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BLAST FURNACE SLAG AND PINE BARK AS POTENTIAL FILTER MEDIA FOR METAL SORPTION FROM LANDFILL LEACHATE

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ABSTRACT

Heavy metals are commonly occurring in landfill leachate and in order to achieve the environmental goal about a non-toxic environment adopted by the Swedish Parliament, the leachate must be treated before being discharged into a nearby surface or groundwater body. There are several technical treatment options based on chemical, biological or physical processes. Examples of these techniques are the SBR technique, oxidation and membrane filtration. These treatment methods are not always suitable at all landfill sites due to economical and/or technical constraints. Other treatment methods have therefore attracted attention. These methods, often natural based such as constructed wetland systems, are more adapted to small landfill sites where high-tech and cost-demanding alternatives are not an option. One natural based method that has attracted attention for leachate treatment in recent years is the filter technique. It is based on the passage of a polluted water flow through a filter media with properties suitable for retention of heavy metals or other pollutants. A large number of different filter materials have been investigated with regard to their metal sorption capacity. The majority of these studies have been carried out in laboratory experiments of different kinds. Industrial by-products such as blast furnace slag and pine bark are filter materials that have been considered interesting for metal removal from landfill leachate. A series of laboratory experiments carried out as batch tests have therefore been conducted in order to learn more about the potential of these filter materials to remove heavy metals from landfill leachate.

KEYWORDS

Amorphous slag; Batch tests; Copper; Crystalline slag; Lead; Zinc

1 INTRODUCTION

There are about 300 active landfills in Sweden of which approximately 25 are regarded as large landfill [1]. At these landfills as well as at the smaller landfill sites, and for any other landfill in the world, landfill leachate is generated. The composition of leachate is dependent on the waste deposited at the landfill site as well as the phase of the landfill, thus landfill leachate at a specific landfill site is unique with regard to composition [2]. In addition, the composition of the leachate within a specified landfill site can also vary if several leachate streams are generated [3]. Commonly occurring pollutants in landfill leachates are ammonium, organic compounds and heavy metals. These pollutants should not be discharged

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into the environment without treatment. A various range of treatment methods have therefore been introduced, e.g. reverse osmosis, ammonium stripping and the SBR technique. These treatment methods are in the majority of cases efficient with regard to the removal of pollutants but on the other hand also very costly for the individual landfill operator.

The high costs and equally high energy input needed, have forced the landfill operators to find new treatment solutions. In recent years, different methods based on environmental engineering concepts have been proposed, for instance constructed wetland systems (CWS) and soil-water systems. One method that can be used solely or be included in a CWS for instance is the filter technique [4]. This technique is based on the passage of the polluted leachate through a special filter media which has demonstrated a high capacity to retain one or several pollutant(s). If necessary, several filter media can be used in combination.

Removal of heavy metals by different filter media is a vast area of research world over. A large number of researchers have investigated the sorption capacity of various groups of filter media such as minerals, organic residues and industrial by-products; see [5] for details. The majority of these filter media are however not easily available in Sweden thus other materials have attracted attention. Two of these are blast furnace slag (BFS) and pine bark, both industrial by-products from the steelworks and forest industries respectively. Blast furnace slag and pine bark have to some extent been investigated in laboratory experiments with regard to removal of heavy metals. The aim with this paper is to present additional investigations demonstrating the capacity of these filter media to remove heavy metals, especially with regard to landfill leachate.

2 MATERIALS AND METHODS

2.1 Materials

The filter media tested are blast furnace slag and pine bark. The former is a by-product derived from the process of separating iron from ore within the steel manufacturing industry. The slag tested originates from the steelworks in Oxelösund, approximately 100 km south of Stockholm, Sweden. The main components of the slag are calcium (Ca), manganese (Mg), silica (Si), but aluminium (Al) and sulphur (S) are important components together with a range of different trace elements, see [6]. For other chemical and physical properties, see *Table 1*.

