

Sorption filters for removal of heavy metals from landfill leachate

Laboratory experiments with leachate from Sysav's landfill Spillepeng

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Summary

As a part of their involvement in the Interreg IIIA project *The Source Partnership Sysav*, South Scania Waste Company, has examined different possibilities to treat leachates within the landfill area. The study described here is a part of this work and aims at studying the possibilities of removing heavy metals from the leachate with sorption filters.

First a batch test was done to evaluate 7 filters and find those that were good enough to study more thoroughly in continuous tests. The studied materials were granular activated carbon (GAC), CAP meal made from animal bones, iron fines (IF), a non-metallic part of bottom ash from a municipal solid waste incineration plant, metal residues from the same bottom ash, lime stone and peat. GAC, CAP meal and IF showed the best capacity to remove heavy metals and were chosen for the continuous test. They were filled into 50 cm high plastic columns. Leachate was pumped from the bottom through the columns for 42 days.

In the sand and GAC columns there were no problems with flow. The CAP columns on the other hand had large problems. With IF one out of three columns had to be stopped before the end of the experiment.

The pH of the untreated leachate in the continuous test was around 7.2. In the GAC columns the pH was around 9 initially but fell to 7.3 at the end of the experiment. In the CAP columns pH was around 6.6 in the beginning but rose to around 8. In the IF columns pH was around 9 in the beginning and after 20 days just above 8.5. The electrical conductivity (EC) was 10 mS/cm in the first batch of untreated leachate, and 9.7 mS/cm in the second. The EC in the blank is slightly lower than that and the GAC columns a little lower still. The CAP meal gives the highest conductivity and the IF the lowest.

GAC showed a good ability to remove Cr, Cu, Ni, Pb and Zn. In the beginning of the experiment As, Cd and Mg concentration were higher in the effluent than in the influent. Especially the As leaching seems to cause problems with complying with limit values.

CAP does not remove metals as efficiently as GAC. About 80 % of Cr and 20 % of Ni are removed. As and Zn seems to be largely unaffected while Mg and Cd are leached.

Removal of Cr and Mg with IF is initially very efficient but concentrations stabilise on 50 % and 80 % of that in the ingoing water, respectively. Some elements are leached from the IF columns initially but only Ni shows a net release during the whole period

Most of the organic carbon is removed by the GAC filter. Nitrogen is unaffected but around 70 % of phosphorous is removed. The CAP meal columns leached large amounts of nutrients and organic carbon. Even at the end of the experiment the outgoing concentrations are a few times higher than the ingoing. Nitrogen was unaffected by the IF but more than 80 % of the phosphorous was removed. TOC concentrations increased due to the fact that the IF were mixed with organic cutting fluids when it was collected at the metal workshop.

The study shows that even though metals can be removed by sorption filters, leaching of unwanted substances can be a problem. Before installing filters, they should be tested to avoid causing new problems.

The bad hydraulic properties of CAP meal probably make it unsuitable for continuous applications. Leaching of carbon and nutrients are also problems that might have to be solved in order to use CAP for water purification. GAC had many good properties. It might be possible to find carbon that does not release As, or to find a way to remove As after filtration, possibly with some kind of IF. A different source for IF has to be found since the results in the continuous test were not good enough.

Table of contents

Summary	1
Table of contents	2
1 Introduction	3
2 Materials and methods	3
2.1 Leachates	3
2.2 Filter materials	3
2.3 Batch test.....	5
2.4 Continuous tests	6
2.5 Statistics	8
3 Results and discussion.....	8
3.1 Batch test.....	8
3.2 Continuous test.....	9
3.2.1 Flow	9
3.2.2 Colour.....	11
3.2.3 pH, conductivity and redox potential	12
3.2.4 Metals.....	13
3.2.5 Organic carbon and nutrients	17
4 Conclusions and recommendations	19
References	19

1 Introduction

The project described here is a part of the Interreg IIIA project *The Source Partnership – Reduction of Sources with Wastewater Discharges of Priority Substances in The Øresund Region*. In connection with the Source Partnership Sysav, South Scania Waste Company, has examined different possibilities of treating leachates from the new part of the landfill Spillepeng within the landfill area.

Various options for removal of nutrients and organic carbon have been studied in other projects. The study described here aims at studying the possibilities of using sorption filter to remove heavy metals from the leachate.

If metals can be removed, the water could be treated successfully in a municipal waste water treatment plant without causing problems. Today the water from Spillepeng is treated at the nearby municipal waste water treatment plant, Sjölanda. In the future however it is expected that SYSAV will be required to purify the water to the extent that it can be released directly to the recipient, Øresund. This means that removal of nutrients and organic carbon within the landfill will be necessary and metal removal, if implemented, will be done in combination with this.

2 Materials and methods

The filter study was done in two steps. Initially a batch test was done. The batch test was a way to evaluate a larger number of filters and find those that were good enough to study more thoroughly. At this stage the potential to remove heavy metals was the only thing considered. The choice of filter materials was based on a literature review previously done within the Source Partnership (Hoyer and Persson 2007).

Following the batch test was continuous experiments with the three filter materials that did best in the batch test. Here the goal was to study their hydraulic properties and their metal removing capacity under more realistic circumstances.

2.1 Leachates

In the batch study two different leachates were used: P2/P6 and Fällning Ut. P2/P6 is a mixture of leachates from two cells with mainly household waste. Both cells are closed. The waste in P2 is 10-15 years old and P6 is 5-10 years old. In a precipitation plant P2/P6 is mixed with leachates from special waste cells. Fällning Ut is the leachate coming from the precipitation. This leachate has a high salinity.

In the continuous study leachate P6 was used. This leachate is fairly stable, i.e. variations are small, and the metals content is rather high. Cr and Ni are especially problematic since they often exceed limits.

Leachate for the batch test was stored in 25 litre containers in a cold room (5°C). Small samples for use were stored in a refrigerator (7°C). Leachate for the column test was stored in a 1 m³ insulated container in a shaded place outdoors. The experiment took place during January and February when the outdoor temperatures were low.

2.2 Filter materials

In the batch study seven different filter materials were used. These were granular activated carbon, CAP meal, iron fines, a non-metallic part of bottom ash from a municipal solid waste incineration plant, metal residues from the same bottom ash, lime stone and peat. Filter materials were stored in sealed containers at room temperature.

Activated carbon is widely used for water purification purposes, however mainly to remove organic pollutants (Corapcioglu and Huang 1987). Activated carbon has a capacity to remove heavy metals as well (Corapcioglu and Huang 1987; Jusoh, Su Shiung et al. 2007). The activated carbon used in this study was granulated to a particle size of 0.25 – 1 mm. The cost for activated carbon for water purification purposes is approximately 13-14 SEK/kg.

Bone meal has been shown to have a potential to reduce metal release from contaminated soils (Hodson, Valsami-Jones et al. 2001; Sneddon, Orueetxebarria et al. 2006). CAP meal is a commercially available powder derived from pig and cow bones, and could be expected to have similar properties. The ash content of CAP meal is just above 70 %, it contains around 20 % protein, some fat and a little moisture. It is delivered sieved to a particle size less than 2 mm. Most particles however are much smaller than this and there are also some larger particles (up to a few mm) present. The cost for CAP meal is approximately 2.75 SEK/kg.

Zero-valent iron is known to have a capacity to remove arsenic from water (Melitas, Wang et al. 2002; Nikolaidis, Dobbs et al. 2003), but other heavy metals can be removed too (Smith 1996). The iron fines used in the batch test was a fine powder aimed for classroom use showing magnetic fields. This is an expensive product so for the continuous study a different material was sought. Metal sawdust from a metal workshop was found to be a more realistic source for metal fines. Residues were collected from two cutting tools in a workshop just south of Lund. Due to the mode of operation of the cutting tools the fines were mixed with cutting fluids consisting of organic oils. This material is normally sold as scrap metal and the price of that is about 1 SEK/kg.

The bottom ash originated from Sysav's waste incinerator in Malmö. If this material would show to have metal removing abilities it would constitute an in house filter material that is produced in large quantities. It would thus provide a cheap and simple solution. The bottom ash is allowed to cool down, is sorted and the non-metallic part is left to harden in large piles outdoors. A sample was taken from a three months old ash. It was sieved to a particle size of 1-2 mm.

The sorting of bottom ash also gives rise to various metallic fractions. The smallest fraction of magnetic residues is hard to sell, and it is therefore desirable to find other uses for it. It could be expected to have properties similar to other iron residues. Metal residues were sampled right after sorting. It was thus considerably fresher than the non-metallic bottom ash. The size variation within the sample was large. For the experiments pieces with a size below approximately 20 mm were chosen.

