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Evaluation of Factors Influencing Lab-Scale Studies to Determine Heavy Metal Removal by Six Sorbents for Stormwater Treatment

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Abstract: For the development of decentralized treatment systems for road runoff, the determination of pollutant removal capacities is essential. The aim of this study was to evaluate the impact of boundary conditions on the simultaneous removal of copper, nickel, and zinc by six sorbents used for urban stormwater treatment (*i.e.*, granular activated alumina, anthracite, granular reactivated carbon, granular ferric hydroxide, calcium carbonate, and granular activated lignite). For batch experiments, capacities were determined at initial concentrations within the range of 2.5–180 mg/L with a rotary shaker. Further influences were investigated: the use of a horizontal shaker for concentrations of up to 1080 mg/L, a variation of the initial pH value (5 and 7), and the presence of a buffer. Furthermore, the influences of the filtration process on the capacities were studied. Kinetic experiments were conducted for contact times between 5 min and 120 min. Lab-scale column experiments with inflow concentrations of 2.5 mg/L (copper and nickel) and 5.0 mg/L (zinc) at an initial pH of 5 and a contact time of 11 min were performed for comparison. Selected experiments were subsequently carried out with changes in initial concentrations and contact time. One result is that it is essential to conduct batch experiments with the metals of interest. The capacities determined by column experiments deviated from batch experiments. Batch experiments under well-defined conditions can be used to evaluate different production batches. Column experiments give a more faithful capacity by considering realistic boundary conditions and should be preferred to determine efficiencies and service lives.

Keywords: batch experiments; column experiments; filter material; filtration; ion exchange; ionic strength; kinetics; pH value; sorption; urban stormwater management

1. Introduction

Metals such as arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), nickel (Ni), and zinc (Zn) are crucial pollutants because of their toxicity, lack of degradability, and their ubiquitous presence in the environment as a consequence of their industrial use [1–3]. Among these metals, the last four elements occur in highest concentrations in highway runoff [4,5]. Pb concentrations have decreased significantly in all traffic area runoff waters in the last few decades because of the phase-out of leaded gasoline and the substitution of Pb in other traffic-related sources. Thus, Cu, Ni, and Zn are, nowadays, measured in the highest runoff concentrations (maxima of mean concentrations per monitored site for the 21st century: 682 µg/L Cu, 458 µg/L Ni, and 2560 µg/L Zn—calculated from the worldwide data presented in [5]). These three heavy metals tend to be less particle-bound

than other heavy metals such as Pb [6,7]. Sources of Cu in runoff water are brake linings [3,8], metal platings, moving engine parts [9], and pesticides applied to road medians [10]. Ni is present in diesel fuel [1], Ni-Cd batteries, stainless steel, and other electronic equipment [11]. The following are products containing Zn: batteries [12], brake linings [13], galvanized car parts [14], motor oils and grease [9], safety fences [15], and tires [16,17]. Furthermore, Cu and Zn show high accumulation potentials, biochemical activities, lifetimes, and solubility; Ni also has a high biochemical activity and lifetime [1].

To retain these heavy metals from traffic area runoff, decentralized stormwater treatment systems are used, which can be designed as an integral part of existing urban infrastructure [18]. Sedimentation and filtration are the retention mechanisms used to remove particle-bound metals. Dissolved heavy metals were retained on filter materials by sorption, ion exchange, and precipitation. To reduce particulate loadings for the filter materials, pretreatment ahead of the filter is required [19]. Both mechanical and chemical steps are necessary to sufficiently reduce dissolved and total metal concentrations [20,21]. Laboratory studies of the filter materials are necessary to develop new treatment systems, to control and optimize existing ones, and to determine application areas and service lives.

In the past, several types of laboratory studies have been conducted to evaluate different filter materials for stormwater treatment. Concerning the determination of cation exchange capacities, metals such as barium and magnesium are sometimes used as surrogates for the removal of heavy metals in time-efficient one-step methods [22]. In equilibrium batch experiments (48 h), the simultaneous removal of As, Cd, Cr, Cu, Ni, and Zn from stormwater was investigated by Genç-Fuhrman *et al.* [23] for eleven different sorbents with eight different initial metal concentrations. An equilibrium batch setup was also used by Wu and Zhou [24] to determine the simultaneous removal of the same six metals with eleven different initial concentrations on granular ferric hydroxide and its mixtures with zeolite and crystal gravel. Liu *et al.* [25] used manganese oxide coated polymeric media to evaluate the removal of Cd, Cu, Pb, and Zn in a recirculating flow-through reactor. In contrast to the static nature of batch experiments and their tendency to reach equilibrium, column experiments can help to assess the behavior of large-scale treatment systems with continuous influent concentrations, specific empty bed contact time (EBCT), and individual influent flow-rates [26]. Therefore, lab-scale column tests, which are less time-consuming and need smaller volumes of stock solution compared with pilot-scale experiments, can be used as an approach to evaluate the performance of sorbents at a small scale [27]. To evaluate filter materials for the removal of heavy metals, Li and Helmreich [28] conducted lab-scale column experiments with granular activated carbon and lignite to determine the removal of Zn. Liu *et al.* [19] used conventional and engineered media to evaluate the removal of Cd, Cu, Pb, and Zn (*i.e.*, silica sand, granular activated carbon, cementitious media, manganese oxide coated media, and other coated media).

However, a standardized protocol to compare filter materials for stormwater treatment systems for both batch and column experiments is missing. Therefore, the hypothesis of this study is that the results of batch- and lab-scale column experiments concerning simultaneous heavy metal removal differ widely because of varying boundary conditions.

The research objectives of this study were to identify relevant boundary conditions concerning the simultaneous removal of Cu, Ni, and Zn and the evaluation of important influencing factors by testing six sorbents with different removal mechanisms. By adjusting and standardizing these boundary conditions, an optimal use of the lab experiments can be achieved for their practical application in the field of stormwater treatment (e.g., type and amount of sorbent, removal efficiencies, ratio of drainage area to filter area, or service life). All of the materials used for this study were relatively coarse (main particle size 1.0–2.0 mm) to secure high permeability during service life and to prevent clogging of the filter. Furthermore, different production batches were evaluated to determine the use of batch experiments with well-defined methods for internal and external quality control.

2. Materials and Methods

2.1. Sorbents and Chemicals

The sorbents used were: granular activated alumina (alumina, Albemarle Corporation, Baton Rouge, LA, USA), anthracite (anthracite, EVERS GmbH & Co. KG, Hopsten, Germany), granular reactivated carbon (GAC, Chemviron Carbon GmbH, Beverungen, Germany), granular ferric hydroxide (GFH, HeGo Biotec GmbH, Berlin, Germany), calcium carbonate (calcium carbonate, Adolf Steinbach Steinindustrie-Schotterwerke GmbH & Co. KG, Bad Neustadt an der Saale, Germany), and granular activated lignite (lignite, Rheinbraun Brennstoff GmbH, Frechen, Germany). The physical characteristics of the sorbents, which were all commercially supplied, are provided in Table 1. Filter materials that retain heavy metals only by ion exchange and that can be improved or regenerated by sodium chloride (e.g., zeolites) [29,30] were not used in this study because they do not fulfill the requirements of a reliable heavy metal removal from traffic area runoff waters containing de-icing salts. All sorbents were sieved to a similar size fraction of 0.5–2.0 mm to avoid the influence of different size fractions of each sorbent on the retention of heavy metals [25,31]. The chosen size fraction (main particle size 1.0–2.0 mm) also fulfills the requirements of technical decentralized treatment systems (*i.e.*, permeability and filtration of particles). The sieved materials were subsequently dried at 105 ± 2 °C to achieve a constant weight, and finally stored in desiccators without additional treatment until usage.

Table 1. Physical characteristics of sorbents (based on dry mass).

