



Simultaneous removal of coexistent heavy metals from simulated urban stormwater using four sorbents: A porous iron sorbent and its mixtures with zeolite and crystal gravel

Peng Wu^{a,b,*}, Yu-shan Zhou^b

^a Institute of Urban Environment, Chinese Academy of Sciences, 2 Huyuan Road, Xiamen, Fujian 361003, China

^b Institute of Environment & Resources, Technical University of Denmark, Lyngby 2800, Denmark

ARTICLE INFO

Article history:

Received 16 April 2008

Received in revised form 2 December 2008

Accepted 17 February 2009

Available online 25 February 2009

Keywords:

Heavy metals

Sorption

Urban stormwater

Iron sorbent

Zeolite

Crystal gravel

ABSTRACT

The selectivity sequence and removal of coexistent heavy metals (namely As, Cd, Cr, Cu, Ni and Zn) in synthetic urban stormwater runoff were investigated by adsorption onto a porous iron sorbent (namely P1) and its mixtures with zeolite and crystal gravel, respectively (namely P2, P3, and P4). A batch method was employed to simulate the sorption processes. The geochemical model PHREEQC was used to calculate the metals' species and saturation data for elucidating the sorption data. The equilibrium data demonstrated a good fit with the Freundlich model and showed affinity in the orders: Cd > Zn > Ni > Cu > As > Cr (sorbents P1, P3 and P4) and Cd > Zn > Ni > As > Cu > Cr (sorbent P2). In addition to this, Calculated Distribution Coefficient (K_d) values were used to compare the overall heavy metal removal efficiencies of the sorbents, which, in decreasing order, was found to be P4 > P1 > P2 > P3. In comparing these four commercial sorbents, sorbent P4 represents a promising material for treatment of urban stormwater runoff containing mixed heavy metals.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Urban stormwater runoff may contain abundant heavy metals such as arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), and zinc (Zn), which may come from a variety of sources including building materials (e.g. roofing, flashing, and walls) and traffic-related sources (e.g. brake linings, tire wear, and auto-catalysts) [1]. If stormwater contaminated with heavy metals is discharged directly into natural water bodies, the non-biodegradable metals can accumulate in the environment, causing both short-term (e.g. acute toxicity) and long-term (e.g. carcinogenic damages) adverse effects on human life. For example, chronic exposure to arsenic compounds may lead to neurotoxicity of both the peripheral and central nervous system [2], while cadmium is known to enhance lipid peroxidation by increasing the production of free radicals in the lungs, which leads to tissue damage and cellular death [3], and chronic lead toxicity affects gastrointestinal, neuromuscular, renal and haematological systems [4]. Furthermore, some non-biodegradable metals like chromium (VI) are thought to be toxic to bacteria, plants and animals [5].

* Corresponding author. Present address: Institute of Urban Environment, Chinese Academy of Sciences, 2 Huyuan Road, Xiamen, Fujian 361003, China.
Tel.: +86 592 2610696; fax: +86 592 2659290.

E-mail address: pwu@iue.ac.cn (P. Wu).

Several treatment methods have been developed to remove pollutants from urban stormwater. The most common forms of treatment are identified as physical/chemical processes (e.g. adsorption, filtration, ion-exchange, membrane systems, etc.). Adsorption was recognized by Hui et al. [6] and McKay [7] as an efficient and economical method of water treatment. It has also proved to be a promising method for removing dissolved metal ions from liquid wastes [8].

Adsorption encourages research of commercially available materials to be used as sorbents in purifying water contaminated with metals. Such materials include sand and sorbents prepared by coating to sand [9,10], sorbents developed from waste materials [11,12], and natural materials and oxides [13,14]. Recently, the use of Granular Ferric Hydroxide (GFH) as a commercial porous iron sorbent has rapidly developed, and to date has proved effective in removal of pollutants such as arsenic [15], phosphorus [16] and coexisting metals [10] from contaminated water. Among other minerals with sorbent-like properties, zeolite has shown promising performance for use in metal purification functions [6,17]. The advantage of zeolite is its three-dimensional structure connected by oxygen vertices, forming channels where H₂O molecules and exchangeable cations counterbalance the negative charge generated from the isomorphous substitution, as well as its low cost [6]. Crystal gravel, another cheap natural material, has also appeared to display a high removal efficiency for Pb and Cu [18]. Despite this however, few if any studies have been published that investigate

the use of a mixture of the above materials for removal of heavy metals from water.

Although many studies investigating removal of heavy metals from urban stormwater have employed a variety of sorbents, they conventionally only report removal efficiency in relation to individual heavy metal systems, despite the fact that urban stormwater may contain significant concentrations of multiple heavy metals [1]. It is therefore important to understand and quantify the heavy metal removal properties of sorbents when metals coexist [9,19]. The typical method for removal of heavy metals is tested under synthetic experimental conditions in terms of stormwater quality, as various pollutants in urban stormwater may confuse investigation of the removal mechanisms. Previously, few studies have been conducted under realistic experimental conditions [14,20].

This study focused on utilizing a typical commercial porous iron sorbent (Ferrocorp Plus, P1) resembling GFH and its mixtures with zeolite and crystal gravel to remove coexistent heavy metals such as As, Cd, Cr, Cu, Ni and Zn from synthetic aqueous samples with similar composition to real life urban stormwater runoff. Coexistence of the most important heavy metals in realistic concentrations as well as the initial pH and ionic strength typical of those found in urban runoff were prioritized properties in this study. Although a very common and important heavy metal contaminant, lead was excluded from this study due to the fact that in stormwater lead is often associated with suspended solids, hence can possibly be removed during pre-filtration treatment (i.e. by settling) [9]. In this research, batch sorption experiments were applied to evaluate the removal efficiency of four sorbents for treatment of urban stormwater containing mixed heavy metals. Heavy metal adsorption performance of the four sorbents was also studied for comparison.