Some studies (Aziz, Othman et al. 2001; Ghaly, Kamal et al. 2007) have shown that limestone have a metal removal capacity. The limestone used in this study was common limestone from Ingaberga in southern Sweden. The limestone was sieved and particles with a size of 1-2 mm were chosen for the experiments. The cost for limestone is around 0.30-0.35 SEK/kg.

Peat is a cheap and widely available material. It is one of few materials that has been used in full scale applications to treat landfill leachate (Heavey 2003; Viberg 2004; Nilsson 2006). The results regarding heavy metals have not been totally convincing, but due to its popularity peat merits further study. The peat used in the experiment was pure Swedish Sphagnum peat. It had been ground into a particle size of 0-30 mm and was used without further sieving. The kind of peat that is relevant for this type of use costs about 0.3 SEK/kg.

In the continuous study sand was used to improve the hydraulic properties in some cases (see Continuous tests below). The sand used was filter sand with a particle size of 0.8 -1.2 mm.

2.3 Batch test

In the batch test each of the two leachates was mixed with each of the seven filter materials in flasks. Details of the different combinations are presented in Table 1. The amount of filter material was chosen so that it would not be limiting to the metal removal. That the volumes rather than the weights were chosen to be similar was because of that this was deemed more representative of the future column study. The metal residues consisted of much larger particles than the other materials and it was had to find a representative mass. Instead a few pieces were used in each flask which made the mass vary.

All equipment used was acid washed. This means it was soaked in, or filled with in the case with larger pieces of equipment, 5 % HNO₃ for 24 hours, rinsed 4 times in ultra pure water and thereafter allowed to dry.

Table 1. Filter samples. All filter materials were mixed with two leachates (Fällning Ut and P2/P6). One sample of peat mixed with P2/P6 was lost, therefore only one sample of this combination could be analysed.

Filter material	Leachate volume [ml]	Weight of filter material [g]	Number of replicates per leachate
Blank	40	0	2
Blank	50	0	3
Activated carbon (GAC)	40	1.00	2
CAP meal (CAP)	40	2.00	2
Iron fines (IF)	40	10.00	2
Iron fines (IF)	50	12.50	3
Peat (PEAT)	40	1.00	1-2
Bottom ash (BA)	40	3.00	2
Metal residues (MR)	40	Approx. 2	2
Metal residues (MR, rinsed)	50	Approx. 3-4	3
Lime stone (LS)	50	5.00 g	3

The flasks with filter material and leachate were mixed for 20 hours at 150 rpm in room temperature. The time was chosen not to limit the metal removal. This requires that there is time to achieve equilibrium distribution of metals between filter material and leachate. The removal capacity of iron is dependent on the formation of iron oxides and these might need some more time to form. The mixing speed was set in order to have a good mixing without breaking the filter particles. After the experiment it showed that in some flasks, especially those with the iron fines, not all filter material was completely mixed with the leachate. In one set of samples metal residues were thoroughly rinsed in tap water before being mixed with leachate. This was done to remove non-metallic particles that could carry contaminants.

After mixing the leachates were transferred to test tubes and centrifuged at 1600 rpm for 20 min. Samples for metal analysis were taken from the supernatant. The samples were not filtrated since this is not normally done with landfill leachate. It is the total amount of pollutants, not the dissolved amount that is of interest. Metals, total nitrogen (TN) and total organic carbon (TOC) were analysed by the laboratory at the Section of Plant Ecology and Systematics at the Department of Ecology at Lund University. pH and conductivity were measured directly in the test tubes. A summary of all analyses can be found in Table 2.

Table 2. Analyses of landfill leachate in batch test with filter materials

Analysis	Method
pH	Buch & Holm WTW Multi 350i
Conductivity	Buch & Holm WTW Multi 350i
As, Cd, Cr, Cu, Ni, Pb, Zn	ICP MS, Elan 6000 (PerkinElmer)
Cu, Zn (all samples mixed with bottom ash and P2/P6 mixed with metallic residues)	ICP AES, OPTIMA 3000 DV (PerkinElmer)
Total organic carbon, TOC	TOC-VCPH (Shimadzu, Tokyo Japan)
Total nitrogen, TN	TOC-VCPH with N-module TNM-1 (Shimadzu, Tokyo Japan)

2.4 Continuous tests

Granular activated carbon (GAC), CAP meal (CAP) and iron fines (IF) were used in the continuous experiments. CAP meal and iron fines were mixed with filter sand in order to increase the hydraulic conductivity. One column was filled with only filter sand in order to act as a blank. Details about the columns can be found in Table 3.

Sand, activated carbon and iron fines were rinsed four times in deionised water and dried before the experiments. CAP meal was not rinsed since this was involved with practical difficulties due to the small particle size. The filter materials were filled into see-through PVC columns. The material was filled in intervals and packed with a 500 g weight. The columns were 50 cm high and had a diameter of 11 cm. In inlet and outlet was 90 μ m HDPE filters whose function was to spread the flow in the inlet and to stop filter materials from escaping in the outlet. The columns were sealed with silicone. Tubing was made of PVC and connections between tubes were made of HDPE.

Table 3. Columns with filter materials used in the continuous filter test.

Column	Filter material type	Filter material dry mass [kg]	Sand mass [kg]	Sand content [vol%]
1	Blank	0.0	6.2	100
2	Activated carbon	0.9	0.0	0
3	Activated carbon	1.0	0.0	0
4	Activated carbon	1.1	0.0	0
5	CAP meal	2.0	4.5	60
6	CAP meal	2.0	4.5	60
7	CAP meal	1.9	4.3	60
8	Iron fines	2.8	3.1	50
9	Iron fines	2.8	3.0	50
10	Iron fines	2.9	3.1	50

When the columns were filled with filter material leachate was pumped in through the bottom. Two identical pumps, Masterflex L/S™ model 7519-15 from Buch & Holm A/S, were

used, one for column 1-4 and one for column 5-10. The tubing used was Masterflex 6424-16 for columns 1-4 and Masterflex 6424-14 for columns 5-10. When the columns were filled with leachate the pumps were stopped for three days before they were started again.

The flow rates in the blank and GAC columns were set to about 1 m/day and the others to about 0.2 m/day. Higher flow in columns 1-4 was chosen since these columns were expected to have better flow properties and achieved by using wider tubing. Overall, low flow rates were chosen in order to avoid problems with the equipment in the start up phase. The flow rates were increased in two steps until they were about 8 m/day and 2.5 m/day respectively. Due to problems these flow rates were not always achieved. More information about actual flow rates can be found in the Results section.

One bath of leachate was used until day 30 when it was replaced with a new one that was used until the end of the experiments. It was carried to the lab in HDPE containers. Leachate from the columns was collected in similar containers. All equipment used was acid washed in the same way as for the batch test, but some silicone seams were made after this.

The experiment went on for 42 days. pH, conductivity, redox potential and flow rate were measured almost daily. Samples for analyses of metals and other compounds were taken when the flow rate was measured and mixed to create three samples per column. The samples represent day 1-10, day 11-20 and day 21-29. Samples from the untreated leachate were not mixed but were taken from the leachate present in the lab on day 2, 10, 20 and 29. The samples were left to the laboratory at the Section of Plant Ecology and Systematics at the Department of Ecology at Lund University and analysed according to Table 4.

Table 4. Analyses of landfill leachate in continuous tests with filter materials

Analysis	Method
Flow rate	Weighing, Precisa 3100D (Precis Instruments AB) or KERN DE60K20N (KERN & Sohn GmbH, Balingen) depending on weight of container
pH	Buch & Holm WTW Multi 340i
Conductivity	Buch & Holm WTW Multi 350i
Redox potential	Buch & Holm WTW Multi 350i
Al, As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Si, Sr, Zn	ICP MS, Elan 6000 (PerkinElmer)
Al, As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Si, Sr, Zn	ICP AES, OPTIMA 3000 DV (PerkinElmer)
F, Cl, NO ₃ -N, PO ₄ -P, SO ₄ -S	Ion Chromatography, 861 Advanced Compact IC, column Metrosep A Supp 5 (Metrohm, Herisau Switzerland)
NH ₄ -N	FIA, FIA-star 5000 Analyzer (FOSS Tecator, Höganäs Sweden)
TOC	TOC-VCPH (Shimadzu, Tokyo Japan)
IC	TOC-VCPH (Shimadzu, Tokyo Japan)
TN	TOC-VCPH with N-module TNM-1 (Shimadzu, Tokyo Japan)

2.5 Statistics

Comparisons in the batch test were done with a two sample equal variance t-test using a two-tailed distribution. Significance levels of 5 % were used.

