

## Article

# Adsorption and Release Characteristics of Purified and Non-Purified Clinoptilolite Tuffs towards Health-Relevant Heavy Metals

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**Abstract:** The occurrence of health-relevant contaminants in water has become a severe global problem. For treating heavy-metal-polluted water, the use of zeolite materials has been extended over the last decades, due to their excellent features of high ion exchange capacity and absorbency. The aim of this study was to assess the effect of heavy metal uptake of one purified (PCT) and two non-purified clinoptilolite tuffs (NPCT1 and NPCT2) in aqueous solutions on monovalent ions Ni<sup>+</sup>, Cd<sup>+</sup>, Cs<sup>+</sup>, Ba<sup>+</sup>, Tl<sup>+</sup>, and Pb<sup>+</sup>. Experiments were furthermore carried out in artificial gastric and intestinal fluids to mimic human digestion and compare removal efficiencies of the adsorbent materials as well as release characteristics in synthetic gastric (SGF) and intestinal fluids (SIF). Batch experiments show low sorption capacities for Ni<sup>+</sup> and Cd<sup>+</sup> for all studied materials; highest affinities were found for Ba<sup>+</sup> (99–100%), Pb<sup>+</sup> (98–100%), Cs<sup>+</sup> (97–98%), and Tl<sup>+</sup> (96%), depending on the experimental setup for the PCT. For the adsorption experiments with SGF, highest adsorption was observed for the PCT for Pb<sup>+</sup>, with an uptake of 99% of the lead content. During artificial digestion, it was proven that the PCT did not release Ba<sup>+</sup> cations into solution, whereas 13574 ng·g<sup>-1</sup> and 4839 ng·g<sup>-1</sup> of Ba<sup>+</sup> were measured in the solutions with NPCT1 and NPCT2, respectively. It was demonstrated that the purified clinoptilolite tuff is most effective in remediating heavy-metal-polluted water, particularly during artificial digestion (99% of Pb<sup>+</sup>, 95% of Tl<sup>+</sup>, 93% of Ba<sup>+</sup>). In addition, it was shown that the released amount of bound heavy metal ions (e.g., barium) from the non-purified clinoptilolite tuffs into the intestinal fluids was significantly higher compared to the purified product.

**Keywords:** clinoptilolite tuff; zeolite; toxic heavy metals; adsorption and release; batch experiment

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## 1. Introduction

Heavy metals are a group of naturally occurring elements with particularly high weight and density of over  $4 \times 10^6$  mg·L<sup>-1</sup> [1]. Some of them are needed as nutrients (zinc, magnesium, iron, molybdenum, selenium), whereas others show toxic effects after uptake, even in very low concentrations (Table 1) [2]. In recent years, environmental contamination by poisonous heavy metal ions has become a public health concern. Heavy metals can enter into water from natural or industrial processes. The former include volcanic eruptions, soil erosion, and weathering of rocks and minerals, whereas the latter comprises mining or smelting procedures, landfills, fuel combustion, and industrial pollutants. Furthermore, the prolonged application of fertilizers and pesticides has resulted in heavy metal accumulation in surface and ground water [3]. Heavy metals can accumulate in tissues and, due to their toxicity, cause cancer and other diseases and disorders [4].

**Table 1.** Comparison of selected heavy metals, their anthropogenic sources, provisional maximum tolerable daily intake (PMTDI) according to the WHO, and related symptoms and diseases.

Heavy Metal	Anthropogenic Sources	PMTDI [mg·L <sup>-1</sup> ]	Symptoms and Diseases	References
Nickel (Ni)	Nickel steel, batteries, non-ferrous alloys, electroplating, coinage, microphone capsules, catalysts, dental and surgical prostheses	0.02	Anemia, diarrhea, encephalopathy, lung and kidney damage, gastrointestinal distress, pulmonary fibrosis, central nervous system dysfunction, skin dermatitis	[1,4]
Cadmium (Cd)	Petroleum refining, electroplating and alloying industry, nickel–cadmium batteries, vapor lamps, coal combustion	0.003	Emphysema, hypertension, nephropathy, diabetes mellitus, skeletal malformation	[1,2,5]
Cesium <sup>1</sup> (Cs)	Vacuum tubes, photoelectric cells, optical and detecting devices	No guideline	Gastrointestinal stress, hypotension, syncope, numbness	[6,7]
Barium (Ba)	Manufacturing of rubber, plastics, electronics, steel, textiles, petroleum industry	1.3	Vomiting, diarrhea, abdominal cramps, anemia, disorders of central nervous system, lung perivascular and peribronchial sclerosis, bronchoconstriction	[8,9]
Thallium (Tl)	Catalyst, coal mining and burning, chemical industries, rodenticide, insecticide, alloys	0.0001	Gastroenteritis, hair loss, peripheral neuropathy, alopecia, high blood pressure, tachycardia, persistent weakness	[10,11]
Lead (Pb)	Fuels, combustion of coal, mining, manufacturing of electronic products, metal processing, painting, pigments, leather tanning	0.01	Anemia, muscle weakness, ataxia, tremors, gastrointestinal disorders, kidney dysfunction	[1,5,12]

<sup>1</sup> Stable cesium only (<sup>133</sup>Cs).

Contamination of aquatic systems constitutes a serious environmental problem. Therefore, development of suitable and efficient technologies to solve this problem is needed [1].

Various processes exist for removing dissolved heavy metals, including chemical precipitation, membrane flotation, and ion exchange or solvent extraction. However, most of these traditional techniques demand high capital or operating costs or cannot reduce heavy metal contamination to an acceptable level [13–16]. Therefore, the development of alternative, low-cost materials as potential sorbents has been emphasized recently [17].

The most cost-effective and best-suited methods to efficiently treat heavy metal polluted water are based on adsorption [13–16]. Numerous adsorbents of different natures have been employed to remove noxious heavy metals from water, including activated carbons, clay minerals, biomaterials, and zeolites [13].

Zeolites are hydrated alumina silicates that can occur naturally or can be produced industrially. Most common natural zeolites are formed by alteration of silicon-rich volcanic rocks (tuffs). They are characterized by a three-dimensional crystalline structure framework of tetrahedral silica (SiO<sub>4</sub>) or alumina ions (AlO<sub>4</sub>), linked by the sharing of all oxygen atoms [13,18]. Partial, isomorphic substitution of Si<sup>4+</sup> by Al<sup>3+</sup> cations leads to a net negative charge in the crystal lattice that is balanced by mono- and divalent cations, such as Na<sup>+</sup>, Ca<sup>2+</sup>, K<sup>+</sup>, and Mg<sup>2+</sup>, which are easily exchangeable for the majority of hazardous metals [16,18]. The fact that these exchangeable cations are relatively innocuous makes natural zeolites suitable for removing undesirable heavy metal ions [17].

Natural zeolites of the clinoptilolite type are among the world's most abundantly occurring and most widely used zeolite minerals. They are found in large deposits and mined all over the world and have high cation selectivity and good resistance to temperature [16,18]. Due to its high ion exchange abilities, as well as molecular sieve properties, clinoptilolite is an excellent low-cost treatment adsorbent for heavy metals from polluted water [14,15,19–22]. That is what makes clinoptilolite a promising material,

not just for the treatment of heavy-metal-polluted water, but also for agronomical applications or in the fields of pharmacy and medicine [18,19,23].

In this study, a purified clinoptilolite tuff and two non-purified clinoptilolite tuffs were examined.

The purified clinoptilolite tuff was produced by applying a sophisticated process [24] to the raw material to lower its natural content of heavy metals and to increase its efficacy and consumer friendliness, enabling it to be safely and extendedly used as a dietary supplement. The NPCTs are medical devices available on the European market.

The adsorption behavior of clinoptilolite tuff towards selected monovalent cations ( $\text{Ni}^+$ ,  $\text{Cd}^+$ ,  $\text{Cs}^+$ ,  $\text{Ba}^+$ ,  $\text{Tl}^+$ , and  $\text{Pb}^+$ ) in drinking water was investigated and discussed.

The aims of this study were to analyse the efficiency of heavy metal reduction by clinoptilolite tuffs and to compare two non-purified tuffs with a purified clinoptilolite tuff in terms of adsorption and release of heavy metals in heavy-metal-spiked aqueous matrix, as well as in gastric and intestinal fluids. This study sought to investigate whether consumption of clinoptilolite can significantly reduce the amount of heavy metals orally ingested via contaminated water and thus contribute to the prevention of heavy metal intoxication in the human body.

In the following study, the isotopes  $^{58}\text{Ni}$ ,  $^{111}\text{Cd}$ ,  $^{133}\text{Cs}$ ,  $^{138}\text{Ba}$ ,  $^{203}\text{Tl}$ , and  $^{208}\text{Pb}$  were examined.

