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Removal of Dissolved Pollutants from Highway Stormwater with Low-cost Adsorbents

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Insitute of Water and River Basin Management
Chair of Hydrology

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Diplom’s Thesis

Removal of Dissolved Pollutants from Highway Stormwater with Low-cost Adsorbents

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Diplom’s Thesis

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Department of Hydraulic and Environmental Engineering

Removal of Dissolved Pollutants from Highway Stormwater with Low-cost Adsorbents

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Declaration for the Diplom’s Thesis

I warrant, that the thesis is my original work and that I have not received outside assistance. Only the sources cited have been used in this draft. Parts that are direct quotes or paraphrases are identified as such.

Karlsruhe, October 7, 2014 ____________________

Abstract

Heavy metal contamination of soil and groundwater have become a harmful issue. Thatswhy effective water treatment utilization were investigated. Low-cost materials, such as industrial waste, secondary waste, by-products, minerals, etc. were found to be efficient and inexpensive adsorbents for heavy metals in aqueous solutions. Twelve sorbents were studied for the heavy metal removal of copper, lead, nickel and zinc in stormwater. The sorbents are bottom ash, fly ash, montmorillonite, kaolinite, zeolite molecular sieve, olivine, bark, sea weed, saw dust, aluminum oxide, iron (III) oxide and granulate activated carbon (GAC). The sorbents were studied to find effiecient soil filter media, therefor sorbents with a smaller particle size were mixed with sand to prevent clogging . Batch test showed that the removal efficiency of all sorbents for four different multi metal concentrations. While the metal uptake of the sorbent/ sand mixtures were mostly not satifying other sorbents was able to remove up to 100 % of each havey metal. The effect of cold climate was analyzed by adding salt into the synthetic stormwater. The leaching ability and the heavy metal removal in a synthetic stormwater with added salt was tested for bark, olivine, granulate activated carbon and zeolite molecular sieve. With increasing salt conentration the removal effectivness of bark decreased, while the other three sorbents was unaffected. Also the adsorbed metals on bark leached in synthetic stormwater with added salt.

Keywords: stormwater, heavy metal removal, low-cost, cold climate, adsorption

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Contents

1 Introduction

The thesis objective is a part of a NORWAT (Nordic road water) funded project in cooperation with the department of hydraulic and environmental engineering of NTNU (Trondheim, Norway) on sorbents for road runoff treatment. NORWAT is a four-year research and development program under the Norwegian Public Roads Administration (www.vegvesen.no). The purpose is to build and operate the road network without causing unacceptable harm to the aquatic environment.

1.1 Thesis description

Rainfall and snowmelt generate massive quantities of storm water from urban surfaces and highways, which contains suspended particles, heavy metals, organic chemicals and even pathogenic bacteria. Compared to organic pollutants, heavy metals are not degradable in the environment. Main emissions are caused by traffic, such as wear of brake lining, vehicle exhaust, tire tread, etc., but also building materials such as roofs (copper) and signs (galvanized steel, zinc) (Genç-Fuhrman, Mikkelsen et al. 2007) . Heavy metals are harmful to the environment; vegetation, animals and human health are also effected. Therefore, heavy metals contamination of surface- and groundwater should be prevented. During the last decades, a great amount of research has been done on elimination of heavy metals from aqueous solutions. Adsorption is one efficient and cost effective method to remove heavy metals, in which heavy metal ions are bound to the surface of the adsorbent, such as granular activated carbon, industrial waste and by-products, minerals, etc.

1.2 Thesis objectives

The overall objective of this thesis is to test the removal efficiency of heavy metals in stormwater and the effect of salt addition on adsorption.

In this study, 12 pre-selected materials were evaluated for their removal efficiency of heavy metals in stormwater. These materials are classified into four groups: secondary waste (i.e. ashes), biosorbents (i.e. pine bark), clays (i.e. montmorillonite) and commercial sorbents (i.e. GAC).

The specific objectives of the project are:

- Conducting literature research to identify suitable low cost sorbents that are effective for the removal of heavy metal from aqueous solutions. Comparing the methods and results with each other.
- Analyzing water quality data to determine the ranges in which heavy metal ions occur.

- To test the removal efficiency of heavy metals using twelve sorbents in synthetic stormwater at four different initial concentrations.
- To test the four most efficient sorbents in saline synthetic stormwater and their leaching ability in a saline solution.
- Analyzing the results to identify the two most effective sorbents that can be selected for upgrade.

1.3 Scope

Multiple studies were conducted to test different parameters such as initial concentration, initial pH, temperature variation, time, and liquid solid ratio, etc., of single adsorbate. The purpose of this thesis was to test and compare removal efficiency of copper, lead, nickel and zinc in stormwater by a variety of low cost sorbents. The stormwater was synthetically prepared in the laboratory. The batch test was done for all four heavy metals at the same time.

The sorbents were tested under equilibrium conditions to get the best possible comparison. The experiments were done with an initial pH between 6.8 and 7.0. Because of the cold climate and the extended use of salt in Northern countries (i.e. Norway) it was interesting to test the most efficient sorbents in saline stormwater and the leaching of the sorbents in saline solutions. The water quality analyses of the heavy metals were done using ISP-MS.

The scope of this work does not include studying the chemical constituents of the adsorbents to determine the chemical reactions involved in the process.

2 Literature review

2.1 Heavy metals

Heavy metals occur in high amounts in highway stormwater mainly due to the automobile industry. Lead, for example, is harmful to human health in small concentrations. While copper, nickel and zinc are indispensable for life in small quantities. However, high intake of heavy metals is harmful and may be cancerous, damaging to organs and the immune system. Accumulation of heavy metals in soil can harm soil flora and fauna by disrupting nutrients cycle, but also it could lead to soil formation due to changes in organic matter decompositions (Crute 2012). Therefore, much attention was focused on the removal of heavy metals from aqueous solutions in the last decades, in order to protect drinking water sources and to assure environmentally friendly conditions for flora and fauna.

The study focuses on the removal of the heavy metals copper, lead, nickel and zinc, which are commonly found in highway stormwater. Table 1 gives the heavy metal concentration in Danish and UK stormwater.

Table 1 Heavy metal ranges in Danish stormwater, highway drainages in the UK and roadside snow Trondheim (Norway)

	Stormwater Danmark (Genç-Fuhrman, Mikkelsen et al. 2007) [µg/l]	Highway drainages during the last 30 years in the UK (Revitt 2004) [µg/l]	In roadside snow Trondheim (Paus 2010) [µg/l]
Copper	0.06 – 1,410	12 – 690	63 – 2142
Lead	-	3 – 2,410	8 - 240
Nickel	1 – 49,000	-	35 – 785
Zinc	0.7 – 22,000	25- 3,550	127 - 6058e

2.1.1 Heavy metal sources

In the highway environment, there are different kinds of pollutants occurring such as heavy metals, inorganic salts and organic pollutants. (Revitt 2004) mentioned that contaminants in the highway environment were caused by vehicle emissions, vehicle part wear and vehicle leakages. Furthermore, there was contribution from seasonal maintenance activities, for instance weed control in the summer and de-icing practices in the wintertime.Table 2 shows sources for the heavy metals, discussed in this study. The table was modified after Loganathan, Vigneswaran et al. (2013).

Table 2: Sources of major heavy metal pollutants and pollutant concentration/ or emission rate

Pollutant	Source	Pollutant concentration/ emission rate	Reference
Cu	Brake disc pad/dust	1.4 – 6.7 %	von Uexkull, Skerfving et al. (2005)
	Brake lining/ dust	5.1 – 11.8 %	Westerlund (2001)
		11 µg/g – 39 %	Thorpe and Harrison (2008)
		6.6 % (mean)	Kadioglu, Ustundag et al. (2010)
	Tire tread	< 1 – 490 µg/g	Thorpe and Harrison (2008)
	Unleaded gasoline exhaust	212 µg/g (mean)	Kadioglu, Ustundag et al. (2010)
	Diesel exhaust	47 µg/g (mean)	Kadioglu, Ustundag et al. (2010)
Ni	Brake lining/dust	70 − 182 µg/g	Westerlund (2001)
		4 – 730 µg/g	Thorpe and Harrison (2008)
	Tire tread	< 1 – 50 µg/g	Thorpe and Harrison (2008)
	Asphalt bitumen	15 – 100 µg/g	
Pb	Gasoline	1.2 g/L in 1970s,	Lovei (1998)
		≤ 0.15 g/L in 1980/1990s	Lindgren (1996)
	Brake lining/dust	0.9 − 1.9 %	Westerlund (2001)
		1 µg/g – 11.9 %	Thorpe and Harrison (2008)
	Tire tread	1 – 160 µg/g	Thorpe and Harrison (2008)
	LPG exhaust	3096 µg/g (mean)	Kadioglu, Ustundag et al. (2010)
Zn	Tire tread	430 – 9640 µg/g	Thorpe and Harrison (2008)
	Brake lining/ dust	25 µg/g – 18.8 %	Thorpe and Harrison (2008)
		0.7 – 2.4 %	Westerlund (2001)
		7.9 % (mean)	Kadioglu, Ustundag et al. (2010)
	Unleaded gasoline exhaust	3225 µg/g (mean)	Kadioglu, Ustundag et al. (2010)
	LPG exhaust	1074 µg/g (mean)	Kadioglu, Ustundag et al. (2010)
	Diesel exhaust	466 µg/g (mean)	Kadioglu, Ustundag et al. (2010)

2.2 Adsorption

Adsorption is the process, where atoms, ions or molecules from a gas, liquid or dissolved solid face adhere to a surface. The adsorbed adsorbate creates a film on the surface of the adsorbent. Another similar process is absorption; it is the filling of pores in a solid. Both processes usually take place simultaneously and are therefore combined into the term “sorption”.

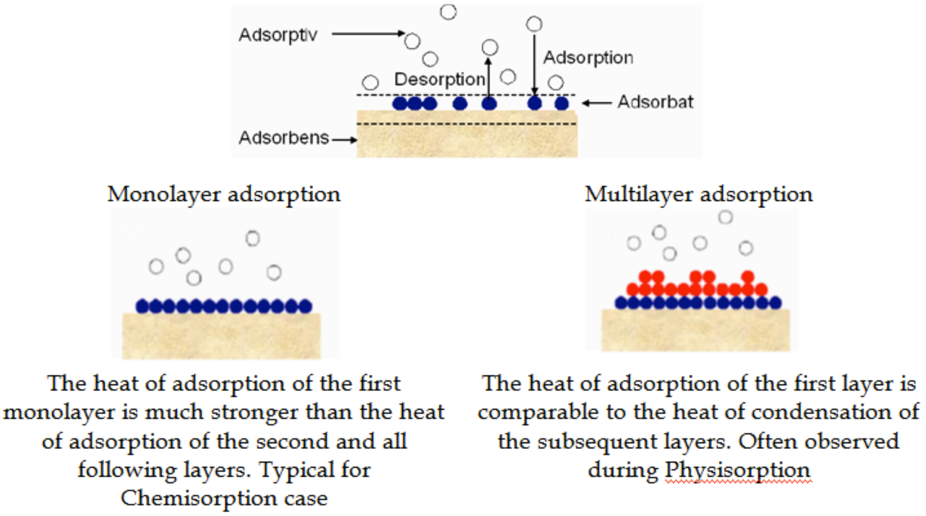

Figure 1 Presentation of the typical adsorption process (after (Christmann, 2010)).

Adsorption is used to separate, purify and to remove impurities in liquid and gas mixtures. Especially in recent years it was found to be an efficient process for water treatment, compared to other processes, and it is cheap due to the possibility of using low-cost materials. Adsorption finds application in drinking water, stormwater and wastewater treatment.

2.2.1 Adsorption types

Adsorption can be classified into physio-sorption, chemisorption and biosorption.

2.2.1.1 Physio-sorption

Physio-sorption describes the interactions between the adsorbate on the adsorbent, based on physical forces. Physio-sorption is the interaction of weak attractive and repulsive electromagnetic forces. Van der Waals interactions are one example of physical bonding forces, while another is fixed dipoles on a polar surface, such as salts.

Van der Waals interactions are the attractive forces between covalent adjacent molecules or atoms, which emerge through spontaneous polarization of a particle and the occurrence of induced dipoles.

2.2.1.2 Chemisorption

Chemisorption is a process by which the adsorbed molecule and the surface form a strong chemical bond. The interaction is irreversible (as long as no chemical treatments or high temperatures are used on the surface), and chemical properties of the adsorbed molecule, and or the surface, are modified. Compared to physio-sorption, chemical interactions form only a monolayer on the surface. Elementary chemical bonds are ionic and covalent bonds.

A metal usually forms a chemical compound with a nonmetal to lose its electrons in the outer energy level. A molecule that is formed by ionic bonds is called polar molecule, and is partly positively and negatively charged. In contrast to the ionic bonds, a covalent bond is about sharing electrons between two atoms, to attain noble gases.

A hydrogen bond is a *dipole – dipole attraction* between polar molecules, which contain interaction between hydrogen and a small, highly electronegative atom such as fluorine, oxygen or nitrogen. Each molecule that contains bonds between hydrogen and one of the three mentioned atoms, are capable of hydrogen bonds. Typical functional groups for hydrogen bonds are the carboxyl group (-COOH), the hydroxyl group (-OH) and the amino group ($-NH_2$).

2.2.1.3 Biosorption

The overall metal uptake by biosorption includes the phenomena of ion exchange, adsorption, complexation and inorganic microprecipitation. Ion exchange tends to be the dominant metal removal mechanism.

Naja and Volesky (2011) illustrate ion exchange of metal ions on biosorbents as the interchange between bivalent metal ions with counterions from active group of polysaccharides, such as alginic acid (ALG) (Equation 2.1).

Equation 2.1

$$2NaALG + Me^{2+} \rightarrow Me(ALG)_2 + 2Na$$

Another example of ion exchange is shown by Bulut and Tez (2007) in Figure 2, where a heavy metal ion is attaching on two hydroxyl groups, while two hydrogen ions become released.

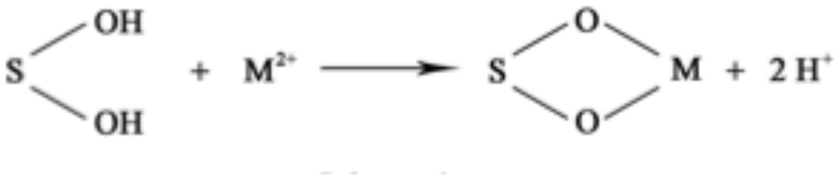

Figure 2 A heavy metal ion is attaching on two hydroxyl groups (Bulut and Tez 2007)

2.2.2 Factors affecting adsorption

Malamis and Katsou (2013) listed several factors, which can enhance or suppress adsorption, such as initial metal concentration, solution pH, temperature, adsorbent grain size, adsorbent concentration, adsorbent type, ionic strength and presence of other ions.