3 Results and discussion

3.1 Batch test

The results from the batch tests are shown in Table 5 and Table 6. The blank, where no filter material was used, differed from the untreated leachate in some cases. This indicates that the shaking itself causes some metals to precipitate or stick to the walls of the flask. Therefore the different samples were compared to the blank rather than to the untreated leachate directly. In the cases where there was a significant difference between blank and the treated leachate the change in metal concentration from untreated to treated leachate was calculated.

Table 5. Difference between untreated leachate (P2/P6) and leachate treated with various filter materials. Information is only given when there is a significant difference between the treated sample and a reference sample (Blank). Blank was compared to the untreated leachate rather than itself. Due to the loss of one PEAT sample no differences were significant; the table shows all values in italics this case.

Material	EC [%]	As [%]	Cd [%]	Cr [%]	Cu [%]	Ni [%]	Pb [%]	Zn [%]	DOC [%]	TN [%]
Blank	-2	-12	-19	-	-	-3	-35	-29	-	-
GAC	-5	+73	-86	-63	-93	-88	-98	-84	-89	-13
CAP	-14	-40	-92	-100	-81	-26	-96	-	+557	+145
IF	-8	-65	-95	-57	-97	-30	-98	-88	-29	-
BA	+5	+6	+90	+3	+6439	+31	+141	+497	-14	-9
MR	-	-47	-	-	+1225	-	-	-	-15	-
LS	-6	-26	-52	-	-	+6	-92	-57	-12	-
PEAT	-7	-17	+62	-35	-29	-3	-72	-46	+2	-6

As can be seen from Table 5 the activated carbon (GAC) removed most of the metals from leachate P2/P6 to a high extent. Cr was removed the least and still the concentration was reduced with 63 %. The significant increase in As concentration could not be explained and seemed still more puzzling since the concentration decreased in Fällning Ut after treatment with GAC. Apart from that GAC did not work as well in Fällning Ut as can be seen from Figure 6. In both leachates the organic carbon content decreased to a large extent.

CAP meal removed large amounts of Cd, Cr and Pb from P2/P6 (Table 5). The other metals were also removed but to a lesser extent except for Zn where no significant change was measured. The results for Fällning Ut (Table 6) were similar except for that here As was not significantly removed but Zn was. Large amounts of nitrogen and carbon were released from the CAP meal. Proteins left in the material may be responsible for this. It is not surprising to find a release of nutrients since this material is sometimes used as a fertiliser, but it can be problematic since there are limits for both organic carbon and nitrogen in the leachate.

Iron fines reduced Cd, Cu and Pb concentrations with more than 90 % in P2/P6 (Table 5). All analysed metals were removed to some extent. Ni was the least affected and 70 % of the Ni concentration was left after treatment. The results in Fällning Ut were similar (Table 6).

The bottom ash and metal residues caused a significant increase of some metals, especially the copper concentration increased greatly. Other metals however were removed. Rinsing the metal residues did not help. There was only one case, Pb in Fällning Ut, where the rinsed residues performed significantly better than the ones that were not rinsed.

Table 6. Difference between untreated leachate (Fällning Ut) and leachate treated with various filter materials. Information is only given when there is a significant difference between the treated sample and a reference sample (Blank). In the case of Blank this comparison was with the untreated leachate.

Material	EC [%]	As [%]	Cd [%]	Cr [%]	Cu [%]	Ni [%]	Pb [%]	Zn [%]	DOC [%]	TN [%]
Blank	-	-11	-	-	-24	-9	-42	-36	-	-
GAC	-4	-27	-	-79	-74	-70	-99	-84	-95	-
CAP	-	-	-55	-100	-68	-53	-96	-79	+543	+102
IF	-2	-25	-81	-76	-69	-56	-100	-86	-35	-
BA	-	-1	+896	-54	+12069	+134	+331	+2260	-17	-8
MR	-	-19	+265	-67	+1168	+64	-92	-	+15	-
LS	-2	-	-45	-34	-40	+11	-100	-67	-12	-
PEAT	-3	-4	-	-56	-	-26	-73	-	-	-5

In P2/P6 the treatment with limestone significantly reduced all metal concentrations except for Cr, Cu and Ni. Only Pb was removed to a really high extent and the Ni concentration increased 6 %. In Fällning Ut As was the only element not significantly affected, but there too the Ni concentration increased significantly.

Unfortunately one sample where P2/P6 was mixed with peat was lost and no statistical analysis could be done in that case. It seems like peat can remove some metals, but not to the same high extent as some other materials. Cd concentrations seemed to have increased after mixing with peat. In the case of Fällning Ut As, Cr, Ni and Pb significantly decreased, but only with between 4 and 73 %.

3.2 Continuous test

The leachate used in the continuous test, P6, often has too high Ni and Cr concentrations. GAC, CAP and IF showed the best ability to reduce these concentrations in the batch tests. Therefore these three materials were chosen for the continuous test.

3.2.1 Flow

The flow rates during the experiment can be seen in Figure 1 through Figure 4. Sand (Figure 1) and GAC (Figure 2) columns faced no problems caused by the filter materials. These materials have rather large and evenly sized particles and were expected to have good flow properties. Therefore the flow rate was set to a higher value in these columns than in those with CAP meal or iron fines. At the end of the experiment the flow in the sand columns was around 8 m/day and in the GAC columns it was around 7 m/day.

One CAP column did not start properly but this seemed to have been caused by incorrect pump settings. Later in the experiment there were big problems with leaking from the columns. This is the cause of most cases of too low flow seen in Figure 3. The flow should have been around 1.2 m/day after day 19 and around 2.5 m/day after day 35. The design of the columns could have been better but it is clear that the nature of the CAP meal is partly responsible for these problems since no other filter material was so problematic.

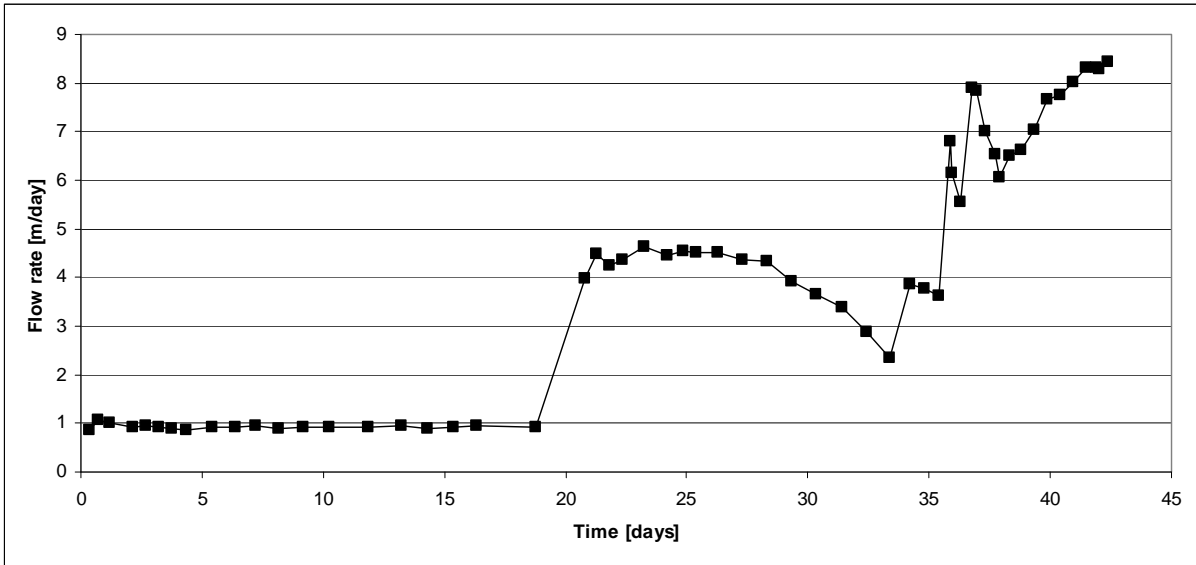


Figure 1. Flow rate in column filled with sand as a blank. Flow was increased on day 18 and day 35. The dip in flow around 33 days was caused by wear on the tubing.