## 2. Materials and Methods

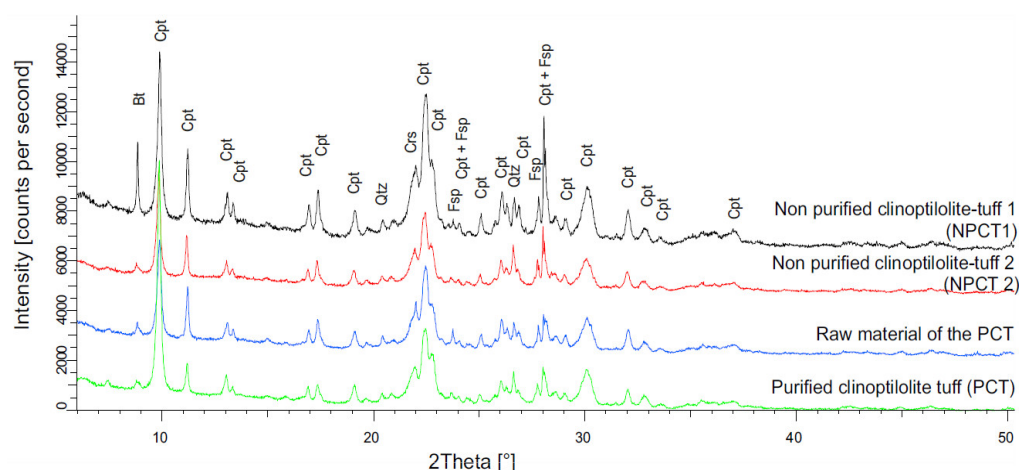
### 2.1. Sorbent Materials

The raw material of the purified clinoptilolite tuff (PCT) originates from the open-pit mine in Nižný Hrabovec (eastern Slovak Republic). It was purified according to a patented treatment, involving several ion exchange steps, micronization, and terminal heat treatment [25]. The heavy-metal-reduced, extremely fine-grained, and dry-sterilized product is available as a dietary supplement on the US market under the trade name G-PUR®. The two non-purified tuffs are commercially available medical devices on the European market.

A detailed investigation of the deposit at Nižný Hrabovec as well as the raw material's characteristics and its evolution were described by Tschegg et al. [18,25].

For characterization of the sorbent materials, the chemical and mineralogical compositions were determined using ICP-MS (NexION 350 D, Perkin Elmer, Waltham, MA, USA) and XRD (D-8 Advance, Bruker, Billerica, MA, USA). For observing the heavy metal content in the zeolite samples of 100 mg from the raw material of the PCT, the PCT and the two NPCTs were taken and primarily digested using an Anton Paar microwave 3000. As digestion reagent, 1% (*w/w*) hydrogen fluoride (HF) and 69% (*w/w*) sub-boiled  $\text{HNO}_3$  were mixed. After digestion, the samples were measured with the ICP-MS (mentioned above). Indium (Merck, Kenilworth, NJ, USA) was added as internal standard to the solutions. For calibration, the multi-element standard VI (Merck) was utilized.

For the mineralogical analyses of the powder samples, XRD (X-Ray Diffractometry) was performed. A Bruker D-8 Advance diffractometer (at Glock Health, Science and Research GmbH) equipped with a Cu source was used. Tube conditions were 40-kV voltage and 40-mA current. Measurements were performed on powdered specimens in top-loaded sample holders using a  $\theta$ - $2\theta$  configuration, scanning angles from  $6^\circ$  to  $70^\circ$ , and  $0.01^\circ$  step size at 0.5 s/step. For the evaluation of the phases, the Bruker software DIFFRAC.EVA (release 2016) was used. The reference sample NIST SRM1976a (sintered alumina) and an intralaboratory clinoptilolite tuff reference sample were analyzed before each batch was run through quality control. XRD analysis is depicted in Figure 1.



**Figure 1.** Powder XRD patterns illustrating the whole-rock mineral composition of the clinoptilolite tuffs. Cpt = clinoptilolite, Bt = biotite, Qtz = quartz, Crs = cristobalite, Fsp = feldspar.

## 2.2. Determination of the Ion Exchange Capacity and Particle Size Distribution

For the purified clinoptilolite tuff and the non-purified tuffs, the ion exchange capacity ( $\text{mol}\cdot\text{kg}^{-1}$ ) was determined using the 930 Compact IC Flex Chamber/SeS/PP/Deg (Metrohm, Herisau, Switzerland).

In total, 0.8 g of the tuff and 20 mL of a  $0.15 \text{ mol}\cdot\text{L}^{-1}$   $\text{NH}_4\text{Cl}$ -solution were mixed by continuous movement (orbital shaker Heidolph Promax 1020) for two hours. In this way, metal cations bound to the tuff were exchanged with the ammonia from  $\text{NH}_4\text{Cl}$ .

Afterwards, the solution was centrifuged for 15 min at 1923 g (Mega Star 1.6R, VWR) to obtain the fluid fraction. The supernatant was filtered through a  $0.45 \mu\text{m}$  PVDF membrane filter, diluted (1:100) with  $\text{HNO}_3$ /dipicolinic acid 34 mM/14 mM (Sigma Aldrich, St. Louis, MO, USA), and analyzed. The ion exchange capacity was calculated over the difference in ammonia content between the blank solution (without sorbent) and the solution after being contacted with the tuff. The samples were measured four times. Results are presented in Table 2.

The particle size of the PCT, its raw material, and the NPCTs were measured with a Mastersizer 2000 (Malvern Panalytical, Malvern, UK). The reference sample NIST SRM 1021 was run with the tuffs to ensure the accuracy and precision of the method. Measurements were carried out in triplicates, and results are given in Table 2.

**Table 2.** Chemical characterization of the sorbent materials.

	Raw Material PCT	PCT	NPCT1	NPCT2
<i>Chemical composition: Oxides [wt%]</i>				
Al <sub>2</sub> O <sub>3</sub>	13	12	14	14
SiO <sub>2</sub>	67	66	82	77
CaO	3	5	4	3
K <sub>2</sub> O	3	1	3	3
MgO	0.6	0.3	0.9	0.7
Na <sub>2</sub> O	1.5	0.5	0.6	1.6
<i>Chemical composition: Elements [μg·g<sup>-1</sup>]</i>				
Aluminium	66,720 ± 421	64,838 ± 1724	70,608 ± 2010	75,577 ± 1939
Silicium	315,242 ± 4986	307,780 ± 7279	315,090 ± 7267	360,084 ± 4318
Nickel	0.20 ± 0.01	4.1 ± 0.3	1.7 ± 0.1	1.6 ± 0.2
Cadmium	<0.05	<0.05	<0.05	<0.05
Cesium	/	/	/	/
Barium	792 ± 7	49 ± 1	817 ± 18	824 ± 11
Thallium	0.33 ± 0.02	0.18 ± 0.003	0.44 ± 0.02	0.44 ± 0.02
Lead	10 ± 0.3	1.6 ± 0.1	13 ± 0.5	14 ± 0.6
<i>Ion exchange capacity [mol·kg<sup>-1</sup>]</i>	0.99 ± 0.02	0.97 ± 0.007	0.65 ± 0.02	0.89 ± 0.02
<i>Particle size [μm]</i>	/	3.2 ± 0.02	22 ± 0.7	7.6 ± 0.1
<i>Si/Al ratio</i>	5	5	4	5

### 2.3. Single-Ion Adsorption Experiments

In the following section, the adsorption of heavy metal cations Ni<sup>+</sup>, Cd<sup>+</sup>, Cs<sup>+</sup>, Ba<sup>+</sup>, Tl<sup>+</sup>, and Pb<sup>+</sup> by the PCT is investigated in single-ion solutions. The batch method was employed, using concentrations from 10 to 1000 ng·g<sup>-1</sup> on the basis of (*w/w*) in non-carbonated mineral water.

Inorganic chemicals were supplied by Merck as analytical-grade reagents.

Stock solutions were prepared by diluting the standard solutions (Merck) of the heavy metal ions with non-carbonated mineral water to the desired concentrations and were then used for heavy metal cation adsorption and release experiments. The heavy-metal-spiked solutions are referred to as “contaminated” in the following sections.

Experiments were conducted batchwise with volumes of 50 mL: tuff samples with masses of 0.2 g (solid solid/liquid ratio of 1:4) were contacted with the heavy-metal-contaminated non-carbonated mineral water with 10 ng·g<sup>-1</sup> and 1000 ng·g<sup>-1</sup> starting concentrations. The solutions were placed in a heating chamber (Binder 9010-0082) at 37 °C for three hours. Experimental conditions of 37 °C as temperature and a maximum reaction time of 180 min were chosen with reference to the body temperature of humans and digestion time in human beings [26,27].

