



Removal of metals from landfill leachate by sorption to activated carbon, bone meal and iron fines

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ABSTRACT

Sorption filters based on granular activated carbon, bone meal and iron fines were tested for their efficiency of removing metals from landfill leachate. Removal of Al, As, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Mo, Ni, Pb, Sr and Zn were studied in a laboratory scale setup. Activated carbon removed more than 90% of Co, Cr, Cu, Fe, Mn and Ni. Ca, Pb, Sr and Zn were removed but less efficiently. Bone meal removed over 80% of Cr, Fe, Hg, Mn and Sr and 20–80% of Al, Ca, Cu, Mo, Ni, Pb and Zn. Iron fines removed most metals (As, Ca, Co, Cr, Cu, Fe, Mg, Mn, Pb, Sr and Zn) to some extent but less efficiently. All materials released unwanted substances (metals, TOC or nutrients), highlighting the need to study the uptake and release of a large number of compounds, not only the target metals. To remove a wide range of metals using these materials two or more filter materials may need to be combined. Sorption mechanisms for all materials include ion exchange, sorption and precipitation. For iron fines oxidation of Fe(0) seems to be important for metal immobilisation.

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1. Introduction

Landfill is still the most common waste disposal option in the European Union [1], in spite of efforts to find alternatives. Landfills affect the environment, for example via leachate, which is water that becomes contaminated due to passing through waste. Its main groups of pollutants are dissolved organic matter, inorganic macro components (including nutrients), heavy metals and xenobiotic organic compounds [2].

Various forms of biological treatment, at the landfill site or in a municipal waste water treatment plant, are the most common methods for dealing with leachates in Sweden. Although biological processes are efficient for organic matter and nutrients, heavy metals are not their main targets [3]. The implementation of new European legislation has dramatically decreased the landfilling of organic waste in Sweden. This is expected to reduce the amount of organic matter and nutrients in the leachate and thus increase the relative importance of heavy metals [4,5]. Therefore, there is a growing interest in finding cost-effective methods to remove heavy metals from landfill leachate.

Sorption filtration has been proposed as a promising technique for removing metals from contaminated waters, since it has shown potential to achieve good removal at relatively low cost and with low energy demands [6,7]. Sorption is here defined as a collective term for adsorption to the surface and absorption into the structure of a material. Strictly speaking, precipitation is not sorption. It is, however, often difficult to distinguish between sorption and precipitation and therefore, in this paper, precipitation is included in the term “sorption”.

The aim of this study was to evaluate the usefulness of sorption filters as a means of removing metals from landfill leachate. Although there is a great deal of research demonstrating that metals can be removed from solution by means of sorption, most of these studies concern idealised conditions and solutions containing only one or a few metals [6–14]. Leachate however is a complex mixture where the interactions between the different pollutants will affect their sorption behaviour. Therefore, there is a need to study sorption of a large number of metals under more realistic conditions using real landfill leachate. For this reason this study was designed to mimic real conditions as closely as possible while restricting the size of the experimental setup to lab scale.

To identify suitable filter materials a literature review and a batch screening test using real landfill leachates [15] were performed. Granular activated carbon (GAC), bone meal (BM) and iron fines (IF) were selected based on their availability, price and ability to remove metals.

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The efficiency of activated carbon for the removal of organic matter from landfill leachate has been demonstrated by a large number of studies [16]. Metal removal from solution has also been thoroughly demonstrated [8,13,14,17]. However, relatively few studies have described heavy metal removal from real landfill leachate using activated carbon. Removal of Cr, Fe, Ni and Pb from real landfill leachate using only activated carbon has been demonstrated [18–20] and Kocasoy [21] achieved the removal of Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, and Zn with coagulation and flocculation followed by activated carbon filtration. The present study attempts to demonstrate the removal of a large number of metals using GAC. Although GAC can originate from various sources, including many by-products and types of waste [7,8,16,22], it is a relatively expensive material.

BM is a by-product from the meat industry. It is currently difficult to find a use for the whole production, which makes it relatively cheap [9]. The usefulness of bone material for removing metals from solution has been demonstrated in several studies [9–11,23,24]. However, no published studies using landfill leachate were found.