2.2.2.1 Competing metals

The presence of competing metals in an aqueous solution affects the adsorption efficiency. Ionic properties like ionic radius, electronegativity and affinity to functional groups are favoring different metal interactions (Shaheen, Derbalah et al. 2012). The ionic properties and the molecular weight of copper, lead, nickel and zinc are shown in Table 3.

Table 3 Ionic properties and molecular weight of copper, lead, nickel and zinc.

	Radius [pm = 10^{-10} cm]		Electronegativity	Molecular weight [g/mol]
	Atomic	Ionic (2^+)		
Copper	145	87	1.9	63.55
Lead	154	133	1.8	207.2
Nickel	149	83	1.8	58.69
Zinc	142	88	1.6	65.38

2.2.2.2 Influence of cold climate and road salt

Woinarski, Snape et al. (2003) studied the effects of cold temperature on copper ion exchange by natural zeolite and the influence of seawater (high salinity). The batch test contained 100 ml of Cu^{2+} concentration and 5g/l dry clinoptilolite, and the pH ranged from 4.5 -6.5. The study shows (Figure 3 A) a copper removal decrease of approximately 32 % due to a colder climate (2 °C) at Cu^{2+} concentrations near mean equilibrium concentration. The change in removal efficiency of Cu^{2+} caused by competitive cations (1 % stormwater) is show in Figure 3 B. For both temperatures, a Cu^{2+} uptake decrease of around 25 % in the saline solution was investigated.

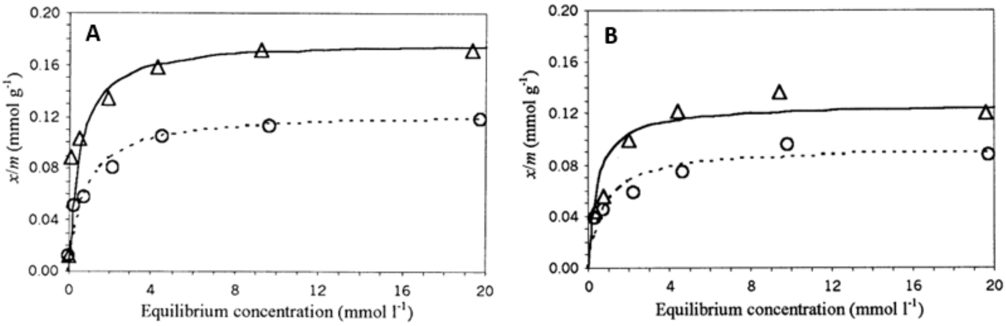

Figure 3 Copper adsorption isotherms for Na clinoptilolite (natural zeolite) at 2 °C (O) and 22 °C (∆), A: without seawater, B: in 1 % seawater.

2.3 Adsorbent

The twelve pre-selected sorbents are fly ash, bottom ash, kaolinite, montmorillonite, olivine, zeolite molecular sieve, bark, sea weed, sawdust, granulate activated carbon, iron (III) oxide and aluminum oxide. Genç-Fuhrman, Mikkelsen et al. (2007) also carried out a study about the comparison of multi sorbents. The experimental comparison of 11 different sorbents was about the simultaneous removal of AS, Cd, Cr, Cu, Ni and Zn. The batch test was run for 48 h with starting pH of 6.5 and a sorbent dosage of 20 g/l. Batches with eight different initial concentrations of eight heavy metals were tested. The adjusted pH after 48 h is shown for some of the sorbents in

Table 4. The increasing pH was mainly due to dissolution of the sorbent minerals. The decreasing pH of bark is explained by the release of natural organic matter containing both acids and phenols.

Table 4 Sorbent pH after 48 h (Genç-Fuhrman, Mikkelsen et al. 2007)

Sorbent	Aluminum oxide	Iron oxide-coated sand	Bark	Fly ash	GAC	Natural zeolites	Sand
pH after 48 h	7.4	7.5	5.8	10.6	8.6	7.7	7.2

To investigate the speciation of the heavy metals obtained in water for a pH range from 5 – 11, the following initial concentrations of 0.588, 0.178 and 1.350 mg/l for Cu, Ni and Zn were used. The speciation of copper, nickel and zinc are shown in Figure 4. The non-charged $CuCO_3$ is the dominating Cu-specie in the pH range 6.5 – 9.0, while the negatively charged species such as $Cu(CO_3)_2^{2-}$ and $CuCO_3(OH)_2^{2-}$ dominate at higher pH values and at lower pH it is Cu^{2+}. Ni^{2+} until a pH of 9.5, succeeded by the hydroxide species $Ni(OH)_2$ and $Ni(OH)_3^-$ at higher pH. Zinc is mainly present as Zn^{2+} below pH 8.5 and as $Zn(OH)_2$ at pH > 9.0

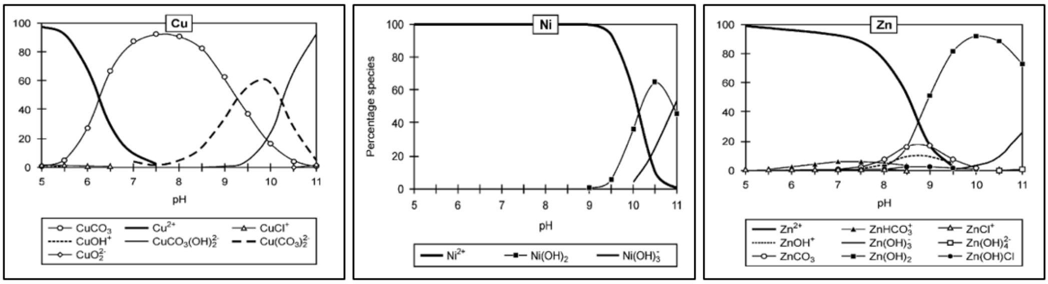

Figure 4 Speciation of Cu, Ni and Zn in water obtained using the PHREEQ-C model with ionic strength of 0.01 M NaCl, 0.003 M NaHCO3 buffer and heavy metal concentrations 0.588, 0.178 and 1.350 mg/l for Cu, Ni and Zn.

2.3.1 Ashes

Bottom ash and fly ash are secondary waste products and are produced by combusting coal or municipal solid waste in incineration plants. Lam, Ip et al. (2010) reported that the properties of the ashes could be separated into physical properties (particle size distribution, moisture content, bulk density, compressive strength, permeability and porosity) and chemical properties (chemical composition, loss on ignition, heavy metals and leachability, organic constituents and chloride content). The composition of municipal solid waste varies from country to country because of the different lifestyles and recycling processes.

The fly ash particles are light in weight and are collected after they got out together with the flue gas of the furnace and drifted away from the high-temperature combustion zone. The main content of fly ash is amorphous or glassy aluminosilicates and a smaller amount is crystalline compounds. The color is dark gray or tan and the particle size typically has a small diameter of 20 – 25 microns.

The particle size of bottom ash can reach much larger sizes up to 50 mm in diameter and has a sandy texture. Therefor, the particles are heavier and fall to the bottom of the furnace. The carbon content of bottom ash is higher than that of fly ash.

Table 5 shows an example that bottom ash and fly ash can also contain heavy metals.

Table 5 Heavy metal concentration in Swedish bottom and fly ash from MSWI.

	Bottom ash (Sweden) (Ribé, Nehrenheim et al. 2014) [mg/kg]	Fly ash (Sweden) (Aguiar del Toro, Calmano et al. 2009) [mg/kg]
Copper	17100	2536
Lead	1250	11513
Nickel	200	-
Zinc	4050	32804

2.3.1.1 Fly ash

Fly ash is basically the material that is produced by incinerating coal in thermoelectric power plants. Cho, Oh et al. (2005) mention that fly ash has a pH of 10 – 13 in water, therefor it is a strong alkali material. The surface of fly ash is negatively charged at high pH. Cetin and Pehlivan (2007) refer to the chemical components of fly ash, which are alumina, silica, ferric oxide, calcium oxide, magnesium oxide and carbon, as making it an efficient sorbent material, but as well its physical properties, such as porosity, particle size distribution and surface area. Komnitsas, Bartzas et al. (2003) mention especially as the most important characteristic the calcium content, which increases the pH to strongly alkaline values, and the $SiO_2 + Al_2O_3 + Fe_2O_3$ content.

Cho, Oh et al. (2005) tested the removal characteristic of heavy metal from aqueous solutions by fly ash. The sorbent was obtained from a bituminous coal-burning power plant in Boryung, Korea. The batch test was conducted at wastewater condition with zinc, copper, lead and cadmium. It was found that for increasing pH in a range from 3 – 12, the percentage of heavy metal removal by precipitation of the total removal increases (Figure 5). At a pH of 12 the removal contain almost only by precipitation.

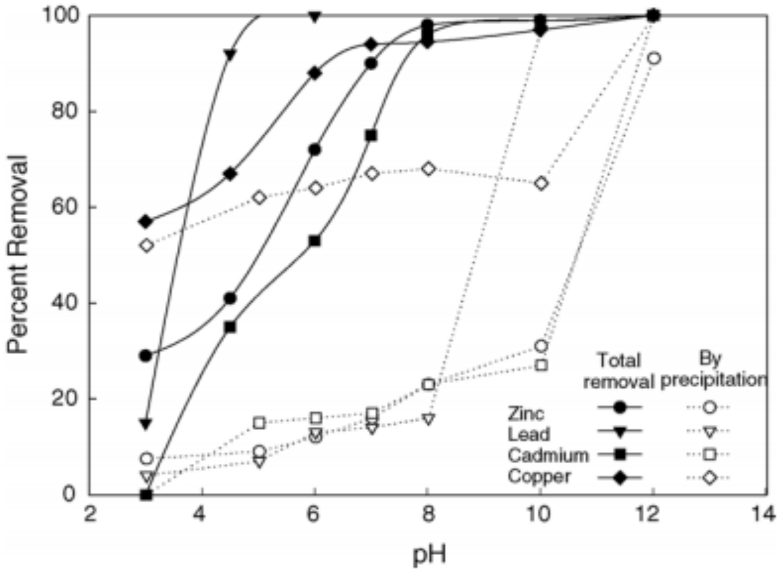

Figure 5 Effect of pH on the percent removal of zinc, lead, cadmium and copper: initial concentration off 100 mg/l and fly ash dosage of 20 g/l (Cho, Oh et al. 2005)

2.3.2 Clays

The mineral clay is a hydrous aluminosilicate, which is broadly defined as the colloid fraction smaller than 2.0 µm of soils, sediments and rocks. Through their ability to take up anions and cations either by ion exchange or adsorption or both, clays are able to immobilize pollutants. Important properties that make clays a good adsorption material are their large specific surface area, chemical stability, layered structure and high cation exchange capacity.

Clay particles can adsorb anions, cations and non-ionics in water on their edges and faces. The pollutants which accumulate on the surface of the clay, become immobilized through the processes of ion exchange, coordination and ion-dipole interactions, but pollutants can also be held trough H-bonding, van der Waals interactions or hydrophobic bonding arising from either strong or weak interactions.

2.3.2.1 Kaolinite

Kaolinite is the most common clay mineral of the kaolin group with the chemical composition $Al_2Si_2O_5(OH)_4$. Kaolinite contains a 1:1 layer structure, which was first suggested by (Pauling 1930), made up for a tetrahedral sheet of SiO_4 and an octahedral sheet Al^{+3}. Both sheets together form one common layer, where the tip of silica points towards the octahedral sheet. Both sheets share the apical oxygen atom. The 1:1 silica-alumina layer is shown in Figure 6.

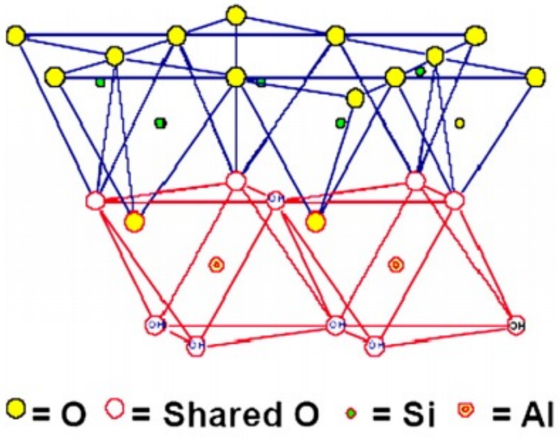

Figure 6 Structure of Kaolinite (Bhattacharyya and Gupta 2008)

Kaolinite has the formula $(Si_4)^{IV}(Al_4)^{VI}O_{10}(OH)_8$ and his theoretical composition of SiO_2 46.54 %, Al_2O_3 39.50 % and H_2O 13,96 %. Murray (1991) mentions that there are limited substitutions in this structure, such as Fe substituting for Al and some Al possibly substituting Si. Therefore, the charge on the layer is minimal.

The theoretical layer charge of kaolinite is 0, but a small negative charge occurs in nature, because of the little substitution and broken edges on the clay crystal (Grim 1968). That is the place where the adsorption of metals takes place, by releasing hydrogen (H^+) ions. Heavy metals could also be adsorbed on the flat exposed planes of the silica and the alumina sheet.

Other properties of kaolinite are low conductivity of both heat and electricity and as well a low surface area (Murray 1991).

Jiang (2010) studied the adsorption of Pb (II), Cd (II), Ni (II) and Cu (II) onto natural kaolinite clay. The results showed that for single metal removal a much higher percentage could be removed, compared to the competitive adsorption, due to the higher ratio of total metal to adsorbing sites. The pH effect shows that there is a lower removal at a low pH, because of the competition with H^+ ions. This competition decreases with increasing pH and the surface of kaolinite becomes more negatively charged. The adsorption capacity for heavy metal ions decrease with an increasing concentration of electrolytes, $NaNO_3$.

2.3.2.2 Montmorillonite

The mineral montmorillonite occurs as calcium and sodium montmorillonite. It belongs to the group called smectite, which contain sodium, calcium, magnesium, iron and lithium aluminum silicates. In contrast to kaolinite, smecites are a three-layer mineral. The structure is shown in Figure 7. Two silica tetrahedral sheets surround a central octahedral sheet. Considerable substitution can occur in each layer; in the octahedral sheet Fe and Mg substitute Al and in the tetrahedral layer it is aluminum for silicon, creating a charge imbalance. Exchangeable cations are adsorbed in the interlayer and around the edges to balance the negative surface charge. If the adsorbed cation is calcium it is a calcium montmorillonite, and if its sodium it is sodium montmorillonite (Murray 1991).