After 10 min, 60 min, and 180 min reaction time, 5 mL of the samples were withdrawn, filtered using a 0.45 μm PVDF filter, and diluted with 1 wt% HNO<sub>3</sub>. The control (no clinoptilolite) and the test solutions (after being contacted with clinoptilolite) were taken for metal-ion concentration analysis using an inductively coupled plasma mass spectrometer (NexION 350 D, Perkin Elmer) for parts-per-billion (ppb) sample concentrations of Ni<sup>+</sup>, Cd<sup>+</sup>, Cs<sup>+</sup>, Ba<sup>+</sup>, Tl<sup>+</sup>, and Pb<sup>+</sup>, with a limit of quantification of 0.10 ng·g<sup>-1</sup> for barium, 0.010 ng·g<sup>-1</sup> for lead, 0.011 ng·g<sup>-1</sup> for cadmium, 0.031 ng·g<sup>-1</sup> for cesium, 0.070 ng·g<sup>-1</sup> for nickel, and 0.0021 ng·g<sup>-1</sup> for thallium. Every experiment was performed with appropriate controls (no sorbent) and blank solutions (non-carbonated mineral water). Accuracy and precision of the analysis were ensured using equidistant calibration (Multi-element Standard Solution VI, Merck). Indium (Merck) was used as an internal standard

and added before the measurements. This was to ensure that the difference in heavy metal concentrations before and after the experiment was due to adsorption processes and not due to, for example, precipitation of heavy metals at high pH. All control solutions underwent the same experimental conditions as the test samples.

Quality assurance checks were run at intervals.

All batch experiments were performed in triplicate, and the averaged values and standard deviations were reported.

A Metrohm pH meter (WTW pH 3210) was used for the pH measurements.

Highest-purity reagents were used throughout this study.

From the results obtained, it was decided to further compare the PCT with NPCTs in terms of adsorption behavior towards heavy metal cations from multi-element solutions.

### 2.3.1. Batch Adsorption and Release Experiments in Contaminated Non-Carbonated Mineral Water

Release experiments were conducted in order to evaluate how strongly heavy metal ions were immobilized by the three different clinoptilolite tuffs. Adsorption behavior was investigated in synthetically prepared multi-ion solutions.

Together with 0.2 g sorbent in a 1:4 solid/liquid ratio, the synthetically treated non-carbonated mineral water spiked with a mix of the heavy metal cations as described above was incubated at 37 °C for three hours. Samples were taken after 10 min, 60 min, and 180 min. The suspension was then filtered through a 0.45 µm PVDF filter in order to remove the sorbent from the solution. The samples of the liquid supernatant were kept in 3 wt% HNO<sub>3</sub>, and the concentrations of the heavy metals in the supernatant were determined by an inductively coupled plasma mass spectrometer. Quality assurance checks with concentrations of 1 ng·g<sup>-1</sup> and 10 ng·g<sup>-1</sup> were used.

Measurements were carried out in triplicates.

### 2.3.2. Batch Adsorption and Release Experiments in Non-Contaminated Non-Carbonated Mineral Water

The experiment was conducted as described above (see Section 2.3.1). However, no heavy-metal-spiked water was used; instead, adsorption/release of heavy metals in naturally occurring amounts was investigated in the non-carbonated mineral water.

The concentrations of heavy metal ions in the sample were analyzed. The limit of quantification was 11 ng·g<sup>-1</sup> for nickel, 0.05 ng·g<sup>-1</sup> for cadmium, 0.012 ng·g<sup>-1</sup> for cesium, 0.21 ng·g<sup>-1</sup> for barium, 0.08 ng·g<sup>-1</sup> for thallium, and 0.44 ng·g<sup>-1</sup> for lead.

### 2.3.3. Heavy Metal Adsorption and Release in Artificial Gastric and Intestinal Fluids

Adsorption and release experiments were performed with multi-component solutions investigating the heavy metals stated above in laboratory-synthesized gastric and intestinal fluids. The simulated gastric fluid (SGF) and simulated intestinal fluid (SIF) were prepared following the instructions of the European Pharmacopoeia [28].

The simulated gastric fluid contained 0.034 mol·L<sup>-1</sup> NaCl and 3.2 g·L<sup>-1</sup> pepsin. The pH was adjusted to 1.5 by using 0.1 M HCl.

The SIF contained 0.05 M KH<sub>2</sub>PO<sub>4</sub>, 19.3 mL 0.2 M NaOH, 40 mL 0.01 M HCl, and 20 g·L<sup>-1</sup> pancreatin in a total volume of 250 mL.

The solution's pH was adjusted to 6.8 using 0.2 M NaOH.

The tuffs were transferred to tubes filled with multi-component heavy metal solution of predetermined concentrations to create a solid/liquid ratio of 1:4 (4 g·L<sup>-1</sup>). Synthetic gastric fluid was added.

These samples were put in a heating chamber (Binder, 9010-0082) at 37 °C. After 20 min, the reaction mixture was centrifuged at 1923 g (Mega Star 1.6R, VWR, Radnor, PA, USA) and the supernatant decanted. A time of 20 min was chosen because of the time it takes for water to pass through the stomach [26].

The remaining tuff was mixed with 20 mL SIF and allowed to equilibrate for another three hours at 37 °C. Afterwards, the samples were centrifuged at 1923 g to separate the solid from the fluid, and the supernatant intestinal juice was withdrawn from the remaining adsorbent.

The SIF was digested in nitric acid. Sub-boiled and then concentrated HNO<sub>3</sub>, concentrated H<sub>2</sub>O<sub>2</sub>, and deionized water were added to the SIF, put in a Teflon vessel, capped, and placed in a laboratory microwave (Anton Paar, Multiwave 3000, Tokyo, Japan). After digestion, the volume was brought to 50 mL with purified water.

The SGF and digested SIF samples were kept in 3 wt% HNO<sub>3</sub> and analyzed using inductively coupled plasma mass spectrometry (described above). Quality assurance checks with concentrations of 0.5 ng·g<sup>-1</sup> and 10 ng·g<sup>-1</sup> were run with the samples. Aliquots of synthetic-heavy-metal-spiked water, pure SGF, and pure SIF (without tuffs) were run as blank and control solutions, respectively, and received the same treatment as the extant samples.

#### 2.4. Adsorption Capacity and Removal Efficiency of PCT for Heavy Metal Ions

For the PCT, the heavy metal concentrations in the sample solution before and after the uptake experiments were measured using ICP-MS. The amount of metal adsorbed by the tuff was determined by calculating the difference between the initial metal concentration and the metal concentration after 180 min reaction time.

The adsorption capacity and removal efficiency of PCT for heavy metal ions could be expressed according to following Equations (1) and (2) [29]:

$$AC = \frac{(C_i - C_f) \times V_f}{W_c} \quad (1)$$

$$RE = 100 \times \frac{(C_i - C_f)}{C_i} \quad (2)$$

where AC [ng·g<sup>-1</sup>] corresponds to the adsorption capacity of PCT for heavy metal ions, RE (%) describes the removal efficiency for heavy metal ions, C<sub>i</sub> [ng·L<sup>-1</sup>] corresponds to the initial heavy metal concentration in the test solution beforehand, and C<sub>f</sub> [ng·L<sup>-1</sup>] to the heavy metal concentration after the adsorption experiments. V<sub>f</sub> [L] stands for the solution volume of the heavy metal ions and W<sub>c</sub> [g] for the dosage of the dry clinoptilolite tuff (0.2 g).

Removal efficiencies were calculated for different times, whereas adsorption capacities were determined only for the last time samples (180 min).

Results are given in Tables 2–5.

**Table 3.** Adsorption of studied heavy metal cations from single-element solutions with concentrations of 10 ng·g<sup>-1</sup> onto PCT.

Heavy Metal Cation	Concentration [10 ng·g <sup>-1</sup> ]				
	Initial Concentration [ng·g <sup>-1</sup> ]	Reaction Time [min]	Residual Concentration [ng·g <sup>-1</sup> ]	SD [ng·g <sup>-1</sup> ]	Removal Efficiency (%)
Nickel (Ni <sup>+</sup> ) <sup>1</sup>	9.8 ± 0.2	10	9.4	0.2	5
		60	8.2	0.5	17
		180	8.3	0.6	16
Cadmium (Cd <sup>+</sup> )	9.8 ± 0.2	10	3.2	0.1	68
		60	2.5	0.01	75
		180	2.0	0.04	80
Cesium (Cs <sup>+</sup> )	9.3 ± 0.1	10	0.30	0.01	97
		60	0.36	0.06	96
		180	0.30	0.009	97
Thallium (Tl <sup>+</sup> )	11 ± 3	10	0.38	0.02	96
		60	0.46	0.009	96
		180	0.44	0.01	96
Lead (Pb <sup>+</sup> ) <sup>2</sup>	9.7 ± 0.2	10	<LOQ	-	100
		60	<LOQ	-	100
		180	<LOQ	-	100

<sup>1</sup>No significant reduction; <sup>2</sup>For lead with concentrations of 10 ng·g<sup>-1</sup>, no uncertainty could be determined.

**Table 4.** Adsorption of studied heavy metal cations from single-element solutions with concentrations of 1000 ng·g<sup>-1</sup> onto PCT.

