

# Kinetic sorption modelling of Cu, Ni, Zn, Pb and Cr ions to pine bark and blast furnace slag by using batch experiments

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## Abstract

Storm water and landfill leachate can both contain significant amounts of toxic metals such as Zn, Cu, Pb, Cr and Ni. Pine bark and blast furnace slag are both residual waste products that have shown a large potential for metal removal from contaminated water. There are however many variables that must be optimized in order to achieve efficient metal retention. One of these variables is the time of which the solution is in contact with each unit of filter material. Metal sorption was studied in two laboratory experiments to improve the knowledge of the effects of contact time. The results showed that pine bark was generally more efficient than blast furnace slag when the metal concentrations were relatively small, whereas blast furnace slag sorbed most metals to a larger extent at increased metal loads. In addition, sorption to blast furnace slag was found to be faster than metal binding to pine bark. A pseudo-second-order kinetic model was able to describe the data well within 1000 s of reaction time.

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## 1. Introduction

Resource optimization implies that we should minimize waste and find new applications for agricultural and industrial by-products. The use of residual waste products in water treatment has been explored all over the world during the past century. For example, technologies have been developed and tested for removal of phosphorus (Johansson, 1998; Nehrenheim et al., in preparation), metals (Färm, 2003; Kietlinska and Renman, 2005) and organic compounds (Ratola et al., 2003). Examples of materials that have been found to efficiently retain metals from water solutions include agricultural wastes such as bagasse (Mohan and Singh, 2002), sewage sludge ash (Pan et al., 2003), cocoa shells (Meunier et al., 2002), barks (Al-Asheh

and Duvnjak, 1997, 1998, 2000) and slags (Dimitrova and Mehandgiev, 1999). The present study focuses on the use of slag and pine bark, which are both residual products available from industries in many parts of the world.

Metals such as copper (Cu), zinc (Zn), nickel (Ni), lead (Pb) and chromium (Cr) are commonly found in storm water run-off and landfill leachate. Recently, an on-site column study revealed that pine bark was more efficient than slag in reducing the concentrations of certain metals from landfill leachate (Nehrenheim, 2005; Nehrenheim et al., 2005). The study also showed that contact time, or the filter hydraulic load, is an important parameter when using reactive filters. Other variables shown to influence the sorption efficiency of a filter are the pH value, the concentration of dissolved complex-forming ligands, and the concentration of target cations. The mechanisms involved in metal retention by slag are thought to be ion exchange with calcium on particle surfaces and precipitation on  $\text{Al}(\text{OH})_3$  and  $\text{SiO}_2$  (Dimitrova and Mehandgiev, 2000), but sorption to

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sulphide components in the slag may also be important at low surface coverage (Gustafsson et al., unpublished results). Sorption to pine bark is mainly dominated by metal complexation to surface functional groups that may include carboxyl, hydroxyl, sulphate, phosphate and amino groups (Al-Asheh and Duvnjak, 1997).

In this study, sorption batch tests were conducted to investigate and compare the sorption capacity of pine bark and blast furnace slag. The objective was to compare single- and multi-component metal retention to the materials and to study the kinetics of the processes. Other modelling approaches have been tested for these materials by other researchers (Dimitrova, 1996; Feng et al., 2004), mostly using simple equilibrium models based on empirical Freundlich or Langmuir equations. However, the retention time in rapid filters may be in the order of seconds, which is much too short for equilibrium to occur. Curcovic et al. (2001) suggested an equilibrium time of 8 h, but the stirring procedure is most often carried out for 24 h in equilibrium experiments (Vázquez et al., 1994; Al-Asheh and Duvnjak, 1997). Hence models built on chemical equilibrium concepts may have limited relevance unless sorption kinetics is well described. Simple kinetic models, derived for individual systems, may be more useful in practical applications.

The aim of this study was to investigate whether a kinetic model could be used to describe the sorption of Zn, Cu, Pb, Cr and Ni to pine bark and blast furnace slag for contact times ranging from 1 to 1000 s. An understanding of the kinetics of sorption to pine bark and slag will hopefully give useful knowledge for on-site full-scale applications. Long retention times are often not desirable on-site for practical reasons (e.g. high flow rate and limited space). Other contact-time experiments have been carried out for sorption of some metals to pine bark by Jang et al. (2005) (Cu, Pb and Zn) and Al-Asheh and Duvnjak (1997) (Cd), and to other similar filter materials by Allen et al. (2005) and Özacar and Sengil (2005).