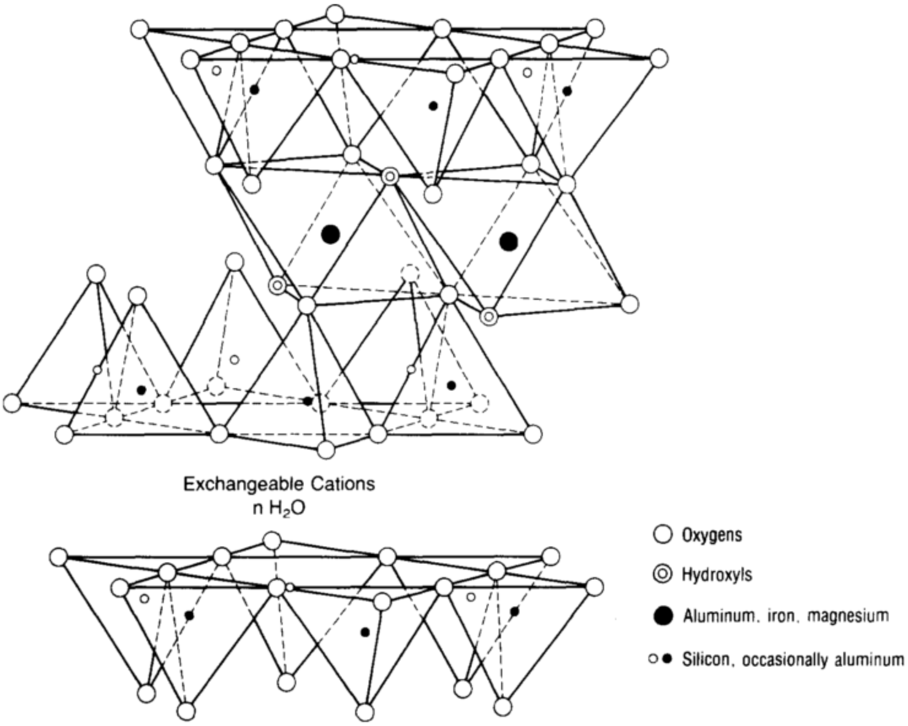

Figure 7 Structure of smectite (Murray 1991)

2.3.2.3 Olivine

Wium-Andersen, Nielsen et al. (2012) evaluated limestone, shell-sand, zeolite and two types of olive for the removal of seven heavy metals and phosphorus from artificial stormwater. The two olivine granulates were produced by Sibelco Nordic. The results of the batch test showed that after only 10 minutes high amounts of the heavy metals were bound on the sorbent surface. The extraction of the adsorbed elements was tested in a ratio of 2 l/kg, whereby the sorbent was gently agitated for 20 h in deionized water. The leaching was tested in three steps, only deionized water, 305 mg NaCl/l in deionized water and in a pH solution of 10. The concentration of the three extraction step have shown that there is no significant different between the tests. For olivine 1 and 2 the release of metal ions is around 10 µg/l and lower, zeolite was highly affected and limestone bound the heavy metals the strongest.

2.3.2.4 Zeolite molecular sieve

Zeolite molecular sieve is produced by UOP (Universal Oil Products). The sorbent is made by a synthetic procedure. To activate the produced crystalline metal aluminosilicates for adsorption, the contained water of hydration has been removed by heating. Zeolite molecular sieve is a highly porous adsorbent. The crystal consists of a tetrahedral structure, in which either silicon or an aluminum cation is surrounded by four oxygen anions. The three-dimensional frameworks are linked together by share oxygen atoms. The molecule interacts with sodium or other cationic ions in order to balance the negative charge. The structure of crystalline zeolite molecular sieve is honeycombed with large cavities. The honeycombed structure makes it highly porous and therefore it acts as a good sorbent. While on the outer surface area molecules of all size can adsorb, on the inner surface only those, which are small enough to pass through the porous. The zeolite molecular sieve used in this study is of type 3Å. During the production of the crystals, some sodium ions have been replaced with potassium. Caused by the larger ionic size of potassium(I) (1.52 Å) compared to sodium(I) (1.16 Å) , the pore size of the crystal decreased to 3.2 angstroms.

Pitcher, Slade et al. (2004) compared a natural (mordenite) and a synthetic zeolite (MAP) in terms of their removal efficiency of Cu, Cd, Pb and Zn in a synthetic solution and in motorway stormwater. MAP performed much better compared to the natural zeolite for the synthetic solution. One reason is the higher aluminum content, hence higher ion exchange capacity in MAP. Another reason is that MAP is a pure zeolite, while mordenite has many mineral impurities and the smaller particle size and larger surface area also makes MAP a better heavy metal removal material. Both zeolites released sodium into the solution, though MAP released more what could be assigned to the higher metal removal and the hydronium ion exchange.

2.3.3 Biosorbents

During the last decades, many studies have analyzed the ability of various kinds of biosorbents to remove heavy metal from aqueous solutions. The functional group of organic ligands, which occurs in large quantities in biosorbents, plays a dominant role in the removal of heavy metal contaminants. The important functional groups are carboxyl, hydroxyl, sulfate, phosphate and amine groups.

Lim, Zheng et al. (2008) shows that biosorbents have a higher cationic metal uptake when the pH is between 4 and 6 than at lower pH. Figure 8 (b) shows the dependence of the heavy metal sorption for different ionic strength intensities. The heavy metal ions compete with light metal ions (which are represented by the ionic strength) for the functional groups.

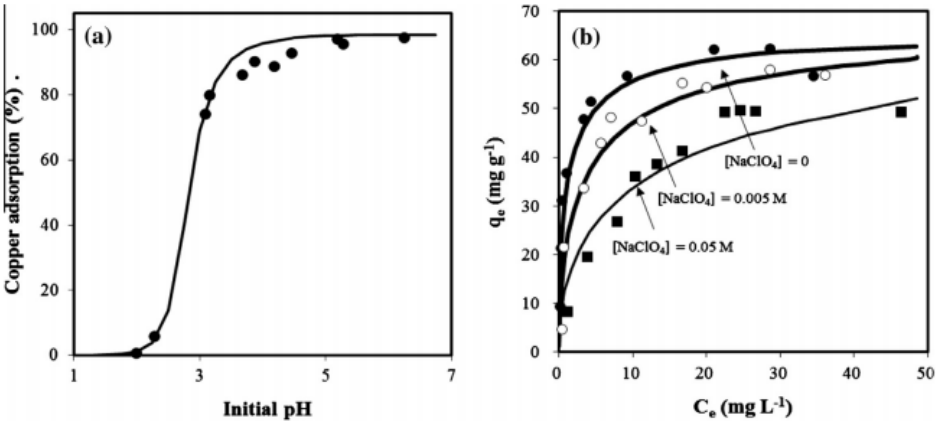

Figure 8 Biosorption of heavy metal ions onto a biosorbent (Lim, Zheng et al. 2008): (a) pH effect; (b) sorption isotherms as a function of ionic strength.

2.3.3.1 Sawdust

Sawdust is a by-product of the wood industry. Important organic compounds in sawdust, which could be useful for binding heavy metals ions are lignin, cellulose and hemicellulose with polyphenolic groups Aksu, Çalik et al. (1999). Bulut and Tez (2007) speculate that phenolic compounds like lignin and tannins are the active ion exchange compounds that immobilize heavy metal and that the active sites of those compounds are the phenolic groups. Figure 9 shows the mechanism of biosorption after Eligwe, Okolue et al. (1999).

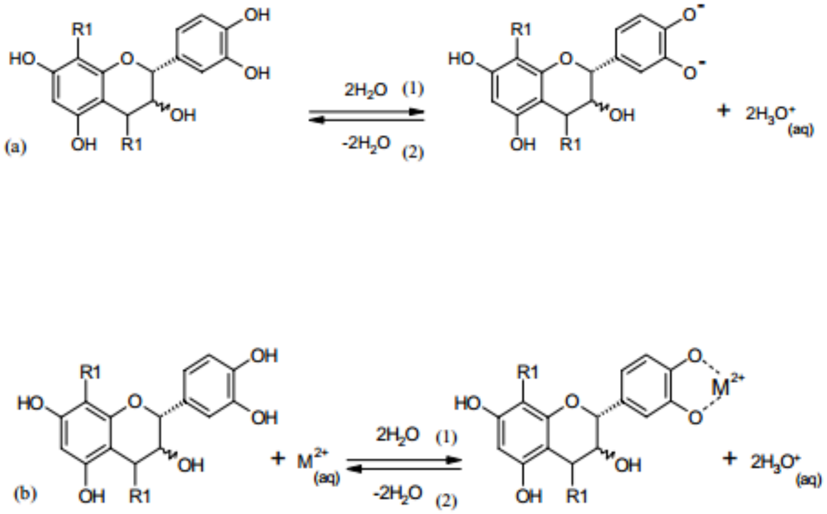

Figure 9 Mechanism of biosorption: (a) represents the first stage of ion exchange (deprotonation), while (b) shows the attachment (adsorption) of the metal cations onto the deprotonated active sites on the sawdust surface. The symbol M is a metal ion of charge 2^+(Eligwe, Okolue et al. 1999).

Taty-Costodes, Fauduet et al. (2003) studied the removal of Cd (II) and Pb (II) onto treated and untreated sawdust of pinus sylvestris. The test was run with an initial concentration 1 to 10 mg/l and sawdust dosages of 1 – 20 g/l for 1 h. There wasn't a difference in the removal efficiency between the untreated and H_2SO_4 and HCHO treated sawdust, but the COD of the treated sorbent is much lower, because of the release of polyphenolic compounds. The highest sorption capacity was at a pH of 5.5. The metal adsorption of sawdust can be explained by the property of containing a large number of active sites and as well by the carboxyl (C=O) and hydroxyl (OH) groups of polyphenols. The oxygen in the functional groups is able to create doublets and make complexes of coordination with metal ions. Sawdust binds the metal ions also by ion exchange shown by (Eligwe, Okolue et al. 1999)

2.3.3.2 Bark

Bark is the outermost layer of woody plants. As a waste product of the paper and pulp industry, it occurs in large quantities and is therefore an interesting low cost adsorbent.

Nehrenheim and Gustafsson (2008) explored the heavy metal uptake of Cu, Ni, Zn, Pb and Cr ions by pine bark and blast furnace slag. Four multi-component solutions with the initial concentrations ranged between 0.2 and 200 mg/l were mixed with the sorbent for 30 minutes to determine equilibrium time and the removal progress by increasing initial concentration. Pine bark shows higher adsorption efficiency for lower initial concentration.

Al-Asheh and Duvnjak (1998) examined copper, cadmium and nickel in single and binary metal sorption by pine bark. In addition Ca^{2+}, Mg^{2+} and K^{2+} were measured in the cell wall, cytoplasm and vacuoles during the ion exchange test to explain the adsorption properties of pine bark. The main area for the metal removal was the cell wall, while only a small amount was able to bind into the cytoplasm. The mechanism of ion exchange was investigated during metal sorption by pine bark by following the release of Ca^{2+}, Mg^{2+}, K^{+} and H^{+} after the sorption process. Thereby the release of calcium, magnesium and potassium cations indicates ion exchange, while the hydrogen cation indicates covalent bonding. The larger amount of Ca^{2+}, Mg^{2+} and K^{+} indicates that the ionic bonding is much more significant than the covalent bonding.

2.3.3.3 Sea weed

Marine algal is a promising biosorbent because it has a high uptake capacity. Furthermore, it is a low cost material, which is renewable and grows in many parts of the world's oceans.

Marine algae are grouped in three pathways, according to their independency of each other. The main difference of the pathways ("green", "red" and "brown") is the structure of their cell wall, where biosorption take place (Romera, Gonzalez et al. 2007).

Romera, Gonzalez et al. (2007) mentions that the cell walls of brown algae exhibit the components cellulose, alginic acid and polymers complexes with light metals (such as sodium, potassium, magnesium and calcium) and polysaccharides.

There are three kinds of interaction between heavy metal ions and algal biomass: Complexation/coordination, ion exchange and surface precipitation. The main reason for the binding metal ions are the cell wall constituents, such as alginate and sulfated polysaccharides (fucoidan). Ion exchange occurs between heavy metal and light metal, such as Ca^{2+} and Mg^{2+} etc.

Vijayaraghavan, Teo et al. (2009) tested Sargassum biomass for removal of heavy metals from synthetic multi-metal solutions. Sargassum biomass shows increasing removal with increasing pH in a pH range from 2 -6 increasing. This is because the concentration of hydrogen ions on the sorbent surface decreases, so the surface is less occupied, hence it is easier for the metals to interact with the negative charged surface. It is also reported that the lead removal (100 %) was much higher than the other ones, cause of the higher electronegativity and the bigger ionic radius. The influence of biomass dosage showed that for an initial concentration of 10 mg/l, a sorbent dosage of 3 g/l is the most efficient. Higher dosages are insufficient and lower the metal uptake because of the interference of the binding sites.

Cochrane, Lu et al. (2006) compared low-cost biosorbents, amongst them the macro algae F. vesiculosus. Batch tests were carried out to investigate effects of initial pH, contact time, initial concentration and sorbent dosages. After only one hour the algae removed 93 % of copper, but equilibrium was not reached after 12 h. Also it was observed that macro algae and the other bio sorbents released a higher amount of ions in the copper solution than in deionised water. This indicates the ion-exchange mechanism. An increasing pH of the algae can be explained by the ion exchange of the metal with of Cu^{2+} or K^{+}. The removal of heavy metal on macro algae increased a lot from a pH of 2 to 3 because the cell walls change their charge from positive to negative.

2.3.4 Metal oxide

Jeong, Fan et al. (2007) evaluated the potential arsenic (V) adsorbents, iron oxide and aluminum oxide. Iron (III) oxide is reddish brown in color and its particles are clustered and aggregated. The surface of aluminum oxide is smooth and the particles are in an acicular form. The color is grayish white. Metal oxides are insoluble in neutral solutions, while in acidic and strongly basic solutions they are easily soluble because of their amphoteric characteristics.

Batch experiment was done for the effect of initial pH and contact time for initial As (V) concentration of 200 – 600 µg/l or adsorbent dosages for Fe_2O_3 0.05 – 1.0 g/l and Al_2O_3 0.5 – 6 g/l. The optimal pH is at 6 for both adsorbents. The arsenic (V) adsorption was better for lower arsenic (V) concentration and higher adsorbent dosages. The As (V) uptake decreases rapidly for iron (III) oxide at $pH > 8$ and for aluminum oxide at $pH > 6$. According to the larger surface area of iron (III) oxide, the sorbent uptake of As (V) is much higher for iron (III) oxide (0.2 mg/g) than for aluminum oxide (0.13 mg/g) at a pH of 6 with 200 µg/l As (V) and a sorbent dosage of 1 g/l.

2.3.5 Commercial sorbents

2.3.5.1 Granular activated carbon

Carbonic materials like wood, peat, brown coal and others are used for the production of activated carbon. There are two procedures to activate those materials, gas activation and chemical activation. The adsorption capacity depends on the manufacturing, activation and the raw material of activated carbon. The adsorption on activated carbon is mostly a physical interaction. If carbon is pretreated with chemical substances, it also shows strong chemisorption (Donau Carbon, Germany). The kind of activated carbon that is used in water treatment has a surface area of 500 - 1500 m^2/g. GAC contains micro (< 1nm), meso (1 – 20 nm) and macro pores (> 20nm). The macro pores only serves as an entrance for the adsorbate, while the adsorption take place in the micro and meso pores.