Heavy Metal Cation	Concentration [1000 ng·g <sup>-1</sup> ]				
	Initial Concentration [ng·g <sup>-1</sup> ]	Reaction Time [min]	Residual Concentration [ng·g <sup>-1</sup> ]	SD [ng·g <sup>-1</sup> ]	Removal Efficiency (%)
Nickel (Ni <sup>+</sup> ) <sup>1</sup>	1136 ± 28	10	853	12	25
		60	810	16	29
		180	865	54	24
Cadmium (Cd <sup>+</sup> )	963 ± 6	10	598	13	68
		60	468	7	75
		180	336	3	80
Cesium (Cs <sup>+</sup> )	998 ± 33	10	18	0.5	98
		60	23	0.9	98
		180	23	1	98
Barium (Ba <sup>+</sup> )	1078 ± 15	10	74	1	93
		60	28	1	97
		180	14	0.4	99
Thallium (Tl <sup>+</sup> )	1108 ± 210	10	36	0.4	97
		60	45	1	96
		180	44	0.8	96
Lead (Pb <sup>+</sup> )	1014 ± 16	10	50	4	95
		60	31	2	97
		180	22	5	98

<sup>1</sup>No significant reduction.



**Table 5.** Adsorption capacities, pH, and removal efficiencies for the adsorption of heavy metal ions by PCT for a contact time of 180 min for an amount of 0.2 g of sorbent.

Concentration [10 ng·g <sup>-1</sup> ]		
Heavy Metal Cation	pH	Adsorption Capacity [ng·g <sup>-1</sup> ]
Nickel (Ni <sup>+</sup> )	7.99	0.375
Cadmium (Cd <sup>+</sup> )	8.08	1.95
Cesium (Cs <sup>+</sup> )	8.02	2.24
Thallium (Tl <sup>+</sup> )	8.02	2.54
Lead (Pb <sup>+</sup> )	8.13	2.43
Concentration [1000 ng·g <sup>-1</sup> ]		
Heavy Metal Cation	pH	Adsorption Capacity [ng·g <sup>-1</sup> ]
Nickel (Ni <sup>+</sup> )	7.94	0.678
Cadmium (Cd <sup>+</sup> )	7.90	1.57
Cesium (Cs <sup>+</sup> )	7.97	2.44
Barium (Ba <sup>+</sup> )	8.08	2.66
Thallium (Tl <sup>+</sup> )	8.04	2.66
Lead (Pb <sup>+</sup> )	7.90	2.48

### 3. Results

#### 3.1. Characterization of Sorbent Materials

The XRD analyses (Figure 1) comprise the whole-rock mineral compositions of the tuffs. The main mineral is clinoptilolite (a heulandite-type zeolite), with cristobalite and feldspars in relatively small amounts, as well as accessory biotite and quartz in traces [18,25]. There is no sign of mineralogical difference between the tuffs. The non-purified clinoptilolite tuffs are distinguished and referred to as 'NPCT1' and 'NPCT2'.

From Table 2, it can be concluded that after the purification process of the PCT, a significant reduction in lead and barium occurred. Furthermore, for thallium, a decrease was found. The NPCTs clearly show more naturally bound barium, lead, and thallium than the PCT. For all three different tuffs and the raw material of the PCT, the cadmium content was below a concentration of 0.05 ng·g<sup>-1</sup>. The two NPCTs show very similar chemical compositions.

The lowest particle size of  $3.2 \pm 0.02 \mu\text{m}$  was determined for the PCT. Higher particle sizes of  $22 \pm 0.58 \mu\text{m}$  and  $7.6 \pm 0.11 \mu\text{m}$  were observed for NPCT1 and NPCT2, respectively.

#### 3.2. Adsorption from Single-Ion Solutions

The adsorption of monovalent heavy metal ions from aqueous media onto purified clinoptilolite tuff (PCT) was investigated for different reaction times. The concentrations of the single-ion solutions prepared were 10 ng·g<sup>-1</sup> and 1000 ng·g<sup>-1</sup> per heavy metal cation, except barium. For barium, adsorption was observed in 50 ng·g<sup>-1</sup> and 1000 ng·g<sup>-1</sup> stock solutions. Because it has the highest PMTDI value and is the least poisonous of the heavy metals (Table 1), higher concentrations were chosen.

pH values of the solutions were measured before and after being contacted with the tuffs. It was found that the pH increased during the experiments. Numbers on the pH values are given in Tables S1 and S2 in the Supplementary Materials.

Tables 3 and 4 summarize the initial and residual amounts of heavy metals in the solution for given reaction times, respectively.

These findings indicate that for each heavy metal, a different physical and chemical binding capacity towards the clinoptilolite tuff was found. Removal efficiencies were calculated taking into account the initial concentration at  $t = 0$  min and the remaining amount of heavy metals measured in the supernatant solutions each time samples were taken. In addition to these data, analytical uncertainties are also given in Tables 3, 4, and 6. Adsorption selectivity series for the removal of heavy metal ions at different times were determined following the results in Table 4 and are presented in Tables 7 and 8.

Adsorption capacities were calculated for every point in time samples were taken. These are shown in Table 5 for two stock solutions with concentrations of  $10 \text{ ng}\cdot\text{g}^{-1}$  and  $1000 \text{ ng}\cdot\text{g}^{-1}$ , respectively. These results are based on the findings shown in Tables 3 and 4.

**Table 6.** Adsorption of barium from a  $50 \text{ ng}\cdot\text{g}^{-1}$  stock solution onto PCT. The initial concentration was  $51.5 \pm 0.3 \text{ ng}\cdot\text{g}^{-1}$ .

Contact Time [min]	Concentration [ $50 \text{ ng}\cdot\text{g}^{-1}$ ]			
	Residual Concentration [ $\text{ng}\cdot\text{g}^{-1}$ ]	SD [ $\text{ng}\cdot\text{g}^{-1}$ ]	Removal Efficiency (%)	Adsorption Capacity [ $\text{ng}\cdot\text{g}^{-1}$ ]
10	2.7	0.09	95	
60	1.1	0.08	98	2.66
180	<LOQ	<LOQ	100	

**Table 7.** Adsorption selectivity series for the PCT from single-element solutions with a heavy metal content of  $1000 \text{ ng}\cdot\text{g}^{-1}$ .

Contact Time [min]	Adsorption Order
10	$\text{Cs}^+ > \text{Tl}^+ > \text{Pb}^+ > \text{Ba}^+ > \text{Cd}^+ > \text{Ni}^+$
60	$\text{Cs}^+ > \text{Ba}^+ \approx \text{Pb}^+ > \text{Tl}^+ > \text{Cd}^+ > \text{Ni}^+$
180	$\text{Ba}^+ > \text{Cs}^+ \approx \text{Pb}^+ > \text{Tl}^+ > \text{Cd}^+ > \text{Ni}^+$

**Table 8.** Adsorption selectivity series for PCT from single-element solutions with a heavy metal content of  $10 \text{ ng}\cdot\text{g}^{-1}$ .

Contact Time [min]	Adsorption Order
10	$\text{Pb}^+ > \text{Cs}^+ \approx \text{Tl}^+ > \text{Cd}^+ > \text{Ni}^+$
60	$\text{Pb}^+ > \text{Cs}^+ \approx \text{Tl}^+ > \text{Cd}^+ > \text{Ni}^+$
180	$\text{Pb}^+ > \text{Cs}^+ \approx \text{Tl}^+ > \text{Cd}^+ > \text{Ni}^+$

After a reaction time of 180 min, the removal efficiency for the adsorption of cesium in the stock solution with a concentration of  $1000 \text{ ng}\cdot\text{g}^{-1}$  was 98%.

