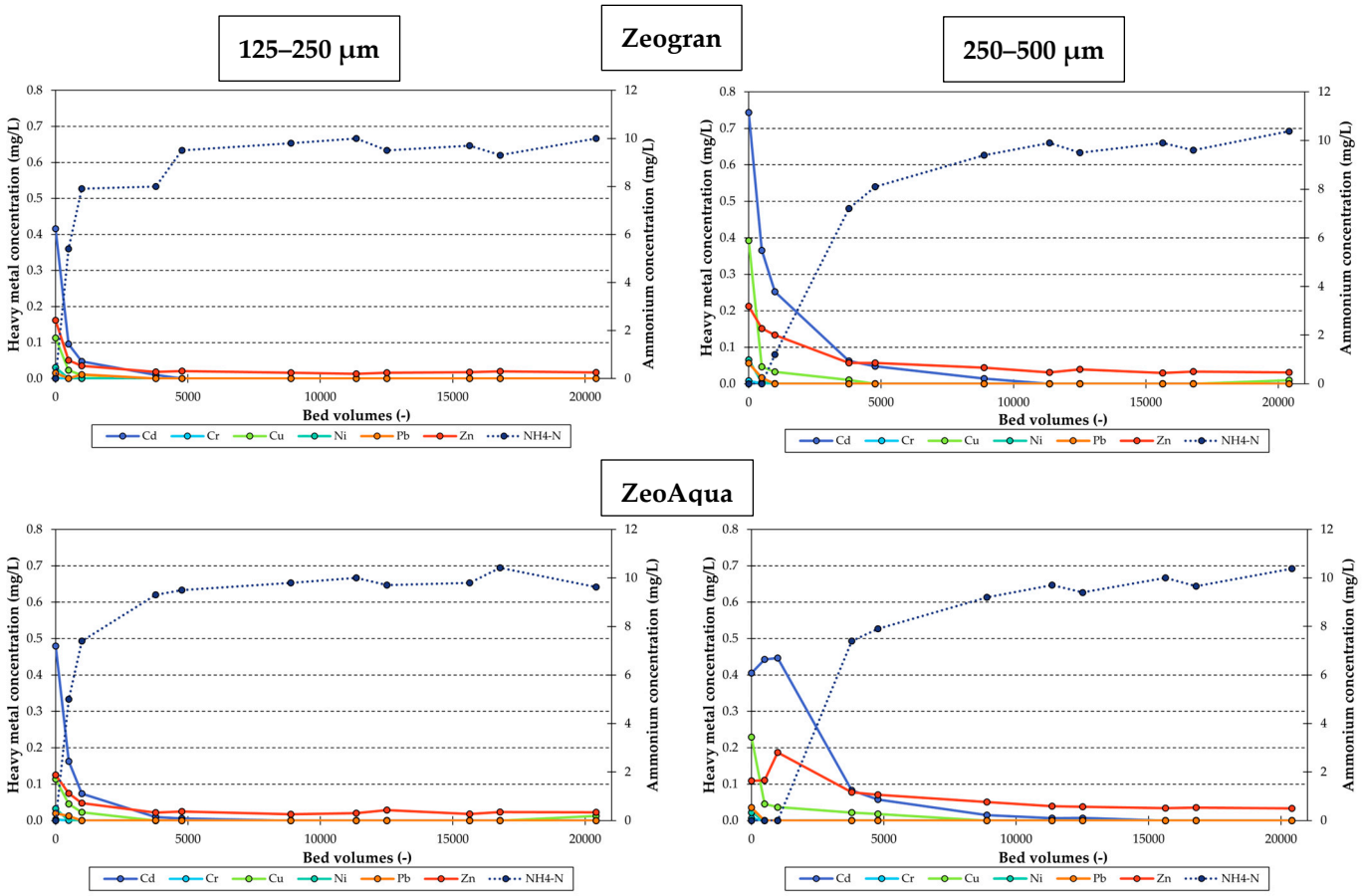


Figure 8. Heavy metal desorption behaviour on preloaded natural zeolites in dependence of the particle size (left figure: d = 125–250 µm; right figure: d = 250–500 µm).

3.3.3. Influence of the pH on Heavy Metal Desorption

To investigate the influence of the H^+-concentration, which also competes for negatively charged binding sites, on the desorption of HMs and the adsorption of NH_4^+, the preloaded zeolites were fed with pH-adjusted NH_4^+-solutions with a pH of 4 and 6 (Figure 9).