## 2. Theoretical approach

The percentage retention rate ( $R$ ) to the material was calculated according to

$$R = \frac{100 \cdot (C_i - C_t)}{C_i}, \quad (1)$$

where  $C_i$  is the initial concentration (normally the same as the added concentration) and  $C_t$  is the concentration in solution at time  $t$  (s). The metals retained in the sorbent phase during the kinetics experiment were calculated according to mass balance

$$m(Q_e - Q_i) = V(C_i - C_e), \quad (2)$$

where  $m$  (g) is the sorbent mass,  $Q_e$  (mg/g) is the sorbed concentration of metal ion (mg/g),  $Q_i$  is the initial metal

ion concentration on the sorbent surface,  $C_e$  (mg/l) is the metal ions removed from solution by retention to the sorbent and  $V$  is the solution volume. The results for the first 100 s of sorption fitted well to the first-order kinetic model, which was expressed in the following way:

$$\ln C_t = \ln C_i - kt, \quad (3)$$

where  $C_t$  (mg/l) is the concentration of metal ions in solution at time  $t$  (s) and  $k$  is the rate of absorption to pine bark at 25 °C (Jang et al., 2005). However, for the entire time span examined (1–1000 s), a pseudo-second-order kinetic model proved to describe the data much better. This model approach has earlier been used by, for example, Ho and Ofomaja (2006) for Cu sorption to palm kernel fibre. In the pseudo-second-order kinetic model, the kinetics was expressed as the change of the mass of sorbed metal with time:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2, \quad (4)$$

where  $k$  is the rate constant of sorption ( $\text{dm}^3/\text{mg s}$ ),  $q_e$  (mg/g) is the amount of metal ions adsorbed at equilibrium and  $q_t$  (mg/g) is the amount of Cu ions adsorbed at time  $t$  (s) (Ho and McKay, 2000).

## 3. Methods

### 3.1. Materials

Pine bark is a by-product from the timber industry. It consists of approximately 85–90% dried and granulated pine bark and 10–15% wood fibre. The material is a commercial product named Zugol™, which was supplied by Zugol AB in Falun, Sweden. The everyday use of the product is to absorb fluids from accidental leakage, i.e. oil, blood or urine. The background metal content of pine bark is shown in Table 1.

Blast furnace slag (BFS) is a by-product from steel manufacturing. Two types of slag were used in the present study, crystalline (BFS-C) and amorphous (BFS-A) slag. The particle size of the tested BFS is 2–4 mm (Merox SSAB, 2005). The difference between the two types of BFS is the procedure (time) when the slag is cooled. BFS-A is cooled rapidly in large water basins leading to a amorphous form, while BFS-C is cooled in the open which gives the slag time to form a crystalline structure. Table 2 shows the chemical composition of the slag.

### 3.2. Methods

Bulk density and porosity were determined after heating three 100 cm<sup>3</sup> replicates of the materials to 105 °C for 64 h.

Table 1  
Metal content of pine bark (Zugol™)

Metal ions	As	Pb	Cd	Co	Cu	Cr	Ni	V	Zn
mg/kg	0.11	2.5	0.6	0.25	6.0	1.8	0.8	0.54	83

Table 2  
Chemical composition of BFS-A and BFS-C

Element (mg/kg)	BFS-C <sup>a</sup>	BFS-A <sup>b</sup>
Ca	214410	214410
Fe	2735	3553
K	4184	4225
Mg	104940	99512
Na	3865	4013
Si	159397	154722
Al	67744	67215
As	0.525	0.966
Ba	369	363
Cd	0.0186	0.0149
Co	10.8	<2
Cr	42.3	30.2
Cu	<2	4.56
Hg	0.132	0.139
Mn	4468	4164
Ni	<2	2.42
Pb	0.595	0.544
Sr	303	300
S	10900	12900
V	611	487
Zn	3.35	3.46

<sup>a</sup> Crystalline blast furnace slag.

<sup>b</sup> Amorphous blast furnace slag.

The materials were then cooled and weighed according to standard procedures (ISO 11272).