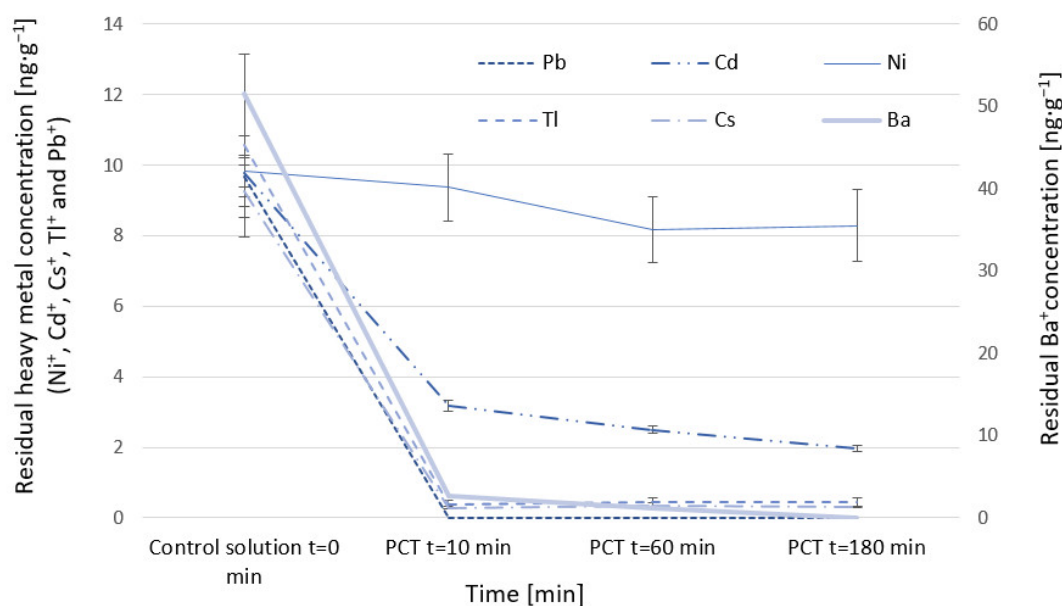
After 180 min, 97% of thallium and 95% of lead was adsorbed. The PCT showed lower affinities towards nickel and cadmium. 65% of cadmium and 24% of nickel were bound from the solution onto the tuff after 180 min reaction time. For cesium and thallium, the adsorption capacity did not increase with longer reaction times. The residual barium content in solution after 180 min was found to be below the limit of quantification.

After 10 min, the purified clinoptilolite tuff had already adsorbed 95% of lead from the solution. Equilibrium was attained. However, even higher uptake percentages of 97% and 98%, respectively, were achieved with longer incubation times (Table 4).

The highest uptake was achieved for barium: the residual barium amount in the solution was found below the limit of quantification (LOQ) after 180 min reaction time with the PCT (Table 6).

Figure 2 illustrates the adsorption behavior of the purified clinoptilolite tuff for different heavy metal cations.

For lead, the residual amount after 10 min reaction time was below the limit of quantification.



**Figure 2.** Adsorption kinetics of heavy metal ions onto purified clinoptilolite tuff (PCT) for concentrations of  $10 \text{ ng}\cdot\text{g}^{-1}$  for  $\text{Ni}^+$ ,  $\text{Cd}^+$ ,  $\text{Cs}^+$ ,  $\text{Tl}^+$  and  $\text{Pb}^+$  and  $50 \text{ ng}\cdot\text{g}^{-1}$  for  $\text{Ba}^+$ . For reaction times longer than 10 min, the lead content was below the limit of quantification (<LOQ). The figure is based on the data presented in Tables 3 and 4.

### 3.3. Adsorption and Release Experiments: Comparison of Purified and Non-Purified Clinoptilolite tuffs

#### 3.3.1. Adsorption and Release of Heavy Metal Ions from Contaminated Non-Carbonated Mineral Water

In order to survey whether heavy metal ions, previously adsorbed by the tuffs, are released again, adsorption/release experiments were performed.

pH values of the solutions were determined before and after contact with the adsorbent materials.

To compare and comprehend adsorption behavior of different adsorbent tuffs, their particle sizes and cation exchange capacities (CEC) were determined.

A particle size of  $3.2 \pm 0.01 \mu\text{m}$  was observed for the PCT,  $22 \pm 0.58 \mu\text{m}$  for NPCT1, and  $7.6 \pm 0.11 \mu\text{m}$  for NPCT2. CEC values of  $0.97 \text{ mol}\cdot\text{kg}^{-1}$  for the PCT,  $0.65 \text{ mol}\cdot\text{kg}^{-1}$  for NPCT1, and  $0.89 \text{ mol}\cdot\text{kg}^{-1}$  for NPCT2 were measured (Table 2).

The pH of the blank solution (non-carbonated mineral water) was 7.56 at the beginning of the experiment ( $t = 0 \text{ min}$ ). After 180 min, the pH increased to 7.68. Measurements of the pH for  $t = 180 \text{ min}$  were carried out in triplicates. Average numbers and standard deviations are reported in Table S3 in the Supplementary Materials. Exact numbers for the pH can be found in Table S1 in the Supplementary Materials.

The heavy metal amount in the solutions before and after adding the tuffs was measured. Adsorption of heavy metal cations from aqueous, heavy-metal-spiked solutions was noted. The residual amounts of heavy metal cations in the solution are reported in Tables 9–11 for each tuff. Resulting from these numbers, removal percentages were calculated, taking into account the initial concentrations and the final concentrations.

As control solution, non-carbonated mineral water was used.

**Table 9.** Adsorption kinetics of studied heavy metal cations from heavy-metal-contaminated non-carbonated mineral water onto PCT.

Heavy Metal Cation	Initial Concentration [ng·g <sup>-1</sup> ]	Reaction Time [min]	Residual Concentration [ng·g <sup>-1</sup> ]	SD [ng·g <sup>-1</sup> ]	Removal Efficiency (%)
Nickel (Ni <sup>+</sup> ) <sup>1</sup>	13.3 ± 0.40	10	14	2	-
		60	15	2	-
		180	13	0.3	-
Cadmium (Cd <sup>+</sup> )	11.9 ± 0.16	10	6.0	0.03	50
		60	4.9	0.1	59
		180	3.9	0.1	67
Cesium (Cs <sup>+</sup> )	2.95 ± 0.038	10	0.11	0.03	96
		60	0.21	0.04	93
		180	0.16	0.01	95
Barium (Ba <sup>+</sup> )	48.5 ± 0.66	10	3.2	0.2	93
		60	3.8	0.6	92
		180	0.53	0.05	99
Thallium (Tl <sup>+</sup> )	3.96 ± 0.086	10	0.15	0.003	96
		60	0.25	0.07	94
		180	0.19	0.01	95
Lead (Pb <sup>+</sup> )	267 ± 4.0	10	5.1	0.9	98
		60	7.3	2	97
		180	2.3	0.4	99

<sup>1</sup>No significant reduction.**Table 10.** Adsorption kinetics of studied heavy metal cations from heavy-metal-contaminated non-carbonated mineral water onto NPCT1.

Heavy Metal Cation	Initial Concentration [ng·g <sup>-1</sup> ]	Reaction Time [min]	Residual Concentration [ng·g <sup>-1</sup> ]	SD [ng·g <sup>-1</sup> ]	Removal Efficiency (%)
Nickel (Ni <sup>+</sup> ) <sup>1</sup>	13.3 ± 0.40	10	13	0.2	/
		60	14	0.3	/
		180	14	0.9	/
Cadmium (Cd <sup>+</sup> )	11.9 ± 0.16	10	9.6	0.2	19
		60	9.4	0.3	21
		180	8.2	0.3	31
Cesium (Cs <sup>+</sup> )	2.95 ± 0.038	10	0.23	0.001	92
		60	0.24	0.02	92
		180	0.25	0.02	92
Barium (Ba <sup>+</sup> )	48.5 ± 0.66	10	22	2	55
		60	16	0.9	67
		180	13	0.2	74
Thallium (Tl <sup>+</sup> )	3.96 ± 0.086	10	0.23	0.009	94
		60	0.22	0.01	95
		180	0.23	0.008	94
Lead (Pb <sup>+</sup> )	267 ± 4.0	10	27	3	90
		60	17	2	99
		180	10	1	96

<sup>1</sup>No significant reduction.

**Table 11.** Adsorption kinetics of different heavy metal cations from heavy-metal-contaminated non-carbonated mineral water onto NPCT2.

Heavy Metal Cation	Initial Concentration [ng·g <sup>-1</sup> ]	Reaction Time [min]	Residual Concentration [ng·g <sup>-1</sup> ]	SD [ng·g <sup>-1</sup> ]	Removal Efficiency (%)
Nickel (Ni <sup>+</sup> ) <sup>1</sup>	13.3 ± 0.40	10	13	0.6	-
		60	13	0.4	-
		180	13	0.3	-
Cadmium (Cd <sup>+</sup> )	11.9 ± 0.16	10	7.5	0.2	37
		60	6.5	0.1	46
		180	5.4	0.06	55
Cesium (Cs <sup>+</sup> )	2.95 ± 0.038	10	0.089	0.002	97
		60	0.15	0.001	95
		180	0.27	0.02	91
Barium (Ba <sup>+</sup> )	48.5 ± 0.66	10	7.8	0.05	84
		60	6.5	0.4	87
		180	15	2	70
Thallium (Tl <sup>+</sup> )	3.96 ± 0.086	10	0.068	0.006	98
		60	0.11	0.004	97
		180	0.15	0.009	96
Lead (Pb <sup>+</sup> )	267 ± 4.0	10	4.6	0.07	98
		60	3.2	0.2	99
		180	5.0	2	98

<sup>1</sup>No significant reduction.

The results show that as far as the PCT in multi-element solutions is concerned, the highest affinity was found for lead (Pb<sup>+</sup>). A maximum removal efficiency of 99% was achieved after 180 min reaction time. The NPCTs showed similar results: after 180 min, 96% and 98% of the lead content was removed by NPCT1 and NPCT2, respectively.