3 Materials and methods

3.1 General

To achieve the objective of finding an effective suitable material, batch test experiments were performed to obtain effective heavy metal removal in synthetic stormwater. The tests were conducted to determine the removal efficiency, change of pH and change of conductivity. To consider the removal efficiency and stability of the sorbents under cold climate conditions, the most efficient sorbents were tested in saline solutions.

3.2 Materials

To prevent clogging in a filter media it is important that the sorbent ensure the permeability of water. Clogging can be caused by powder form sorbents; therefor it was decided to test sorbents with small particle in a mixture with sand.

Table 6 Dividation into sorbents which are tested in their pure form or as sorbent/sand mixtures

Sorbents		Pure sorbent	Sorbent/sand mixture
Ashes	Bottom Ash	X	X
	Fly ash	X	X
Clays	Kaolinite		X
	Montmorillonite		X
	Zeolite molecular sieve	X	
Blueguard®	63	X	X
	120	X	X
	G 1-3	X	X
Biosorbent	Pine bark	X	
	Spruce-pine bark	X	
	Sea weed	X	
	Saw dust	X	
Metal oxide	Aluminum oxide		X
	Iron(III) oxide		X
Commercial sorbent	Granular activated carbon	X	

3.2.1 Ashes

Bottom and fly ash samples were collected at the Heimdal incinerator, which is the main incineration Center of Sør Trøndelag County. It is an incineration plant where household and commercial waste are combusted. The samples were picked from different parts of the ash heaps and were randomly filled into several buckets. To create a representative sample, the sample was reduced by following the coning and quartering method of Gerlach, Dobb et al. (2002). Afterwards the ashes were dehydrated in the oven at 80 °C overnight and sieved through a 4 mm sieve.

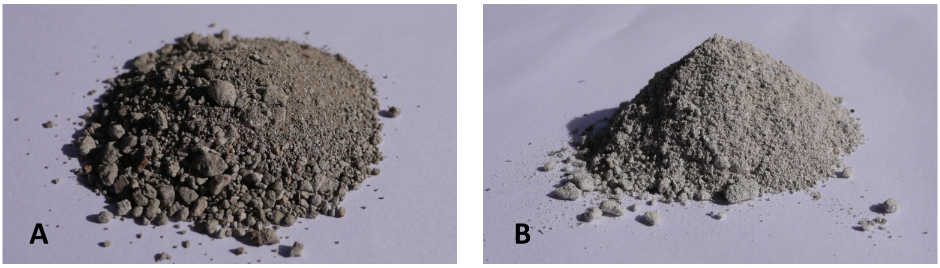

Figure 10 Ashes: A) Bottom ash and B) fly ash

3.2.1.1 Coning and quartering of bottom ash and fly ash

The coning and quartering method starts with the mixing of the samples on a piece of paper on a flat surface (Figure 11 A). Then the mixed conical pile was flattened and quartered with a firm piece of cardboard into four equal quarters (Figure 11 B). The first and the third quarters on a clockwise-observed view, starting at the upper right were combined, and afterwards coned and quartered again. The other two opposing quarters was always taken away and kept in a bucket. This process was repeated until the sample became the desired size.

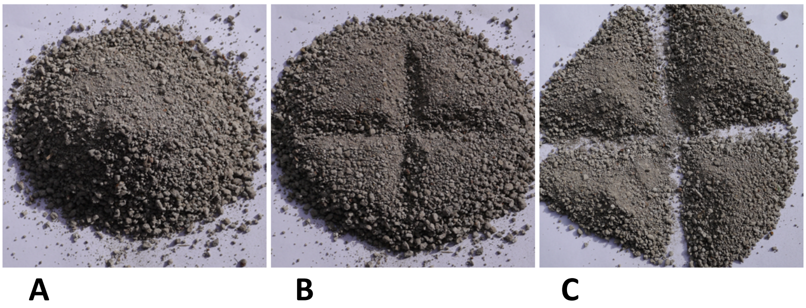

Figure 11 Coning and quartering of bottom ash

3.2.2 Clays

Sibelco Nordic AS produces the olivine's sorbents of the Blueguard® series. Table 7 includes some details of the three Blueguard® products, which was tested in the batch test. Figure 12 show the olivine sorbents Blueguard ® 63 (A), Blueguard ® 120 (B) and Blueguard ® G 1-13 (C),

Table 7 Particle distribution, characteristic properties and chemical composition of Blueguard® (Sibelco Nordic AS)

	Particle distribution (mm)			Characteristic properties		Chemical composition Weight (%)			
	D_{90}	D_{50}	D_{10}	Surface area (m^2/g)	pH	MgO	SiO_2	Fe_2O_3	CaO
Blueguard® 63	0.063	0.025	0.006	8.0	8.9 – 9.5	46.1	42.1	7.2	
Blueguard® 120	0.125	0.044	0.007	6.0	8.9 – 9.5	48.0	41.6	7.4	
Blueguard® G1-3	2.5	2.5	1.0	2.0	11 – 12	45.0	40.0	7.0	4.0

Sigma Aldrich produced all other clay sorbents including kaolinite, montmorillonite and molecular sieve. Molecular sieve has a bead form and mesh size of 4 – 8 (Figure 12 D). Kaolinite has the formula $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ and a molecular weight of 258.16 g/mol (Figure 12 E) and according to Sigma Aldrich montmorillonite (Figure 12 F) has a powder form, a surface area of 250 m^2/g and a pH between 3 and 4.

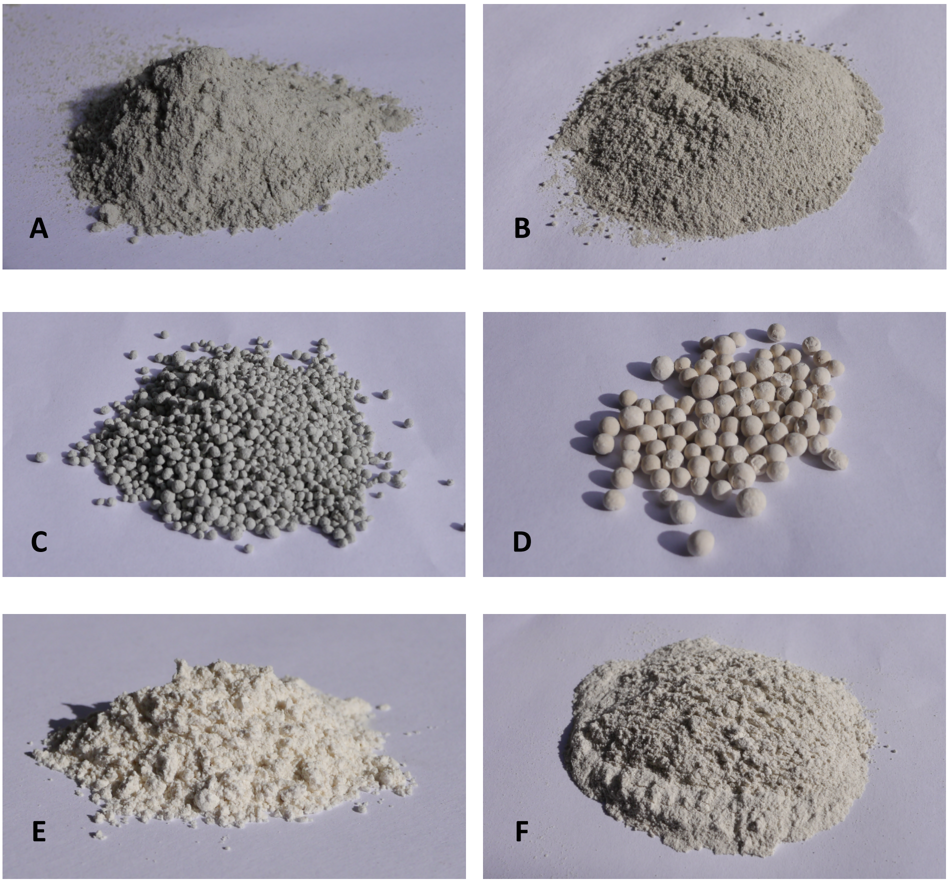

Figure 12 Clays: A) Blueguard® 63, B) Blueguard® 120, C) Blueguard® G1-3, D) zeolite molecular sieve, E) kaolinite and F) montmorillonite

3.2.3 Biosorbents

The pine bark used (Figure 13 A) is a product of Nittedal Torvindustri A.S. The other bark is a product of Nordic garden; it is a mixture of 50 % spruce to 50 % pine bark (Figure 13 B). Both types of bark have, according to their description, a pH of 5. The barks were dried at 80 °C overnight and crushed to a particle size smaller than 4 mm.

Sawdust (Figure 13 C) was produced by Kjelstad. It was crushed to a particle size smaller 2 mm.

The brown algae ascophyllum nodosum (Figure 13 D) was collected at the Korsvika beach in Trondheim.

The seaweed was washed with deionized water and air dried for one week before it was completely dehydrated in the oven at 80 °C for 24 h. Afterwards the pieces were crushed to a smaller particle size.

Figure 13 Biosorbents: A) Pine bark, B) Spruce-pine bark, C) sawdust and D) ascophyllum nodosum.

3.2.4 Metal oxide and GAC

Sigma Aldrich also produced aluminum oxide, Activated Charcoal Norit® (granulate activated carbon - GAC) and iron (III) oxide. The formula of aluminum oxide (Figure 14 A) is Al_2O_3 and its molecular weight is 101.96 g/mol. Activated Charcoal Norit® (Figure 14 B) has a granular form with a particle size of 1 mm, a molecular weight of 12.01 g/mol and its biological source is coal. Iron (III) oxide (Figure 14 C) is a powder with a particle size smaller than 5 µm, the formula is Fe_2O_3 and the molecular weight is 159.69 g/mol. The sand (Figure 14 D), which was used in the mixed sorbents, was manufactured by Rådasand AB, Sweden.

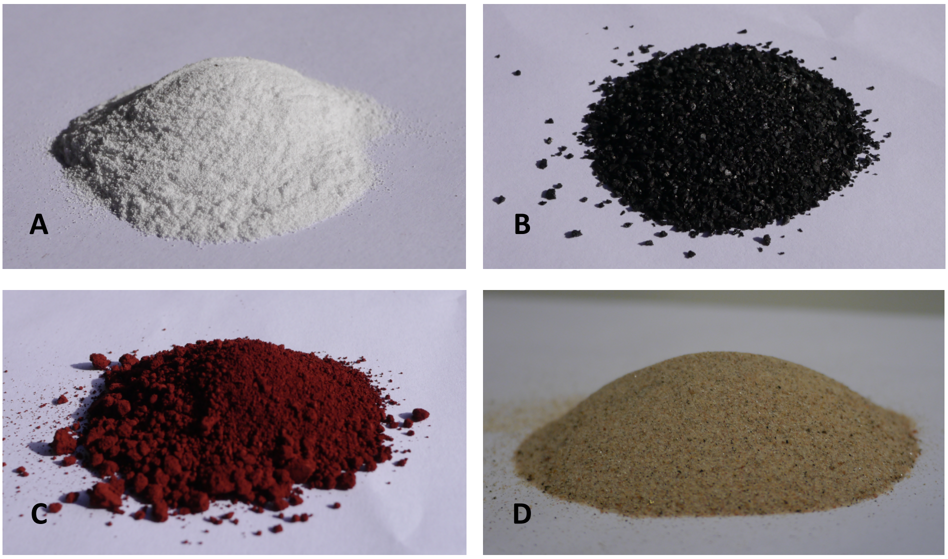

Figure 14 Other sorbents: A) Aluminum oxide, B) activated charcoal Norit®, C) Iron(III) oxide and D) sand

3.2.5 PH and conductivity of the sorbents

To determine the pH and the conductivity of the sorbents, 80 grams of a material was left over night in a beaker with 800 ml of deionized water. Afterwards the pH and conductivity of the solution was measured with a pH meter. Each sorbent was tested three times (two duplicates). The average value represented the pH and conductivity value of each sorbent.

To identify a good sorbent/sand mixture for the powder form sorbents, their pH and conductivity was also determined for 5, 10, 15 and 20 % sorbent of the total mixture weight.

3.3 Synthetic stormwater

The study focuses on the removal of the heavy metals of copper, lead, nickel and zinc from highway stormwater. To achieve this objective a synthetic stormwater based on a concentration range for the actual highway stormwater was used. Adsorption can be at different initial metal concentration differently strong, therefore it is important to test the sorbent with the right profil of requirement.

Detected stormwater ranges in Denmark, the UK and Trondheim are shown in Table 1 and the detection range of the spectrometer method is shown in Table 8.

Table 8 Detection range of heavy metal analyzing with ICP/MS

	Detection range (mg/l)
Copper	0.001 – 8
Lead	0.003 – 2
Nickel	0.006 – 6
Zinc	0.01 – 3

By considering the ranges of Table 8 and Table 1, four concentration levels with the initial concentrations levels of Table 9 were chosen to represent stormwater.

Table 9 Initial heavy metal concentration for the batch test

Concentration level	Copper (mg/l)	Lead (mg/l)	Nickel (mg/l)	Zinc (mg/l)
1	1.0	1.0	2.5	5.0
2	2.0	2.0	5.0	10.0
3	3.0	3.0	7.5	15.0
4	4.0	4.0	10.0	20.0

3.3.1 Stock solution

Diluting a prepared stock solution with milli-Q water made the different synthetic stormwater concentrations. The strength of the stock solution was determined on the condition that 2, 4, 6 or 8 ml of the stock solution diluted with milli-Q water made up the concentration levels. The chosen amount of the four heavy metals copper, lead, nickel and zinc (

Table 10) dissolved in a solution of 1.0 liter of milli-Q water makes the stock solution.

Table 10: Amount of heavy metal in 1 liter of stock solution

Heavy metal	[mg]
Copper (Cu)	50.0
Lead (Pb)	50.0
Nickel (Ni)	125.0
Zinc (Zn)	250.0

The heavy metals, however, are not available in the pure form, but they occur in other chemicals. In Table 11 is more information about the ratio of the heavy metals in the heavy metal chloride.

Table 11: Properties of the heavy metal: Copper, lead, nickel and Zinc

Heavy metal	Molecular Weight [g/mol]	Chemical	Formula	Molecular Weight [g/mol]	Form
Copper (Cu)	65.55	Copper (II) chloride	Cl_2Cu	134.45	Powder
Lead (Pb)	207.20	Lead (II) chloride	Cl_2Pb	278.11	Powder with lumps
Nickel (Ni)	58.69	Nickel (II) chloride	Cl_2Ni	129.60	Powder
Zinc (Zn)	65.38	Zinc (II) chloride	Cl_2Zn	136.30	Crystals with lumps

With the ratio of the molecular weight of the chemical to the molecular weight of the heavy metal it is possible to calculate the amount of the chemical (Table 12), which is required to contain the right concentration of heavy metal in the stock solution.