The relationship between contact time and sorption efficiency of metal ions was determined in a batch test (150 rpm). Three multi-component solutions were prepared containing 0.2 mg/l, 2 mg/l and 20 mg/l of Zn(NO<sub>3</sub>)<sub>2</sub>, Pb(NO<sub>3</sub>)<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, Cr(NO<sub>3</sub>)<sub>3</sub>, and Ni(NO<sub>3</sub>)<sub>2</sub>. Three replicates of each solution were mixed with 10 g of slag and 5 g of pine bark in glass bottles and shaken to determine metal retention. Ten grams of slag corresponded approximately to 5 g of pine bark, by volumetric measures. A potential future full-scale application of the technique would be limited by e.g. space demand, which was taken into consideration in this way. The contact times examined were 1, 10, 100 and 1000 s. A second batch experiment was conducted for 30 min to investigate the removal efficiency for all three materials. This corresponds to what can be considered as a reasonable retention time in a compact filter in full-scale applications (Nehrenheim, 2005). In this experiment, the metal concentrations ranged between 0.2 and 200 mg/l (0.2, 2, 20 and 200 mg/l); metal solutions and sorbent concentrations were the same as in the contact-time experiment. After centrifugation and filtration, metal concentrations in the solutions were analyzed by atomic absorption spectrometry (AAS) with an AAS Vario 6 instrument in accordance with Swedish Standard methods (SS-EN 028150). The detection limits were for Zn: 0.0014 mg/l, Pb: 0.013 mg/l, Cu: 0.003 mg/l, Ni: 0.004 mg/l and Cr: 0.0054 mg/l, respectively. Directly after shaking filtration, the solution pH was measured to be around 4.5 (range 4.0–5.1).

## 4. Results and discussion

### 4.1. Bulk density and porosity of the materials

Slags had a higher bulk density and porosity than pine bark (Table 3). The values for BFS were similar to what was determined earlier for this material (Johansson, 1999).

### 4.2. Metal sorption to slag and pine bark

Fig. 1 illustrates the results from sorption experiments with multi-metal solutions shaken for 30 min. Pine bark retained more than 75% of all metals at the 0.2 and 2 mg/l concentration levels. Metal retention was lower at initial metal concentrations ( $C_i$ ) of 20 and 200 mg/l except for Cu for which 98% was retained at  $C_i = 200$  mg/l.

Cr(III) and Cu ions (80–100%) were retained by BFS-A at all initial concentrations. The retention of Pb increased with increased Pb concentration and Cr(III) retention was more than 90% at  $C_i = 2$  and 20 mg/l but less efficient at smaller or larger concentrations. The retention of Zn at large concentrations (i.e. at  $C_i = 20$  and 200 mg/l) was less than 60%, perhaps due to competition for sorption sites in the multi-component solutions used. BFS-C was a rather strong sorbent (between 70% and 90% sorption retention) for Zn, Cu and Pb in all batch experiments. Taken together the results show that the materials consistently sorbed Pb, Cu and Cr(III) relatively strongly (Fig. 1). For Zn strong sorption was observed at low concentrations, whereas mixed results were obtained at larger concentrations. In most cases the sorption of Ni was relatively weak. These trends were not unexpected since Pb, Cu and Cr(III) are hydrolyzed more easily and thus can be bound strongly through hydroxide precipitation and complexation to surfaces with oxygen-containing functional groups. In addition, Ni forms relatively soluble sulphides (Morse and Arakaki, 1993), which could be of importance in the case of BFS.

### 4.3. Kinetics

The contact time between the water and the sorbent in a filter application is limited by the space available on-site and by the leachate flow rate. Batch experiments can provide information on the contact time required to achieve the optimum conditions for metal removal.

The concentration of metal ions remaining in solution ( $C_f/C_i$ ) at different contact times was largest in the pine

Table 3  
Density and porosity of the evaluated materials

	BFS-A <sup>a</sup>	BFS-C <sup>b</sup>	Pine bark
Density (g/cm <sup>3</sup> )	1.2–1.6	0.8–1.5	0.6–0.9
Porosity (%)	40–58	44–55	38–49

<sup>a</sup> Amorphous blast furnace slag.

<sup>b</sup> Crystalline blast furnace slag.