Filter Material	Surface Area m ² /g	TC %	TS %	Al mg/kg	Ca mg/kg	Fe mg/kg	Mn mg/kg	Cu mg/kg	Ni mg/kg	Zn mg/kg
Alumina	263	-	-	462000	87.6	1270	7.43	18.6	1.98	9.11
Anthracite	1.4	88.2	0.91	931	1010	2260	20.5	16.0	2.57	1.56
Calcium carbonate	3.1	-	-	3520	318500	4370	78.7	3.50	2.91	5.04
GAC	896	91.6	0.83	6300	3050	3260	61.8	458	28.4	7.92
GFH	224	-	-	753	56300	431000	9090	2.00	41.3	87.6
Lignite	262	89.2	0.46	1090	18800	2330	83.1	0.17	1.69	0.37

The heavy metals used were: copper(II) nitrate trihydrate pure (AppliChem GmbH, Darmstadt, Germany), nickel(II) nitrate hexahydrate p.a. (Merck KGaA, Darmstadt, Germany), and zinc nitrate hexahydrate pure (AppliChem GmbH, Darmstadt, Germany). To determine the cation exchange capacities, barium chloride dehydrate p.a. (Merck KGaA, Darmstadt, Germany), magnesium sulfate heptahydrate p.a. (Merck KGaA, Darmstadt, Germany), sodium chloride 99.9% (AppliChem GmbH, Darmstadt, Germany), and ammonium chloride pure (Merck KGaA, Darmstadt, Germany) were used. pH adjustments and conservation of samples were performed with nitric acid 65% p.a. (Merck KGaA, Darmstadt, Germany). A combination of potassium dihydrogen phosphate p.a. (Th. Geyer GmbH & Co. KG, Renningen, Germany) and disodium hydrogen phosphate dihydrate p.a. (Merck KGaA, Darmstadt, Germany) was used as a buffer.

2.2. Experimental Setup

For all of the experiments with heavy metals, the concentration of Zn was always twice as high as the concentration of Cu and Ni, respectively. This represents the higher concentrations of Zn in traffic area runoff waters [5]. Equal concentrations of Cu and Ni made it easier to detect a possible competition between the removals of each metal.

2.2.1. Batch Experiments with Heavy Metals

For the equilibrium batch tests, sorption experiments were carried out in 250 mL low-density polyethylene (LDPE) bottles, at pH 5, and with initial metal concentrations from 2.5 mg/L to 90 mg/L

for Cu and Ni, and from 5.0 mg/L to 180 mg/L for Zn. Deionized water (electric conductivity of $<1 \mu\text{S}/\text{cm}$) was used for preparing all stock solutions and the initial pH value was adjusted with nitric acid. At pH 5, all three heavy metals are present in dissolved form [23]. This initial pH value was chosen because filter materials in stormwater treatment systems are mainly designed to retain dissolved substances. The filter material dosage was always 8.0 g of filter material in 200 mL stock solution. No delay occurred between the addition of the solution to the sorbent in the bottles and the beginning of the shaking. Shaking was performed on a rotary shaker at a speed of 16 rpm for 24 ± 0.5 h. Subsequently, samples were filtrated with a cellulose nitrate membrane filter ($0.45 \mu\text{m}$ pore size, Sartorius, Göttingen, Germany) to separate the dissolved and solid phases. All experiments were carried out in duplicate at room temperature ($21 \pm 2 \text{ }^\circ\text{C}$).

Control experiments were conducted with all six sorbents without adding heavy metals. They followed the same experimental procedure as described previously to observe a possible release of heavy metals from the sorbents. In addition, further blank and spike samples were included into the experimental setup to detect possible sample contaminations during the filtration process and subsequent sample preparations and analyses. Samples with the same heavy metal concentrations, but without sorbents, were used to evaluate any possible heavy metal losses because of adsorption to the flasks and bottles. No significant losses of heavy metals were detected for any materials.

Differences between the rotary shaker (16 rpm) and a horizontal shaker (125 rpm) were examined for concentrations of up to 540 mg/L (Cu and Ni) and 1080 mg/L (Zn). In addition, the presence of a buffer was tested at pH 5 and pH 7 with the rotary shaker. A pH value of 7 represents commonly observed values for traffic area runoff [5]. Since the runoff water from traffic areas consists of several compounds that constitute a buffer capacity, other studies used sodium hydrogen carbonate buffers in the stock solution [23,24]. Since carbonate leads to a precipitation of heavy metals similar to the sorbent calcium carbonate and its addition influences the removal mechanisms, a phosphate buffer was used to minimize pH changes in this evaluation. Furthermore, the influence of the filtration process on the measured concentrations was studied by using further samples without sorbents, and by following the same experimental procedure.

Batch kinetic experiments were conducted with two concentration ranges (10 mg/L and 90 mg/L for Cu and Ni, respectively; 20 mg/L and 180 mg/L for Zn). The contact times were 5 min, 10 min, 20 min, 30 min, 60 min, and 120 min, respectively.

For the evaluation of different production batches, only Cu with an initial concentration of 63.5 mg/L was used. In contrast to the other experiments, the dosages were 0.4 ± 0.05 g material and 0.3 ± 0.05 g material in 250 mL solution.

2.2.2. Column Experiments

Lab-scale column experiments were conducted with inflow concentrations of 2.5 mg/L (Cu and Ni) and 5.0 mg/L (Zn) at an initial pH of 5 and at ambient temperature ($21 \pm 2 \text{ }^\circ\text{C}$). Deionized water (electric conductivity of $<1 \mu\text{S}/\text{cm}$) was used for influent preparation. pH adjustments were performed with nitric acid. The experimental apparatus was constructed of glass and all pipes were of polyvinyl chloride. The glass column had an inner diameter of 2.0 cm and a length of 40 cm, providing a sorbent bed height of 23 cm. A glass screen was placed at the bottom of the column to support the filter materials. The feed water percolated through the glass columns in down-flow mode (from top to bottom) and the flow-rate was adjusted to about 6.5 mL/min by a peristaltic pump (ECOLINE VC-MS/CA8-6, Ismatec SA, Glattbrugg, Switzerland). As a result, the EBCT was maintained at 11 min. The experiments were performed in duplicate from Monday to Friday. During weekends, the filter materials were kept saturated without flow. Operation of all columns was terminated when the removal efficiencies of all metals were less than 20%. However, for the two tests representing the best performing removal efficiencies, this operational criterion was not achieved during a four-week testing period.

One influent sample per stock solution and several effluent samples at designated times were collected in 250 mL LDPE bottles. Filtration of samples was not conducted. Selected experiments were done with changes in initial concentrations and contact time.

2.2.3. Batch Experiments According to Standard Methods

Further batch experiments were performed according to two standard protocols [32,33]. Both procedures were often used in the field of stormwater treatment to determine sorption capacities of heavy metals although they do not use heavy metals as adsorbates, but other cations as substitutes.

The cation exchange capacity of the first method (CEC 1) is determined by shaking 2.50 g of filter material with 30 mL of barium chloride solution three times each for 60 min to extract sodium, potassium, calcium, and magnesium [32]. After each step, the solution is separated from the filter material by centrifugation and subsequently rejected. The filter material is then shaken again with a fresh barium chloride solution to preload the material with barium for 17 h. After centrifugation, 30 mL of magnesium sulfate solution is added to the filter material to exchange the sorbed barium ions with magnesium under the precipitation of barium sulfate. After 24 h of shaking, the decrease of dissolved magnesium is determined in filtrated samples of the last step. The result of the magnesium sorption is given in cmol^+/kg and this value is often proposed to be valid for other metal cations. This standard protocol was developed for soils but is also used for technical filter materials. All experiments were done in quadruplicate.

The cation exchange capacity of the second method (CEC 2) is determined by preparing a sample of the filter material (10 g) with sodium chloride and then adding the sorbent to a 300 mL solution of ammonium chloride [33]. This cation exchange capacity is calculated by the decrease of ammonium in a filtrated sample after 2 h of shaking. It is assumed that the exchange capacity related to ammonium is comparable to the total cation exchange capacity. This standard was developed for natural zeolites. All experiments were carried out in triplicate.

2.3. Analytical Procedures

The same analytical procedures and equipment were used during all experiments to minimize the influences of sample preparation and analysis on the results.