Two variants of the BFS were tested; amorphous and crystalline slag. The former has a porous structure while the latter has a more glassy structure. The differences in structure are due to different cooling processes; the amorphous slag (BFS-A) is rapidly cooled in water while the crystalline slag (BFS-C) is air-cooled.

Table 1. Chemical and physical properties of blast furnace slag (from [6]).

Parameter	Crystalline BFS	Amorphous BFS
Ca (mg/kg)	214410	214410
Fe (mg/kg)	2735	3553
K (mg/kg)	4184	4225
Mg (mg/kg)	104940	99512
Na (mg/kg)	3865	4013
Si (mg/kg)	159397	154722
Al (mg/kg)	67744	67215
As (mg/kg)	0.525	0.966
Ba (mg/kg)	369	363
Cd (mg/kg)	0.0186	0.0149
Co (mg/kg)	10.8	< 2
Cr (mg/kg)	42.3	30.2
Cu (mg/kg)	< 2	4.56
Hg (mg/kg)	0.132	0.139
Mn (mg/kg)	4468	4164
Ni (mg/kg)	< 2	2.42
Pb (mg/kg)	0.595	0.544
Sr (mg/kg)	303	300
S (mg/kg)	10900	12900
V (mg/kg)	611	487
Zn (mg/kg)	3.35	3.46
pH	10.2-10.3	10.3-10.6
Density (g/cm^3)	1.2-1.61	0.8-1.47
Porosity (%)	40-58	44-55
Hydraulic conductivity (m/day)	0.8-15.9	3.2-40.6
Specific surface area (m^2/g)	0.5-0.7	n.a.

The pine bark used (*Pinus sylvestris*) is a by-product from the forest industry. The material originates from non-irrigated timber which is barked off at the saw-mill and thereafter delivered for use. The material is composed of a mixture of bark and wood fibre, see *Table 2*. The major components of these compounds are lignins and tannins. Other properties of the material can be seen in *Table 2*.

Table 2. Chemical and physical properties of pine bark (Pinus sylvestris) (from [7])

Parameter	**Pine bark**
Pine bark (%)	85-90
Wood fibre (%)	10-15
Density (g/cm^3)	0.25

2.2 Methods

The blast furnace slag and the pine bark have been the subjects of numerous laboratory tests; e.g. batch tests in which a range of heavy metal solutions have been used in order to investigate the sorption capacities of the materials. The selected metals presented in this paper were copper (Cu), lead (Pb) and zinc (Zn) since these metals are commonly occurring in landfill leachate according to [2].

2.2.1 Batch tests

Metal solutions were prepared in the laboratory using different metal salts. Stock solutions were prepared and diluted to various concentrations that ranged from 1.0-100 mg/l; see also [8], [7] and [9] for further details. The pH of the solutions also varied; e.g. pH 4 and pH 7 were used in the tests. The metal solutions were added to a known volume of the filter media (ratio 5:50) and shaken for 60 seconds in all tests. The samples were thereafter analysed by means of atomic absorption spectrophotometer (AAS) (Vario 6). The difference between the initial concentration and the final concentration was assumed to be due to sorption.

3. RESULTS

3.1 Metal sorption by blast furnace slag

The results from the batch tests using blast furnace slag as filter media are presented in Figures 1-3. In *Figure 1*, results from a sorption experiment in which a Cu-solution was used for sorption by BFS-A and BFS-C are presented.

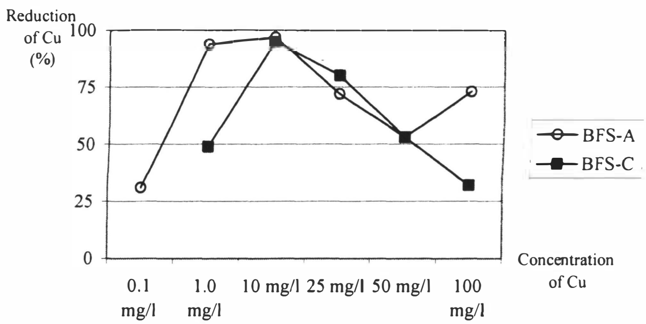

Figure 1. Examples of reduction of Cu by amorphous blast furnace slag (BFS-A) and crystalline blast furnace slag (BFS-C) at pH 7 (adapted from [9]).