Furthermore, it was found that longer incubation times lead to increased heavy metal uptake from the test matrices. However, 10 min after the start, the largest part of lead is adsorbed.

The most efficient adsorption for thallium was found with NPCT2. A removal percentage of 98% was obtained after 10 min reaction time.

For PCT and NPCT1, longer contact times did not lead to an improvement in the uptake of thallium from the solution.

Cesium adsorption kinetics revealed that the percentage of metals removed from the solution by NPCT1 decreased with longer incubation times. It is thus assumed that neither NPCT would bind cesium stably over the duration of the experiment. The uptake of cesium by the PCT and NPCT1 remained constant, with 95% and 92%, respectively, found to be removed after 180 min contact time with each tuff.

When it comes to barium, the greatest removal was achieved with the PCT. A 99% reduction in metal content in solution was achieved with the PCT after 180 min reaction time.

Lower affinities were noticed for cadmium concerning all three tuffs. A maximum removal efficiency of 67% with the PCT was obtained, whereas for NPCT1 and NPCT2, percentage uptakes of 31% and 55%, respectively, were found after 180 min reaction time.

No significant adsorption of nickel was found for either of the adsorbents.

From the results, it becomes clear that all the tuffs showed great affinity towards lead. This effect will be elaborated in the discussion section.

Compared with NPCT1, the PCT showed higher affinity towards the studied target species. PCT and NPCT2 showed similar results for the adsorption of thallium, lead, and cesium. For these heavy metal cations, the highest removal efficiencies were found to be 99% and 98%, respectively.

Overall, in this experiment, the PCT and NPCT2 showed better removal efficiencies than NPCT1.

### 3.3.2. Adsorption and Release Characteristics of Heavy Metal Ions in Non-Contaminated Non-Carbonated Mineral Water

Whether or not heavy metals are adsorbed and/or released by the tuff in non-carbonated mineral water with only low heavy metal concentrations was examined. Therefore, experiments as described in Section 2.3.2 were carried out.

Adsorption for the metal ions of cesium, barium, and thallium was found.

For lead, cadmium, and nickel, no results could be obtained. The concentration of these cations in the non-spiked non-carbonated mineral water was below the limit of quantification of  $0.44 \text{ ng}\cdot\text{g}^{-1}$  for lead,  $11 \text{ ng}\cdot\text{g}^{-1}$  for nickel, and  $0.05 \text{ ng}\cdot\text{g}^{-1}$  for cadmium.

For the matrix (non-carbonated mineral water), pH values were determined before being contacted with the tuffs. Its initial pH was 7.34 and increased to 7.59 after 180 min reaction time.

The tuffs were compared regarding their adsorption behavior with respect to the target metals. Removal efficiencies were calculated and are given in Tables 12–14 for the PCT and the NPCTs.

The experimental results revealed that none of the observed heavy metals ( $\text{Ni}^+$ ,  $\text{Cd}^+$ ,  $\text{Cs}^+$ ,  $\text{Ba}^+$ ,  $\text{Tl}^+$ , and  $\text{Pb}^+$ ) were released.

The average pH values and standard deviations for the matrix components are given in Table S4 in the Supplementary Materials.

**Table 12.** Adsorption kinetics of different heavy metal cations for the PCT in non-contaminated non-carbonated mineral water.

Heavy Metal Cation	Initial Concentration [ $\text{ng}\cdot\text{g}^{-1}$ ]	Reaction Time [min]	Residual Concentration [ $\text{ng}\cdot\text{g}^{-1}$ ]	SD [ $\text{ng}\cdot\text{g}^{-1}$ ]	Removal Efficiency (%)
Cesium ( $\text{Cs}^+$ )	$0.31 \pm 0.001$	10	0.067	0.02	71
		60	0.066	0.001	79
		180	0.091	0.005	79
Barium ( $\text{Ba}^+$ )	$35 \pm 0.2$	10	2.4	0.4	99
		60	0.91	0.2	97
		180	0.38	0.01	99
Thallium ( $\text{Tl}^+$ )	$0.38 \pm 0.02$	10	0.023	0.002	94
		60	0.023	0.0007	89
		180	0.021	0.001	92

**Table 13.** Adsorption kinetics of different heavy metal cations for NPCT1 in non-contaminated non-carbonated mineral water.

Heavy Metal Cation	Initial Concentration [ $\text{ng}\cdot\text{g}^{-1}$ ]	Reaction Time [min]	Residual Concentration [ $\text{ng}\cdot\text{g}^{-1}$ ]	SD [ $\text{ng}\cdot\text{g}^{-1}$ ]	Removal Efficiency (%)
Cesium ( $\text{Cs}^+$ )	$0.31 \pm 0.001$	10	0.14	0.01	39
		60	0.15	0.01	53
		180	0.19	0.01	55
Barium ( $\text{Ba}^+$ )	$35 \pm 0.2$	10	17	0.8	64
		60	13	1	64
		180	13	0.6	53
Thallium ( $\text{Tl}^+$ )	$0.38 \pm 0.02$	10	0.043	0.005	90
		60	0.048	0.004	87
		180	0.039	0.03	89

**Table 14.** Adsorption kinetics of different heavy metal cations for NPCT2 in non-contaminated non-carbonated mineral water.

Heavy Metal Cation	Initial Concentration [ng·g <sup>-1</sup> ]	Reaction Time [min]	Residual Concentration [ng·g <sup>-1</sup> ]	SD [ng·g <sup>-1</sup> ]	Removal Efficiency (%)
Cesium (Cs <sup>+</sup> )	0.31 ± 0.001	10	0.083	0.006	46
		60	0.13	0.0007	60
		180	0.17	0.02	74
Barium (Ba <sup>+</sup> )	35 ± 0.2	10	7.2	0.3	79
		60	6.9	0.3	81
		180	7.5	2	80
Thallium (Tl <sup>+</sup> )	0.38 ± 0.02	10	0.014	0.005	85
		60	0.025	0.001	93
		180	0.058	0.005	96

About 79% of the cesium in solution was removed by the PCT after 180 min reaction time (Table 12). NPCT1 would bind 55% of the metal ions after the same amount of time (Table 13), and NPCT2 showed a removal efficiency of 74% for cesium ions in solution with other ions (Table 14). Longer reaction times did not lead to a significant increase in the removal efficiency for either of the observed adsorbents.

Great efficiency in the removal of barium ions from the non-carbonated mineral water by the PCT was observed. The maximum removal efficiency of barium was found to be 99% after 180 min reaction time (Table 12). Less affinity towards barium was observed with the NPCTs. About 60% and 80%, respectively, of the barium metal content were adsorbed by the non-purified tuffs.

After only 10 min, 94% of thallium in the solution was adsorbed. The NPCTs showed removal efficiencies of 89% and 92%, respectively. With longer incubation times, no change in the removal efficiency was observed.

In general, the PCT showed higher affinities towards the target heavy metal ions than NPCT1/2.

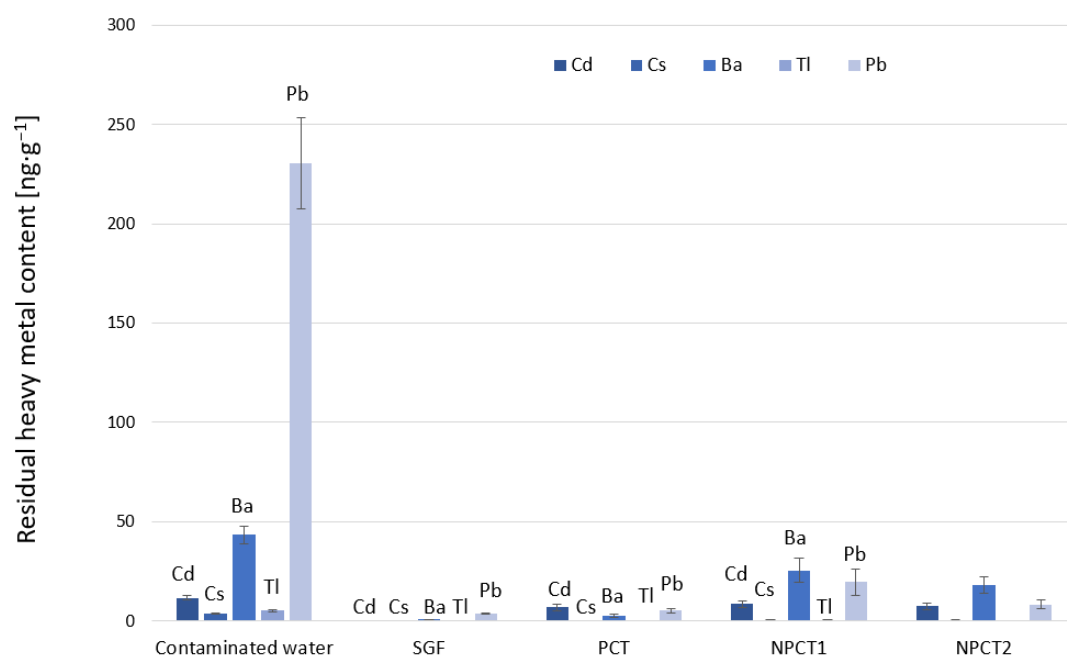
### 3.3.3. Adsorption and Release Characteristics of Heavy Metal Ions from Artificial Gastric Fluids

This experiment served to answer the question of whether heavy metals can be bound from contaminated non-carbonated mineral water mixed with synthetic gastric fluids (SGF) by the clinoptilolite tuffs, thus preventing intoxication of the human body. The experiment was performed in two steps. In the first step, adsorption/release in contaminated non-carbonated mineral water mixed with synthetic gastric fluids (with heavy-metal-spiked non-carbonated mineral water) was examined (Tables S5–S7 in the Supplementary Materials). In the second part of the experiment, adsorption/release of metals from the tuffs was investigated in synthetic intestinal fluids (SIF). The tuffs were incubated with the SIF, in order to investigate whether heavy metals previously bound onto the tuff are released again into solution during artificial digestion.