The concentrations of heavy metals were measured by flame atomic absorption spectrometry (AAS, Varian Spectrometer AA-240FS, Palo Alto, CA, USA) according to Standard Method 3111 [34] with detection limits of 50 $\mu\text{g}/\text{L}$ (Cu), 50 $\mu\text{g}/\text{L}$ (Ni), 20 $\mu\text{g}/\text{L}$ (Zn), 2500 $\mu\text{g}/\text{L}$ (aluminum), 100 $\mu\text{g}/\text{L}$ (calcium), 100 $\mu\text{g}/\text{L}$ (iron), 50 $\mu\text{g}/\text{L}$ (manganese), and 50 $\mu\text{g}/\text{L}$ (magnesium). Some samples were also measured with a graphite furnace AAS (Varian Spectrometer AA-240Z with GTA 120, Palo Alto, CA, USA) according to Standard Method 3113 [34] with detection limits of 5 $\mu\text{g}/\text{L}$ (Cu) and 5 $\mu\text{g}/\text{L}$ (Ni). Total metal concentrations were measured with AAS in an *aqua regia* digestion of the samples to quantify their contents in the filter materials. Quality control was maintained by using control and blank samples, and taking standard solution quantity checks of every five samples.

Ammonium was measured using cuvette tests (Hach Lange GmbH, Düsseldorf, Germany). Total carbon (TC) and total sulfur (TS) were determined with a multi EA 4000 element analyzer (Analytik Jena AG, Jena, Germany). The solid samples were directly decomposed and oxidized at 1350 °C and the resulting oxides were quantified simultaneously with a non-dispersive infrared (NDIR) detector. Specific surface areas of the sorbents were determined according to ISO standard 9277 [35] using a SA 3100 plus (Beckman Coulter, Brea, CA, USA) with nitrogen as adsorption gas (BET method).

For all samples, the pH value and electric conductivity were measured immediately after sample collection. Measurements of the pH value were performed with a glass electrode (WTW Sentix 60, Weilheim, Germany) according to Standard Method 4500- H^+ and electric conductivity (detection limit: 0.1 $\mu\text{S}/\text{cm}$) was determined by using a WTW ProfiLine Cond 1970i (WTW, Weilheim, Germany) according to Standard Method 2520 B [34]. Subsequently, all samples were conserved with nitric acid

at pH < 2. Sorbent samples were weighed using an analytical balance (Sartorius MC1 Research RC 210D, Göttingen, Germany) with an accuracy of ± 0.1 mg.

2.4. Data Evaluation

Heavy metal capacities, representing their contents on the sorbent, were calculated for each experiment and each sorbent. This was done by using the analyses of the corresponding metal concentrations before and after the experiments with Equation (1):

$$q_e = (c_0 - c)/X, \quad (1)$$

where q_e (mg/g) is the sorbed amount of adsorbate on the filter material, c_0 (mg/L) is the initial metal concentration, c (mg/L) is the equilibrium or averaged effluent metal concentration of adsorbate in solution, and X is the filter material dosage (g/L).

The Langmuir isotherm model (a non-linear isotherm with two-fitting parameters) was used for the calculation of q_m (2):

$$q_e = q_m K_1 c / (1 + K_1 c), \quad (2)$$

where q_m (mg/g) is the saturated amount of adsorbate on the filter material, and K_1 (L/mg) is the Langmuir parameter representing the consumed energy in the sorption process.

For the column experiments, breakthroughs in this study were defined at $c/c_0 = 0.1$ and $c/c_0 = 0.5$. The corresponding capacities were $q_{10\%}$ and $q_{50\%}$, respectively.

3. Results and Discussion

3.1. Batch Experiments

Comparing the removal of heavy metals by all investigated materials, anthracite had the lowest capacities because it was not pretreated and it had the smallest specific surface area (1.4 m²/g). Anthracite was the only sorbent with metal leaching in the control batches without any heavy metals being present in the stock solution. The leached concentrations observed after shaking were 13.5 $\mu\text{g/L}$ Cu, 41.4 $\mu\text{g/L}$ Ni, and 30.3 $\mu\text{g/L}$ Zn.

For all other equilibrium experiments, Cu showed the highest affinity for all sorbents. For the highest concentrations, smaller quantities of Ni and Zn were retained. Almost no removal of Ni was observed at initial concentrations of 540 mg/L Ni (pH 5, no buffer) for alumina or calcium carbonate. Zn was not removed by GAC or calcium carbonate at an initial concentration of 1080 mg/L Zn under competitive conditions (*i.e.*, in the presence of other metals). At the same concentrations and pH values, the removal mechanisms including sorption, ion exchange, and precipitation preferentially removed Cu from the solutions. With increasing metal concentrations, the equilibrium pH value decreased for all sorbents. This trend was also reported by Wu and Zhou [24] for GFH. During the shaking, the shift of the pH value of the solution is linked to the presence of the filter material, the removal of metals from the solution, and the exposure to limited amount of atmosphere in the bottle. In the case of poor removal (e.g., by anthracite in this study), the difference between the concentration measurements of the stock solution and after shaking is very small, which might lead to small calculated capacities because of the analytical accuracy (Figure 1).

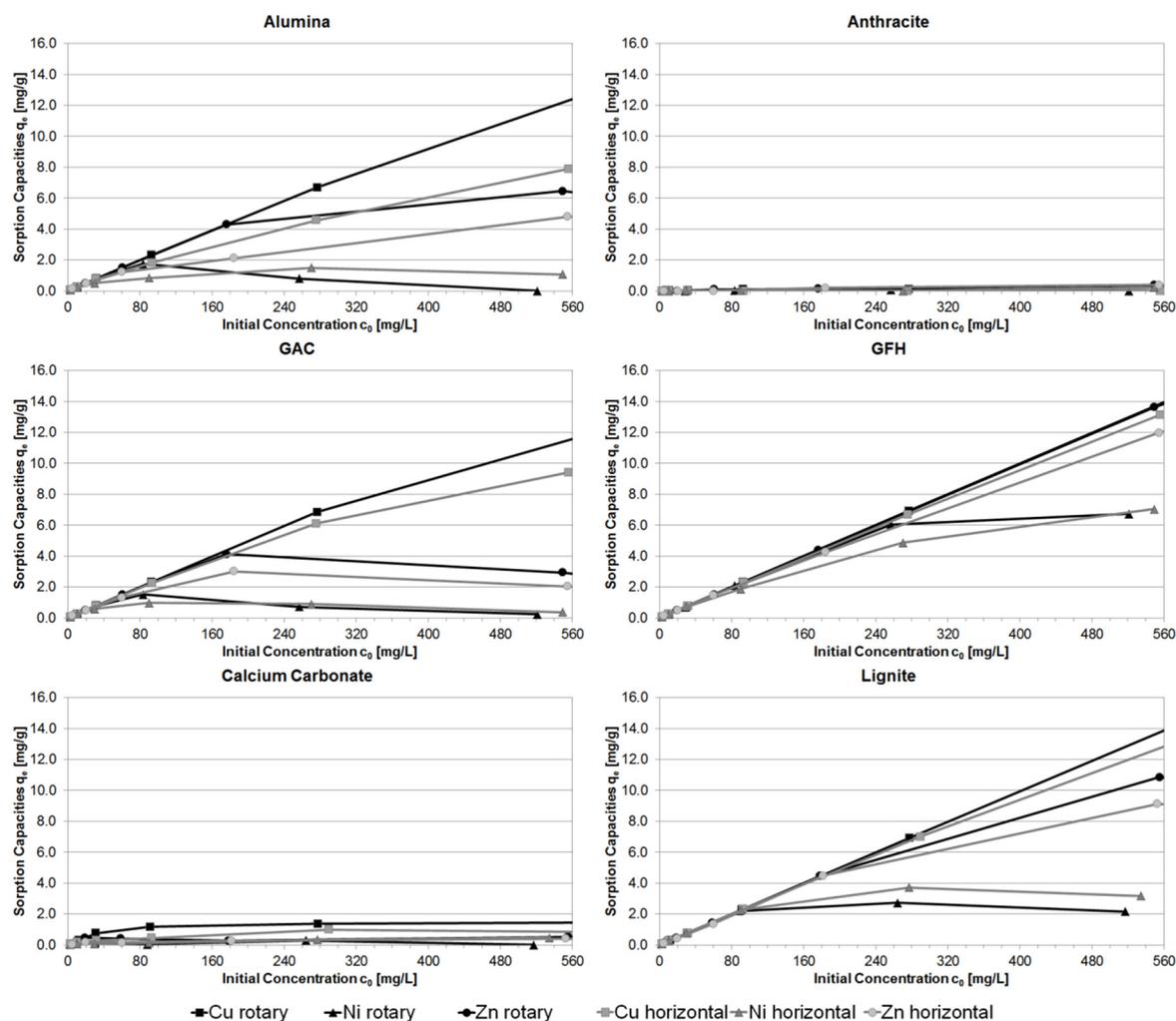


Figure 1. Influences of a rotary shaker (16 rpm) and a horizontal shaker (125 rpm) on sorption capacities at pH 5 without a buffer.