Equation (3.1)

$$m_{chemical,X} = \frac{mw_{chemical,X}}{mw_X} * m_X$$

$m_{chemical,X}$ = *amount of the chemical in the stock solution (mg)*

mw_X = *molecular weight of the heavy metal X (g/mol)*

$mw_{chemical}$ = *molecular weight of the chemical in which occur heavy metal X (g/mol)*

Table 12: Amount of chemical for the stock solution

chemical	$m_{chemical}$ [mg]
Copper(II) chloride	105.8
Lead(II) chloride	67.1
Nickel(II) chloride	276.0
Zinc(II) chloride	521.2

The heavy metal chlorides were weighted with a special accuracy-weighing machine and given into a volumetric flask with 1 liter of milli-Q water.

3.4 Batch Tests

To test the removal efficiency of the sorbents, 100 ml of synthetic storm water, which is described in section above, was used. A 15 ml sample was taken of the initial concentration. The pH of the solution was adjusted between the range of 6.8 and 7.0 by adding either 0.1 M NaOH or 0.1 M HNO_3. This range reflects the pH of storm water, how it occurs in nature. Also the conductivity was measured of the pure synthetic storm water.

Afterwards 10 g (+- 0.1%) of the sorbent was added to the solution, for the sand mixtures it was 9 g of sand and 1 gram of the literal sorbent. Than it was mixed on micro-shaker with 170 rpm for 24 h. Time and turns (rpm) were determined after previous studies and OECD protocol.

After 24 h shaking, the flasks of the sorbent liquid mixture were directly centrifuged with SORVALL® RC 5C Plus. To separate the solid from the liquid face, the samples were rotated for 10 min with an rpm of 6000. A solution sample and a duplicate were taken out of the flask with a 20 ml syringe. The samples were filtered through a 0.45 µm syringe filters into 15 ml. The tubes were acidified with 5 drops (0.25 % of the total volume of the sample) of 0.1 M HNO3 and stored at 4 °C until the heavy metal analyses with ICP/MS which were performed by laboratory at chemistry department of NTNU.

To separate the sample from the liquid, the content of the flasks was filtered through a whatman filter paper using a water jet pump. The sorbent was filled in a plastic bag and was frozen, while the most efficient sorbents were defrosted again for the leaching test.

3.4.1 Initial heavy metal concentration

Each of the 20 sorbents was tested for the four initial concentration levels (Table 9). For each test two duplicates was also run.

3.4.2 Initial sodium chloride concentration

The four most efficient sorbents of the initial concentration test were also tested in a saline solution to determine their ability to remove heavy metal in highly salt loaded solution, caused by de-icing practices in the wintertime . The tests were run like before, 10 g of a sorbent was given into a 100 ml saline heavy metal solution. The chloride concentrations are shown in Table 13. The chloride concentrations were determined after the Cl^- range 6 – 1204 mg/l given by Paus (2010)

Table 13 Chloride concentration, Trondheim (2010)

Salt level	Chloride concentration (mg/l)
1	10
2	400
3	800
4	1200

3.4.3 Leaching test

To test how the sorbents perform under saline conditions, the frozen sample of the four earlier determined sorbents (concentration level 4) was refrozen and dried for 24 h at 105 °C in an oven. 5 g of the refrozen sorbents was tested in a 50 ml Cl^- solution to analyze the leaching of the sorbents. The test followed further the steps of the general batch test.

3.4.4 Theoretical approach

The percentage removal rate (R) of the material was calculated according to

Equation (3.2)

$$R = \frac{100 * (C_i - C_t)}{C_i}$$

where C_i is the initial concentration and C_t is the concentration in solution at time t (h).

3.5 Analytical method

The solution samples were analyzed with Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) by the chemistry department of NTNU. To evaluate if the initial concentration is in desired range cuvette tests of Dr. Lange (HACH-Company) was used.

4 Results and discussion

4.1 PH and conductivity of the sorbents

The results for conductivity and pH value of the sorbents in deionized water at a liquid solid ratio of 10 are presented in . The pH value of deionized water is 7.0. Many sorbents release positive ions like sodium, magnesium, potassium and calcium in an aquatic solution. The sorbents surface becomes negatively charged and is able to adsorb hydrogen (H+), which changes the hydroxide-hydrogen balance, leading to a pH increase.

Table 14 PH value and conductivity of the sorbents in deionized water

Sorbents		pH	Conductivity (µS/cm)
Ashes	Bottom Ash	9.03	1411.3
	Fly ash	11.35	27566.7
Clays	Kaolinite	7.01	39.0
	Montmorillonite	3.84	157.3
	Zeolite molecular sieve	10.26	791.0
Blueguard®	63	9.49	253.3
	120	9.41	122.7
	G 1-3	11.05	266.3
Biosorbent	Pine bark	4.64	163.5
	Spruce-pine bark	5.31	1762
	Sea weed	5.71	5010
	Saw dust	5.05	95.3
Metal oxide	Aluminum oxide	8.80	69.3
	Iron(III) oxide	7.04	73.6
Commercial sorbents	GAC	8.45	27.7

Biosorbents make an exception, their pH is between 5 and 6 due to their release of organic molecules containing both acids and phenols there is a decrease of the pH (Genç-Fuhrman, Mikkelsen et al. 2007). The low conductivity value and unchanging pH value of kaolinite can be explained by its low surface area and limited substitution in its structure (Murray 1991). Therefor it can be assumed that kaolinite released only a small amount of ions, which is indicated by the low conductivity.

4.2 Sorbent-sand mixture

Figure 15 shows the pH of the powder sorbents for a sorbent-sand mixture with 0, 5, 10, 15, 20 and 100 % of the pure sorbent, whereby the pH value of 0 % sorbent accord to 100 % sand. For each sorbent it shows the change from the sand pH (6.41 measured in deionized water) to the pure sorbent pH depending on the mixing ratio. It is noticeable that for only 5 % of the pure sorbent the pH is changing remarkably compared to the pH value of 100 % pure sorbent. Hence the mixture was not able to adjust the pH of those pure sorbents, which normally have a very acidic or basic pH at a neutral level. But an advantage of the sorbent-sand mixture is to create a bigger pore volume, which would help to avoid clogging in a filter media, and that is the purpose for all the sorbents. The sorbent-sand mixture with 10 % pure sorbent was chosen for the small particle sorbents for use in the batch test. It was considered that for a 5 % mixture the active sites for the pure sorbents could be too little. The conductivity of the sorbent-sand mixture at 10 % sorbent was lowered to 14 - 25 % of the conductivity of the pure sorbent.

Table 15 PH and conductivity values for sorbent/sand mixtures in deionized water

	pH				Conductivity [µS/cm]			
	5%	10%	15%	20%	5%	10%	15%	20%
Bottom ash	8.65	8.81	8.89	9.02	257	346	475	495
Fly ash	10.5	10.78	10.77	10.86	2750	5030	6790	8770
Kaolinite	6.58	6.83	6.92	7.12	9.1	9.8	11.2	12.9
Montmorillonite	4.82	4.53	4.31	4.22	14.4	22	30	37.4
Blueguard® 63	9.17	9.41	9.48	9.54	33.4	52.5	69.6	84.1
Blueguard® 120	8.35	8.86	9.05	9.18	16.6	24.8	32.2	39.4
Blueguard® G 1-3	9.54	10.1	10.1	10.24	20.4	41.8	53.8	71.2
Aluminum oxide	7.12	7.48	7.67	7.92	8.1	11.3	13.8	17.8
Iron (III) oxide	7.07	7.17	7.27	7.52	10.8	13.7	17.7	22.9

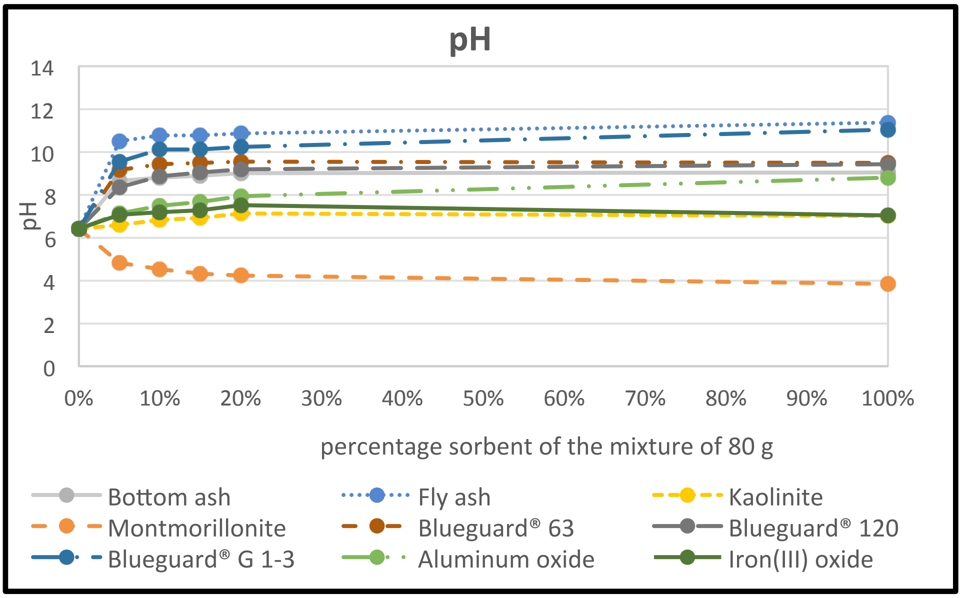

Figure 15 PH of the powder sorbents at different sorbent/ sand ratios

4.3 Batch test

Table 16 shows a literature review of the removal efficiency for sorbent materials, which were used in the current study.

Table 16 Literature review for the removal of copper, lead, nickel and zinc with low cost sorbents

Heavy metal	Adsorbent	Co (mg/l)	pH	Adsorbent (g/l)	Removal efficiency (%)	Reference
Cu (II)	Fly ash	10 – 100	5.0 – 8.0	20	60 – 99	Cho, Oh et al. (2005)
	Coal bottom ash	10	8.0	20	95	Lin and Yang (2002)
	Mordenite (nat. zeolite)	0.25	3.6	10	53.4	Pitcher, Slade et al. (2004)
	MAP (synthetic zeolite)	0.25	8.5 – 9.0	10	98.4	Pitcher, Slade et al. (2004)
	Natural kaolinite	10 – 150	7.0	25	30 – 65	Jiang, Jin et al. (2010)
	Zeolite	2	3.0 – 4.0	10	92.5	Wium-Andersen, Nielsen et al. (2012)
	Olivine I	40	3.0 – 4.0	10	97.8	Wium-Andersen, Nielsen et al. (2012)
	Olivine II (less cement)	8	3.0 – 4.0	10	96.6	Wium-Andersen, Nielsen et al. (2012)
	Pine bark	0.2 – 20			75 – 80	Nehrenheim and Gustafsson (2008)
	Sargassum	10	2 – 6	3	20 – 80	Vijayaraghavan, Teo et al. (2009)
	Macroalgae F.vesiculosus	10 - 100	4.6	5	80 – 90	Cochrane, Lu et al. (2006)
Pb (II)	Fly ash	10 – 100	5.0– 8.0	20	96 – 99	Cho, Oh et al. (2005)
	Mordenite (nat. zeolite)	0.05	3.6	10	89.2	Pitcher, Slade et al. (2004)
	MAP (synthetic zeolite)	0.05	8.5 – 9.0	10	100	Pitcher, Slade et al. (2004)
	Natural kaolinite	10 - 150	7.0	25	65 – 95	Jiang, Jin et al. (2010)
	Zeolite	40	3.0 – 4.0	10	86.3	Wium-Andersen, Nielsen et al. (2012)
	Olivine I	40	3.0 – 4.0	10	92.4	Wium-Andersen, Nielsen et al. (2012)
	Olivine II (less cement)	40	3.0 – 4.0	10	91.9	Wium-Andersen, Nielsen et al. (2012)
	Pine bark	0.2 – 20			85 – 95	Nehrenheim and Gustafsson (2008)
	Sargassum	10	2 – 6	3	40 – 100	Vijayaraghavan, Teo et al. (2009)
	Pinus sylvestris	1 – 10	5.5	1	84 – 98	Taty-Costodes, Fauduet et al. (2003)

Ni (II)	Natural kaolinite	10 – 150	7.0	25	35 – 85	Jiang, Jin et al. (2010)
	Zeolite	4	3.0 – 4.0	10	90.7	Wium-Andersen, Nielsen et al. (2012)
	Olivine I	8	3.0 – 4.0	10	98.8	Wium-Andersen, Nielsen et al. (2012)
	Olivine II (less cement)	4	3.0 – 4.0	10	99.7	Wium-Andersen, Nielsen et al. (2012)
	Pine bark	0.2 – 20			55 – 80	Nehrenheim and Gustafsson (2008)
Zn (II)	Fly ash	10 – 100	5.0 – 8.0	20	86 – 98	Cho, Oh et al. (2005)
	Mordenite (nat. Zeolite)	0.5	3.6	10	41.8	Pitcher, Slade et al. (2004)
	MAP (synthetic zeolite)	0.5	8.5 – 9.0	10	96.8	Pitcher, Slade et al. (2004)
	Zeolite	2	3.0 – 4.0	10	95.3	Wium-Andersen, Nielsen et al. (2012)
	Olivine I	40	3.0 – 4.0	10	95.6	Wium-Andersen, Nielsen et al. (2012)
	Olivine II (less cement)	4	3.0 – 4.0	10	99.8	Wium-Andersen, Nielsen et al. (2012)
	Pine bark	0.2 – 20			75 – 85	Nehrenheim and Gustafsson (2008)
	Sargassum	10	2 – 6	3	15 – 50	Vijayaraghavan, Teo et al. (2009)