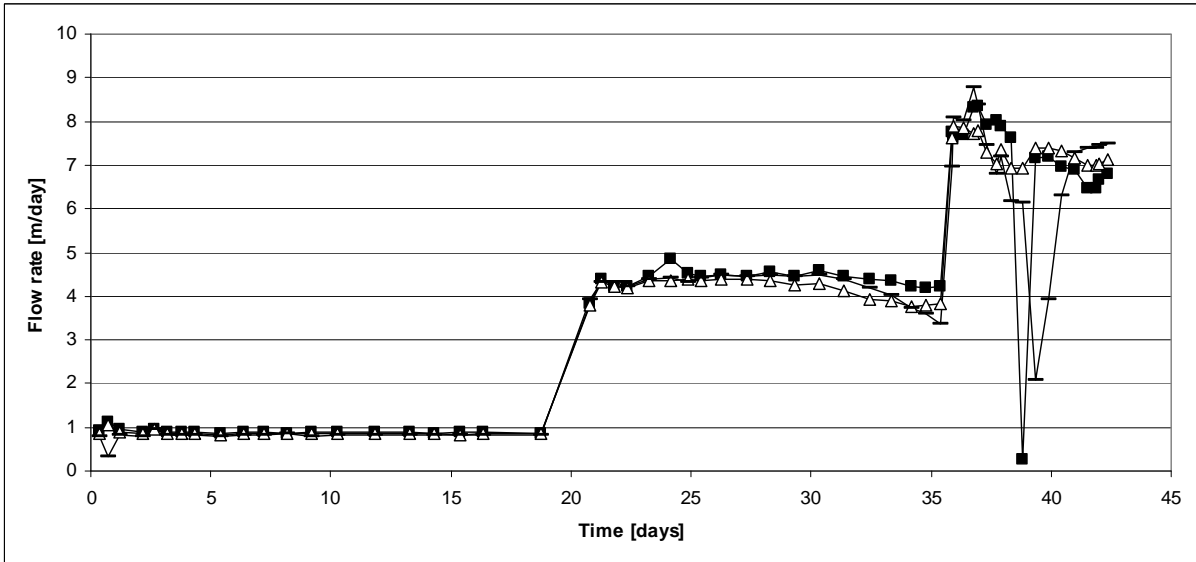


Figure 2. Flow rate in three activated carbon columns. Flow rate was increased day 18 and day 35. The dip in flow on day 0 was caused by a leaking column. The dips in flow around day 39 were caused by wear on the tubing.

The flow rate in the iron fine columns was set to the same as in the CAP columns which was a smaller flow than the GAC and sand columns. After some initial problems with the pump there were no problems until one column started leaking around day 36. Two columns worked until the end of the study.

When the columns were taken apart after the experiment it was clear that particles from the leachate had been accumulated in the bottom of the columns, especially where the particle size of the filter was small. This is likely to have been one cause of the problems in the CAP columns.

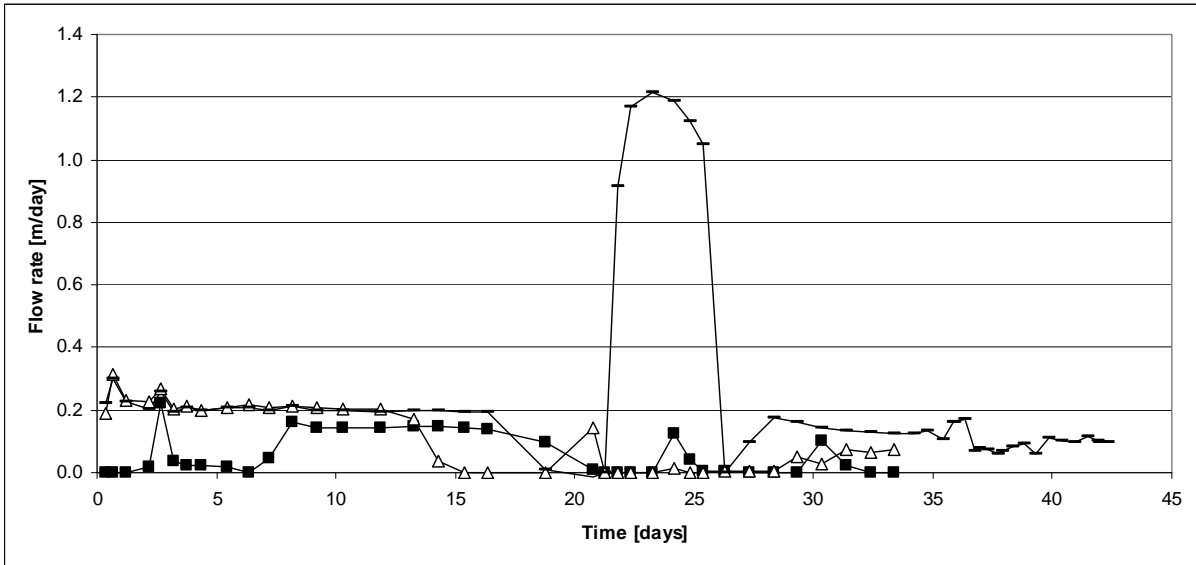


Figure 3. Flow rate in columns with CAP meal. The pump speed was increased day 18 and day 35. Problems with leaking columns were common and are explained in more detail in the text.

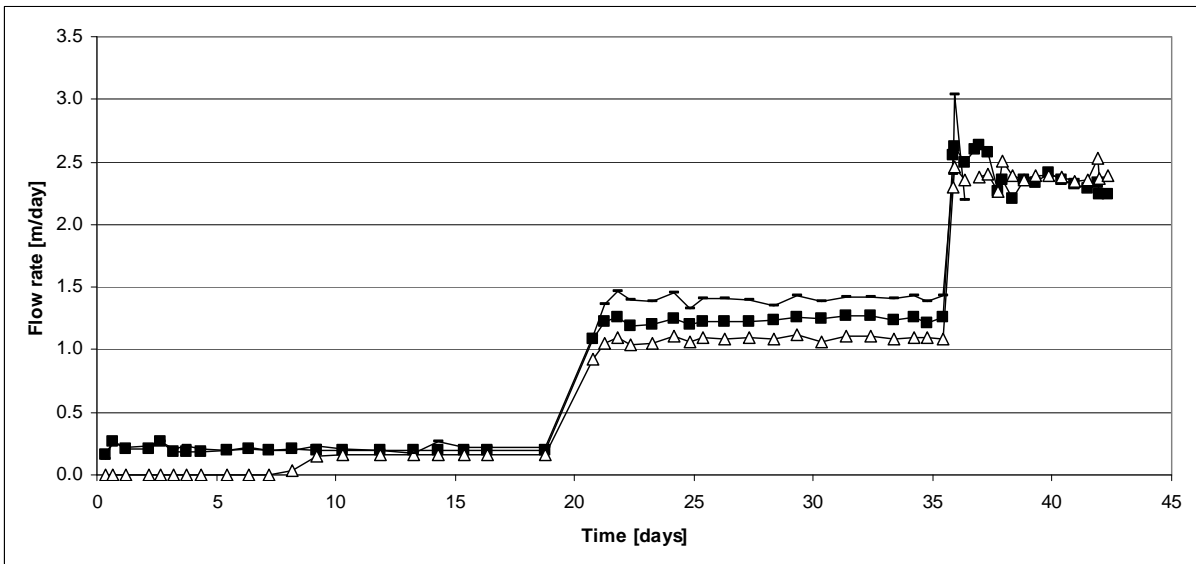


Figure 4. Flow rate in column with iron fines. Flow rate was increased on day 18 and day 35. In one column the flow did not start properly, but the problem could be solved by changing the setting of the pump. One column started leaking around day 36 and was stopped.

3.2.2 Colour

The appearances of the unfiltered and filtered leachates can be seen in Figure 5. Most of the colour is removed by the activated carbon. As will be discussed below GAC can remove organic content from the leachate, which is probably what causes the colour change. Iron fines and CAP meal gives the leachate a yellow colour, which is turbid in the case of CAP.

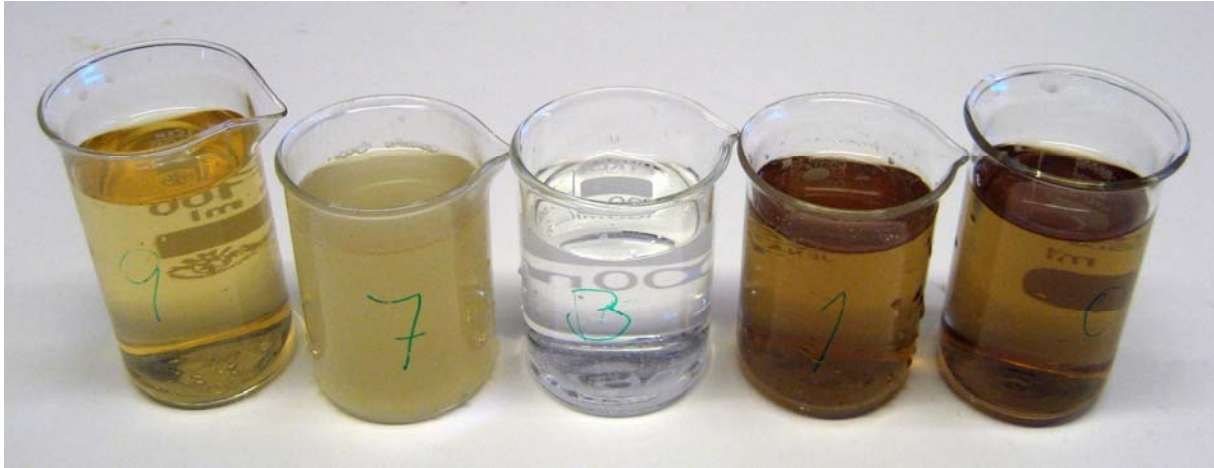


Figure 5. Leachate before and after filtration. From left: Filtered with iron fines, filtered with CAP meal, filtered with activated carbon, filtered with sand, unfiltered.