The effect of different types of shakers on the removal capacities was determined for the equilibrium experiments. The speed of each shaker was adapted in order to ensure that the sorbents were in suspension. The same substrate dosage and stock solutions (*i.e.*, initial heavy metal concentrations, pH 5, and no buffer) were used. The capacities determined in the experiments with the rotary shaker were often higher (Figure 1). These differences are likely because of material abrasion and dispersion during shaking [36], which subsequently led to larger surface areas. This effect depends on the type of material and, as a consequence, different behaviors between the sorbents occurred. The absolute differences were low for anthracite and high for alumina. For Cu, the capacities of all of the substrates, determined using the rotary shaker, were between 98% and 268% of the ones determined using the horizontal shaker. At the lowest concentrations, when nearly all of the Cu ions were removed, the difference was very small for all sorbents (factor 1.05) but increased for the highest concentration (factor 1.37). The higher capacities of Ni determined using the horizontal shaker at increasing concentrations can be explained by minor retention of Cu and Zn compared with the rotary shaker on the material surface. Therefore, the competition was lower and Ni ions had more opportunities to sorb onto the material.

Quevauviller *et al.* [37] investigated the influence of shaking types and speed on the determination of extractable trace metals in sediments. They reported that lower amounts of metals were extracted by experiments with horizontal shakers at a speed of less than 40 rpm compared with speeds of up

to 150 rpm. In experiments with rotary shakers operated at 30 rpm, 20% more Cu was extracted, compared with experiments using a horizontal shaker at 130 rpm. This effect was less pronounced for Ni than for Cu [37].

Due to the small amount of materials used in batch experiments (8.0 g) an extensive disintegration of the material was possible during rotary shaking intervals of 24 h. This was observed during the experiments with calcium carbonate. Abrasion led to significant experimental difficulty and representative analyses were hardly possible, which was also observed by Liu *et al.* [25] for manganese oxide-coated polymeric media. Therefore, it is essential to record the type of shaker and its speed to assure reproducible and reliable results.

The initial pH value has an influence on the sorption capacities. For example, Smith [31] investigated the Cd removal by a recycled iron sorbent and determined a capacity increase as the pH increased within the range of 4–7. Liu *et al.* [25] calculated the equilibrium capacities for Pb removal that was observed at pH 5, 6, and 7. Between pH 5 and 6 the capacity increased slightly, whereas it was several times higher for pH 7 compared with pH 6. Reed *et al.* [38] also reported higher Pb removal by GAC for elevated pH values. Athanasiadis *et al.* [30] measured higher Zn uptakes of a zeolite with an increasing initial pH value. For example, at higher pH values more metals are precipitated [24], the pH value is at or above the point of zero charge that leads to negatively charged sorbent surfaces and higher retention of cations [23], and sorption also increases because metal ions exchange hydrogen ions of the sorbent surfaces more likely [39]. Thus, higher capacities for all six sorbents were expected for an initial pH value of 7 instead of 5.

The results of the experiments with the variation of the initial pH value are presented in Figure 2. A buffer was used for all curves and the results without a buffer are shown as single points for comparison. For the best materials (alumina and GFH), nearly no differences in the removal of heavy metals occurred with and without buffer. Anthracite, which showed nearly no removal for experiments without a buffer, had removal capacities for all heavy metals for the experiments with a pH buffer at pH 5 and all capacities increased for the experiments at pH 7. The behavior of calcium carbonate was similar. For GAC, differences occurred only for the removal of Ni that was better removed at pH 7 instead of pH 5. However, the use of a buffer had a negative effect on the Ni capacities compared with experiments without buffer addition. Lignite that has larger amounts of primarily oxygen-containing functional groups (e.g., carboxylic, phenolic, and carbonyl groups) than GAC [40–42] also showed differences in the Ni capacities. At pH 5 without a buffer, Ni was completely removed. For the experiments with a buffer, Ni was not completely removed and the removal increased with increasing pH value. This might be related to the functional groups and to a preferred removal of the cations present in the buffer (*i.e.*, potassium and sodium) compared with Ni. In consequence, an increase of the initial pH value led to higher removal capacities whereas the addition of a buffer showed different results.

The difference of the removal capacities for the used buffer and the pH values correlated with the filtration step at the end of the equilibrium experiments. Some heavy metals can be associated with colloidal sorbent compounds and can pass through the 0.45 μm -filter and are subsequently analyzed [31]. In contrast, larger colloids and particulate heavy metals are retained by the filter. The greatest difference between total and filtrated heavy metal concentrations was observed for a stock solution with a buffer at an initial pH of 7. This difference in initial and equilibrium concentrations could be related to a capacity that is equal for all experiments at pH 7 (Figure 3). A comparison of this capacity (equilibrium experiment with no sorbent) with the total capacities of alumina and anthracite (equilibrium experiments with sorbents) illustrated that all heavy metals were partially removed by the filtration process. Thus, the capacities of anthracite at pH 7 and in the presence of a pH buffer (Figure 2) were not related to the sorbent but mainly to the experimental setup. Similar results were obtained by Liu *et al.* [25]. They investigated the removal of Pb during equilibrium batch experiments for pH values between 5 and 11. At pH values > 6, Pb was not only adsorbed onto the sorbent surface but also precipitated. Thus, 89% of Pb was removed at pH 7 by precipitation in the presence of the

sorbent, and 62% of Pb was precipitated in the solution without sorbent (same experimental setup) and, therefore, retained during the filtration process. Results consistent with this study were also reported by Genç-Fuhrman *et al.* [23] and Wu and Zhou [24] at an initial pH of 6.5.