Iron fines are by-product from many industries. Its cost depends on the price of scrap metal but it is relatively inexpensive. Zero-valent iron and iron oxide containing materials have been thoroughly demonstrated to remove arsenic from contaminated waters [25,26]. Heavy metals can also be removed [6,12,27–29]. Dong et al. [30] evaluated metal removal from landfill leachate with promising results motivating further study.

2. Experimental

2.1. Filter materials

The activated carbon used in this study was a commercially available, peat derived, steam activated granular activated carbon (GAC) with a particle size of 0.25–1 mm. According to the supplier (Brenntag Nordic AB, Malmö, Sweden), it is suitable for various uses including improvement of drinking water quality.

A commercially available bone meal (BM) from Elco Food AB (Klippan, Sweden) was used. This product is derived from cow and pig bones and contains 73% ash, 19% protein, 7% fat and 2% moisture. The product is sterilised and the particle size specified as less than 2 mm with most particles being a very fine powder.

Iron fines (IF) were collected from two cutting tools at a local metal workshop. Due to the mode of operation at the workshop, the fines were mixed with cutting fluids consisting of organic oils (CAS numbers 8002-13-9, 112-80-1, 2717-15-9, 143-19-1 and 34590-94-0). Most of the particles in this material could pass through a 2 mm sieve but there was considerable variation.

To ensure acceptable flow properties, BM and IF were mixed with filter sand (Rådasand AB, Göteborg, Sweden) with a particle size of 0.8–1.2 mm (60 vol% and 50 vol%, respectively). GAC, IF and filter sand were rinsed 4 times in deionised water and oven-dried at 105 °C. BM was not rinsed since that was not practical due to its fine, powdery particles.

2.2. Landfill leachate

Leachate was collected from a landfill cell containing 7–14 years old mixed industrial and municipal solid waste. The cell is in the methanogenic phase. Methanogenic leachate is characterised by near-neutral pH and strongly reducing conditions [2]. This leachate's composition is stable over time and some metal concentrations (especially Ni and Cr) are high enough to be considered a problem. Therefore it was chosen for the study.

One batch of leachate (1 m³) was collected and employed throughout the study. The leachate was stored in an insulated con-

tainer in a sheltered outdoor area. Outdoor temperatures remained below 10 °C throughout the study. Smaller portions of leachate needed for the experiment were stored at ambient room temperature for a maximum of three days. The composition of the leachate was analysed initially, and on three additional occasions during the experiment.

2.3. Filtration study

Ten acid washed PVC columns with a height of approximately 50 cm and an inner diameter of 10.5 cm were used. 90 µm HDPE filters were installed at the bottom and top of the columns, which were sealed with silicone. PVC tubing and HDPE connections were employed. The filter materials were filled into the columns and compacted using a 500 g weight. Three replicate columns were used for each filter material and one control was filled with filter sand.

The leachate was pumped through the columns in an up flow mode to avoid channelling. The flow rate was initially set to 1 m/day in the GAC and sand columns and to 0.2 m/day in the BM and IF columns. The smaller flow rate was chosen for materials expected to have lower hydraulic conductivity. After 18 days the flow rate was increased to approximately 4.4 and 1.2 m/day, respectively.

The experiments continued for 29 days. The pH was measured most working days in the effluent from each column. Leachate for further analysis was collected and mixed to approximately flow proportional samples representing days 1–10, days 11–20 and days 21–29, respectively. Samples from the untreated leachate were taken on days 2, 10, 20 and 29.

2.4. Analyses

All analyses were performed on unfiltered samples, as when landfill leachate is analysed for compliance control, since the aim of the study was to imitate real conditions. The pH was analysed with a handheld pH meter (Buch & Holm WTW Multi 340i). All other analyses were performed by the Plant Ecology and Systematics section of the Department of Ecology at Lund University. Element analyses were conducted using ICP MS (Elan 6000, PerkinElmer) or ICP AES (OPTIMA 3000 DV, PerkinElmer) depending on the concentration. Total organic carbon (TOC) and total nitrogen (TN) were analysed using a TOC analyser (TOV-VCPH with N-module TNM-1, Shimadzu) and Cl by means of ion chromatography (861 Advanced Compact IC, column Metrosep A Supp 5, Metrohm, Herisau, Switzerland).