3.2.3 pH, conductivity and redox potential

Figure 6 shows pH in the effluent from the columns and in the untreated leachate. pH in the ingoing water was around 7.2 during the whole experiment. The sand filtered leachate (blank) has a slightly higher pH. On day 20, after the first increase in flow rate, it falls closer to the blank, but stays above.

The pH in the GAC columns is 9 in the beginning but decreases slowly until it is around 8 at day 20. Thereafter it falls down to 7.3 and follows the sand column till the end of the experiment. The CAP columns have the largest variation in between them, especially between day 15 and 20. After day 20 only one column worked so the figure does not present the average in this case. The pH in the outlet from the CAP columns starts out low, around 6.6. Around day 15 it increases to around 8 and stays there for the rest of the experiment. The iron fines columns follow each other closely (not shown in the figure). The first 20 days the pH is around 9 and after that it is just above 8.5.

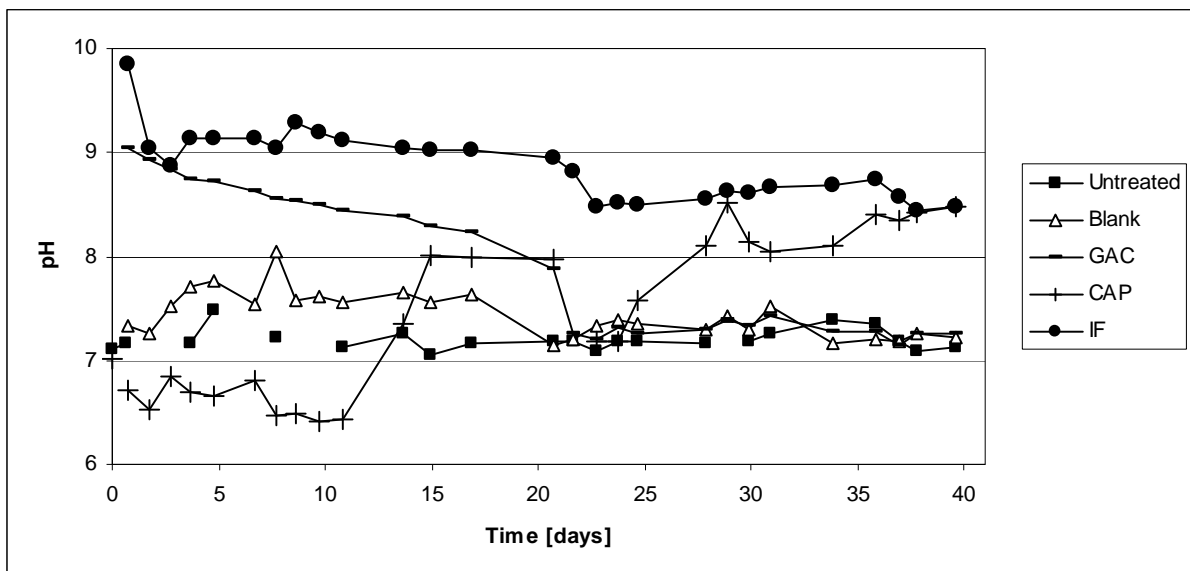


Figure 6. pH values in leachate before and after treatment in filter columns. Values for activated carbon (GAC), CAP meal (CAP) and iron fines (IF) are averages of three columns with some exceptions for CAP and IF.

The electrical conductivity (EC) in the different leachates is shown in Figure 7. The EC was 10 in the first batch of untreated leachate, and 9.7 in the second. The EC in the blank is slightly lower than in the untreated leachate and after the GAC columns a little lower still.

Towards the end of the experiments the differences between the three have disappeared. The CAP meal gives the highest EC but once again the internal variations are quite large. The leachate filtered with iron has the lowest conductivity.

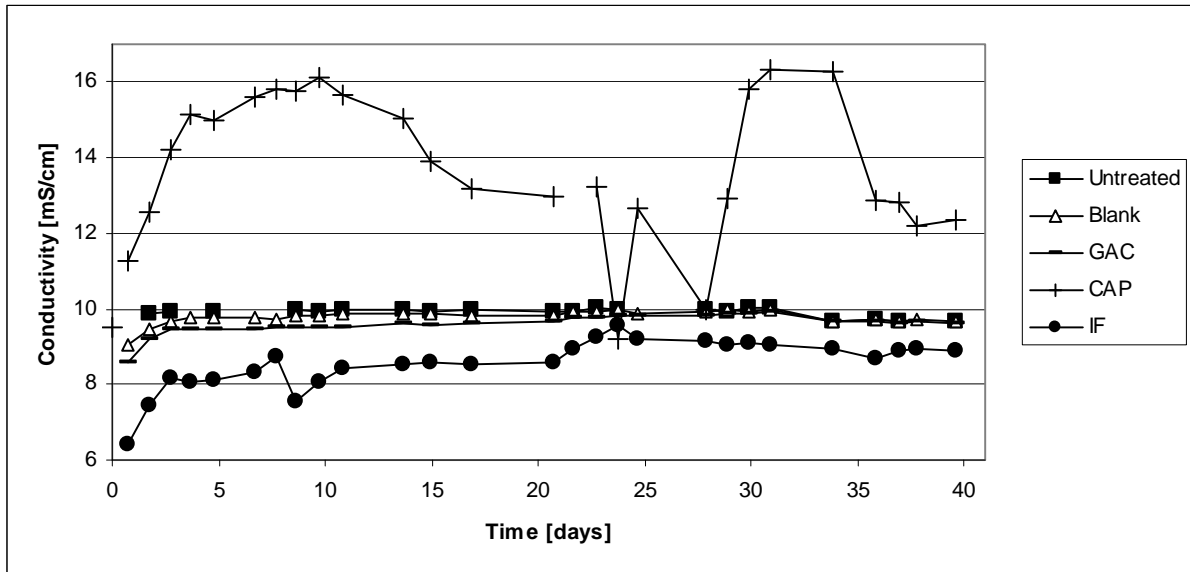


Figure 7. Electric conductivity in leachate before and after filter treatment. Values for activated carbon (GAC), CAP meal (CAP) and iron fines (IF) are averages of three columns with some exceptions for CAP and IF.

Redox measurements can be quite unreliable, and quantitative conclusions should not be drawn from measurements with a redox electrode (Appelo and Postma 2007). However some qualitative information should still be possible to get from Figure 8. The lowest redox potential can be found in the water from the CAP column, conditions are reducing during the whole experiment. The activated carbon gives the highest and most stable redox potential. The other ones vary in between the two extremes.

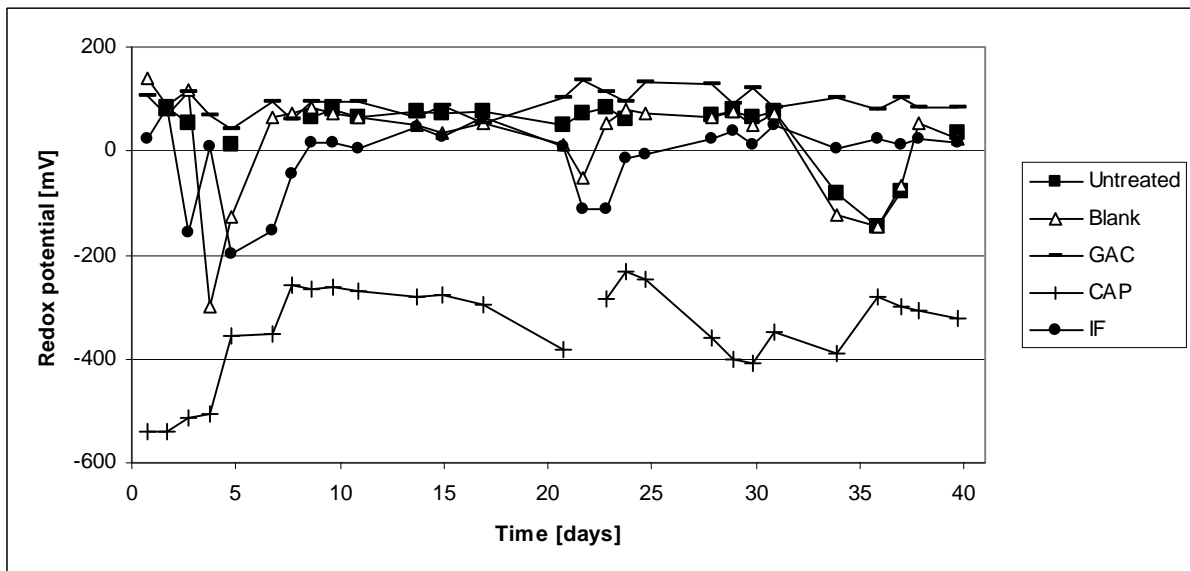


Figure 8. Redox potential in leachate before and after filter treatment. Values for activated carbon (GAC), CAP meal (CAP) and iron fines (IF) are averages of three columns with some exceptions for CAP and IF.