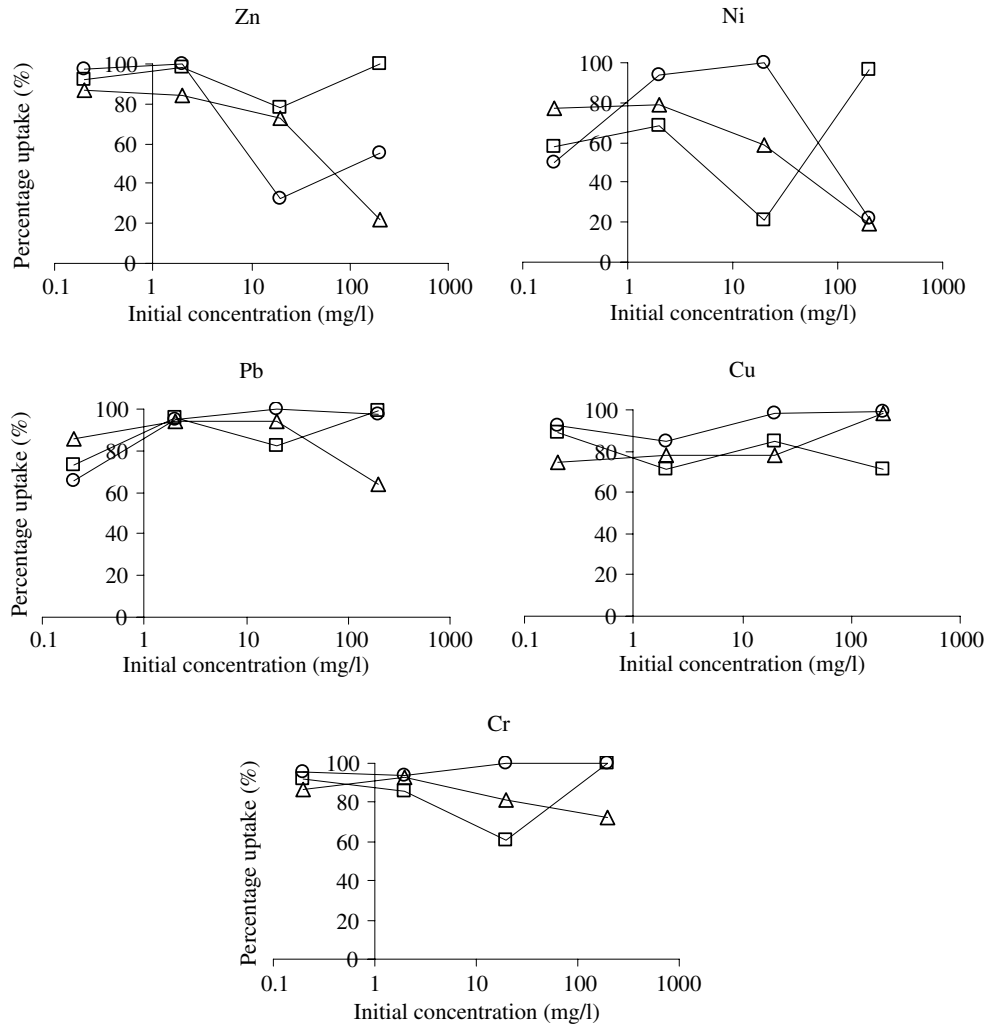


Fig. 1. Sorption percentage of Zn, Ni, Pb, Cu and Cr(III) to BFS-A (○), BFS-C (□) and pine bark (△) after 30 min.

Table 4

Pseudo-second-order model parameters by using the linear method for pine bark, BFS-A and BFS-C, respectively

	Pine bark				BFS-A <sup>a</sup>			BFS-C <sup>b</sup>		
	$C_i$	$q_e$	$k$	$R^2$	$q_e$	$k$	$R^2$	$q_e$	$k$	$R^2$
Zn	0.2	0.03	35.1	0.97	0.03	22.8	0.96	0.04	3.62	0.89
	2	0.39	1.92	1.00	0.40	7.66	0.92	0.40	7.08	0.99
	20	3.98	0.77	1.00	3.99	18.38	0.97	4.00	12.29	1.00
Cu	0.2	0.03	7.24	0.99	0.01	-0.17	0.79	0.02	3.53	0.87
	2	0.37	0.64	0.99	0.20	1.91	0.81	0.20	5.50	0.97
	20	3.94	0.37	1.00	2.00	2.40	0.93	2.00	6.13	0.96
Pb	0.2	0.01	1.41	0.79	0.02	7.3	0.95	0.01	33.94	1.00
	2	0.20	1.79	0.97	0.19	78.37	0.68	0.20	28.33	1.00
	20	2.00	2.40	0.93	2.00	25.47	0.89	2.00	24.33	1.00
Ni	0.2	0.02	340	1.00	0.01	4.21	0.93	0.01	10.18	0.99
	2	0.19	1.29	0.83	0.01	4.21	0.93	0.17	1.69	0.95
	20	1.97	0.76	0.77	1.99	150	0.96	1.95	0.99	0.86
Cr	0.2	0.02	70.15	0.98	0.02	6.46	0.97	0.02	7.27	0.89
	2	0.19	2.03	0.87	0.20	22.03	0.92	0.20	14.61	0.99
	20	1.99	1.18	0.85	1.99	90.83	0.96	2.00	25.49	1.00