2. Materials and methods

2.1. Sorbents and reagents

In accordance with information from the supplier (Ingenieurgesellschaft Prof. Dr. Sieker mbH, Germany), characteristics of the commercial porous iron sorbent and its mixtures with zeolite (1–4 mm) and crystal gravel (3.15–5.6 mm) are provided in Table 1. Particles of various diameters were created through a combination of crushing and sieving procedures. The composition of sorbent P1 was introduced as pure ironhydroxide, also evident by the distinctive color (dark brown) of the sorbent compared with the color of common iron oxides [21]. During the manufacturing process, sorbent P2 was produced from a ferric chloride solution by neutralization and precipitation with zeolite and sodium hydroxide. The ratio of ironhydroxide to zeolite in sorbent P2 was approximately 50/50 (w/w). All sorbents were sieved to 0.6–1.0 mm diameter particles using ENDECOTTS sieves series that meet US standards. The four sorbents appeared similar to each other after sieving, all displaying a dark brown color. The presence of white particles found

in sorbents P2, P3, and P4 after sieving indicated that some zeolite and crystal gravel particles had passed through the sieves. Upon sieving, the sorbents were stored in a desiccator to avoid moisture.

The Brunauer–Emmett–Teller (BET) surface area of the sorbents was determined using Flowsorb 2300 (Micromeritics Instrument Corp., USA). The single point nitrogen isotherm method was employed to determine surface area of the samples. The results of this are displayed in Table 1. It is noted that the surface area of sorbent P1 is similar with a previously reported 176 m²/g for sorbent GFH [15]. The pH of the point of zero charge (pH_{PZC}) for GFH was reported between 7.5 and 8.0 [22]. For this study, the pH_{PZC} of sorbent P1 was also expected to lie within a similar range. The pH_{PZC} of zeolite has been reported to be around 8.0 [6].

Analytical grade heavy metal stock solutions (PerkinElmer, Denmark) at 1.0 g/L were used for the study. Cd, Cu, Ni and Zn were all pure metal ions in 2% (v/v) HNO₃, while the As stock solution was H₃AsO₄·(1/2)H₂O in 2% (v/v) HNO₃, and the Cr stock solution was Cr(NO₃)₃·9H₂O in 2% (v/v) HNO₃. Initial synthetic adsorbate solutions were prepared using the stock solutions as well as NaCl (Riedel-deHaën, Germany) and NaHCO₃ (Fluka, Switzerland). The pH values were adjusted by HNO₃ (Riedel-deHaën, Germany) and NaOH (Riedel-deHaën, Germany). All reagent solutions were made of analytic grade reagents with Milli-Q water (Milli-Q Academic A10 system, Millipore, USA).

2.2. Instrumentation

A Varian model VISTA-MPX (Varian, Australia) Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) with an Ultrasonic Nebulizer U5000AT⁺ (CETAC Technologies, USA) was employed to measure metal ion concentrations, in which the detection limits were 0.4, 0.2, 0.1, 0.8, 0.2 and 1.1 µg/L for As, Cd, Cr, Cu, Ni and Zn, respectively. The pH of the solutions was measured with a MeterLab PHM210 standard pH meter (Radiometer Analytical, France). Two standard buffer solutions at pH 4.0 ± 0.01 (duracal buffer) and 7.0 ± 0.02 (potassium dihydrogen phosphate) were used for calibration of the meter. Sorbent samples were weighed using an analytical balance model BL60S (Sartorius, Germany) with an accuracy limit of ±0.1 mg.

2.3. Batch sorption experiments

The experiments were performed in 50 mL screw top polyethylene batch reactors at 25 ± 0.5 °C. Before testing, all batch reactors and bottles were soaked overnight in 10% (v/v) HNO₃ solution, triple rinsed with de-ionized water, and dried. Each reactor contained 1 g sieved sorbent (namely P1, P2, P3, and P4) to obtain a 20 g/L sorbent dosage. The desired concentrations of heavy metals (As, Cd, Cr, Cu, Ni, and Zn) were obtained by step-by-step dilution of the commercial stock solutions with 2% (v/v) HNO₃. This trial included 11 batches, where the initial heavy metal concentrations ranged from 6.00 to 1003, 2.83 to 4430, 6.67 to 2967, 15.2 to 2370, 2.81 to 8340, and 58.9 to 58,400 µg/L for As, Cd, Cr, Cu, Ni, and Zn, respectively. In addition to heavy metals, the synthetic samples consisted of 0.01 M NaCl to control ionic strength, and 0.003 M NaHCO₃ as a buffer to minimize pH changes during experiments. The pH of the samples was adjusted to approximately 6.5 by using 1.44 M HNO₃ or 1.0 M NaOH, depending on need. After gently mixing the sorbent and solution in each batch, the pH was immediately adjusted to approximately 6.5 again. All batches were capped tightly and placed into an end-over-end tumbling mixer, which had been refitted at 1 rpm. After 48 h constant shaking, the batches were removed from the tumbler and centrifuged for 20 min at 2000 rpm. The batch solutions were then transferred carefully to clean bottles, acidified to pH 1.5–2.0 using 1.44 M HNO₃

Table 1

Characteristics of the sorbents used in this study.