3.2.4 Metals

The results from the analysis of the untreated P6 leachate are presented in Table 7. The As, Ni, phosphorous and total nitrogen concentrations exceeded relevant limit values. The limit

value for organic matter is expressed as COD but here TOC was analysed. However, COD in untreated P6 is usually high.

Table 7. Characterisation of leachate P6 used in continuous experiments. Numbers in italics indicate that the value is above a relevant limit. Values shown are averages of 4 measurements except for pH (22 measurements) and conductivity (21 measurements).

Parameters with limit values		Parameters without limit values		Parameters without limit values	
Parameter	Concentration [mg/l]	Parameter	Concentration [mg/l]	Parameter	Concentration [mg/l]
As	<i>0.023</i>	Al	0.076	NO ₃ -N	0.104
Cd	0.000019	Ca	202.35	NH ₄ -N	325
Cr	0.038	Co	0.012	PO ₄ -P	1.42
Cu	0.018	Fe	2.08	SO ₄ -S	35.08
Hg	0.00023	K	316.34	TOC	234.23
Ni	<i>0.066</i>	Mn	0.27	IC	650.55
Pb	0.00070	Mo	0.0025		
Zn	0.051	Na	1504.53		
Mg	103.83	S	37.24		
P	<i>1.68</i>	Si	17.63		
TN	<i>363.9</i>	Sr	5.30		
pH (no unit)	7.2	F	0.46		
Cond. [mS/cm]	9.9	Cl	2406		

To evaluate the filter materials' capacity to remove metals the concentration after filtration, C , was compared to the concentration before treatment, C_0 . Samples representing day 1-10 were compared to an average of the untreated leachates from day 2 and 10, samples from day 11-20 was compared to untreated from day 10 and 20 and samples from day 21-29 was compared to untreated samples from day 20 and 29. At a given time not all columns with the same filter material had reached the same liquid to solid (L/S) ratio. Therefore they are not entirely comparable to one another and averages were not used.

The water did not pass the sand column totally unaffected. Most metal concentrations increased slightly, but the Zn concentration was halved. In the comparison to the untreated leachate the effect of the sand was not considered. The results from comparisons are shown in Figure 9 through Figure 14. With few exceptions the figures show only the parameters where there are relevant limit values.

As can be seen from Figure 9 activated carbon has a good ability to remove Cr, Cu, Ni, Pb and Zn from leachate P6. Cr and Ni which are the most problematic metals in this leachate are removed to more than 90 % throughout the experiment which is very encouraging. Some metals are removed less in the beginning. This can be an indication that there are some minerals being leached from the carbon.

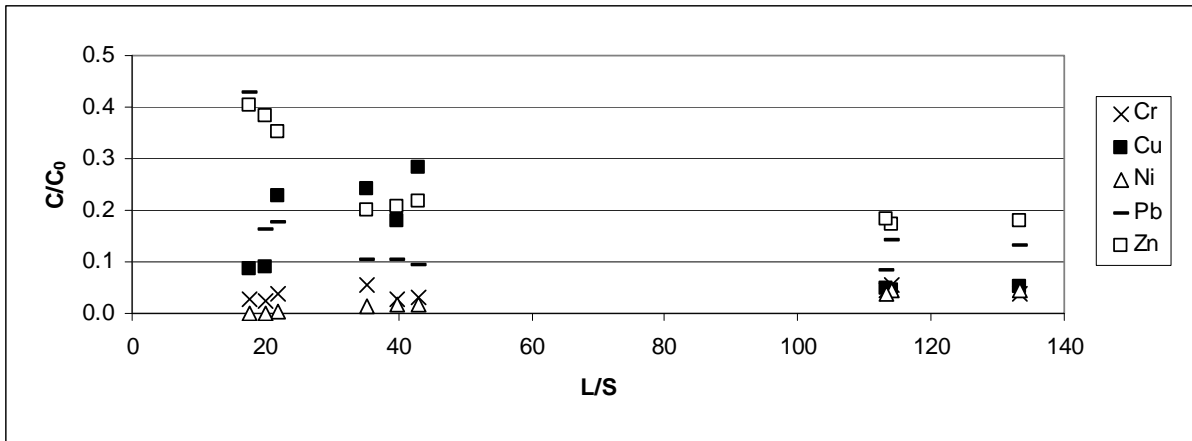


Figure 9. The effect on Cr, Cu, Ni, Pb and Zn from filtration with activated carbon. Ingoing concentration (C_0) compared to outgoing concentration (C) at different liquid to solid ratios.

Figure 10 shows that some elements indeed can be released from the activated carbon. In the beginning of the experiment As, Cd, Hg and Mg concentrations are higher in the effluent than in the influent. This confirms the findings from the batch test that As can be leached from activated carbon.

At the end of the experiment there has been a net removal of Cd. There still is a net release of Mg, but all Mg concentrations are below the limit. As, and possibly Hg, still seems to be a problem. There is a net release of both and the As concentration was above the limit already in the influent. As release from activated carbon has been known to occur before (Gandy and Maas 2004). In that case it was not considered a big problem, but since As will need to be removed from the leachate in this case it is of course a problem if the filter releases the element. After filtration Hg concentrations were above the limit value.

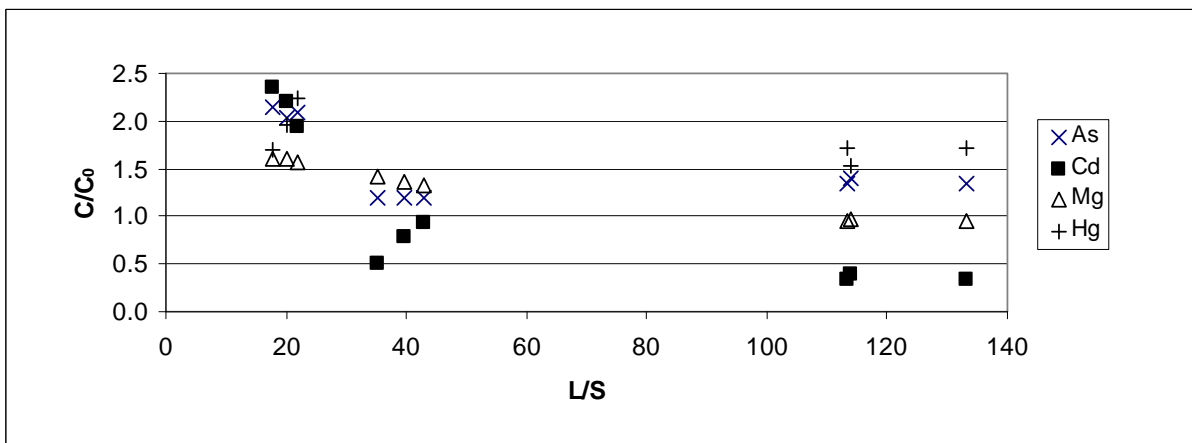


Figure 10. The effect on As, Cd, Hg and Mg from filtration with activated carbon. Ingoing concentration (C_0) compared to outgoing concentration (C) at different liquid to solid ratios. There is less information about Hg since the concentration was below detection limits in several cases.

Figure 11 shows the metals that were removed most efficiently in the CAP columns. It is clear that CAP is not as efficient as activated carbon. About 80 % of Cr and 20 % of Ni are removed. These results are similar to those from the batch study. In two cases the Ni concentration is above a limit.