<sup>a</sup> Amorphous blast furnace slag.

<sup>b</sup> Crystalline blast furnace slag.

bark batches. The sorption to each mass unit of sorbent was greatest for the slags at short contact times; in other words sorption to pine bark was a relatively slow process. Pine bark was a more efficient sorbent than slag for Cu, but slag appeared to be more efficient for Zn and Pb. The removal rate for Zn and Pb was equal at 1000 s. For both metals, the sorption rate was fast and substantial sorption efficiency was obtained already after 100 s. However, the uptake of Pb was linear during the entire period of 1000 s and more extended contact times would be required to fully evaluate Pb retention by pine bark.

Jang et al. (2005) conducted sorption kinetics experiments for three types of mulch. Their results could be sat-

isfactorily fitted to a first-order kinetic model for the first 10 min of shaking, but after this initial reaction, sorption deviated from the model. A similar observation can be made for the experimental data of this study. Second-order or pseudo-second-order models have often been found to provide acceptable descriptions of kinetic sorption data. A recent example is the study of Allen et al. (2005), who showed that the sorption of basic dyes to kudzu was more successfully described by the pseudo-second-order model than by the pseudo-first-order model. Table 4 gives empirical  $k$  data and  $R^2$  value from the first 1000 s of contact to the sorbent for concentrations of 0.2, 2 and 20 mg/l. Pine bark sorbed metals relatively strongly when the initial con-