Symbol	Compositions	Surface areas ^c , m ² /g
P1	Ferrocorp Plus ^a	173
P2	Ferrocorp RWR ^b	166
P3	Mixture of P2 and crystal gravel (50/50%, w/w)	168
P4	Mixture of P1 and zeolite (50/50%, w/w)	198

^a Ferrocorp Plus = pure ironhydroxide.

^b Ferrocorp RWR = consist of ironhydroxide and zeolite (approximately 50/50%, w/w).

^c Sorbents were sieved with 0.6–1.0 mm screens before determinations.

and stored at 4 °C until heavy metal measurements were conducted.

Two series of control batches were also run under the same experimental procedure. One series included each sorbent dosage without the heavy metal stock solutions in order to determine whether the sorbents would release any investigated metal during the adsorption process. The other series included the investigated metals, but excluded the sorbents in order to quantify any loss or addition due to sorption to the reactors or contamination during the handling of samples.

2.4. Heavy metal speciation calculations

The computer program PHREEQC (version 2) with a thermodynamic database (namely LLNL.DAT) [23] was used to calculate the distribution of the heavy metals' aqueous species and the saturation state of any relevant metallic minerals/salts during the experiments. The calculation processes have been described by Genç-Fuhrman et al. [9]. The speciation modeling applied a chemical analysis of water to calculate the aqueous species distribution. The chemical equations for mole-balance and mass-action expressions, $\log K$ and its temperature dependence, and activity coefficient parameters of each aqueous species are defined in the LLNL.DAT database [23]. The essential data needed for the speciation calculation (e.g. temperature, pH and concentrations of the elements) were the same as the initial conditions of the batch sorption experiments.

2.5. Analyzing sorption data

The solid phase heavy metal concentration, q_e ($\mu\text{g/g}$), was evaluated by analyzing the corresponding heavy metal concentrations before and after adsorption using the following equation:

$$q_e = \frac{C_0 - C_e}{X} \quad (1)$$

where C_0 and C_e are the initial and equilibrium heavy metal concentrations in the solution ($\mu\text{g/L}$), and X is the sorbent dosage (g/L).

Analysis of the isotherm data is important to develop an equation that both accurately represents the results and could be used for design purposes. The Freundlich isotherm, a common mathematical expression which is suitable for analysis of highly heterogeneous surfaces [9,24], was used to analyze the adsorption results of the batch experiments as follows:

$$\log q_e = \log K + \frac{1}{n} \log C_e \quad (2)$$

where K is correlated with the quantity of sorbate associated with the sorbent (L/g), and n is a Freundlich isotherm constant related to the strength of the sorption at a particular temperature. By plotting Eq. (2) with the logarithmic equilibrium heavy metal concentrations ($\log C_e$) depicted on the horizontal axis and the logarithmic solid phase metal concentrations ($\log q_e$) on the vertical axis, values of K and n can be determined from the slope and intercept of the plot.

The overall efficiency of the sorbents in terms of heavy metal removal was determined using a distribution coefficient K_d (L/g) as below:

$$K_d = \frac{q_e}{C_e} \quad (3)$$

where K_d values were calculated corresponding to the initial concentrations used, and average K_d values were calculated and used to rank the overall heavy metal removal efficiency of sorbents.

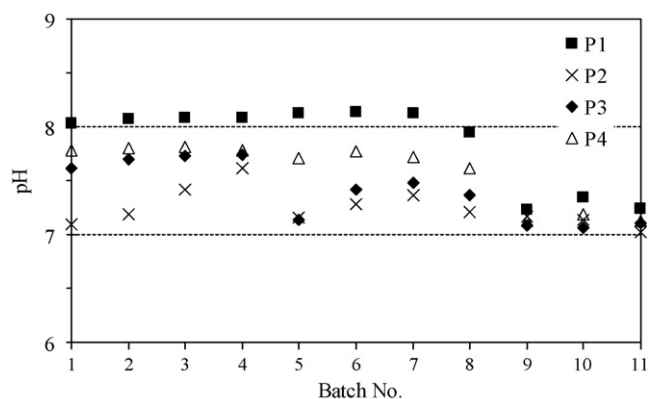


Fig. 1. The pH values after adsorption of the investigated metals onto different sorbents in batch sorption experiments.

3. Results and discussion

3.1. Equilibrium pH

The pH values of aqueous solutions were examined after sorption of the mixed heavy metals onto the four sorbents (see Fig. 1). Here, it can be observed that the pH values displayed no significant variations among different batches after the adsorption processes, with average values of 7.9, 7.2, 7.4, and 7.6 for sorbents P1, P2, P3, and P4, respectively, although the average pH of the inflow was around 6.5 in all batches. The pH values of the sorption experiments were controlled mainly by dissolution of the sorbents' minerals [10] and the release of $-\text{OH}$ groups from each sorbent as it formed inner-sphere complexes with metal ions [25,26].