3. Results

3.1. Influent leachate composition

The results from the analyses of the untreated leachate are presented in Table 1 which also includes the median values in samples taken from this leachate on site during the two years preceding the study and median values from 12 Swedish leachates from Öman and Junestedt [31]. The leachate used in this study is very similar to the median leachate on site. Also, most metal concentrations are in the same order of magnitude as those found in other Swedish leachates. Most metal concentrations remained constant throughout the study, the important exceptions being Cu and Hg. Chloride concentrations are high in this leachate.

3.2. Metal removal and leaching

The removal efficiencies in the columns are presented in Table 2 as effluent concentration/influent concentration (C/C_0). Effluent samples from each column were mixed using aliquots from several days during a time period. The sample from each column was

Table 1

Concentrations in mg/l in one batch of landfill leachate used for sorption experiments measured at four occasions, results from samples collected on site (median values from the two years preceding the collection of leachate for the experiment), and median values from 12 Swedish landfills presented by Öman and Junestedt [31]. –, not reported.

Sample	Day 2	Day 10	Day 20	Day 29	On site	Sweden
pH	7.5	7.1	7.1	7.4	7.2	7.6
BOD ₇	–	–	–	–	33	12
COD	–	–	–	–	700	560
TOC	240	240	240	230	250	150
Alkalinity ^a	670	660	630	650	–	300
Cl	2200	2600	2600	2200	2400	780
N	350	380	370	360	390	190
P	2.6	1.3	0.48	2.3	1.6	0.59
Al	0.049	0.077	0.078	0.10	–	0.10
As	0.022	0.027	0.025	0.020	0.0080	0.0017
Ca	200	210	200	200	–	0.11
Cd	0.000027	0.000012	0.000016	0.000019	<0.0001	0.00020
Co	0.012	0.013	0.013	0.010	0.011	0.0066
Cr	0.039	0.037	0.037	0.041	0.054	0.0082
Cu	0.034	0.0079	0.0025	0.027	0.0098	0.013
Fe	2.3	1.2	1.5	3.3	3.1	2.9
Hg	0.00019	<0.00001	<0.00001	0.00072	<0.0001	0.000022
Mg	110	100	100	100	–	39
Mn	0.26	0.27	0.27	0.27	0.41	0.58
Mo	0.0023	0.0032	0.0023	0.0020	–	0.22
Ni	0.061	0.072	0.073	0.059	0.057	0.026
Pb	0.00082	0.00024	0.00025	0.0015	0.0021	0.0037
Sr	5.3	5.3	5.3	5.3	–	1.0
Zn	0.084	0.054	0.020	0.045	0.061	0.046

^a Carbonate alkalinity given as mg C/l. Data for Sweden [31] calculated from bicarbonate concentrations.

Table 2

Removal efficiencies by filtration in columns filled with granular activated carbon (GAC), bone meal (BM) and iron fines (IF). Numbers represent effluent concentration/influent concentration (C/C_0). Averages for three columns are presented with the exception of the final BM sample where data were only available for two columns. Statistically significant differences ($p < 0.1$) between C and C_0 are underlined. n.d., not detected in the influent.