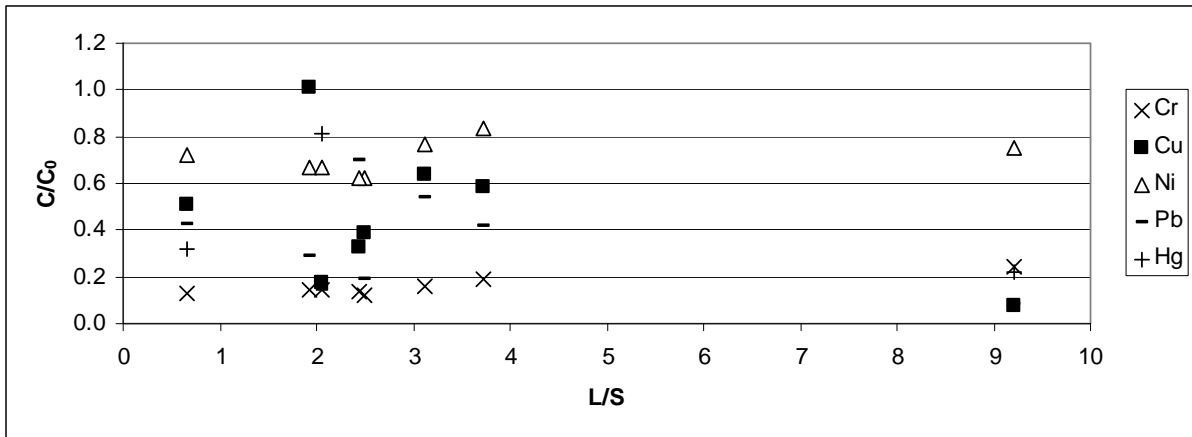


Figure 11. The effect on Cr, Cu, Hg, Ni and Pb from filtration with CAP meal. Incoming concentration (C_0) compared to outgoing concentration (C) at different liquid to solid (L/S) ratios. There is less information about Hg since the concentration in several cases was below detection limits.

Figure 12 shows that some important elements are leached or unaffected by the CAP meal filter. As and Zn seems to be largely unaffected while Mg and Cd are leached. In absolute numbers the difference between C and C_0 is small for Cd, and all measured concentrations were still below the limit except for As that was above already in the influent.

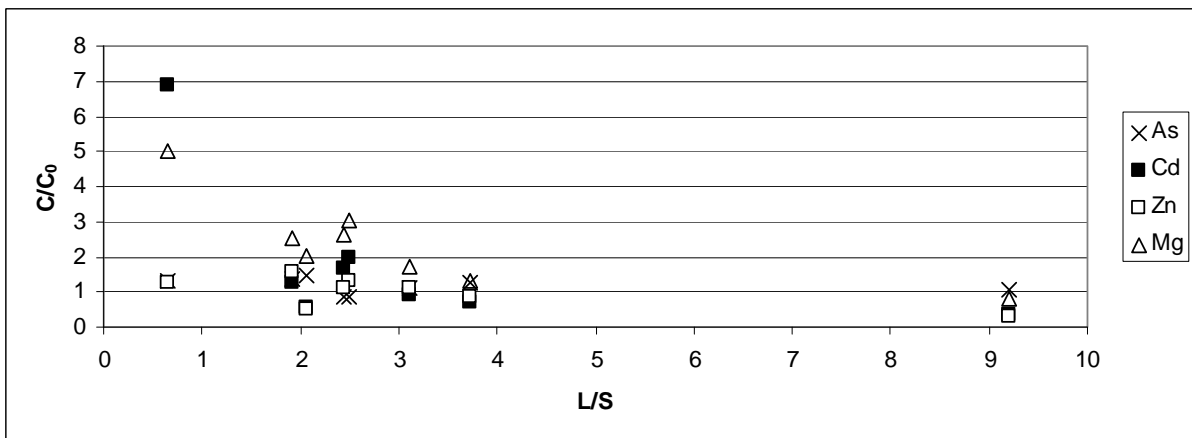


Figure 12. The effect on As, Cd, Zn and Mg from filtration with CAP meal. Incoming concentration (C_0) compared to outgoing concentration (C) at different liquid to solid (L/S) ratios.

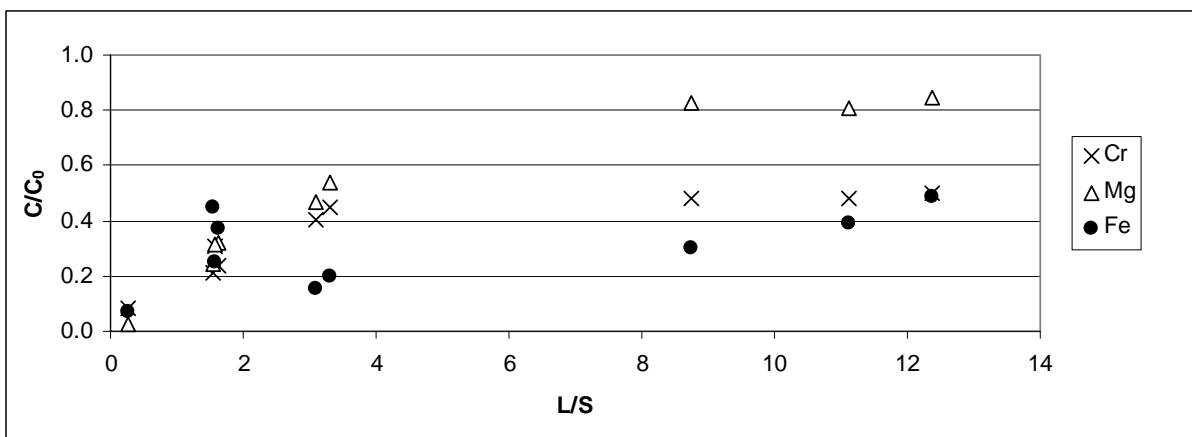


Figure 13. The effect on Cr, Mg and Fe from filtration with iron fines. Incoming concentration (C_0) compared to outgoing concentration (C) at different liquid to solid (L/S) ratios.

As can be see from Figure 13 removal of Cr and Mg with iron fines is initially very efficient. After some time the concentrations seem to stabilise on 50 % and 80 % of that in the ingoing water, respectively. Since the columns were filled with iron and rust could be seen in the tubing leading away from them it could be expected that the iron concentration would increase but Figure 13 shows that this is not the case; the outgoing concentration is less than half the ingoing. A lot of iron is probably precipitating in the columns and co-precipitation could be one mechanism that other elements are removed.

As can be seen from Figure 14 some elements are leached from the iron columns initially, but reach lower concentrations towards the end of the experiment. Only Ni shows a net release during the whole period, but this is problematic enough since this is one of the most important elements to remove. Cu and Pb reach very low C/C_0 values. Cd (not shown in the figure) is released in large amounts; initially the outgoing concentration is more than 40 times the ingoing, but is still below the limit value.

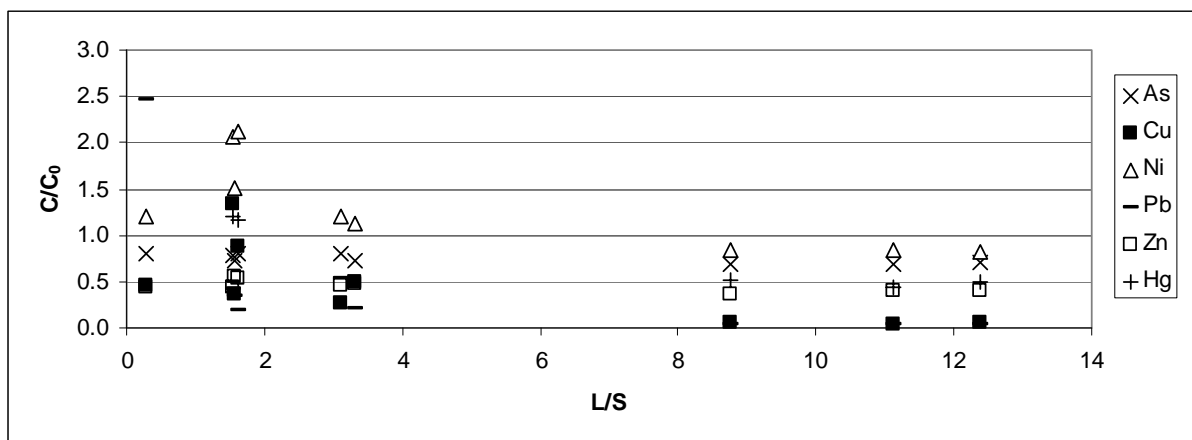


Figure 14. The effect on As, Cu, Hg, Ni, Pb and Zn from filtration with iron fines. Ingoing concentration (C_0) compared to outgoing concentration (C) at different liquid to solid ratios. There is less information about Hg since the concentration in several cases was below detection limits.

3.2.5 Organic carbon and nutrients

The goal of this study is not to find ways to remove organic carbon or nutrients, but there are limits to the chemical oxygen demand (COD), total nitrogen (N) and phosphorous (P) in the leachate so it is interesting to have a look on how the different materials affect these parameters (Figure 15 through Figure 17).