3.2. Heavy metal speciation and saturation conditions

Species of the mixed heavy metal ions (as calculated by PHREEQC) at experimental conditions are shown in Fig. 2. Within the concentration ranges of the investigated metals, the dominant species for each metal were HAsO_4^{2-} , CdCl^+ , CrO_4^{2-} , CuCO_3 , Ni^{2+} and Zn^{2+} at the relevant pH. The varieties of dominant species were not obvious among the 11 batches, even though the solute concentrations increased with each batch. In this study, metals As and Cr conceivably existed as anions of the species HAsO_4^{2-} (97 mol% of As) and CrO_4^{2-} (99 mol% of Cr). H_2AsO_4^- and HCrO_4^- were the second most common species of As and Cr, following HAsO_4^{2-} and CrO_4^{2-} . The major cations present in the solutions existed as CdCl^+ (70 mol% of Cd), Ni^{2+} (100 mol% of Ni) and Zn^{2+} (74 mol% of Zn). The non-charged CuCO_3 (89 mol% of Cu) was the dominant species of Cu, while charged species such as CuOH^+ (5 mol%) and $\{\text{Cu}(\text{CO}_3)_2\}^{2-}$ (5 mol%) represented only minor percentages within the solutions.

Oversaturated heavy metal minerals/salts in the synthetic solutions are displayed in Table 2. From Table 2, it can be seen that the oversaturated minerals/salts increased as the initial heavy metal concentration increased. Similar results were reported by Genç-Fuhrman et al. [9]. Therefore, as precipitation of minerals/salts occurs, sorption may no longer be the primary removal process in those batches. Oversaturated conditions and consequently precipitation of Cd, Cu and Zn minerals/salts with high heavy metal concentrations will contribute to the overall removal.

3.3. Equilibrium concentrations and sorption isotherms

The results of simultaneous removal of heavy metals by the tested sorbents are presented in Fig. 3. As expected, the level of heavy metal removal increased as the initial heavy metal concen-

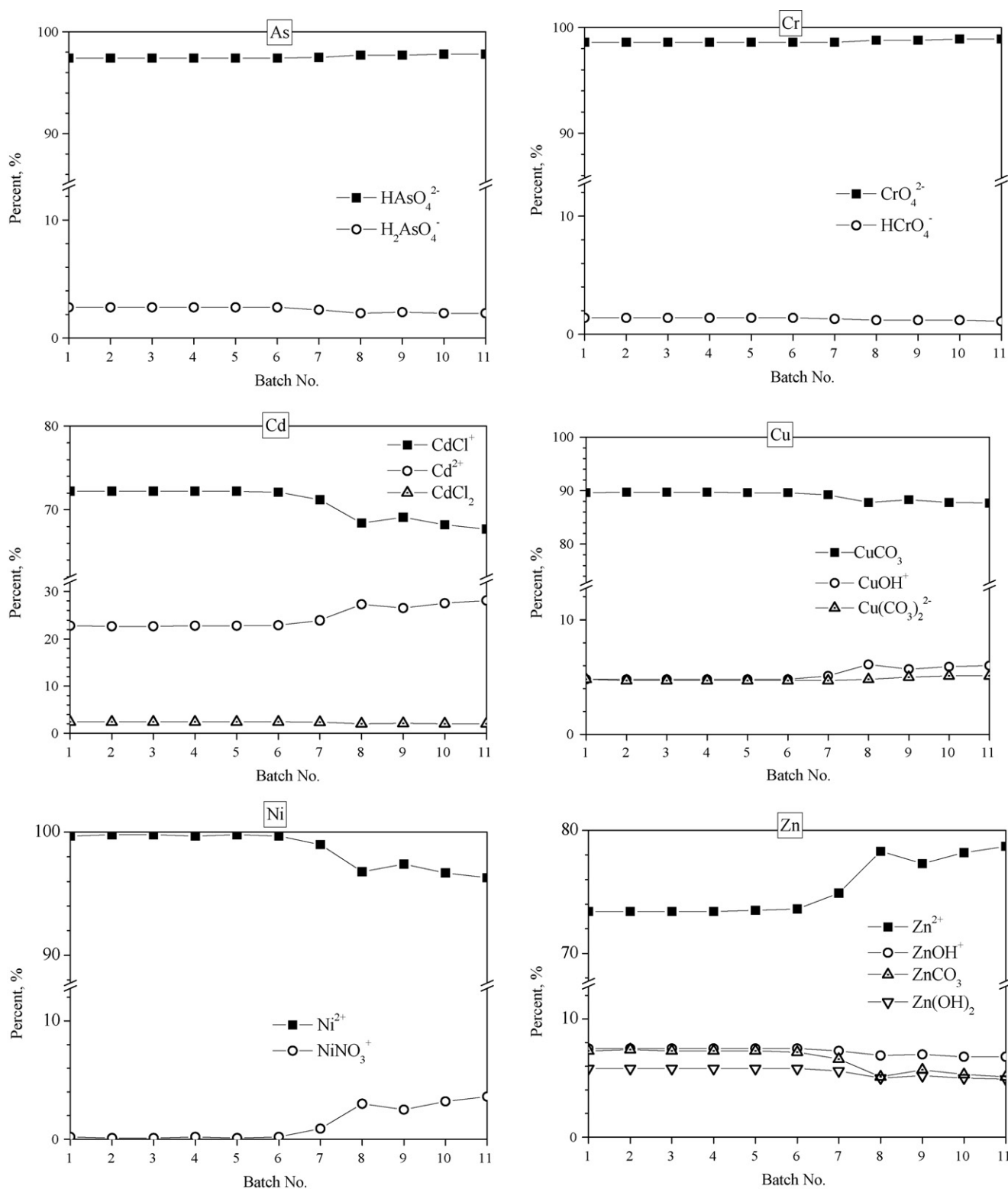


Fig. 2. Species of As, Cd, Cr, Cu, Ni and Zn in aqueous solutions obtained using the PHREEQC program (input data the same as the initial conditions of the batch sorption experiments).

trations increased in all batches. It was noted that leaching of Cr (14.3 $\mu\text{g/L}$) and Zn (120 $\mu\text{g/L}$) was observed in the control batches involving sorbent P1. In the second series of control batches, involving the investigated metals but without any sorbent, leaching of Zn (812 $\mu\text{g/L}$) was also observed, however a loss of 30 $\mu\text{g/L}$ Cd was detected.