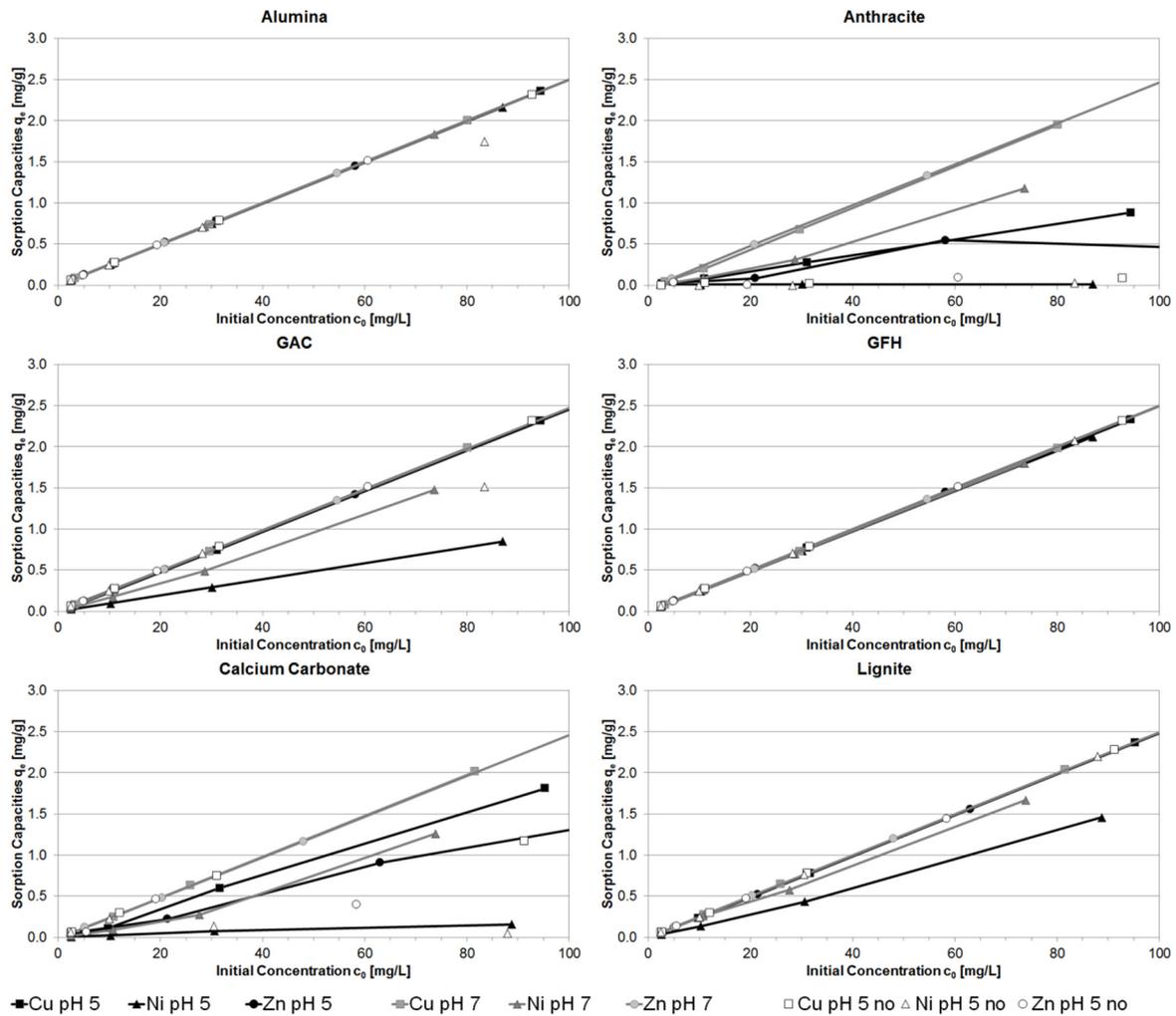


Figure 2. Influences of a buffer at pH 5 and pH 7 for the rotary shaker. For comparison, pH 5 without a buffer (metal pH 5 no) is also presented.

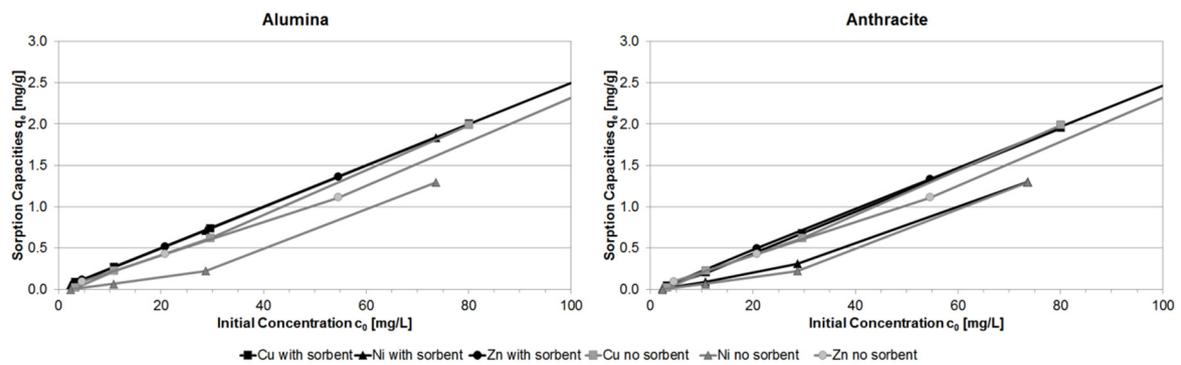


Figure 3. Influence of the filtration process at pH 7 for experiments using a buffer and a rotary shaker: heavy metal removal for different initial concentrations for two sorbents and for the same initial concentrations without any sorbent (metal no sorbent).

The addition of a buffer and other chemicals to adjust the ionic strength, led to an oversaturation of the heavy metal minerals and salts in the synthetic solutions. Thus, higher metal concentrations tended to precipitate with compounds of the added chemicals and not with the constituents of the sorbents. They were also retained during the filtration process and contributed to the overall removal. Consequently, the removal of dissolved heavy metals by sorbents for stormwater treatment systems should be determined at pH 5 without the addition of a buffer.

Batch kinetic experiments can be used to evaluate capacities for the design of treatment systems. In stormwater treatment systems, the contact time between the influent and the filter material is in the order of several minutes and varies widely because rain intensities can be very heterogeneous and the retention volumes are very small in decentralized systems. These short EBCTs can lead to an incomplete reaction of the heavy metals with the sorbents. Therefore, the kinetics of the heavy metal removal is very important to characterize the suitability of a material for this application. Since the removal mechanisms in porous media are controlled by physical-chemical processes or by chemical-dominant surface reactions (*i.e.*, adsorption, desorption, surface complexation, ion exchange, and precipitation), the capacities after several minutes or hours depend on the filter material and the substances of interest as some processes are rate limited (e.g., intraparticle transport and dissolution of carbonates) [31,43,44].

For all kinetic experiments, a higher initial concentration correlated with less heavy metal removal efficiencies at the same time, and the pH values increased with time for all sorbents except anthracite because of the sorbent specific removal mechanisms (e.g., dissolution of the sorbent minerals or release of phenols) [23]. Following an initial fast reaction stage, a slower stage continued for the four sorbents having the best removal capacities (Figure 4).

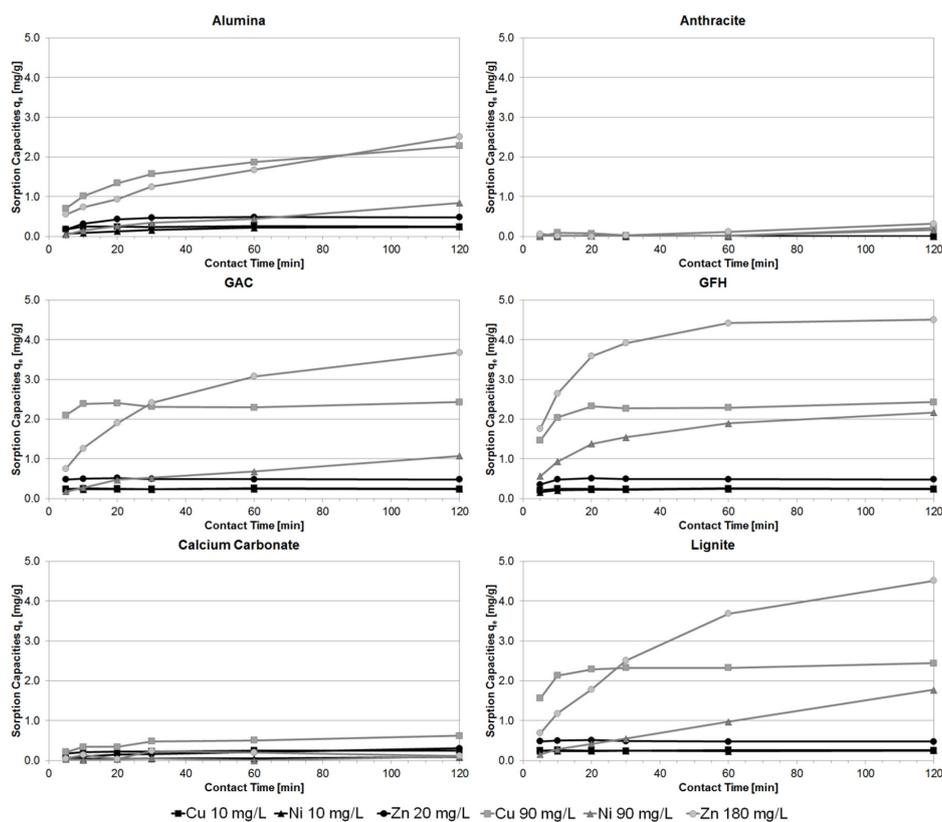


Figure 4. Results of the kinetic experiments with two initial concentrations (rotary shaker, pH 5, and no buffer).