4.3.1 Ashes

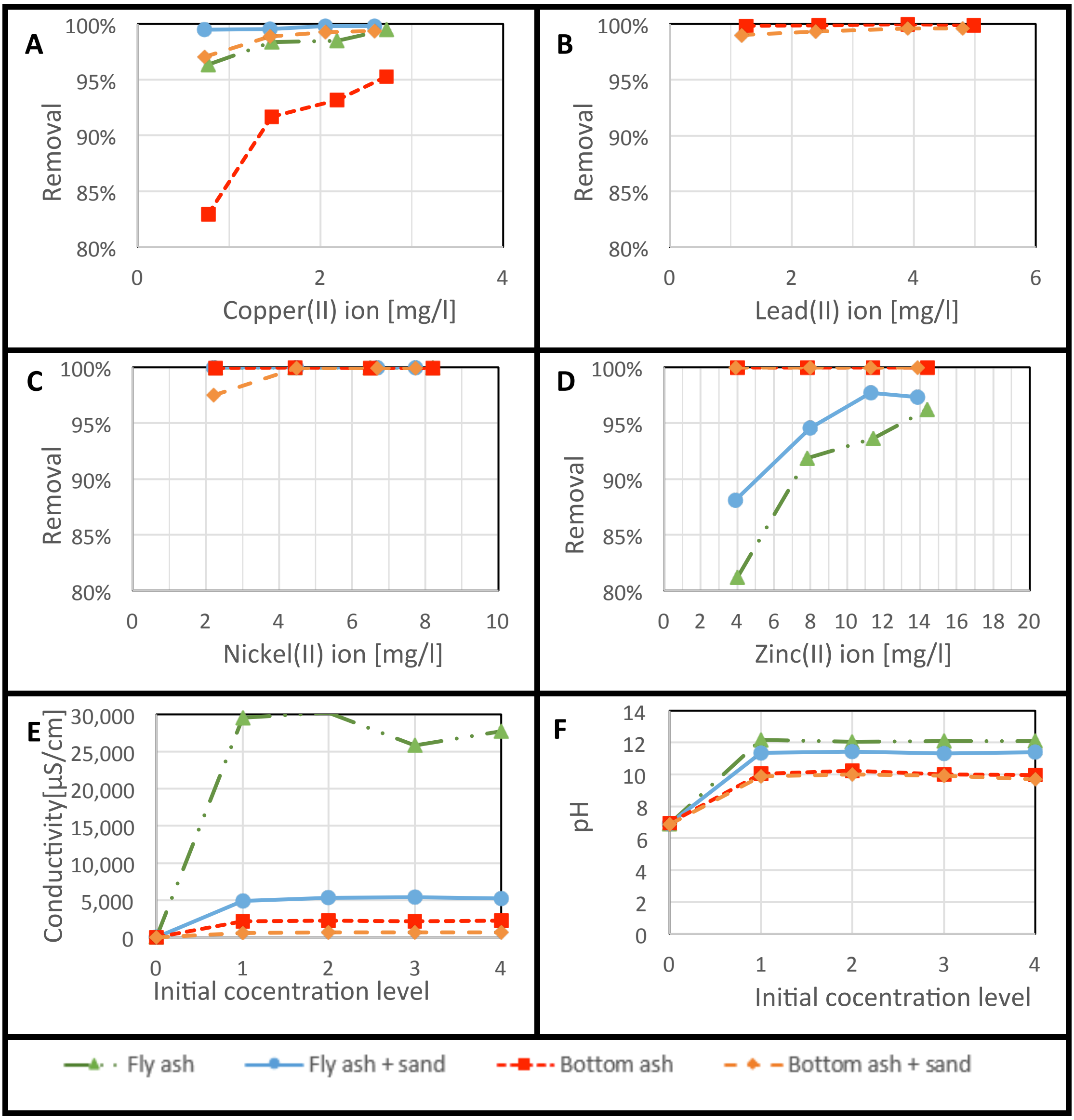

Figure 16 Removal efficiency of bottom ash and fly ash for copper (II) (A), lead (II) (B), nickel (II) (C) and zinc (II) (D), in addition their conductivity (E) and pH (F).

Table 17 Heavy metal removal in synthetic stormwater with ashes

	Copper removal (%)	Lead removal (%)	Nickel removal (%)	Zinc removal (%)	pH	Conductivity (µS/cm)
Bottom ash	83.0 – 95.3	99.8 – 100	99.9 – 100	100	10.0 – 10.3	2,200 – 2,300
Bottom ash + sand	97.0 – 99.4	99.0 – 99.6	97.5 – 99.9	100	9.7 – 10.0	602 – 708
Fly ash	96.4 – 99.5	-357 – -23.0	100	81.2 – 96.2	12.0 – 12.2	25,800 - 30,200
Fly ash + sand	99.5 – 99.8	-92.1 – 54.3	100	88.1 – 97.7	11.3 – 11.5	4,880 – 5,400

4.3.1.1 Bottom ash

Results of ashes need more discussion and references

The batch test shows that bottom ash has a removal of almost 100 % for Pb (II), Zn (II) and Ni (II), while Cu (II) shows by an increase of initial concentration an increase of removal efficiency from 83.0 % up to 95.3 %. For the mixture of bottom ash and sand the results look very similar. The removal of Zn (II) and Pb (II) to over 99.0 %, Cu (II) and Ni (II) remove between 97.0 % and 100.0 %. The pH of both systems adjusted itself to around 10.

4.3.1.2 Fly ash

Both fly ash and the mixture with sand were able to adsorb high amounts of Cu (II) over 96 % and 100 % of Ni (II). The removal of Zn (II) is in the range of 81.2 – 96.2 % for fly ash without sand and between 88.1 – 97.7 % with sand. The results show that for Pb (II), there is a higher concentration after the test than before the test, due to the origin of the fly ash. Table 5 shows that fly ash is able to contain high lead concentration (10 mg/kg). The mixture with sand obtained a better result for all heavy metals, which could be because of the lower conductivity of the sand mixture, which would mean that less light metal ions are in competition for the free spots of the surface. The pH of the tests adjusted for fly ash around 12.1 and for the sand mixture around 11.4. Figure 5 shows the removal of the heavy metal zinc, copper, lead and cadmium at different pH levels. It also shows how much of the total removal was caused by precipitation. For pH of 11 the figure shows that 80 % of copper, 60 % of zinc and almost 100 % of lead was mainly eliminated by precipitation. That is why it could be very likely that the main heavy metal ions were removed by precipitation. The problem with removed metals caused by precipitation is that for pH changes, the sorbent could start to leach the precipitated metals.

4.3.2 Clays

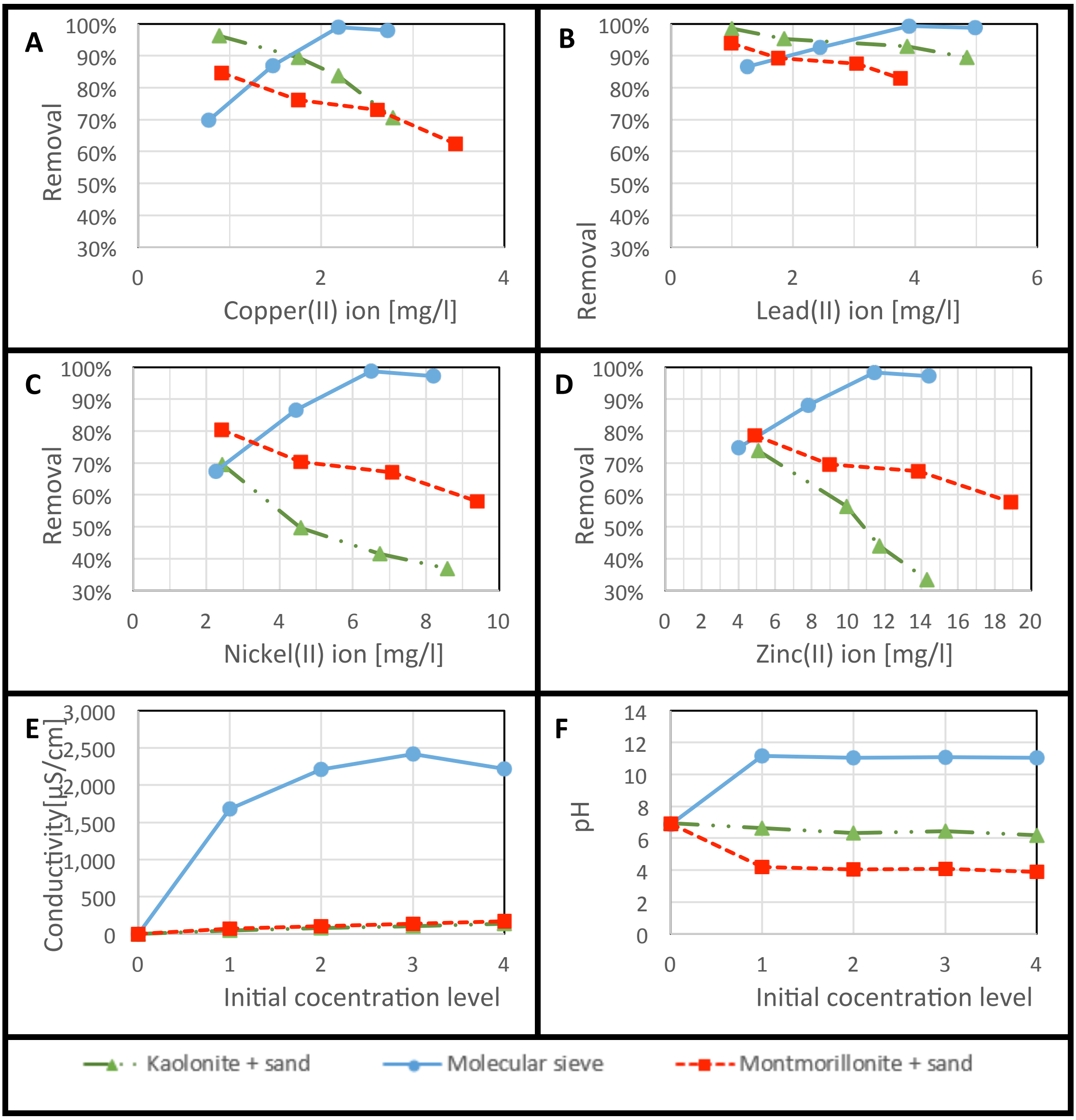

Figure 17 Removal efficiency of Kaolinite, montmorillonite and molecular sieve for copper(II) (A), lead(II) (B), nickel(II) (C) and zinc(II) (D), in addition their conductivity (E) and pH (F).

Table 18 Heavy metal removal in synthetic stormwater with clays

	Copper removal (%)	Lead removal (%)	Nickel removal (%)	Zinc removal (%)	pH	Conductivity (µS/cm)
Kaolinite + sand	70.4 – 96.2	69.8 – 99.0	36.8 – 69.5	33.4 – 73.9	6.2 – 6.6	46.5 – 133.8
Molecular sieve	89.5 – 98.6	86.5 – 99.3	67.5 – 98.8	74.8 – 98.4	11.1 – 11.2	1,682 – 2,420
Montmorillonite + sand	62.3 – 84.6	82.9 – 94.0	57.9 – 80.4	57.8 – 78.6	3.9 – 4.2	71.5 – 173.8

4.3.2.1 Kaolinite

The adsorption capabilities of kaolinite sand mixture were in the order of Pb > Cu > Zn > Ni, thereby the sorbent was able to remove 89.5 – 98.6 % of lead, for the other metals it removed 70.4 – 96.2 % copper, 36.8 – 69.5 % of nickel and 33.4 – 73.9 % of zinc. The pH was adjusted between 6.2 – 6.6 and the conductivity stayed smaller than 140 µS/cm. The lower conductivity can be explained by the low substitution in the structure of kaolinite, for this reason there is a smaller release of ions, also (Murray 1991) mentioned the low electricity conductivity.

The removal capacity decreases with increasing initial concentration that may be because kaolinite has lower surface sites and larger particles (Murray 1991).

Jiang, Jin et al. (2010) reported the removal with a natural kaolinite of 90.0 % Pb and around 47 % of Ni and Cu, in a multi-metal solution (10 mg/l) with 25 g/l of natural kaolinite. The removal is higher than in the current study, which could be explained by the higher kaolinite dosage in the study of Jiang, Jin et al. (2010) (2.5 times higher).

4.3.2.2 Zeolite molecular sieve

For the first and second initial concentration stages the sorbents shows lower removal capacity than for the higher initial concentrations. While for stage 1 and 2 the removal efficiency is between 69.8 – 86.9 % for copper, 86.5 – 92.7 % for lead, 67.5 – 86.5 % for nickel and 74.8 – 88.2 % for zinc, the heavy metal uptake increases to over 97.2 % for all heavy metals at stage 3 and 4. The pH adjusts itself around 11.1 and the conductivity establish over 2000 µS/cm for stage 2, 3 and 4. The conductivity is almost 3 times higher than the blank test (deionized water). The higher conductivity (release of sodium and potassium ions) caused by the surrounded heavy metal ions could be an indication of ion exchange (Pitcher, Slade et al. 2004). Also the increasing conductivity and adsorption for increasing heavy metal initial concentration can be an indication that ion exchange is the dominant process. Zeolite molecular sieve is a good removal material for very high stormwater concentration. But stage 1 and 2 represent more common concentration in stormwater, for those concentrations molecular sieve was not able to gain satisfying remove. Pitcher (2004) had reported a heavy metal removal for a synthetic zeolite (MAP) of over 96.8 % (for all heavy metals) in a synthetic stormwater with initial concentrations lower than 500 µg/l. That leads to the assumption that the results for stage 1 and 2 could be uncertain. According to the larger particle size and the very porous structure, molecular sieve can be considered as a very efficient adsorbent.

4.3.2.3 Montmorillonite

The montmorillonite sand mixture lowered the start pH to between 3.9 and 4.2, this pH was also reported by the producer of montmorillonite Sigma Aldrich. An explanation could therefor be the release of hydrogen ions from the interlayer of montmorillonite, which would make the solution more acidic. Hence the adsorption of the ions took place in an acid medium, where no or only less removal by precipitation is given. The conductivity was measured in a range of 71.5 – 173.8 µS/cm. The removal efficiency is decreases with increasing initial metal concentration. Lead had the highest removal with 82.9 – 94.0 % followed by copper (62.3 – 84.6%), nickel (57.9 – 80.4) and zinc (57.8 – 78.6 %).