The adsorption isotherms of the investigated metals by the four sorbents are shown in Table 3. The experimental data results displayed a good fit with the Freundlich isotherm equation, suggesting that the four sorbents contained heterogeneous surface characteristics. Based on the quantity of sorbate associated with the sorbents (as the Freundlich constant K), the

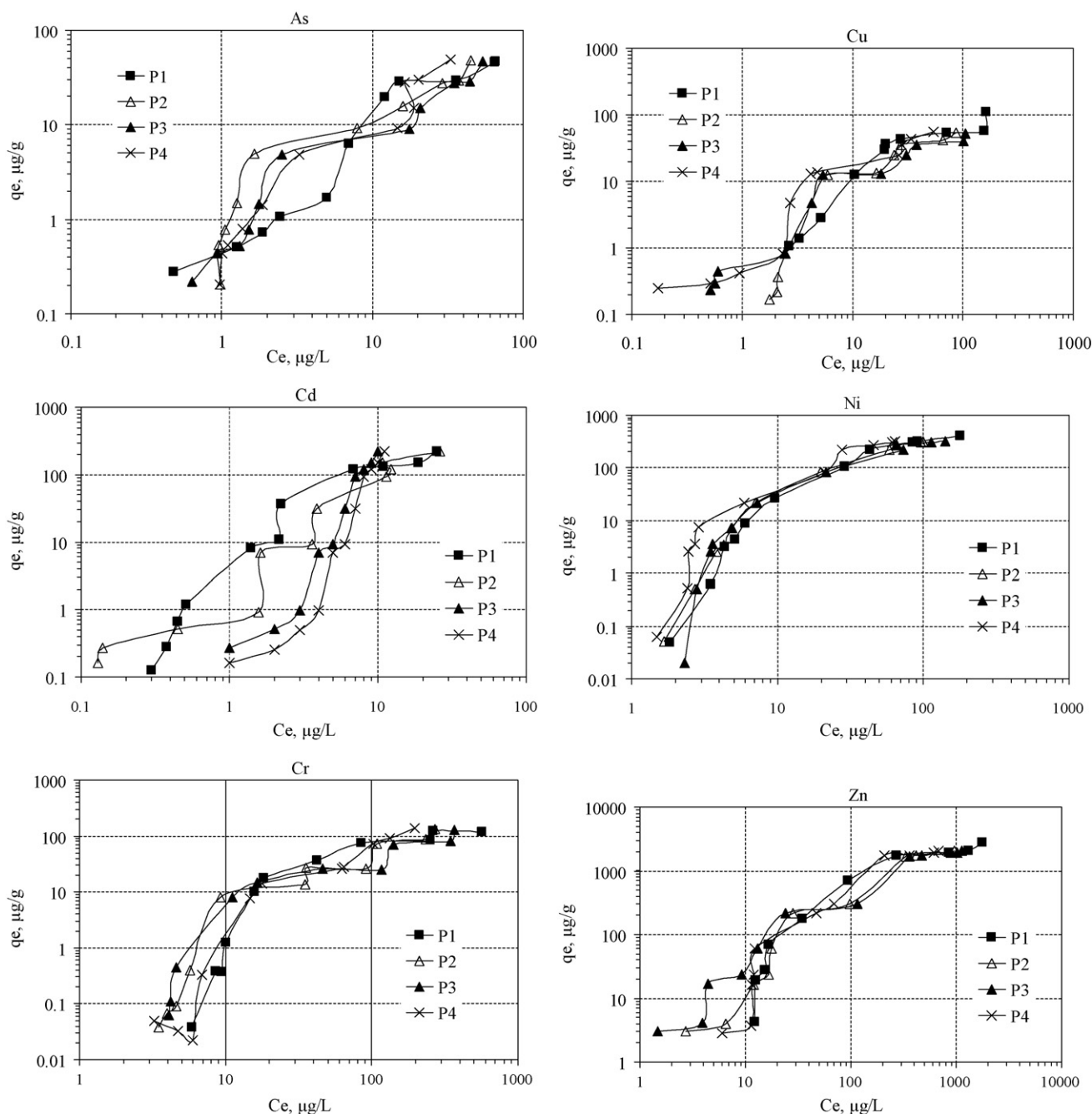


Fig. 3. Removal of coexistent heavy metals (As, Cd, Cr, Cu, Ni and Zn) using the investigated sorbents.

sorption sequence of metals for sorbents P1, P3, and P4 was $\text{Cd} > \text{Zn} > \text{Ni} > \text{Cu} > \text{As} > \text{Cr}$, while the sorption sequence of metals for sorbent P2 was $\text{Cd} > \text{Zn} > \text{Ni} > \text{As} > \text{Cu} > \text{Cr}$. The different sorption of As and Cu between sorbent P2 and the other sorbents was most likely the result of competition among HAsO_4^{2-} , CrO_4^{2-} and hydroxyl ions for sorption on the surface Lewis acid sites of the sorbents [25,26]. The sorption of anions onto the hydroxylated mineral surface might also be explained by the ligand exchange mechanism [27]. The sorption mechanism in this study was confirmed by the fact that the final pH values were higher than the initial pH values for all batch experiments (see Fig. 1).