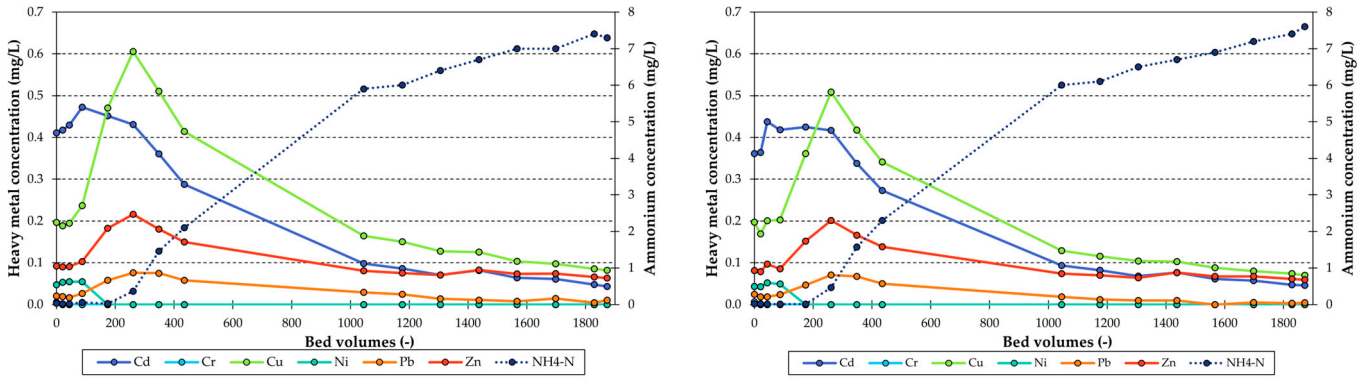


Figure 9. Concentrations as a function of bed volumes of preloaded ZeoAqua at different pH values: 4 (**left**) and 6 (**right**) (NH_4-N and HM concentrations = 10 mg/L).

The speciation of HMs depends on the pH of the solution, which strongly influences the adsorption and ion exchange processes as well as the mobility of the HMs. Furthermore, the pH influences the removal mechanism of HMs by natural zeolites since it affects the

surface charge [40,41]. No decreasing effects of acidic conditions on the ion exchange, caused by the competition of hydrogen and metal ions for binding sites on the natural zeolite, were observed for Cr and Ni. It should also be noted that low pH values change the sorption processes and increase the mobility and remobilisation of already adsorbed HMs, rereleasing them into the environment [42]. Cu was the most sensitive to acidic conditions, releasing up to 0.61 µg/L after 260 BV, compared to 0.51 µg/L at a higher pH.

The behaviour of NH_4-N showed similar trends in both pH scenarios. In the pH range between 4 and 6, more than 99% of the total ammonia nitrogen exists in the form of NH_4^+ and not the conjugate base NH_3, which is not exchangeable via ion exchange [43]. As the pH went up during the experiment to 6.5 under the higher-pH conditions, a slight drift in the speciation of NH_4^+ and NH_3 caused the small decline in adsorption capability. This pH-dependent speciation underscores the importance of operating under mildly acidic to neutral conditions in systems relying on zeolite-mediated ammonium removal. However, the breakthrough of NH_4-N began at approximately 260 BV in both cases.

These findings underline the critical role of pH in controlling both the stability of adsorbed HMs and the ammonium removal capacity of zeolites. Near-neutral pH conditions are thus more favourable for minimising HM remobilisation while optimising ammonium removal in treatment systems using natural zeolites.

4. Conclusions

This study explored the competitive interactions between NH_4^+ and the heavy metals Cd, Cr, Cu, Ni, Pb, and Zn in their adsorption and desorption behaviour in natural zeolites (Zeogran and ZeoAqua). The results showed that NH_4^+ strongly competed with HMs for the zeolite's cation exchange sites. This competition was particularly evident at higher NH_4^+ concentrations, where the adsorption of HMs significantly decreased, with a reduction in the overall adsorption capacity of the zeolites by approximately 45% at 100 mg/L NH_4-N in the kinetic experiments. Among the selected HMs, Pb consistently exhibited the highest affinity for both zeolites and was nearly completely retained up to 14,000 BC in the absence of NH_4^+, while Cd, Cr, Ni, and Zn were most affected due to the competing effects between NH_4^+ and HMs on the zeolite surface. The adsorption behaviour was well described by the Hill isotherm, indicating a narrow concentration window in which uptake rises sharply. The consistently small C_{50} range shows that most of the capacity is achieved over only a slight change in equilibrium concentration. Such steep Hill slopes may reflect genuine cooperativity or apparent cooperativity arising from heterogeneity or particle aggregation. Material-specific differences in site density, accessibility, and ion exchange selectivity account for the contrasting performance of Zeogran and ZeoAqua under competitive conditions.

Desorption experiments further confirmed the strong competitive elution effect of ammonium, particularly under higher NH_4^+ concentrations, which rapidly remobilised pre-adsorbed metals, in particular Cd, Cu, and Zn. This is due to the monovalence, the relatively small hydration radius, and the relatively low hydration enthalpy of ammonium. The particle size of the zeolite influenced desorption dynamics, with larger particles exhibiting higher initial desorption rates. Additionally, pH played a role in Cu desorption, with slightly higher desorption at a pH of 4 compared to 6.

Overall, these results highlight the complex interactions between NH_4^+ and HMs on natural zeolites, emphasising the importance of considering parameters such as NH_4^+ concentrations, pH, and zeolite particle size when designing wastewater treatment systems. This study provides vital insights for enhancing the application of zeolite-based technologies in ammonium-rich environments, such as constructed wetlands, soil filters, or

other decentralised applications where competitive adsorption and potential desorption can occur.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/pr13082647/s1, Figure S1: Loading over time during the adsorption kinetic tests (C_0 = 10 mg/L per HM); Figure S2: NH_4-N concentrations (1 mg/L) and pH in the competitive adsorption column tests; Figure S3: NH_4-N concentrations (10 mg/L) and pH in the competitive adsorption column tests.

Author Contributions: L.M.O.: conceptualization, methodology, formal analysis, investigation, writing—original draft preparation, and writing—review and editing; C.K.: conceptualization, validation, resources, supervision, and writing—review and editing. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The raw data supporting the conclusions of this article will be made available by the authors on request.

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Conflicts of Interest: The authors declare no conflicts of interest.

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