4.3.2.4 Olivine – Blueguard ®

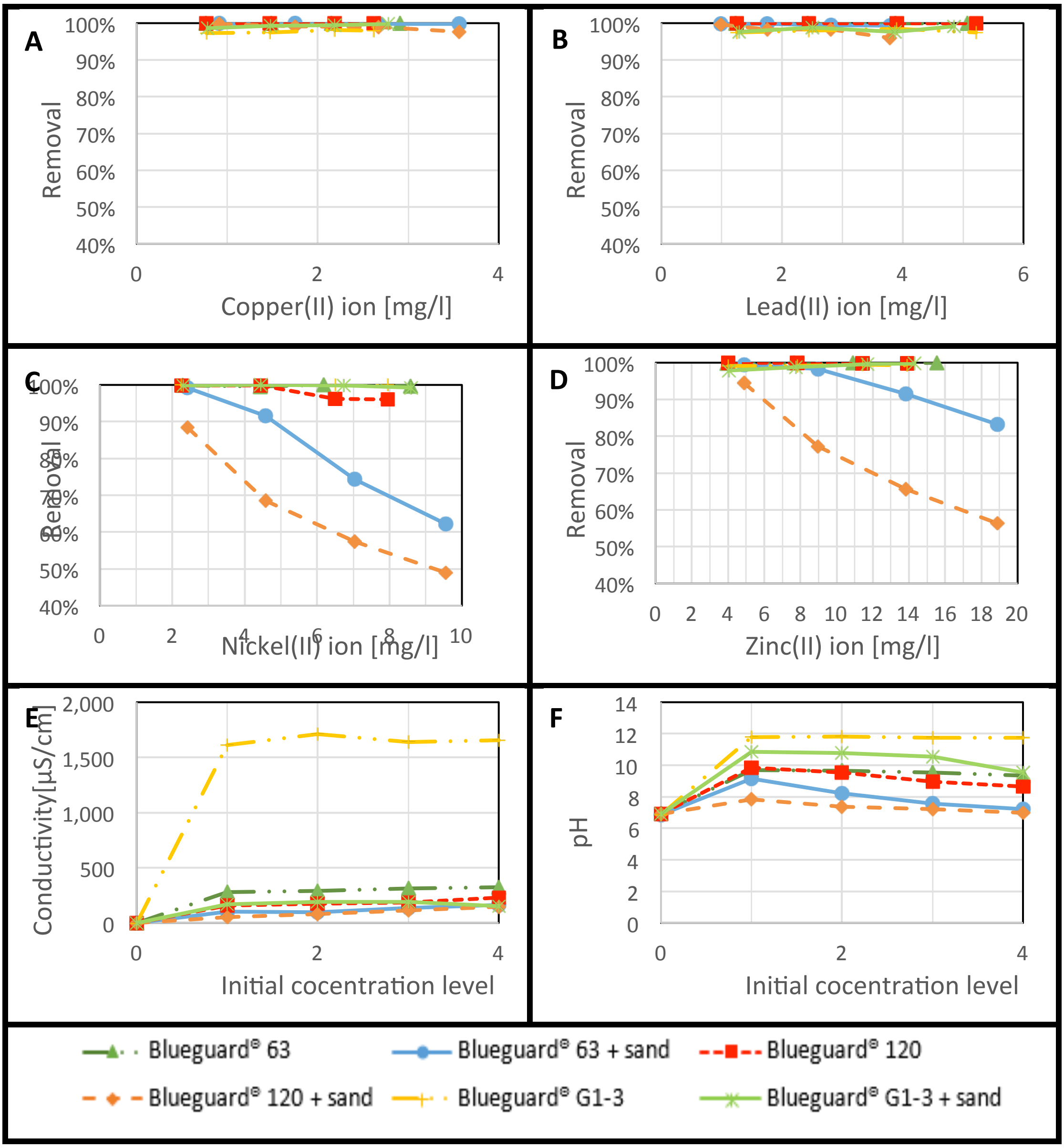

Figure 18 Removal efficiency of Blueguard® 63, 120 and G 1-3 for copper(II) (A), lead(II) (B), nickel(II) (C) and zinc(II) (D), in addition their conductivity (E) and pH (F).

Table 19 Heavy metal removal in synthetic stormwater with products of the Blueguard ® series

	Copper removal (%)	Lead removal (%)	Nickel removal (%)	Zinc removal (%)	pH	Conductivity (µS/cm)
Blueguard ® 63	100	99.9 – 100	99.6 – 99.9	99.8 – 100	9.4 – 9.7	280 - 323
Blueguard ® 63 + sand	99.8 – 99.9	99.3 – 99.8	62.1 – 99.2	83.2 – 99.5	7.2 – 9.2	99.0 – 162.5
Blueguard ® 120	100	99.9 – 100	96.0 – 99.9	99.7 – 100	8.7 – 9.8	158.6 – 230
Blueguard ® 120 + sand	97.7 – 99.7	96.0 – 99.7	49.0 – 88.5	56.3 – 94.5	7.0 – 7.8	53.3 – 148.0
Blueguard ® G1-3	97.2 – 98.2	97.4 – 98.5	100	99.1 – 99.4	11.7 – 11.8	1,580 – 1,723
Blueguard ® G1-3 + sand	98.6 – 99.9	97.6 – 99.2	99.3 – 100	97.9 – 99.8	9.5 – 10.9	150.3 – 193.0

All Blueguard ® products show a high capacity to remove heavy metals from synthetic stormwater, except the sand mixture of Blueguard ® 63 and Blueguard ® 120. For the sand mixture of Blueguard ® G 1-3 there is almost no difference compared to the pure Blueguard ® sorbents. The lower removal with sand may be caused by the lower dosage of Blueguard ®, and therefor fewer active sites. Another explanation would be the lower pH of the sand mixtures of Blueguard ® 63 and Blueguard ® 120. At their pH nickel and zinc still occur in a high amount as positive cations, while at a higher pH the hydroxide predominate (which are not measured in the end concentration).

Blueguard ® 63 gained for each heavy metal nearly 100.0 % removal, the same counts for Blueguard ® 120 with the exception of Ni (II), where the removal decreased to 96.0 % at higher initial concentrations. For

Blueguard ® G 1-3 with and without sand the removal is still over 97.2 % for lead, zinc and copper and nearly 100.0 % for nickel. The Blueguard ® products increase the pH because of their high amount of MgO, which react in water to magnesium hydroxide. The pH of Blueguard ® G 1-3 is even higher because it also contain CaO, which react to calcium hydroxide and has according to aqion (www.aqion.de) a higher pH than magnesium hydroxide. Blueguard ® G 1-3 has the highest pH with 11.7, than Blueguard ® 63 (9.4 – 9.7) and Blueguard ® 120 (8.7 - 9.9). The conductivity increases for Blueguard ® 63 and Blueguard ® 120 with increasing initial concentration, while for Blueguard ® G1-3 it deviates between 1,580 – 1,723 µS/cm (sand mixture 150.3 – 193 µS/cm). The Blueguard ® products have low particle sizes and have therefore quantity of actives sites, on which they are able to bind the heavy metals.

The olivine sorbents Blueguard ® 63 and Blueguard ® 120 proofed to be very good heavy metal removal adsorbents , but it have to be considered that they have very low porosity, what could make them unsuitable in field because they would inhibit infiltration. The sand mixture with 10 % sorbent was not satisfying, maybe a sand mixture with a higher amount of sorsorbent could be considered, or another r possibility could be the mixture with bottom ash, what contain also larger particles and showed a good removal effiency.

4.3.3 Biosorbents

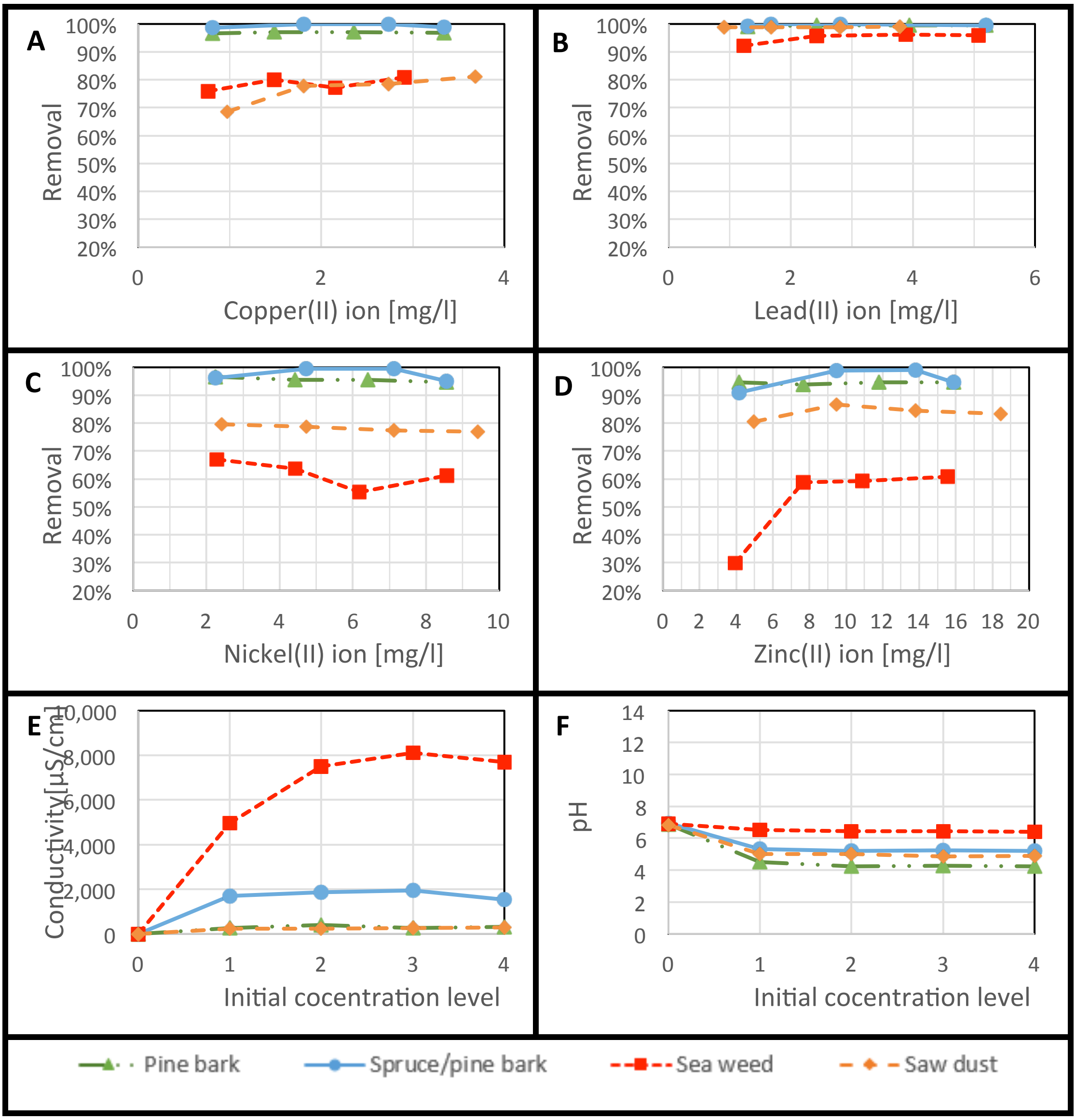

Figure 19 Removal efficiency of pine bark, spruce/pine bark, sea weed and saw dust for copper (II) (A), lead (II) (B), nickel (II) (C) and zinc (II) (D), in addition their conductivity (E) and pH (F).

Table 20 Heavy metal removal in synthetic stormwater with biosorbents

	Copper removal (%)	Lead removal (%)	Nickel removal (%)	Zinc removal (%)	pH	Conductivity (µS/cm)
Pine bark	96.6 – 97.1	99.1 – 99.5	94.7 – 96.5	93.8 – 94.7	4.2 – 4.5	255 – 415
Spruce/pine bark	98.6 – 99.9	99.4 – 99.9	95.0 – 99.5	91.0 – 94.7	5.2 – 5.3	1,535 – 1,941
Sea weed	75.9 – 80.8	92.1 – 96.1	55.2 – 67.0	29.8 – 60.7	6.4 – 6.5	4,970 – 8,100
Saw dust	68.5 – 81.2	98.8 – 99.1	76.8 – 79.5	80.5 – 86.6	4.9 – 5.0	233 – 290

4.3.3.1 Bark

Bark has the ability to lower the pH value, because of the release of organic molecules, containing acidic and phenolic functional groups. The phenomenon is confirmed by water discoloration from clear to yellow (Genç-Fuhrman, Mikkelsen et al. (2007). The batch tests containing bark decreased the pH value for pine bark to 4.2 - 4.5 and the pH of spruce/pine bark to 5.2 - 5.3. Nehrenheim (2008) also measured a pH of around 4.5 for pine bark in a multi metal solution.

The metal uptake for both types of bark is relatively stable even for higher initial metal concentrations that were tested. Nehrenheim (2008) also observed a strong metal uptake (around 80 %) for initial concentration smaller than 2 mg/l by 5 g of pine bark, but unfortunately the solution volume of the batch tests was not documented. In general, the spruce/pine bark mix removed more than pine bark. Both bark sorbents show metal uptakes over 91 % for all heavy metals. Most effective for lead (> 99 %) followed by copper, nickel and zinc.

The conductivity of spruce/pine bark (1,535 – 1,941 µS/cm) is much higher than for pine bark (255 – 415 µS/cm). A possible explanation could be the thickness/structure of the bark. It was observed that pine bark contain pieces with a greater thickness than spruce/pine bark. Legrand, Asta et al. (1996)found that the conductivity and acidity of Norway spruce and silver fir bark correlated with its thickness. Thick bark from the lower part of a tree trunk has a lower conductivity and acidity compared to the thinner bark from the upper parts of the tree. The thinner bark has a closer proximity to the internal tissues, which makes it richer in K^+ ions. This is a possible explanation for the variation in conductivity and acidity between the pine bark and spruce/pine bark.

The pH and conductivity values for bark in deionized water (shown in) are equivalent to the values in the batch test. Therefore, it is likely that the metal ions do not strongly influence the release of cations from bark.

4.3.3.2 Sea weed

The brown algae ascophyllum nodosum lowered the pH during the batch test to around 6.5, this is slightly lower than the initial pH.

The heavy metal removal from the synthetic stormwater with sea weed was moderate except for lead (92.1 -96.1 %). The removal efficiency ranged from around 80 % for copper, to 60 % for nickel and zinc. The removal efficiency for the first zinc concentration was only 29.8 % (shown in Figure 19). The reliability of this value is uncertain.

Vijayaraghavan, Teo et al. (2009) shows similar results for the removal efficiency of heavy metals with sea weed. In this study, 3 g Sargassum biomass were used at a pH of 6 to remove heavy metals from a synthetic multi-metal solution (10 mg/l of copper, lead, manganese and zinc). Under these conditions around 95 % of Pb, 85 % Cu and 55 % Zn were removed.

Ascophyllum nodosum grows in seawater that contains around 3 % NaCl. When sodium chloride is dissolved in an aquatic solution, it divides into the ions $Na^{+}_{(aq)}$ and $Cl^{-}_{(aq)}$, which increases the conductivity and therefor it led to high conductivity values (4,970 – 8,100 µS/cm) during the batch test. As an attempt to avoid this, the sea weed was washed with deionized water, but the results still show high conductivity values.

4.3.3.3 Sawdust

The biosorbent sawdust also lowers the pH down to 5.0. The highest removal efficiency was gained for lead (98.8 – 99.1 %). The uptake for nickel decreases with increasing metal concentration (76.8 – 79.5 %), the removal of copper is increasing with increasing metal concentration (68.5 -81.2 %) and the values of zinc range between 80.5 – 86.6 %. The conductivty increases with metal concentration (233 – 290 µS/cm).

Taty-Costodes, Fauduet et al. (2003) obtained a similar result for lead uptake in a lead-cadmium solution with an initial concentration of 1 – 10 mg/l and a pH of 5.5, where 0.1 g of sawdust was able to remove 84 – 98 % of lead.