The pH of the aqueous solution is an important controlling parameter in the sorption process. As mentioned in Section 3.1, the average equilibrium pH values of the four sorbents were similar to the reported pH_{PZC} range for GFH (between 7.5 and 8.0)

[22]. Because both positively and negatively charged groups were available at the sorbents' surface, electrostatic attraction as well as surface complexation should be considered as an important mechanism in heavy metal removal. The size and charge intensity of dominant species, which can affect the accessibility of species to the surface of pores, must also be considered. Based on electrostatic attraction, the smaller ionic radius and greater valence, the more closely and strongly is the ion adsorbed onto the sorbent [28].

For cationic metal ions, there is a direct relationship between the charge to radius ratio (Z/r) and adsorption [28]. As Section 3.2 mentioned, the dominant species for each metal at equilibrium pH were HAsO_4^{2-} , CdCl^+ , CrO_4^{2-} , CuCO_3 , Ni^{2+} and Zn^{2+} . Thus, according to the Z/r ratio of the cations Cd^{2+} (2.11), Cu^{2+} (2.82), Ni^{2+} (2.90) and Zn^{2+} (2.70) [28–30], the selectivity sequence is

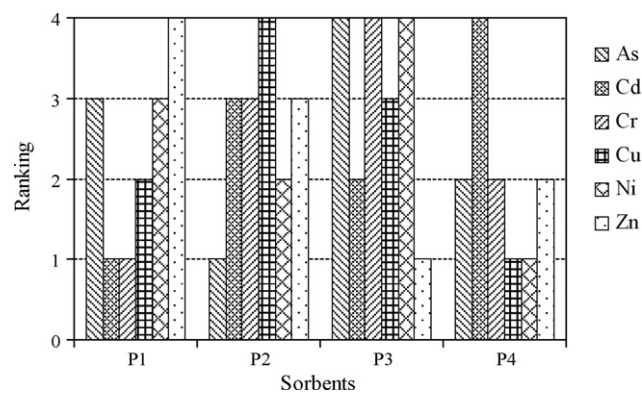
Table 2
Oversaturated heavy metal minerals/salts in the batch experiments.

	Oversaturated heavy metal minerals/salts ^a					
	As	Cd	Cr	Cu	Ni	Zn
Batch.1						
Batch.2				2		
Batch.3				2		5
Batch.4				2		5
Batch.5		1		2, 3, 4		5, 6, 7, 8
Batch.6		1		2, 3, 4		5, 6, 7, 8, 9
Batch.7		1		2, 3, 4		5, 6, 7, 8, 9, 10, 11
Batch.8		1		2, 3, 4		5, 6, 7, 8, 9, 10, 11
Batch.9		1		2, 3, 4		5, 6, 7, 8, 9, 10, 11, 12
Batch.10		1		2, 3, 4		5, 6, 7, 8, 9, 10, 11, 12
Batch.11		1		2, 3, 4		5, 6, 7, 8, 9, 10, 11, 12

^a The minerals/salts are referred to as follows: 1 = Otavite, 2 = Tenorite, 3 = Atacamite, 4 = Malachite, 5 = Hydrozincite, 6 = Smithsonite, 7 = Zincite, 8 = ZnCO₃·H₂O, 9 = Zn(OH)₂(epsilon), 10 = Zn(OH)₂(beta), 11 = Zn(OH)₂(gamma), and 12 = Zn₂(OH)₃Cl.

recognized as Ni²⁺ > Cu²⁺ > Zn²⁺ > Cd²⁺. However, the sorption sequences observed for sorbents P1, P3 and P4 and that for sorbent P2 did not accurately explain the greater selectivity of Ni and Cu compared to that of Zn and Cd. It was postulated that the actual selectivity factor also depends on other removal mechanisms, such as surface complexation (hydroxide groups), precipitation of metallic minerals/salts and adsorption to the walls of the reactors.

Cu is generally considered to be adsorbed more easily than other metal ions [24], however studies have reported that the adsorption of Cu only occurred with a high H⁺ concentration (pH ≤ 2.5) [31]. In this study however, Cu did not show preferential selectivity in the adsorption system, as the major species of Cu were CuCO₃ (89 mol%), CuOH⁺ (5 mol%) and {Cu(CO₃)₂}²⁻ (5 mol%) at the equilibrium pH (see Fig. 2). Moreover, precipitation of Cd, Cu and Zn minerals/salts (e.g. Otavite, Tenorite, Smithsonite, and so on, as Table 2 shows) in batches 5–11 may also be counted as a removal

**Fig. 4.** Ranking of the sorbents based on the average K_d values (lower values indicating greater removal efficiency).

process. It was inferred that the sorption processes were affected by several possible removal mechanisms and the selectivity sequence of sorbent may show specifications concerning properties of the sorbents and the experimental set-up applied.