Sorption rates were fast for GAC with nearly 100% of the equilibrium capacities within 5 min for all metals at lower concentrations and Cu at higher concentrations, where the removal of Zn was slower and the removal capacity of Ni was only 71% after 2 h compared with the result of the equilibrium experiment (Zn 89%, respectively). Lignite had a similar behavior but had slower efficiencies compared with GAC for the higher concentrations until 20–30 min. The initial fast rates can be explained by the large surface areas (*cf.* Table 1) and the following reactions were rate-limited by diffusion through the micropores of the sorbent because easily available surface areas were occupied by previously-sorbed metals [39]. Similar results were calculated for GFH with slower rates in the first 5 min for the lower concentrations and a subsequent faster increase in removal efficiencies. For higher concentrations, GFH had the highest removal rates compared with all other sorbents. For alumina, the capacities increased slowly, especially for Ni. Calcium carbonate exhibited slow increases in the removal capacities over time (rate-limited dissolution) with varying results likely because of the abrasion of the material. Therefore, in the range of 5–20 min, which is relevant for stormwater treatment systems, differences occurred between all sorbents for all heavy metals. However, batch kinetic experiments are not suitable to evaluate contact times shorter than 5 min. Thus, these conditions representative of high rain intensities should be simulated using column experiments.

The effect of different temperatures was not evaluated as lab-experiments were always performed at ambient temperatures. Changes in the behavior of heavy metals because of temperature effects in labs were not considered significant according to Quevauviller *et al.* [37] and Pehlivan and Arslan [39].

3.2. Column Experiments

Column studies were carried out with appropriate solid-to-solution-ratios [36] and filtration was not conducted when preparing the samples. The differing behavior of the sorbents during the batch kinetic experiments were reflected in the performance of the filter materials in the lab-scale column tests. One of the aims of these column studies was to achieve maximum capacities of a sorbent under specific boundary conditions. These capacities are needed to design full-scale systems for stormwater treatment (e.g., amount of sorbent and service life) [45]. The design of a full-scale system requires the prediction of the concentration-time profile or the breakthrough curve using lab-scale experiments. The breakthrough curves had a very high coincidence with the pH drift curve for all sorbents (Figure 5). In general, the pH drop correlated with decreasing heavy metal removal for the experiments with an EBCT of 11 min. This pH effect can be used in monitoring the removal process.

The best material (GFH) had a breakthrough of 10% at *ca.* > 2200, 1300, and 1470 bed volumes for Cu, Ni, and Zn, respectively. The capacities of the column experiments were also comparable to the ones of the batch experiments (Table 2). No differences occurred between alumina and GFH in the equilibrium batch experiments for concentrations <100 mg/L and there were only small differences in the kinetic studies for lower concentrations. For the column experiments, the differences were more evident. A 10%(50%)-breakthrough of Ni, Zn, and Cu was observed after treatment of approximately 70(240), 190(310), and 380(950) bed volumes by alumina, respectively. The high efficiency of GFH compared with alumina cannot be linked exclusively to the specific surface area [24] and the medium pore diameter because they are both similar. However, GFH has a 4.5 times larger pore volume (0.717 cm³/g) that supports heavy metal pore diffusion, surface interaction, surface complexation with hydroxide groups, and precipitation with calcium carbonate (*cf.* Table 1). Furthermore, a regeneration of the filter material during weekends was observed (Figure 5).

Although GAC had the largest specific surface area (896 m²/g), it had very low capacities in the column experiments and the steepest gradient from breakthrough to exhaustion. The simultaneous steep decrease of the pH value can be linked to the formation of hydroxide complexes of Zn and Ni after the breakthrough point, when the surface area is limited for sorption of metal ions. These low capacities of GAC limits its applicability for stormwater treatment systems as it was also reported by Liu *et al.* [19] and Li and Helmreich [28]. Both GAC and lignite had Zn and Ni values above 1.0 for c/c_0 as a result of competition because Cu is preferentially retained. As sorption is one of the key

removal mechanisms, a partial displacement of previously sorbed Ni and Zn occurred as the remaining capacity decreased and led to effluent concentrations that were higher than the influent concentrations. A higher selectivity of lignite for Cu removal (followed by Zn and Ni) was also measured by Jochová *et al.* [44].

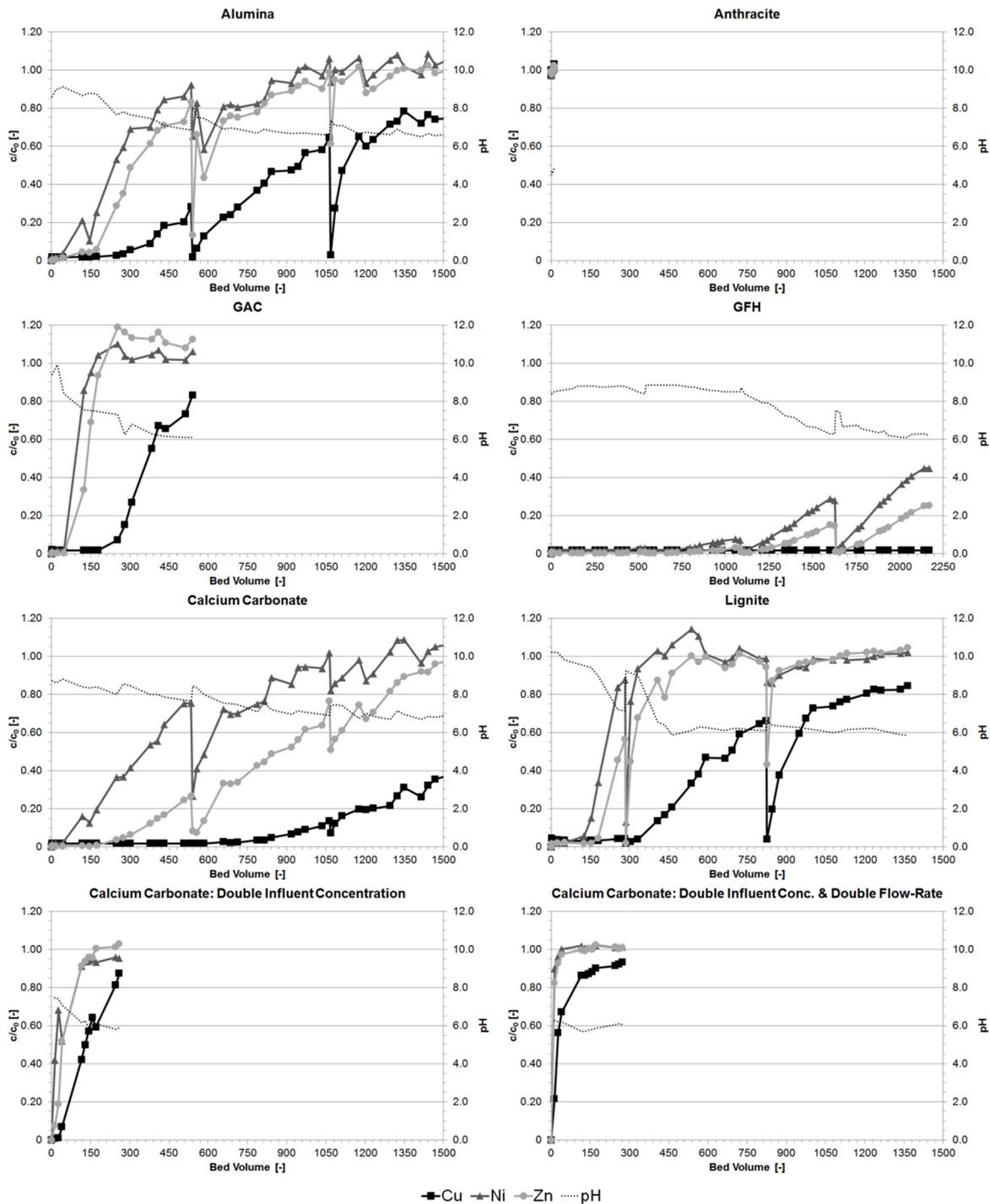


Figure 5. Heavy metal removal and pH drift curves of all column experiments conducted with influent concentrations of 2.5 mg/L Cu, 2.5 mg/L Ni, and 5.0 mg/L Zn at a flow-rate of 6.5 mL/min (exceptions: two calcium carbonate experiments with variations; GFH has a different scale).

Anthracite had an exhaustion of the capacity before the first sampling (Figure 5).

In contrast to the batch experiments, calcium carbonate had higher capacities in column experiments (Table 2). Therefore, the batch experiment setup had a negative effect while determining sorption capacities because of the abrasion and disintegration of the material. Despite its medium Ni and Zn removal efficiencies, calcium carbonate showed a high Cu removal because Cu is predominantly precipitated as copper carbonate at the prevailing pH values (*cf.* Figure 5) [23].