The pH of the test matrix was measured before incubation with the tuffs. The pH of the SGF was measured at the beginning and at the end of the experiment. Before contacting the solution with the tuffs, a pH value of  $6.57 \pm 0.0056$  was determined.

The pH values of the solutions after 180 min reaction time with the tuffs are summarized in Table S8 in the Supplementary Materials. The heavy metal content of the SGF is given in Table S9 in the Supplementary Materials.

Figure 3 demonstrates the adsorption of heavy metal cations from the SGF mixed with contaminated non-carbonated mineral water onto PCT, NPCT1, and NPCT2.



**Figure 3.** Adsorption of heavy metal ions from SGF onto PCT and NPCTs after 20 min contact time. The figure is based on data from Tables S5–S7 in the Supplementary Materials.

From Figure 3, it becomes evident that all tuffs did adsorb heavy metals from the contaminated non-carbonated mineral water mixed with the SGF.

The results indicate that the strongest adsorption took place for lead and thallium, followed by cesium. The adsorbent tuffs showed the greatest affinity towards lead. As already seen in the experiment with adsorption from single-ion solutions (Figure 2), no adsorption for nickel was observed.

### 3.3.4. Adsorption and Release Characteristics of Heavy Metal Ions in Artificial Intestinal Fluids Regarding the Three Single Tuffs

After the adsorption in synthetic gastric fluids, release of the various heavy metals into synthetic intestinal fluids was observed. As no significant adsorption took place with nickel and cadmium, these two heavy metal cations were no longer considered in the release experiments.

Results on the adsorption/release of heavy metals in the SIF onto the PCT and NPCTs are given in Tables S10–S12 in the Supplementary Materials and illustrated by Figure 4.

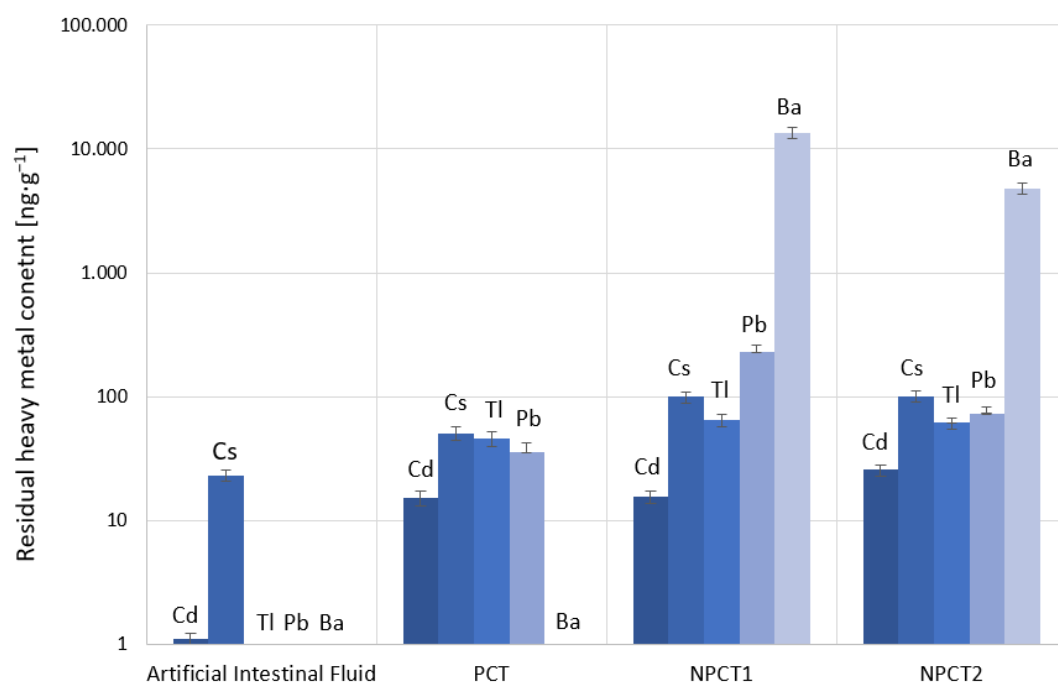
Prior to the experiments, the pH of the synthesized intestinal fluid was measured and is summarized in Table S13 in the Supplementary Materials. The pH values for the test matrices contacted with tuffs (before and after 180 min contact time) and the SIF are also given in Table S13 in the Supplementary Materials.

The SIF served as control solution.

The test matrices (pure SGF and SIF) were analyzed before the adsorbents were added. The concentrations of barium, lead, and cadmium in the pure artificial intestinal fluids were below the limits of quantification of  $6.5 \times 10^{-5} \mu\text{g}\cdot\text{g}^{-1}$ ,  $1.1 \times 10^{-1} \text{ng}\cdot\text{g}^{-1}$ , and  $1.1 \times 10^{-2} \text{ng}\cdot\text{g}^{-1}$ , respectively.

After mixing the solution with the tuffs, which had adsorbed the heavy metals before, and incubating the compounds for 180 min, the heavy metal content was again measured. The experimental results revealed that all tuffs released lead into the solution. The concentration of lead in the solution incubated with PCT was  $36 \text{ng}\cdot\text{g}^{-1}$ . For NPCT1/NPCT2, the release of lead was remarkably higher, with concentrations of  $227 \text{ng}\cdot\text{g}^{-1}$  and  $73 \text{ng}\cdot\text{g}^{-1}$ , respectively.





**Figure 4.** Adsorption/release of heavy metal ions in SIF from the PCT, NPCT1, and NPCT2 (log-scale). The figure is based on data from Tables S10–S12 in the Supplementary Materials.

Also for thallium, the initially measured concentration was below the limit of quantification of  $2.1 \times 10^{-3} \text{ ng}\cdot\text{g}^{-1}$ . Concentrations of  $46 \text{ ng}\cdot\text{g}^{-1}$ ,  $65 \text{ ng}\cdot\text{g}^{-1}$ , and  $61 \text{ ng}\cdot\text{g}^{-1}$  could be determined after reaction time with PCT, NPCT1, and NPCT2, respectively.

The amount of barium released by the PCT after 180 min reaction time remained below the detection limit. After contacting the solutions with the NPCTs, however, concentrations of  $13574 \text{ ng}\cdot\text{g}^{-1}$  and  $4839 \text{ ng}\cdot\text{g}^{-1}$ , respectively, were measured.

In the control solution (SIF), a concentration of  $23 \text{ ng}\cdot\text{g}^{-1}$  for cesium was determined. After a reaction time of 180 min with the PCT,  $51 \text{ ng}\cdot\text{g}^{-1}$  were found. NPCT1/2 revealed concentrations of  $99 \text{ ng}\cdot\text{g}^{-1}$  and  $100 \text{ ng}\cdot\text{g}^{-1}$ , respectively, which are almost twice as high as observed for the PCT after 180 min contact duration.

For nickel and cadmium, no significant adsorption was observed in the first part of the experiment. Hence, no release of any of these metals could subsequently be observed (Tables S5–S7 in the Supplementary Materials).

#### 4. Discussion

The present study aims to assess the adsorption behavior of clinoptilolite tuffs for various, health-relevant heavy metal cations from aqueous media.

For adsorption from single-ion solutions with concentrations of  $10 \text{ ng}\cdot\text{g}^{-1}$  onto the PCT, highest removal was achieved with lead (100%) and cesium (97%). In a solution of  $1000 \text{ ng}\cdot\text{g}^{-1}$ , removal efficiencies for cesium, barium, thallium, and lead were very similar. The measurable amount of barium was removed from the solution of initially  $50 \text{ ng}\cdot\text{g}^{-1}$  by the PCT after 180 min contact time, proving high affinity of the tuffs towards this element.