3.4. Comparing the removal capacities of the sorbents

The calculated average distribution coefficient (K_d) values for each set of batches are listed in Table 3, while the overall results are displayed in Fig. 4. From Table 3, each sorbent demonstrated a similar removal efficiency for each heavy metal, displaying a very high affinity for Cd, Zn, and Ni, but less so for Cu, As and Cr. It was observed that the metal removal efficiency of the sorbents increased with greater surface area, with the sorbents containing the least available surface area (P2 and P3) displaying a lower removal efficiency at the tested concentrations than those with a higher surface area (sorbents P4 and P1). Sorbent P4 displayed the greatest removal efficiency, followed by sorbent P1.

Table 3
Characteristics of adsorption constants using the Freundlich isotherms and the average K_d values.

	Conc. range, $\mu\text{g/L}$	Sorbents	Freundlich constants			K_d , L/g	
			K , L/g	$1/n$	R^2	Avg. ^a	S.D. ^b
As	6.00 –1003	P1	0.49	1.16	0.93	0.80	0.06
		P2	0.70	1.12	0.89	1.24	0.14
		P3	0.56	1.03	0.93	0.74	0.14
		P4	0.45	1.34	0.95	0.91	0.15
Cd	2.83 –4430	P1	2.58	1.63	0.93	7.19	0.61
		P2	2.50	1.44	0.94	5.49	0.79
		P3	4.58	1.96	0.93	6.07	1.17
		P4	2.30	1.71	0.95	4.98	1.01
Cr	6.67 –2967	P1	0.18	1.16	0.75	0.41	0.10
		P2	0.19	1.19	0.83	0.36	0.13
		P3	0.11	1.25	0.82	0.33	0.11
		P4	0.03	2.16	0.88	0.40	0.06
Cu	15.2 –2370	P1	0.67	1.06	0.87	0.85	0.21
		P2	0.39	1.28	0.83	0.76	0.21
		P3	0.67	1.01	0.93	0.80	0.10
		P4	0.99	1.08	0.90	1.36	0.15
Ni	2.81 –8340	P1	1.01	1.28	0.94	2.19	0.65
		P2	0.99	1.31	0.96	2.22	0.51
		P3	0.94	1.27	0.95	2.01	0.27
		P4	1.19	1.41	0.96	3.38	0.54
Zn	58.9 –58,400	P1	1.87	1.06	0.85	2.94	0.40
		P2	1.86	1.09	0.98	2.95	0.46
		P3	2.83	1.01	0.95	3.44	0.74
		P4	2.11	1.12	0.94	3.39	0.72

^a Average of K_d values.

^b Each standard deviation (S.D.) was based on each set of values (11 batches).

It is interesting to note however that this trend was not observed between sorbents P3 and P2, where sorbent P3 displayed a lower removal efficiency than that of sorbent P2 despite having a greater surface area. Sorbents P3 and P2 had relatively similar compositions (Ferrosorp RWR), the only difference being the addition of crystal gravel to sorbent P3. The lower removal efficiency of sorbent P3 compared to sorbent P2 suggests that while cheap, crystal gravel does not appear to be viable as a sorbent for removing metals from urban stormwater.

4. Conclusions

This study examined the selectivity sequence and removal efficiency of the Ferrosorp Plus sorbent and its mixture with other minerals in treating water containing mixed heavy metal contaminants. The results from the present study show that the sorption processes were affected by several possible factors, including the pH of the sample, surface complexation of the sorbent and electrostatic attraction at the sorbent surface, interacted in a complex manner.

The Freundlich isotherm was applied to the sorption data. It is found that sorbents with a Ferrosorp base displayed a high affinity for Cd, Zn and Ni, but were less effective at removing Cu, As and Cr. It is also interesting to note that the addition of both zeolite and crystal gravel did not significantly alter this selectivity sequence.

According to the Calculated Distribution Coefficient (K_d), the results of this study indicate a potential for use of P4 (mixture of Ferrosorp Plus and zeolite) as a sorbent in stormwater treatment, especially in removal of Cd, Zn and Ni. Further research however is required to test the promising sorbent with real life urban stormwater, as well as testing the performance of different sorbents to achieve greater removal efficiency in waters containing high levels of Cu, As and Cr.

Acknowledgements

The authors would like to thank Assistant Prof. Dr. Genç-Fuhrman and Prof. Dr. Ledin for their guidance from the Institute of Environment & Resources, Technical University of Denmark. The authors also express their sincere gratitude to Harald Sommer at Ingenieurgesellschaft Prof. Dr. Sieker mbH, Germany for supplying sorbents.

References

- [1] D.K. Makepeace, D.W. Smith, S.J. Stanley, Urban stormwater quality: summary of contaminant data, *Crit. Rev. Environ. Sci. Technol.* 25 (1995) 93–139.
- [2] R.A. Goyer, W.T. Clarksom, Toxic effects of metals, in: C.D. Klaassen (Ed.), *Casarett and Doull's Toxicology: The Basic Science of Poisons*, McGraw-Hill, New York, 2001, pp. 811–867.
- [3] M. Méndez-Armenta, C. Ríos, Cadmium neurotoxicity, *Environ. Toxicol. Pharmacol.* 23 (2007) 350–358.
- [4] Agency for Toxic Substance and Disease Registry (ATSDR), *Toxicological Profile for Lead*, U.S. Department of Health and Humans Services, Public Health Service, Atlanta, GA, 2005.