Table 2. Comparison of different sorption capacities; batch experiments: highest values measured (q_e) for two initial concentrations (mg/L) at pH 5 with the rotary shaker without a buffer and calculated using the Langmuir isotherm model (q_m); column experiments: at 10% breakthrough point ($q_{10\%}$) and at 50% breakthrough point ($q_{50\%}$)—all values in mg/g.

Filter Material	Cu					Ni					Zn				
	$q_{e,2.5}$	$q_{e,540}$	q_m	$q_{10\%}$	$q_{50\%}$	$q_{e,2.5}$	$q_{e,540}$	q_m	$q_{10\%}$	$q_{50\%}$	$q_{e,2.5}$	$q_{e,540}$	q_m	$q_{10\%}$	$q_{50\%}$
Alumina	0.06	12.7	13.5	1.46	3.07	0.06	1.75	1.77	0.25	0.71	0.12	6.45	6.47	1.35	2.01
Anthracite	0	0.09	-	-	-	0	0.06	-	-	-	0	0.36	-	-	-
Calcium carbonate	0.06	1.45	1.45	1.60	>2.27	0.06	0.30	0.31	0.13	0.42	0.12	0.53	0.53	1.06	2.25
GAC	0.06	11.9	12.0	1.40	1.81	0.06	1.51	1.52	0.28	0.41	0.12	4.11	4.44	0.71	1.22
GFH	0.06	14.4	21.8	>8.92	>8.92	0.06	6.73	6.82	4.90	>7.57	0.12	24.0	23.5	11.1	>11.3
Lignite	0.06	14.6	16.6	1.27	2.00	0.06	2.73	2.73	0.44	0.60	0.12	10.9	11.2	1.26	1.62

Selected experiments were performed with calcium carbonate because of its rate-limiting removal mechanism to evaluate the influence of changes in initial concentrations and contact time. These are the main factors varying between different rain events treated in decentralized systems. For decreasing EBCT, capacities and efficiently treated bed volumes decreased (Figure 5). The $q_{50\%}$ -capacity decreased for Zn from 2.25 mg/g to 0.42 mg/g (double influent concentration) and to 0.14 mg/g (double influent concentration and double flow-rate). These results indicated that the impact of the EBCT for calcium carbonate was comparable to the ones for GAC and manganese oxide-coated media [19,38]. Inglezakis *et al.* [43] also determined for a zeolite that the breakthrough point (set at $c/c_0 = 10\%$) could be observed after a smaller amount of treated bed volumes as the flow-rate increased and the EBCT decreased. This effect also occurred in the experiments of this study (Figure 5) and it influenced the capacities negatively because the steepness of the breakthrough curve also increased. In contrast to the manganese oxide-coated media tested by Liu *et al.* [19], the breakthrough capacities of calcium carbonate decreased with increasing concentrations for the same EBCT. For the same removal efficiencies, a longer EBCT must be maintained for higher influent concentrations [38]. Therefore, for the same EBCT and higher influent concentrations, the removal efficiencies decreased and the steepness of the breakthrough curve increased (Figure 5). All breakthrough curves can be used to evaluate service lives for specific removal efficiencies under defined boundary conditions of the column experiments. These individual breakthroughs can be linked to meeting regulatory requirements.

3.3. Comparison of Batch and Column Experiment Capacities

A comparison of the capacities determined for the three heavy metals is summarized in Table 2. These removal capacities are important because they are needed to design full-scale systems for stormwater treatment (e.g., type and amount of sorbent, ratio of drainage area to filter area, or service life) [45]. For realistic stormwater runoff concentrations (2.5 mg/L and 5.0 mg/L) in batch experiments, all filter materials exhibited approximately 100% removal (with the exception of anthracite) and, therefore, achieved the same capacities (0.06 mg/g for Cu and Ni, 0.12 mg/g for Zn). For the highest initial concentrations of the batch experiments (540 mg/L and 1080 mg/L) the sorbents can be differentiated by the capacities. However, aspects such as a decrease in the equilibrium pH value because of the high metal concentrations make it difficult to evaluate the results as some metals were not removed. These capacities are comparable with the ones calculated using the Langmuir isotherm model.

In column experiments, the sorbents were evaluated by realistic concentrations under an EBCT of 11 min, which represents lower rain intensities. The capacities were much lower than the maximal sorption capacities calculated from the batch experiments, with the exception of GFH and calcium carbonate. GFH was the best material in the lab-scale column tests and calcium carbonate was disintegrated during the batch experiments. These differences were observed because of the reaction kinetics and the experimental setup. For a calcareous soil, a comparison of the retention of heavy metals in batch and column experiments showed similar results [46]. A comparison of the batch ($q_{e,2.5}$ or $q_{e,5.0}$) and column capacities ($q_{10\%}$ and $q_{50\%}$) using the same stock solution concentrations showed that larger amounts are sorbed on the column materials because of the higher solid-to-solution-ratios [36].

Lab-scale column experiments are more representative than batch experiments because of a constant flow, higher solid-to-solution-ratios, and the missing of the filtration step, which makes it possible to compare the efficiencies of filter materials and the effluent water quality [47]. A variation of the flow-rate to evaluate varying rain intensities can be achieved without high efforts during one experimental run by considering the site-specific hydrology and the flow-rate that is relevant for the filter system. Column experiments are applicable to simulate the behavior of stormwater filter materials for high rain intensities (contact times < 5 min) and, therefore, kinetic effects are better considered compared with batch kinetic experiments. In addition, there is no abrasion of filter materials that could influence the results. Thus, column experiments give a more realistic capacity by considering real boundary conditions and should be preferred to determine efficiencies and service lives. The determined service life is only valid for the dissolved substances and further field experiments are needed to verify the performance in the presence of particulate matter that can cause clogging. Batch experiments can be used to exclude sorbents that are not appropriate for the removal of a specific metal from subsequent and more expensive column experiments and to evaluate different production batches (*cf.* Section 3.6). To date, a lack of standardized methods does not allow a comparison of various results of one sorbent used in different research programs [37].

3.4. Comparison of Different Batch Experiment Capacities

In addition to the batch experiments with heavy metals, further batch experiments were conducted with surrogates according to standard methods to evaluate their ability to determine the capacities of different sorbents. Both methods use other cations (magnesium and ammonium) that replace previously exchanged cations (barium and sodium, respectively). Due to the exchange of cations being a selective process, the use of surrogates assumes that their affinity for being removed is comparable with the cations of interest. This is especially critical for the method CEC 2 because it was developed for natural zeolites and not for filter materials in general. It must be noted that the method CEC 1 is not suitable for materials containing significant amounts of calcite or gypsum [32]. This applies to the sorbent calcium carbonate.

The results of both methods that are described in Section 2.2.3 are shown in comparison with sorption capacities of Cu, Ni, and Zn in Table 3. All capacities are presented in the unit cmol^+/kg to enable a comparison as it is suggested by the two standard methods. By comparing the absolute numbers of the sorption capacities with the results of CEC 1, differences between each sorbent are apparent. GFH and lignite have comparable results regarding the sorption capacities for all three heavy metals, although they have different CEC 1 values. Therefore, different removal mechanisms are responsible for the retention of heavy metals. For alumina, CEC 1 values and the sum of the heavy metal sorption capacities are comparable. However, the individual heavy metal capacities indicate that Cu is completely retained, Zn less, and Ni only up to 67%. Thus, the method CEC 1 does not consider the diverse behavior of the heavy metals and overestimates the capacity for more mobile metals such as Ni. By using the method CEC 2, a capacity was calculated for anthracite that does not retain any heavy metals (*cf.* Figure 1). Furthermore, a ranking of the capacities according to CEC 2 is not comparable with the results of the batch experiments with heavy metals. The use of the method CEC 2 for natural zeolites is also limited because sodium chloride is used to enhance the sorption

behavior of natural zeolites by pretreatment [30]. The use of sodium chloride during application of CEC 2 would, therefore, falsify the capacity results for pretreated and untreated zeolites.

Table 3. Comparison of different capacities determined by batch experiments at pH 5 with the rotary shaker and without a buffer, CEC 1, and CEC 2—all values in cmol^+/kg .