Material	GAC			BM			IF		
	1–10	11–20	21–29	1–10	11–20	21–29	1–10	11–20	21–29
TOC	<u>0.032</u>	<u>0.011</u>	<u>0.054</u>	78	<u>19</u>	13	2.6	<u>1.4</u>	<u>1.1</u>
Cl	0.98	0.96	0.96	1.1	<u>0.85</u>	1.0	0.93	<u>0.89</u>	0.96
Alkalinity	<u>0.96</u>	0.99	0.98	<u>0.59</u>	<u>1.1</u>	0.82	<u>0.35</u>	<u>0.60</u>	<u>0.81</u>
N	0.89	<u>0.91</u>	<u>1.1</u>	<u>17</u>	<u>5.2</u>	3.9	0.81	<u>0.85</u>	1.0
P	0.31	0.28	0.27	<u>8.1</u>	<u>16</u>	<u>5.5</u>	0.16	<u>0.21</u>	0.10
Al	1.0	0.73	0.72	<u>1.0</u>	<u>0.27</u>	0.66	<u>4.4</u>	<u>0.33</u>	0.70
As	<u>2.1</u>	1.2	1.4	0.99	<u>1.3</u>	1.3	0.80	<u>0.75</u>	0.69
Ca	<u>0.04</u>	<u>0.16</u>	<u>0.45</u>	0.94	<u>0.46</u>	0.36	<u>0.09</u>	<u>0.03</u>	<u>0.06</u>
Cd	2.2	0.74	<u>0.36</u>	2.8	0.98	0.57	<u>31</u>	<u>19</u>	<u>4.4</u>
Co	<u>0.013</u>	<u>0.017</u>	<u>0.023</u>	1.1	1.1	0.95	<u>0.55</u>	0.91	0.69
Cr	<u>0.031</u>	<u>0.038</u>	<u>0.045</u>	<u>0.13</u>	<u>0.16</u>	<u>0.19</u>	<u>0.18</u>	<u>0.39</u>	<u>0.48</u>
Cu	0.11	0.23	0.060	0.40	0.75	0.13	0.89	0.38	0.054
Fe	0.0067	<u>0.0080</u>	0.0058	0.089	<u>0.12</u>	0.12	0.37	<u>0.20</u>	0.32
Hg	3.9	n.d.	3.3	0.21	n.d.	1.0	1.6	n.d.	0.98
Mg	<u>1.6</u>	<u>1.4</u>	<u>0.96</u>	<u>3.5</u>	1.9	1.5	<u>0.19</u>	<u>0.44</u>	<u>0.85</u>
Mn	<u>0.027</u>	<u>0.080</u>	<u>0.078</u>	<u>0.095</u>	<u>0.056</u>	<u>0.047</u>	0.78	<u>0.67</u>	<u>0.43</u>
Mo	<u>5.6</u>	1.4	<u>0.48</u>	0.39	0.15	<u>0.24</u>	<u>99</u>	<u>47</u>	<u>18</u>
Ni	<u>0.0010</u>	<u>0.016</u>	<u>0.043</u>	0.65	<u>0.76</u>	0.71	1.8	1.3	0.83
Pb	0.42	<u>0.10</u>	<u>0.073</u>	0.44	<u>0.42</u>	0.12	1.0	<u>0.36</u>	0.04
Sr	<u>0.23</u>	<u>0.73</u>	<u>0.77</u>	<u>0.054</u>	<u>0.030</u>	<u>0.023</u>	<u>0.039</u>	<u>0.073</u>	<u>0.39</u>
Zn	0.27	0.21	0.28	0.88	1.2	0.66	0.47	0.49	0.39

analysed separately and the average of the three columns with each material was used in the calculations. Influent concentrations were taken as the average in the two influent samples collected at the beginning and the end of each period. Numbers below one indicate removal and above indicate release. The effluent concentrations were compared to the influent concentrations using two-sided heteroscedastic t -tests. The statistically significant ($p < 0.1$) differences are underlined in Table 2.

3.2.1. Granular activated carbon

The granular activated carbon (GAC) columns removed many metals very efficiently (Table 2). More than 90% of Co, Cr, Fe, Mn and Ni were removed. Ca, Cu, Pb, Sr and Zn were removed in all

samples but not to the same extent. As, Cd, Hg, Mg and Mo were released from the filters in one or more samples.

3.2.2. Bone meal

Bone meal (BM) removed more than 90% of Sr and Mn and approximately 80% or more of Cr, Fe and Hg (Table 2). Between 20 and 80% of Al, Ca, Cu, Mo, Ni, Pb and Zn were removed in most samples. Cd and Mg were released initially.

3.2.3. Iron fines

In the columns with iron fines (IF) only Ca was removed by over 90% throughout the filtration, but most metals (As, Co, Cr, Cu, Fe, Mg, Mn, Pb, Sr and Zn) were removed to some extent in most samples

Table 3
Filtration removal efficiencies in one column filled with filter sand. Numbers represent influent concentration/effluent concentration (C/C_0).