- [5] F.C. Richard, A.C.M. Bourg, Aqueous geochemistry of chromium: a review, *Water Res.* 25 (1991) 807–816.
- [6] K.S. Hui, C.Y.H. Chao, S.C. Kot, Removal of mixed heavy metal ions in wastewater by zeolite 4A and residual products from recycled coal fly ash, *J. Hazard. Mater.* 127 (2005) 89–101.
- [7] G. McKay, *Use of Adsorbents for the Removal of Pollutants from Wastewaters*, first ed., CRC Press, New York, 1996.
- [8] B. Bayat, Comparative study of adsorption properties of Turkish fly ashes. I. The case of nickel (II), copper (II) and zinc (II), *J. Hazard. Mater.* B95 (2002) 251–273.
- [9] H. Genç-Fuhrman, P.S. Mikkelsen, A. Ledin, Simultaneous removal of As, Cd, Cr, Cu, Ni and Zn from stormwater: experimental comparison of 11 different sorbents, *Water Res.* 41 (2007) 591–602.
- [10] H. Genç-Fuhrman, P. Wu, Y.S. Zhou, A. Ledin, Removal of As, Cd, Cr, Cu, Ni and Zn from polluted water using an iron based sorbent, *Desalination* 226 (2008) 357–370.
- [11] W.S. Wan-Ngah, M.A.K.M. Hanafiah, Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: a review, *Bioresour. Technol.* 99 (2008) 3935–3948.
- [12] E. Malkoc, Y. Nuhoglu, M. Dundar, Adsorption of chromium (VI) on pomace—an olive oil industry waste: batch and column studies, *J. Hazard. Mater.* 138 (2006) 142–151.
- [13] J.H. Potgieter, S.S. Potgieter-Vermaak, P.D. Kalibantonga, Heavy metals removal from solution by palygorskite clay, *Miner. Eng.* 19 (2006) 463–470.
- [14] S.k. Pitcher, R.C.T. Slade, N.I. Wards, Heavy metal removal from motorway stormwater using zeolites, *Sci. Total Environ.* 334 (2004) 161–166.
- [15] M. Badruzzaman, P. Westerhoff, D.R.U. Knappe, Intraparticle diffusion and adsorption of arsenate onto granular ferric hydroxide (GFH), *Water Res.* 38 (2004) 4002–4012.
- [16] A. Genz, A. Kornmüller, M. Jekel, Advanced phosphorus removal from membrane filtrates by adsorption on activated aluminium oxide and granulated ferric hydroxide, *Water Res.* 38 (2004) 3523–3530.
- [17] D.W. Breck, *Zeolite Molecular Sieves: Structure, Chemistry, and Use*, first ed., Wiley, New York, 1974.
- [18] M. Scholz, J. Xu, Performance comparison of experimental constructed wetlands with different filter media and macrophytes treating industrial wastewater contaminated with lead and copper, *Bioresour. Technol.* 83 (2002) 71–79.
- [19] A. Jang, Y. Seo, P.L. Bishop, The removal of heavy metals in urban runoff by sorption on mulch, *Environ. Pollut.* 133 (2005) 117–127.
- [20] D. Liu, J.J. Sansalone, F.K. Cartledge, Comparison of sorptive filter media for treatment of metals in runoff, *J. Environ. Eng.* 131 (2005) 1178–1186.
- [21] R.M. Cornell, U. Schwertmann, *The Iron Oxides: Structure, Properties, Reactions, Occurrence and Uses*, VCH Press, New York, 1996.
- [22] A. Sperlich, A. Werner, A. Genz, G. Amy, E. Worch, M. Jekel, Breakthrough behavior of granular ferric hydroxide (GFH) fixed-bed adsorption filters: modeling and experimental approaches, *Water Res.* 39 (2005) 1190–1198.
- [23] C.A.J. Appelo, D. Postma, *Geochemistry, Groundwater and Pollution*, second ed., Taylor & Francis, Amsterdam, 2005.
- [24] R. Coşkun, C. Soykan, M. Saçak, Adsorption of copper (II), nickel (II) and cobalt (II) ions from aqueous solution by methacrylic acid/acrylamide monomer mixture grafted poly (ethylene terphthalate) fiber, *Sep. Purif. Technol.* 49 (2006) 107–114.
- [25] W. Stumm, J.J. Morgan, *Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters*, John Wiley and Sons, New York, 1981.
- [26] M. Streat, K. Hellgardt, N.L.R. Newton, Hydrous ferric oxide as an adsorbent in water treatment. Part 2. Adsorption studies, *Process Saf. Environ. Prot.* 86 (2008) 11–20.
- [27] G. Sposito, *The Chemistry of Soils*, Oxford University Press, New York, 1989.
- [28] A. Demirbas, E. Pehlivan, F. Gode, T. Altun, G. Arslan, Adsorption of Cu (II), Zn (II), Ni (II), Pb (II), and Cd (II) from aqueous solution on Amberlite IR-120 synthetic resin, *J. Colloid Interface Sci.* 282 (2005) 20–25.
- [29] S.T. Breviglieri, E. T.G. Cavalherio, G.O. Chierice, Correlation between ionic radius and thermal decomposition of Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) diethanoldithiocarbamates, *Thermochim. Acta* 356 (2000) 79–84.
- [30] B.K. Kim, S.B. Cha, J.H. Park, Ordering behaviors of divalent and pentavalent cations in lead magnesium niobates modified by lanthanum, nickel, zinc, and cadmium, *Mater. Sci. Eng. B* 58 (1999) 244–250.
- [31] M. Malandrino, O. Abollino, A. Giacomino, M. Aceto, E. Mentasti, Adsorption of heavy metals on vermiculite: influence of pH and organic ligands, *J. Colloid Interface Sci.* 299 (2006) 537–546.