The results indicate that Cu is sorbed by both the amorphous and crystalline slag. The amorphous slag demonstrated a slightly better removal rate than the crystalline slag. This was the case also for Pb which also was removed by both slag types, and again, the amorphous slag demonstrated a more efficient removal rate than did the crystalline slag, see *Figure 2*.

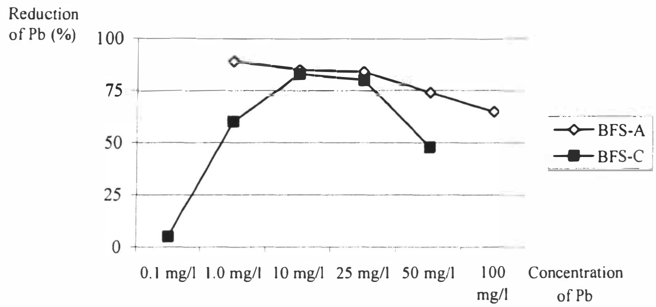

Figure 2. Examples of reduction of Pb by amorphous blast furnace slag (BFS-A) and crystalline blast furnace slag (BFS-C) at pH 7 (adapted from [9]).

Zink did not show the same sorption pattern as Cu and Pb. The removal rate for this metal was less than those for Cu and Pb, and the Zn-sorption decreased with increasing concentration, see *Figure 3*. In this case, the crystalline slag performed better than the amorphous slag.

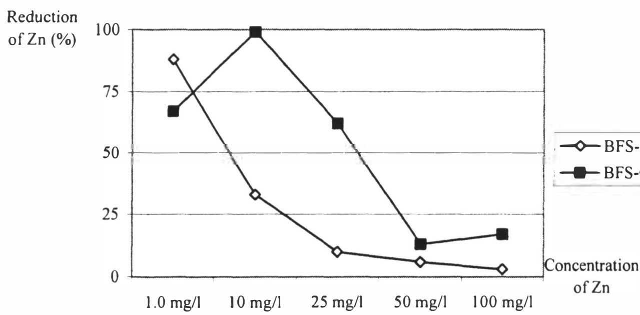

Figure 3. Examples of reduction of Zn by amorphous blast furnace slag (BFS-A) and crystalline blast furnace slag (BFS-C) at pH 7 (adapted from [9]).

3.2 Metal sorption by pine bark

The removal rates of metals by pine bark are shown in Figures 4-6. *Figure 4* shows the removal of Cu which is rather stable between 1.0 and 10 mg/l, but thereafter it decreased slightly.

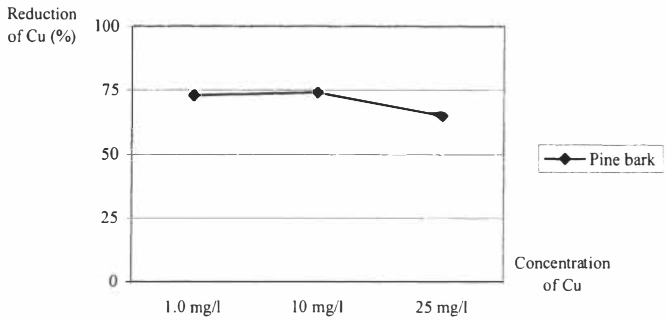

Figure 4. Examples of reduction of Cu by pine bark at pH 5 (adapted from [7])

In *Figure 5*, the removal of Pb is shown. It can be seen that the removal is increasing but it should be noted that this phenomenon occurred at rather low concentrations, e.g. between 1.0 and 5.0 mg/l.