Day	1–10	11–20	21–29
P	0.72	1.9	1.0
Al	1.6	1.2	1.1
Cd	9.6	1.1	0.86
Co	4.2	1.6	0.92
Cu	2.2	1.1	0.21
Fe	0.17	2.6	0.97
Mn	4.8	3.2	1.2
Mo	3.5	1.6	1.0
Pb	2.5	1.4	0.32
Zn	0.34	0.44	0.50

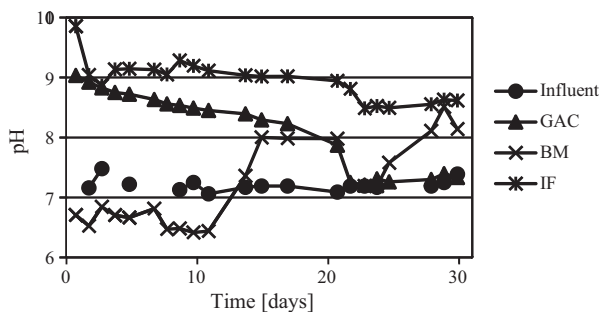


Fig. 1. pH in influent and effluent from filter columns. Data for granular activated carbon (GAC), iron fines (IF) and bone meal (BM) are the average of three columns, with the exception of BM after day 15, where the average of one to three columns is presented. Influent data are single values.

(Table 2). Concentrations of Cd and Mo increased greatly. Al, Hg and Ni were released initially.

3.2.4. Filter sand

Since BM and IF were mixed with sand, the leachate was filtered through a sand filled column for comparison. Most concentrations were unaffected by sand filtration but those affected are presented in Table 3. Since there was only one sand column it was not possible to treat this data statistically.

3.3. Other changes in leachate quality

The untreated leachate had a grey/brown colour. The effluent from the GAC columns was clear and colourless. The effluent from BM columns was cloudy and yellow, initially very strongly coloured, and smelled strongly. The IF effluent was clear and had a light yellow colour.

Changes in pH during filtration are presented in Fig. 1.

Although nutrients and organic carbon were not the main targets of this study, they are of interest because of the problems, such as eutrophication, that they can cause in the environment. In the GAC filters more than 90% of the organic carbon (measured as TOC) was removed, while the other filter materials released this material (Table 2). GAC and IF did not affect the N concentration but removed some P (Table 2). BM released large quantities of N and P (Table 2).

3.4. Flow rate

The desired flow rate was maintained in the GAC, IF and sand columns except for some startup problems in one IF column. However the BM columns had frequent leaks and after day 15 the flow rate varied between 0 and 0.2 m/day with the exception for one column that reached the target of 1.2 m/day during approximately

four days. Most likely the problems were due to clogging in the very fine BM.

4. Discussion

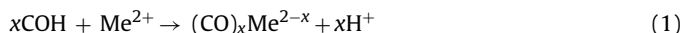
As clogging was observed in some of the columns part of the metal removal might be attributed to the removal of particulate matter. However, the only metal that was consistently removed by the sand filter was Zn (Table 3). Therefore it is not likely that particulate matter removal was an important removal mechanism for the other metals.

Oxidation of methanogenic landfill leachate can cause metals to precipitate [32]. In the batch tests preceding this study [15] removal of some metals was observed without the addition of filter material. However, all filter materials used in this study significantly improved the metal removal during the batch test, compared to the samples without filter material. Some oxygen was most likely available in the columns, although not to the same extent as in the batch test. Therefore part of the metal removal in the column study could be attributed to oxidation but the filter materials played a crucial role. The mechanisms for metal sorption to the filter materials are discussed in the following.

4.1. Granular activated carbon

The sorption of metals to activated carbon is affected by factors including solution pH [13,14,33] and the acidic/basic character of the carbon surface [13,17]. In this study the pH in the leachate increased from 7.2 to 9 (Fig. 1) during the initial equilibration in the columns, suggesting that the GAC was basic.

Sorption of heavy metals to activated carbon is often attributed to acidic (most notably carboxylic) sites [17,22]. The mechanism of sorption in that case is via ion exchange with H^+ (Reaction (1)) [14,17,34] or complex formation with negatively charged sites (Reaction (2)) [8,13]. In the reactions Me stands for any metal removed.



Reaction (1) causes pH to decrease. When the exchangeable H^+ is depleted the pH reaches that of the influent and sorption ceases [14]. However, in this study, the metal removal was not affected when the solution pH stabilised at the influent level after 22 days (Fig. 1 and Table 2). Thus ion exchange cannot have been the dominating mechanism.

Sorption to basic sites, such as graphene layers, proceeds without pH decrease [17,34] which makes this mechanism more likely and, unlike Reaction (2), it is consistent with the suggested basic character of the carbon used in this study. Another mechanism that is most likely to have occurred is sorption together with organic matter since more than 90% of the organic matter was removed in the columns (Table 2) and heavy metals in landfill leachate are thought to form complexes with organic matter [35].