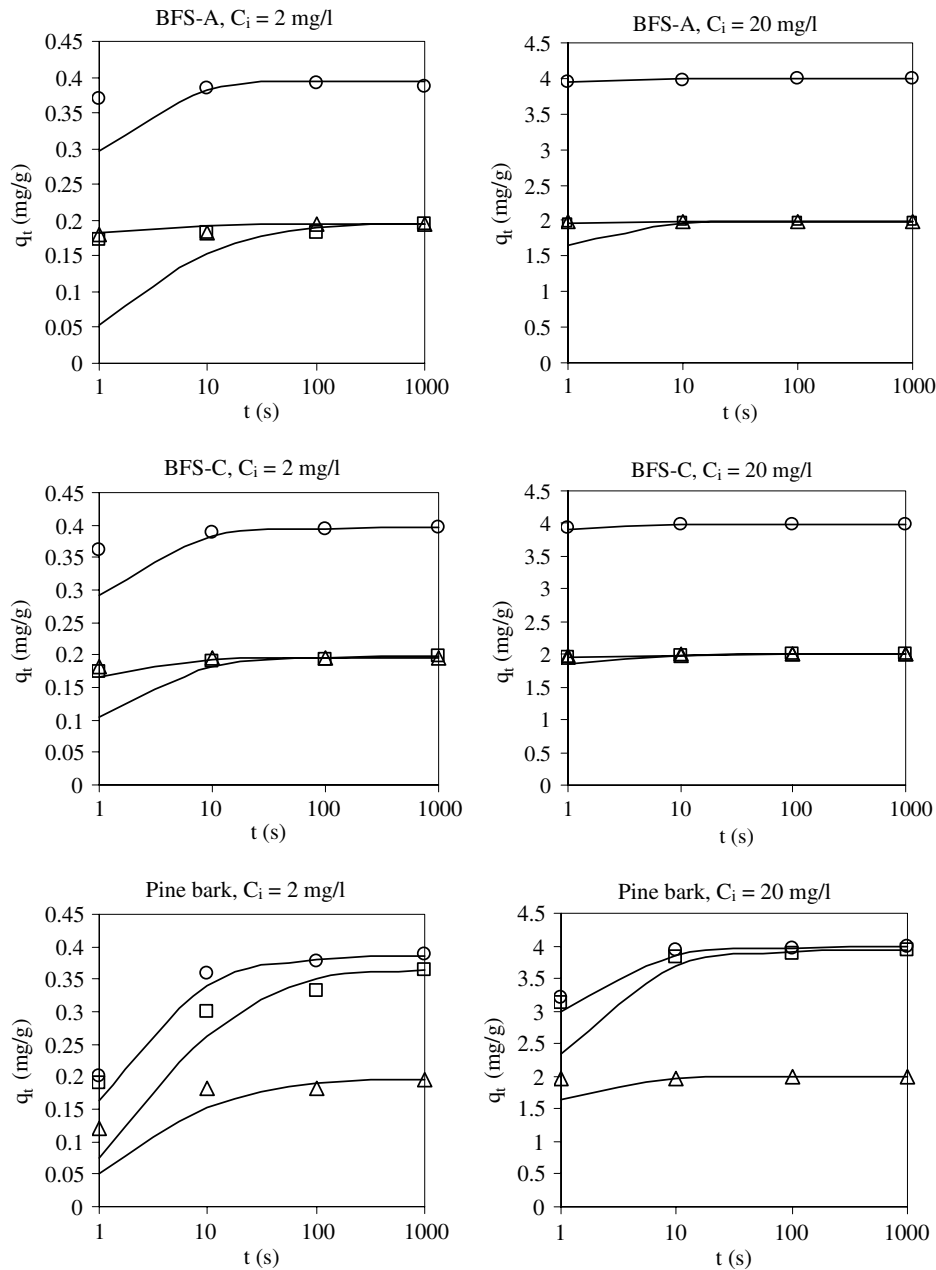


Fig. 2. Pseudo-second-order model (curves) and data (symbols) on the metal uptake to the sorbent materials (mg/g). The metals in the model are: Pb ( $\Delta$ ), Zn ( $\circ$ ) and Cu ( $\square$ ) and the initial concentrations 2 and 20 mg/l.

centration ( $C_r$ ) was small (Fig. 2), while the slags were more efficient in the higher metal concentration range. The results for pine bark conformed very well to the model except for low concentrations of Pb and Ni. Although this may be related to deficiencies in the model, it might also be explained by contamination or uncertainties in the analytical procedures. For Cr(III) the retention was strong for all the three sorbents tested.

## 5. Conclusions

Single laboratory batch experiments give little reliable information on metal retention in full-scale leachate treatment filters, since they exclude many important variables. For example, the leachate can contain dissolved organic matter, which can bind metal ions through complexation, thus reducing metal sorption to the filter materials. However, laboratory experiments, together with complementary studies on additional crucial parameters (e.g. composition of the leachate matrix), enable the processes involved in filter technology to be monitored and optimized. Increased contact time and low leachate concentrations of metals were favourable for sorption to pine bark whereas sorption to slag was more efficient at larger metal concentrations (with the exception of Cu). This agrees well with the conclusions drawn by Nehrenheim (2005) in a pilot experiment.

The pH examined after shaking the materials (4.5) is not optimal for metal retention by either inorganic or organic sorbents. For example, Cu, Zn, Pb and Ni sorption to blast furnace slag is much stronger at higher pH, i.e. above pH 6–7 (Dimitrova, 1996; Dimitrova and Mehandgiev, 1998). This is due to pH-dependent sorption (i.e., to oxides and organic matter) and to the formation of hydroxides and carbonates at high pH. In a full-scale application, it is of great importance to ensure that retained metals are not subsequently released and thus that the pH is kept at a sufficiently high level. A pilot study conducted during 2005 showed that there is a risk of metal leaching at low metal concentrations in the percolating water (Nehrenheim, 2005). If pH varies, the risk of leaching could increase even further if metals are precipitated in the filters.

From this study, we conclude that

- With the exception of copper, pine bark retained metals more strongly at small metal concentrations whereas slag was a more efficient metal sorbent at larger concentrations.
- Metal retention to pine bark and to two inorganic slag sorbents fitted well to a pseudo-second-order kinetic model, which suggests that the use of this model approach can be a reliable tool when predicting metal sorption in systems with short contact times.

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