In comparison with the NPCTs, better removal efficiencies were obtained with the PCT in the uptake experiments in multi-element solutions. During the release experiments, lower heavy metal amounts were found to be released by the PCT into the SIF. It was observed that each of the adsorbing tuffs released cesium in the synthetic intestinal fluids. Exchange of cesium for potassium in the intestinal fluid was noticed in the supernatant, due to the high concentration of potassium in the SIF [28]. Furthermore, as the results show, far more barium and lead were released by the NPCTs than by the PCT. Since the raw materials are compositionally similar, the reason for the higher

performance has to be owed to the purification process the PCT went through. During that process, the naturally bound metals are removed, and free crystal-lattice positions are created. The data indicate that pre-conditioning of zeolites leads to an enhanced performance.

Heavy metal ions can be immobilized on zeolites by two different mechanisms: ion exchange and chemisorption. However, ion exchange generally dominates chemisorption and occurs through substitution of ions in the zeolite by metal cations from the solution, whereas chemisorption results in the formation of inner-sphere complexes with the metals. The ion exchange efficiency is determined by the type of cation (affinity) and the cation concentration in the solution [29,30].

The process of adsorption is furthermore affected by experimental conditions, such as temperature, pH, solid/liquid ratio, and the concentration of ions in solution, that may influence the binding efficiency. Exchange capacities also depend on the crystal structure, chemistry of sorbents, and the particle size: the smaller the particle and therefore higher the surface area, the higher the exchange capacity [30,31]. This is also in conformity with the findings of this study. Zeolite particles provide a highly reactive surface for sorption of heavy metals [1].

Mihaly-Cozmata et al. [32] found that zeolites have higher preference for  $Pb^{2+}$  than for  $Cd^{2+}$  and  $Ni^{2+}$ , which resembles the findings in this study. They suggested this happens because  $Pb^{2+}$  shows lower hydration radius, lower dehydration energy, and higher mobility than the other heavy metals. In solution, ions are in hydrated forms. The radius of the hydrated form depends on the dehydrated ionic radius and the electric charge of ions. This greatly affects the mobility of ions and the adsorption onto the zeolite surface.

According to Liu et al. [21] polarization effects also contribute to adsorption properties. Polarization occurs in an electric field, generated by tuffs with their negatively charged surface, which is related to its Si/Al ratio [20]. In an electric field, cations are differently polarized. Cesium, barium, and lead, as reported by Liu [21], represent metals with large polarizability due to their size and are thus preferably adsorbed by zeolites. Steric factors also contribute to adsorption affinities, leading to different degrees in adsorption for various cations. Heavy metals are generally bound on the surface rather than on the inside because of their size [33–36].

Similar results concerning the adsorption of heavy metal cations and resulting selectivity order for divalent cations are demonstrated by Qiu et al. [37]. Their results revealed the strongest adsorption for lead cations onto zeolitic minerals. Panayotova et al. [29] described selectivity series for uptake from both single- and mixed-element solutions for bivalent heavy metal ions. In both cases, the highest adsorption was found for  $Pb^{2+}$ .

Only recently, Samekova et al. [34] were able to prove the efficiency of the PCT to prevent enteral lead uptake. A significant reduction in lead concentrations in the blood of the study's participants after consumption of the PCT through heavy metal adsorption was examined.

The binding of radioactive metals onto zeolitic minerals from different deposits, Nižný Hrabovec (Slovakia) and Metaphysxedes (Greece), was studied by Rajec et al. [38] using batch techniques. They reported a very efficient uptake of cesium and lead.

As mentioned above, pH is an influential factor in the adsorption process. At low pH, high concentrations of  $H^+$  ions are available in the solution, which might be bound onto the tuff and thus block adsorption sites for competing cations [39]. During the experiments, pH values changed. At the beginning of the experiments, values measured were slightly lower than at the end. It is assumed that natural  $CO_2$ , which is contained in the non-carbonated mineral water, would come off the solution after warming up (to 37 °C). After vaporization of  $CO_2$  (dissolved in water as carbonic acid) the solution's pH becomes more basic. Solubility of  $CO_2$  in water increases with increasing temperature. Solvated  $CO_2$  reduces a solution's pH due to the formation of carbonic acid [40,41].

## 5. Conclusions

Two non-purified clinoptilolite tuffs (NPCT) and one purified clinoptilolite tuff (PCT) were studied in order to investigate adsorption of health-relevant heavy metal cations from aqueous solutions.

No significant adsorption took place for nickel, and the lowest adsorption was found for cadmium in all of the solutions (with different concentrations) for each of the tuffs.

In single-element solutions mixed with the PCT, highest sorption capacities were found for lead (100% and 98%), cesium (97% and 98%), and thallium (96% and 96%) for concentrations of both  $10 \text{ ng}\cdot\text{g}^{-1}$  and  $1000 \text{ ng}\cdot\text{g}^{-1}$ , respectively. Furthermore, high removal efficiencies (100% and 99%) were found for barium in single-element solutions of  $50 \text{ ng}\cdot\text{g}^{-1}$  and  $1000 \text{ ng}\cdot\text{g}^{-1}$ , respectively.

The adsorption order for removal in  $1000 \text{ ng}\cdot\text{g}^{-1}$  solutions after 180 min was determined as follows:  $\text{Ba}^+ > \text{Cs}^+ \approx \text{Pb}^+ > \text{Tl}^+ > \text{Cd}^+ > \text{Ni}^+$ .

In non-contaminated non-carbonated mineral water, the elements  $\text{Cs}^+$ ,  $\text{Ba}^+$ , and  $\text{Tl}^+$  were investigated, whereby it was found that the PCT showed significantly higher removal efficiencies for  $\text{Cs}^+$ ,  $\text{Ba}^+$ , and  $\text{Tl}^+$  of 79%, 99%, and 92%, respectively, than the tuffs compared.

In contaminated multi-element solutions mixed with the synthetic gastric fluids, highest affinity of the PCT was observed for  $\text{Pb}^+$ , with 99% removal after 20 min. Lower removal percentages of 91% and 96% were obtained for the NPCT1 and the NPCT2, respectively.

Remarkably, the experiments demonstrate that  $\text{Pb}^+$  was again released in the SIF from the NPCTs in significantly higher amounts than from the PCT ( $227 \text{ ng}\cdot\text{g}^{-1}$  for the NPCT1 and  $73 \text{ ng}\cdot\text{g}^{-1}$  for the NPCT2). After incubation of the tuff with the PCT, no barium could have been detected in the solution, whereas high barium concentrations of  $13574 \text{ ng}\cdot\text{g}^{-1}$  and  $4839 \text{ ng}\cdot\text{g}^{-1}$  were measured in the solutions incubated with NPCT1 and NPCT2, respectively. This indicates that preconditioning and purifying such materials is an essential manufacturing step for products with intended use in human consumption, as it increases not only the sorption capacity but also the sorption strength.

**Supplementary Materials:** The following are available online at [www.mdpi.com/article/10.3390/cryst11111343/s1](http://www.mdpi.com/article/10.3390/cryst11111343/s1), Table S1: Data of pH values and standard deviations before and after the adsorption experiments in single-ion solutions with concentrations of  $10 \text{ ng}\cdot\text{g}^{-1}$  for  $\text{Ni}^+$ ,  $\text{Cd}^+$ ,  $\text{Cs}^+$ ,  $\text{Tl}^+$ , and  $\text{Pb}^+$  and  $50 \text{ ng}\cdot\text{g}^{-1}$  for  $\text{Ba}^+$ , Table S2: Data of pH values and standard deviations before and after the adsorption experiments in single-ion solutions with concentrations of  $1000 \text{ ng}\cdot\text{g}^{-1}$  for all studied heavy metals, Table S3: Average pH values and standard deviations of the supernatant solutions after contact with the PCT and NPCTs after 180 min reaction time in contaminated non-carbonated mineral water, Table S4: Average pH values and standard deviations for non-contaminated non-carbonated mineral water after contact with the tuffs after 180 min reaction time, Table S5: Adsorption/release of different heavy metal cations from SGF mixed with contaminated non-carbonated mineral water from the PCT, Table S6: Adsorption/release of different heavy metal cations from SGF mixed with contaminated non-carbonated mineral water from the NPCT1, Table S7: Adsorption/release of different heavy metal cations from SGF mixed with contaminated non-carbonated mineral water from the NPCT2, Table S8: Average pH values and standard deviations of synthetic gastric fluids mixed with contaminated non-carbonated mineral water, contacted with PCT and NPCTs after 180 min reaction time. Synthetic gastric fluid served as control solution, Table S9: Heavy metal content of the SGF, Table S10: Adsorption/release of different heavy metal cations from SIF onto the PCT, Table S11: Adsorption/release of different heavy metal cations from SIF onto the NPCT1, Table S12: Adsorption/release of different heavy metal cations from SIF onto the NPCT2, Table S13: Average pH values and standard deviations of the PCT, NPCT1 and NPCT2 after 180 min reaction time in SIF. The artificial intestinal fluid served as control solution.

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