Precipitation of new metal containing phases can contribute to sorption [14,22] when pH is elevated. This can have occurred initially but if this was a dominating mechanism sorption should have decreased when pH was back to the influent level. Therefore this mechanism is not thought to have been important in this study.

Among the metals that were released from the GAC As, Cd, Mg and Mo were only released in the first effluent sample (Table 2), indicating that easily leachable impurities on the carbon were behind the release. In the long term, the filter might be effective also against these contaminants. After release, Cd and Mo concentrations were still not high compared to what has been found

in an earlier study of Swedish leachates [31] but As, Hg and Mg concentrations were above the highest found there.

Release of As from activated carbon has been observed previously [36]. There are, however, studies (e.g. [7]) that report successful As removal with activated carbon, while others have found the opposite [26]. In a screening test [15] preceding this study the sorption from two different leachates was studied using the same GAC as in this study. In one leachate the As concentration increased by 70% and in the other it decreased by 30%. This shows that the nature of the leachate treated is important for the treatment result.

For no metal that was sorbed the maximum sorption capacity seems to have been reached after 29 days of filtration since complete breakthrough was not reached. Within the pH range in this study (approximately 7–9) the pH does not seem to have a significant effect on metal sorption. In order to optimise a granular activated carbon process for the sorption of heavy metals from landfill leachate the maximum sorption capacity of the carbon will be the most important parameter to assess.

4.2. Bone meal

The high amount of non-degraded organic matter in the BM and the long retention time could have favoured microbial activity in these columns. The strong smell of the effluent supports this. Microbial activity would affect the conditions in the columns, including pH and redox potential. Variations in metal removal and pH were largest in these columns (Table 2 and Fig. 1) which can depend partly on microbial activity and partly on the variations in flow rate caused by the low hydraulic conductivity.

Poorly crystalline hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, the major inorganic constituent of bones, is believed to be mainly responsible for the ability of BM to remove metals. Ion exchange with Ca^{2+} has been proposed as an important mechanism of metal sorption to this mineral. This can occur as the substitution of Ca^{2+} ions in the original matrix or dissolution of hydroxyapatite followed by precipitation of other apatites, where some or all Ca are replaced by other metals. Precipitation of new, heavy metal containing phosphate minerals has also been shown to occur. It is also possible that the complexation to organic matter in the bone meal contributes to the sorption. [9,10]

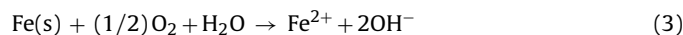
Ion exchange causes Ca release [24]. Dybowska et al. [10] found that meat and bone meal dissolving in water released balanced amounts of Ca and P. In this study, however, there was an uptake of Ca and a release of P. This suggests that ion exchange with Ca was not the major metal removal mechanism. But even so, Ca must have been released at some stage since large amount of P was released. The Ca that thus must have been released on the dissolution of apatite could either have precipitated with other counter ions such as CO_3^{2-} (although variations in alkalinity does not support this as seen in Table 2) or metal anions or been sorbed to other parts of the BM, e.g. organic matter.

In the BM effluent Cd concentrations were elevated in the first sample and Mg concentrations in the first two samples. Compared to other Swedish leachates [31] Cd concentrations were close to the median even after this release but Mg concentrations were many times higher than the maximum observed. Cd was also released by the sand columns (Table 3), thus the Cd release could have originated from the sand mixed with the BM.

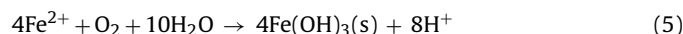
4.3. Iron fines

Metal removal by zero-valent iron is usually attributed to adsorption to or co-precipitation with iron corrosion products on the surface of the sorbent [25,27,28]. Iron corrosion is thus a crucial process. It can proceed aerobically (Reaction (3)) or anaer-

obically (Reaction (4)). Although the leachate used in this study was reduced some oxygen has undoubtedly been introduced during handling. Reaction (4) releases H_2 but no significant gas formation was observed in the columns. Therefore Reaction (3) is thought to have been dominating.