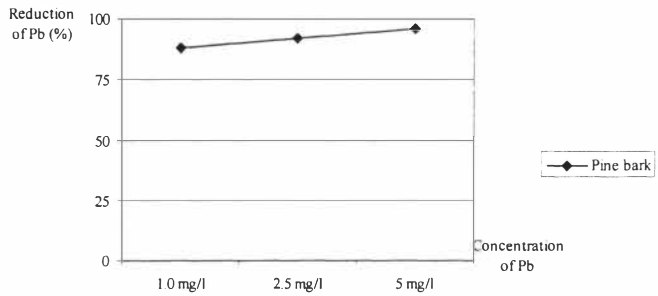

Figure 5. Examples of reduction of Pb by pine bark at pH 5 (adapted from [7])

The sorption pattern for Zn is shown in *Figure 6*. From the figure, a decreasing sorption can be observed. The removal of Zn is highest at the lowest concentration.

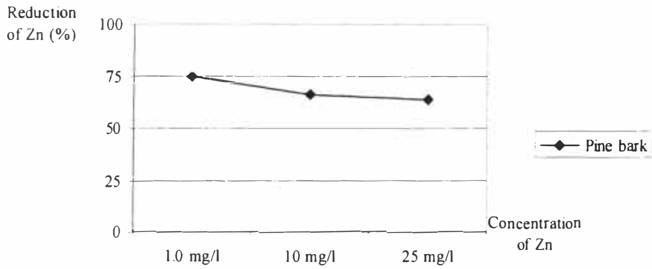

Figure 6. Examples of reduction of Pb by pine bark at pH 5 (adapted from [7])

4 DISCUSSION

The results in the present paper indicate that both blast furnace slag and pine bark demonstrate an adequate capacity to sorb heavy metals from metal solutions. The results are in agreement with other similar investigations; see for instance [8], [10], [11] and [12]. It should however be kept in mind that the experiments described are carried out in the laboratory where conditions can be kept stable compared to the conditions in the field where they might vary considerable. Thus the results are therefore to be regarded as indicators of the filter media's capacity to sorb metals rather than a maximum value of the sorption capacity.

The batch tests have also been carried out with single metal solutions; e.g. there has been solely one metal species in the solution. In a real landfill leachate, the chance to find more than one metal is very large, and the results might therefore be completely different if using metal solutions or leachates with a more complex composition since competition for sorption sites might occur in that case. Further studies using multi-metal solutions and/or landfill leachates are therefore needed in order to learn more about the capacity by the filter media to sorb metals under more realistic conditions. An *on-site* column test indicates that the metal sorption capacity is more various and less efficient in the field than in the laboratory investigations presented in the present paper [3].

All metals were however sorbed to the filter media tested, in particular copper and lead which demonstrated a high affinity regardless of pH and concentrations used. This might be due to the fact that these metals are strongly adsorbing metals; e.g. strongly bound to humic substances and variable-charged particles surfaces in the soil [13]. Zinc is also an adsorbing metal but its mobility depends on the pH-value to a much larger extent than for the other metals tested.

The fact that the filter media tested sorb metals at various metal concentrations also vouch for removal of metals from different types of landfill leachates. A landfill will undergo several stages depending on the degradation of the waste it contains. The landfill leachate generated at the different stages will reflect the degradation processes leading to variations in metal concentrations in the leachate for instance.

Further on, the amorphous blast furnace slag seemed to be more efficient than the crystalline blast furnace slag with regard to sorption of the metals in general, and Cu and Pb in particular. This might be explained by the properties of the slag types. The amorphous slag is much more porous than the crystalline one, thus allowing a more efficient sorption due to larges sorption sites available.

Compared to the slag materials, the pine bark is also an efficient filter media with regard to sorption of metals. The pattern is the same for the different metals; copper and lead are sorbed to a larger extent than zinc. The same reasons can be quoted as for the slag materials.

5 CONCLUSIONS

The laboratory investigations that have been carried out demonstrate the both the blast furnace slag and the pine bark are capable of sorbing heavy metals. In general the amorphous slag demonstrates a higher sorption capacity than the crystalline slag. The pine bark has also performed well indicating that this media is interesting for further investigations. Further studies are however needed in order to learn more about the filter media behaviour when fed with multi-metal solutions and/or landfill leachate.

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