Filter Material	Four Sorption Capacities				CEC 1	CEC 2
	120 mg/L Cu	120 mg/L Ni	240 mg/L Zn	480 mg/L $\Sigma(\text{Cu}+\text{Ni}+\text{Zn})$	480 mg/L Mg	180 mg/L NH_4^+
Alumina	8.42	5.93	15.0	29.4	28.5	7.33
Anthracite	0	0	0	0	0	5.37
Calcium carbonate	3.00	1.34	0	4.34	7.94	3.45
GAC	8.38	3.39	12.4	24.2	3.99	3.63
GFH	8.44	8.96	17.0	34.4	40.2	10.7
Lignite	8.44	8.93	17.0	34.4	9.39	2.98

3.5. Implementation of Ionic Strength and the pH value of Stormwater Runoff

In lab-scale experiments with sorbents for stormwater treatment systems, chemicals such as NaCl [23,24], NaClO_4 [31], and NaNO_3 [19,25,39] are used to adjust ionic strength, which shall represent the one measured in traffic area runoff. These chemicals contain further cations and chloride that might have an effect on sorption efficiencies (e.g., the presence of other cations can diminish the available number of sorption sites and chloride can form complexes that enhance the mobility of heavy metals [48]).

The parameter of field measurements that is often quantified and mostly related to ionic strength is the electric conductivity because hardness is only sometimes measured. However, the values vary between $11.3 \mu\text{S}/\text{cm}$ and $52000 \mu\text{S}/\text{cm}$ in the dataset presented in [5] with a median value of $160 \mu\text{S}/\text{cm}$. Thus, the ionic strength relates to site-specific factors that are mainly influenced by the road surface and road maintenance. It should at least be distinguished between warm and cold climates and between asphalt and concrete surface runoff waters. Hence, a median ionic strength is not representative for several sites or seasons. Winter maintenance practices, such as de-icing salt applications, generate chlorides and associated cations, in particular sodium and calcium, that can have an effect on the removal of heavy metals [49,50]. Thus, the ionic strength previously used in lab experiments does not reflect the amount and composition of the cations and anions of real stormwater runoff. Since each element has a unique effect on the removal, additional compounds to simulate ionic strength should be used carefully.

In summary, the consideration of ionic strength in lab-scale experiments is ambiguous as it varies in reality because of de-icing salt maintenance and other site-specific factors that lead to different compositions of the stormwater runoff, which cannot be reproduced in the lab. Therefore, the use of no buffer or ionic strength might be a worst case scenario for the determination of dissolved heavy metal removal to prevent oversaturated systems. However, for treatment systems in cold climates, de-icing salts must be considered. Additional experiments might be a better solution to observe their mobility and remobilization behavior.

The initial pH value has an effect on the measured capacities (*cf.* Figure 2). The pH values of 6.0, 6.5, and 7.0 [23–25,31] are often used in lab experiments that represent the median value of 6.9 for traffic area runoff waters [5]. A higher initial pH value results in more metals being precipitated because of the experimental setup [25]. This leads to an overestimation of the capacities of sorbents (especially for higher metal concentrations), which are predominantly increased by the filtration step at the end of all batch experiments by which larger colloids and particulate heavy metals are retained (*cf.* Figure 3). This effect does not occur in real stormwater treatment systems because the wire mesh or geotextile that is used to restrain the sorbents has larger pore diameters and these fine heavy metals can pass through them. Therefore, the enhanced precipitation has a great influence on the results, and

the comparability between the real situation and the lab experiments is limited. Using realistic influent pH values is not suitable to test the performance of filters for stormwater treatment systems that have to remove dissolved heavy metals. Therefore, to determine the sorbent performance and to investigate the removal mechanisms of decentralized stormwater treatment systems, it is preferred to perform batch experiments with the dissolved heavy metals of interest using synthetic water at pH 5.

3.6. Evaluation of Different Production Batches

A well-defined method for batch experiments can also be used to evaluate different production batches in a fast and inexpensive way. This method must contain information on the initial pH value, the concentrations of the metals of interest, the substrate dosage, the type and speed of the shaker, the shaking time, the temperature, and the sample preparation. The addition of a buffer or ionic strength should be avoided. All experiments should be performed in triplicate and blank samples are recommended.

The evaluation of different production batches of GFH for the removal of Cu is plotted in Figure 6. All samples were filtrated ($0.45\ \mu\text{m}$) after 24 h of shaking and before analysis. The first two batch experiments marked with * contained $0.4 \pm 0.05\ \text{g}$ material instead of $0.3 \pm 0.05\ \text{g}$ material in 250 mL solution. A lower filter material dosage had an effect on the results that is comparable to the one of increasing concentrations for the same dosages. A decreased dosage led to fewer variations of the results (Figure 6). Comparing the four batches with the same experimental setup, it can be seen that the results are reproducible for each production batch and there is only a slight variation between different production batches.

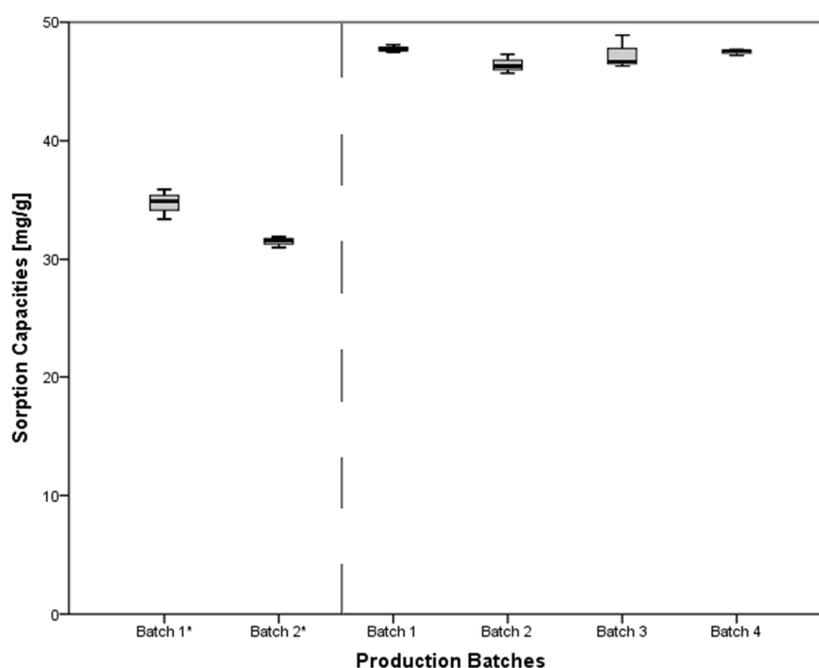


Figure 6. Evaluation of different production batches of GFH by sorption capacities for Cu: batch experiments marked with * contained $0.4 \pm 0.05\ \text{g}$ sorbent instead of $0.3 \pm 0.05\ \text{g}$ sorbent in 250 mL solution.

This method can be used to evaluate the performance of the sorbent in comparison with different production batches under identical experimental conditions. Such an evaluation is needed for internal and external quality control, which is conducted several times per year by the manufactures of technical decentralized stormwater treatment systems. This quality control proves that the filter materials of one treatment system always have the same characteristics. Therefore, the performance of different plants

should be comparable. However, this method is not suitable to design full-scale treatment systems or to predict the service life because it overestimates the sorbent capacity.

4. Conclusions

For testing sorbents for urban stormwater treatment systems, it is important to assure that reproducible and reliable results were obtained. Hence, the following influencing factors must be considered for the determination of capacities:

- Experiments with the dissolved heavy metals of interest using synthetic water at pH 5 is suggested and the influence of the type and speed of the shaker must be considered.
- Adjustments of ionic strength and pH > 5 are more sensitive and should be avoided because they mostly lead to an overestimation of the removal capacities of sorbents.
- The filtration step at the end of the batch experiments has an effect on the results and does not simulate real situations.
- Batch experiments with other cations (e.g., magnesium and ammonium) should not be used as surrogates.

The results of batch and lab-scale column experiments concerning simultaneous heavy metal removal differed widely for each sorbent. Thus, the following applications are recommended:

- Batch experiments with heavy metals can only be used under identical and well-defined conditions to prove the comparability of different production batches and to select sorbents for subsequent column experiments.
- Column experiments can be used as an indicator to determine the efficiencies and service lives of treatment systems.

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