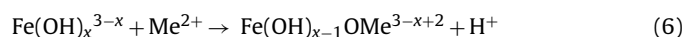


The Fe^{2+} can be further oxidised, e.g. through hydrolysis (Reaction (5)). If the oxidation proceeds to this step it is a pH neutral process. Since there was a net removal of Fe in the IF columns (Table 2) all Fe seem to have precipitated either through this or other mechanisms. Examples of other Fe minerals that cause H^+ release upon precipitation are summarised by Su and Puls [25].



The pH was elevated compared to the influent (Fig. 1). Other authors have seen an elevated and/or fluctuating pH in water in contact with iron sorbents and attributed that to dissolution of surface minerals and ion exchange between OH^- and metal anions [27,29]. Cl^- could also take part in ion exchange. OH^- release due to anion exchange is likely to have been an important pH controlling process in this study due to the high chloride concentration (Table 1) and its apparent decrease (Table 2).

Most metals are assumed to be in the form of positive ions in the leachate. Therefore ion exchange with OH^- cannot have been the dominating removal mechanism although it is likely to have controlled pH. Another possible mechanism is ion exchange with H^+ , e.g. as in Reaction (6) where Me^{2+} is a metal cation.



However, if this mechanism would occur on a large scale it should significantly have contributed to lowering the pH and this does not seem to have been the case. Therefore co-precipitation with Fe minerals is more likely to have been the dominating mechanism. Due to the elevated pH, precipitation of other metal containing minerals, such as hydroxides, is also possible [12,27,29,30].

Although the concentrations of Cd and Mo increased drastically in the IF columns (Table 2), the Cd concentrations were still well below the highest concentrations found in Swedish leachates [31] and the Mo concentrations had the same order of magnitude. Among the elements that were released only initially (Al, Hg and Ni) only Ni showed a net release throughout the experiment. Ni had high concentrations compared to other landfills only in the first effluent sample [31]. Mo and Ni are common in stainless steel alloys that could have been present in the fines. There could also be unwanted impurities in the scrap metal. The filter sand that was mixed with the fines released Cd and Mo (Table 3) but not to an extent that explains the release from the IF columns.

The removal of some metals in the iron columns was better at the end of filtration. This could be due to initial release of these metals, but as oxidation of the iron in the columns proceeds that would create more sorption sites. To optimise metal removal the leachate should be well aerated to ensure oxidation of the IF.

5. Conclusions

This study has demonstrated that granular activated carbon (GAC), bone meal (BM) and iron fines (IF) can sorb heavy metals from real landfill leachate. It is encouraging to note that the cheaper by-products BM and IF can be used to sorb metals, and that BM showed high sorption efficiencies (>80%) for several metals. No material was efficient for removing all the studied metals. In order to remove a wide range of metals with these materials two or more filter materials need to be combined.

All materials released unwanted substances which highlights the need to study the uptake and release of a large number of compounds, not only the target metals, when assessing the usefulness of a potential filter material.

Granular activated carbon (GAC) was by far the most effective of the tested materials with regard to removal of metals. The main drawbacks of this material are its high price and the risk of As release. The dominating metal removal mechanisms by GAC seem to have been cation interaction with basic surface sites and immobilisation of metals together with organic matter being sorbed to the GAC. Ion exchange does not seem to have been among the important mechanisms of sorption in this study. Neither precipitation was among the dominating mechanisms in spite of an elevated pH.

BM released less metal than GAC, but its removal was in less effective for most metals. The main drawback of BM is the release of large amounts of organic carbon and nutrients, probably from proteins. BM could however be useful whenever these substances cannot cause a problem, e.g. where further treatment is applied or there is a need of nutrient addition. Microbial activity in the columns most likely affected sorption in the BM columns. Although ion exchange with Ca^{2+} is usually thought to be an important mechanism, there was an uptake of Ca in the columns.

Iron fines (IF) were the least effective for removing metals. The possibility of reducing As concentrations, however, is an advantage. Before using scrap iron, its leaching characteristics need to be assessed to avoid release of metals. Since the sorption improved considerably during the course of this study, IF is thought to be a promising filter material, but the source of the material must be carefully chosen and oxidation of the leachate must be ensured. Co-precipitation with iron corrosion products was likely the dominating removal mechanism. Ion exchange seems to have been less important for metal removal but can have had indirect effects as it is likely to have controlled the pH.

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