Figure 15 shows that most of the organic carbon is removed by the activated carbon filter. This could be expected and is also consistent with the results from the batch test. Nitrogen is unaffected but around 70 % of phosphorous is removed.

As Figure 16 shows leaching of nutrients and organic carbon from CAP meal columns is extensive. Even at the end of the experiment the outgoing concentrations are a few times higher than the ingoing. CAP meal consists partly of calcium phosphate but calcium is not released from the columns. Two proposed mechanisms for metal removal with similar materials are ion exchange with calcium and precipitation as phosphates (Xu and Schwartz 1994; Sneddon, Orueetxebarria et al. 2006). These mechanisms can not explain why large amounts of phosphate but no calcium is released.

Organic carbon and nitrogen release from CAP meal could at least partly be explained by the fact that there is about 20 % protein still left in the CAP meal even though the production process aims at minimising this. This can prove to be a big obstacle to the use of CAP meal for water purification purposes. Some studies have used bone char as a sorbent for heavy

metals (Cheung, Porter et al. 2002; Wilson, Pulford et al. 2003). Bone char should not contain proteins like CAP meal and could therefore be a better alternative. It can however be expected that bone char be more expensive than CAP meal.

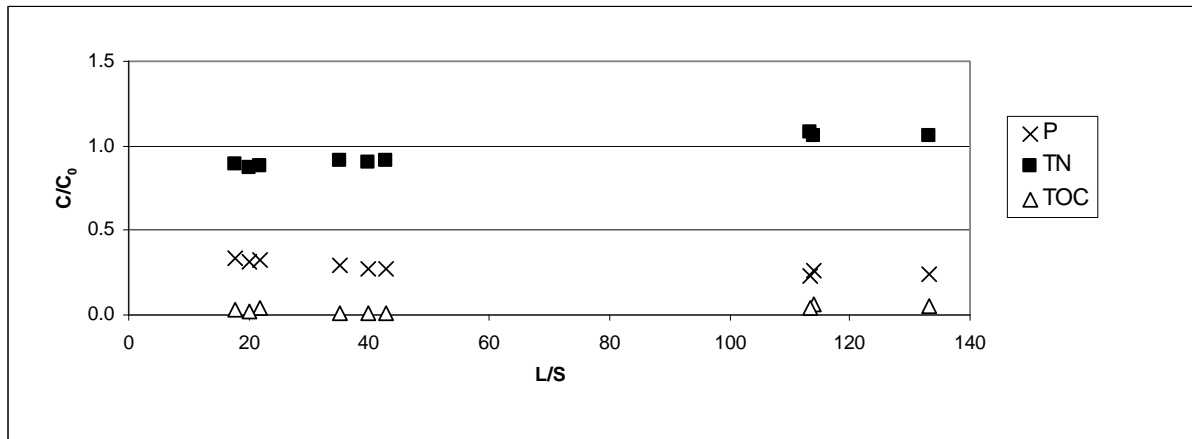


Figure 15. The effect on total organic carbon (TOC), total nitrogen (TN) and phosphorous (P) from filtration with activated carbon. Ingoing concentration (C_0) compared to outgoing concentration (C) at different liquid to solid ratios.

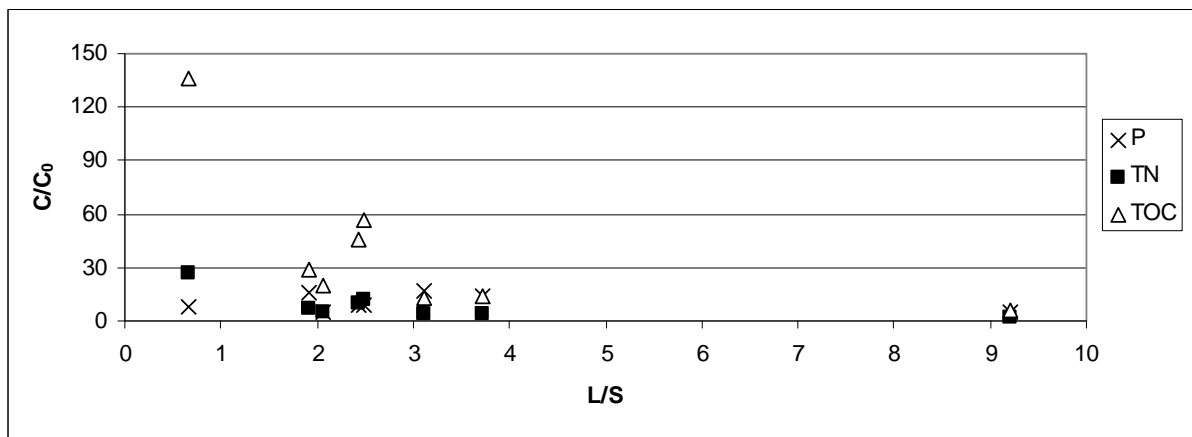


Figure 16. The effect on total organic carbon (TOC), total nitrogen (TN) and phosphorous (P) from filtration with CAP meal. Ingoing concentration (C_0) compared to outgoing concentration (C) at different liquid to solid ratios.

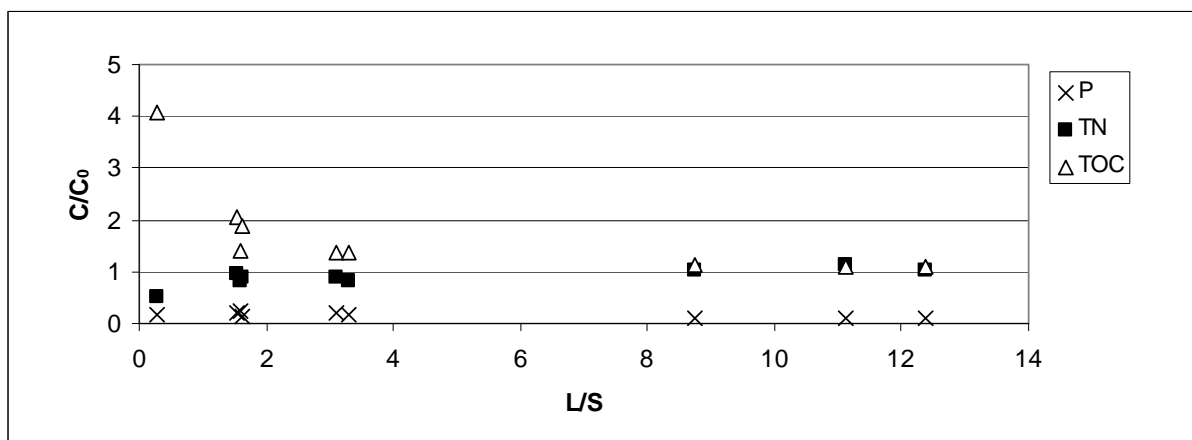


Figure 17. The effect on total organic carbon (TOC), total nitrogen (TN) and phosphorous (P) from filtration with iron fines. Ingoing concentration (C_0) compared to outgoing concentration (C) at different liquid to solid ratios.

Figure 17 shows how the iron columns affected nutrients and organic carbon. Nitrogen is unaffected but more than 80 % of the phosphorous is removed, possibly due to precipitation with iron. TOC concentrations increased. This might be surprising but is probably due to the fact that the iron fines were mixed with organic cutting fluids when it was collected at the metal workshop.

4 Conclusions and recommendations

The study clearly shows that metals can be removed by sorption filters. All three filter materials from the continuous test showed good results for at least a few elements. Activated carbon had the best ability to remove heavy metals from the leachate, and also the best hydraulic properties.

CAP meal had the worst hydraulic properties, and the small particle size might make CAP meal unsuitable for continuous applications even though better equipment could make the problem smaller. To avoid this problem, larger particles will be needed. This could be achieved by using a larger fraction from the sieving or by trying to granulate the CAP meal. Alternatively the CAP meal could be used as a reactive barrier but release of nutrients and carbon is a problem if the filtered leachate is to be released into the environment. Production of bone char could be one way of solving this problem.

Leaching of unwanted substances has proven to be a possible problem when working with reactive filters. Leaching of As from activated carbon, nutrients and organic carbon from CAP meal and Ni from iron fines were the worst disadvantages in this case. Before installing filters, they should be tested to avoid similar problems.

In order to find alternatives for filter applications in the future there are several different options. Different activated carbon can be studied to find one that does not release As. The As release seems to be dependent on the leachate chemistry since there was no release with Fällning Ut in the batch test. This proves how important it is to always test a filter material with the leachate in question.

Another alternative would be to search for a material that could remove the As being released from a CAG filter. Iron fines of some kind could be an alternative since the batch test showed that iron fines can remove As to a high extent.

The iron fines used in the filter study did not give as good results as those in the batch test. However there are other possible sources of scrap metal fines that might merit studying.

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