4.3.4 Metal oxide and granulate activated carbon

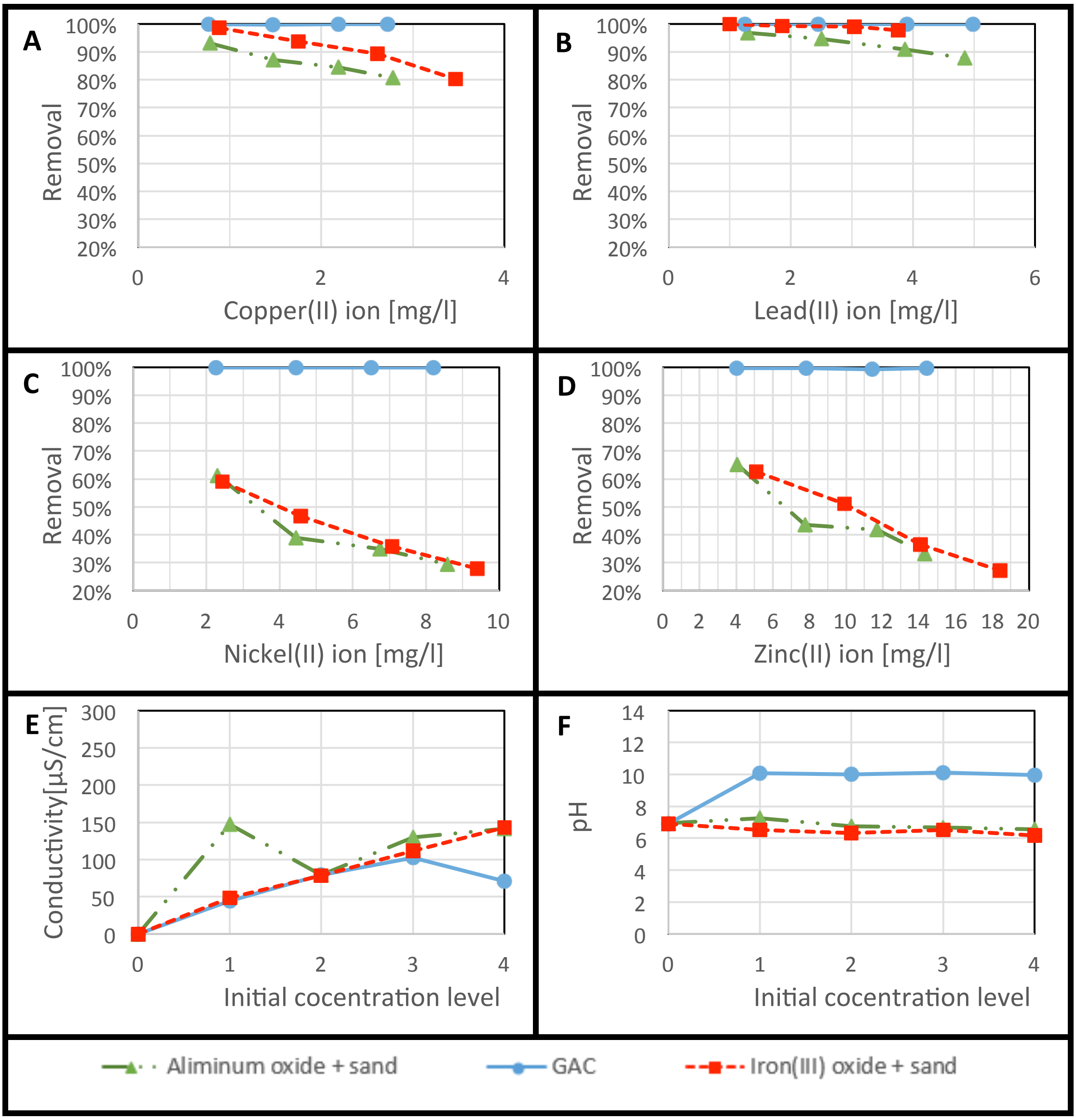

Figure 20 Removal efficiency of aluminum oxide, GAC and iron (III) oxide for copper (II) (A), lead (II) (B), nickel (II) (C) and zinc (II) (D), in addition their conductivity (E) and pH (F).

Table 21 Heavy metal removal in synthetic stormwater with metal oxides and GAC

	Copper removal (%)	Lead removal (%)	Nickel removal (%)	Zinc removal (%)	pH	Conductivity (µS/cm)
Aluminum oxide + sand	80.6 – 93.1	87.7 – 96.9	29.4 – 61.1	33.3 – 65.3	6.6 – 7.3	79.6 – 146.9
GAC	99.7 – 99.9	99.9	99.9 – 100	99.2 – 99.8	10.0 – 10.1	44.4 – 102.4
Iron (III) oxide + sand	80.1 – 98.5	97.6 – 99.9	27.8 – 59.1	27.2 – 62.5	6.2 – 6.5	48.9 – 143.1

4.3.4.1 Metal oxide

The aluminum sand mixture and iron (III) oxide sand mixture show similarities in their application to remove metals. Both have good removal ability for copper (80.6 – 93.1 % for Al_2O_3 and 80.1 – 98.5 % for Fe_2O_3) and lead (87.7 – 96.9 % for Al_2O_3 and 97.6 – 99.9 for Fe_2O_3), while for the higher concentration of nickel and zinc the removal ability does not prove satisfactory. The pH adjusted itself in a neutral medium between 6.6 and 7.3 for aluminum oxide and around 6.5 for iron (III) oxide. The conductivity rose for both sorbents only a little bit higher than the initial conductivity, which is due to the small amount of released ions.

Metal oxides could be considered to mix with ashes to lower the solution pH and to improve the consistency against leaching.

4.3.4.2 Granulate activated carbon

The commercial sorbent granulate activated carbon is a very efficient sorbent, for each initial concentration level and type of heavy metal it removed over 99 %. The pH adjusts itself constantly at 10 and the conductivity is even lower than the start conductivity value. Genç-Fuhrman, Mikkelsen et al. (2007)reported that GAC have a very huge surface area and is also very porous. These are the main reasons for the excellent removal of heavy metals.

4.4 Classification of the removal efficiency of the sorbents

To determine the four most efficient sorbents, which were tested in a saline solution, the sorbents were classified into non-satisfactory, moderate, good and very good sorbents, depending on the removal efficiency of each of the sorbents. Table 22 shows the classified removal efficiency and pH of the sorbents in stormwater.

The heavy metal ions with lower initial concentration (copper and lead) were removed in higher percentages than nickel and zinc, which was contained in much higher concentration in the synthetic stormwater. All sorbents show a high average removal efficiency for lead (> 90 %), except fly ash (which contained high amounts of lead) and montmorillonite + sand.

Table 22 Average removal percentage: Very good (++: > 97 %), good (+: 90 – 97 %), moderate (0: 70 – 90 %), non-satisfactory sorbents (-: 50 – 70 % and --: < 50 %). pH difference to a neutral pH 7.0: Very good (++: Δ = 0 - 1), good (+: Δ = 1 - 2), moderate (0: Δ = 2 - 3) and non-satisfactory pH values (-: Δ = 3- 4 and --: Δ > 4)

Sorbents		Copper removal	Lead removal	Nickel removal	Zinc removal	pH
Ashes	Bottom ash	+	++	++	++	-
	Bottom ash + sand	++	++	++	++	0
	Fly ash	++	--	+	++	--
	Fly ash + sand	++	--	+	++	--
Clays	Kaolinite + sand	0	+	-	--	++
	Montmorillonite + sand	0	0	-	-	0
	Zeolite molecular sieve	++	++	++	++	--
Blueguard®	63	++	++	++	++	0
	63 + sand	++	++	+	0	+
	120	++	++	++	++	0
	120 + sand	++	++	-	-	+
	G 1-3	++	++	++	++	--
	G 1-3 + sand	++	++	++	++	-
Biosorbent	Pine bark	+	++	+	+	0
	Spruce-pine bark	++	++	++	++	+
	Sea weed	0	+	-	-	++
	Saw dust	0	++	0	0	0
Metal oxide	Aluminum oxide + sand	0	+	--	--	++
	Iron (III) oxide + sand	+	++	--	--	++
Commercial sorbent	GAC	++	++	++	++	0

Non-satisfactory sorbents: The sorbent sand mixture of kaolinite, montmorillonite, Blueguard ® 120, aluminum oxide, iron (III) oxide and the pure sorbent seaweed removed an unsatisfactory percentage (< 70 %) of the heavy metal nickel and zinc. Also the tested fly ash type cannot be considered as a filter material in the column tests, because of its high amount of lead, whereby it increased the lead concentration in the solution.

Moderate sorbents: Saw dust removed moderate values (70 – 90 %) for copper, nickel and zinc. While Blueguard ® 63 was able to adsorb high amounts of lead, copper and nickel, the removal efficiency of zinc was moderate.

Good sorbents: A good sorbent released at least 90 % of each sorbent. Pine bark and bottom ash have removal efficiency higher than 90 %, but both sorbents eliminate less than 97 % of copper out of the solution. Pine bark was only able to remove over 97 % for lead, while bottom ash gained very good removal percentages for all other heavy metals.

Very good sorbents: The sorbent sand mixture of bottom ash and Blueguard ® G 1-3, and the pure sorbents of molecular sieve, Blueguard ® 63, Blueguard ® 120, Blueguard ® G 1-3, spruce/pine bark and granulate activated carbon removed over 97 %for all heavy metals.

Four of the very good sorbents were chosen to test in a saline solution. One sorbent of the Blueguard ® series was picked. The pH of Blueguard ® G 1-3 is too high and therefor hard to adjust to a neutral pH. Therefor Blueguard ® 63 was chosen because of the higher removal efficiency and the better sorbent/mixture. The other sorbents are GAC, spruce/pine bark and molecular sieve. Molecular sieve was given precedence to bottom ash, because of its good reputation, despite the non-satisfaction pH.

4.5 Adsorption in a saline solution

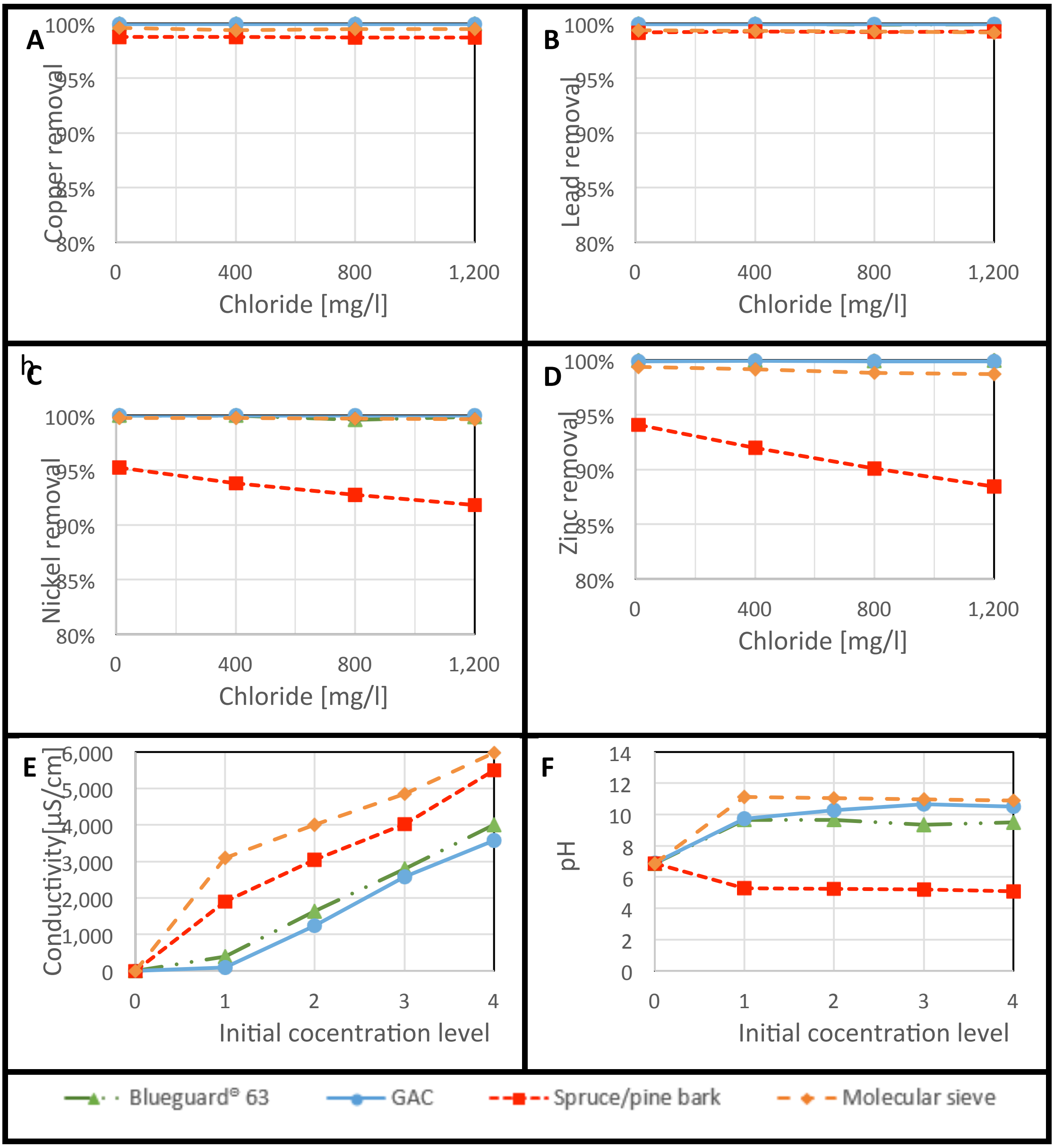

Figure 21 Removal efficiency of Blueguard® 63, GAC, spruce/pine bark and molecular sieve in a saline solution for copper (II) (A), lead (II) (B), nickel (II) (C) and zinc (II) (D), in addition their conductivity (E) and pH (F).

Table 23 Heavy metal removal in a saline solution

	Copper removal (%)	Lead removal (%)	Nickel removal (%)	Zinc removal (%)	pH	Conductivity (µS/cm)
Blueguard 63 ®	100	99.9 – 100	99.6 – 100	99.9 – 100	9.3 – 9.7	397 – 4,000
GAC	99.9 – 100	99.9	100	99.9	9.7 – 10.7	93.9 – 3,570
Spruce/pine bark	98.7 – 98.8	99.2 – 99.3	91.8 – 95.2	88.4 – 94.1	5.1 – 5.3	1,905 – 5,500
Zeolite molecular sieve	99.4 – 99.6	99.2 – 99.4	99.7 – 99.8	98.7 – 99.4	10.9 – 11.1	3,090 – 5,980

The adsorption test in a saline stormwater solution with initial heavy metal concentration of 4 mg/l copper, 4 mg/l lead, 10 mg/l nickel and 20 mg/l zinc showed that the removal efficiency of Blueguard 63, GAC and molecular sieve are not inhibited by an increasing chloride concentration. Spruce/pine bark instead shows a decreasing nickel and zinc adsorption for an increasing salt concentration. The uptake for nickel decreases from 95.2 to 91.8 % and from 94.1 to 88.4 % for zinc. GAC lowers the initial conductivity. There is no change of pH compared to the test with synthetic stormwater.

4.6 Leaching test

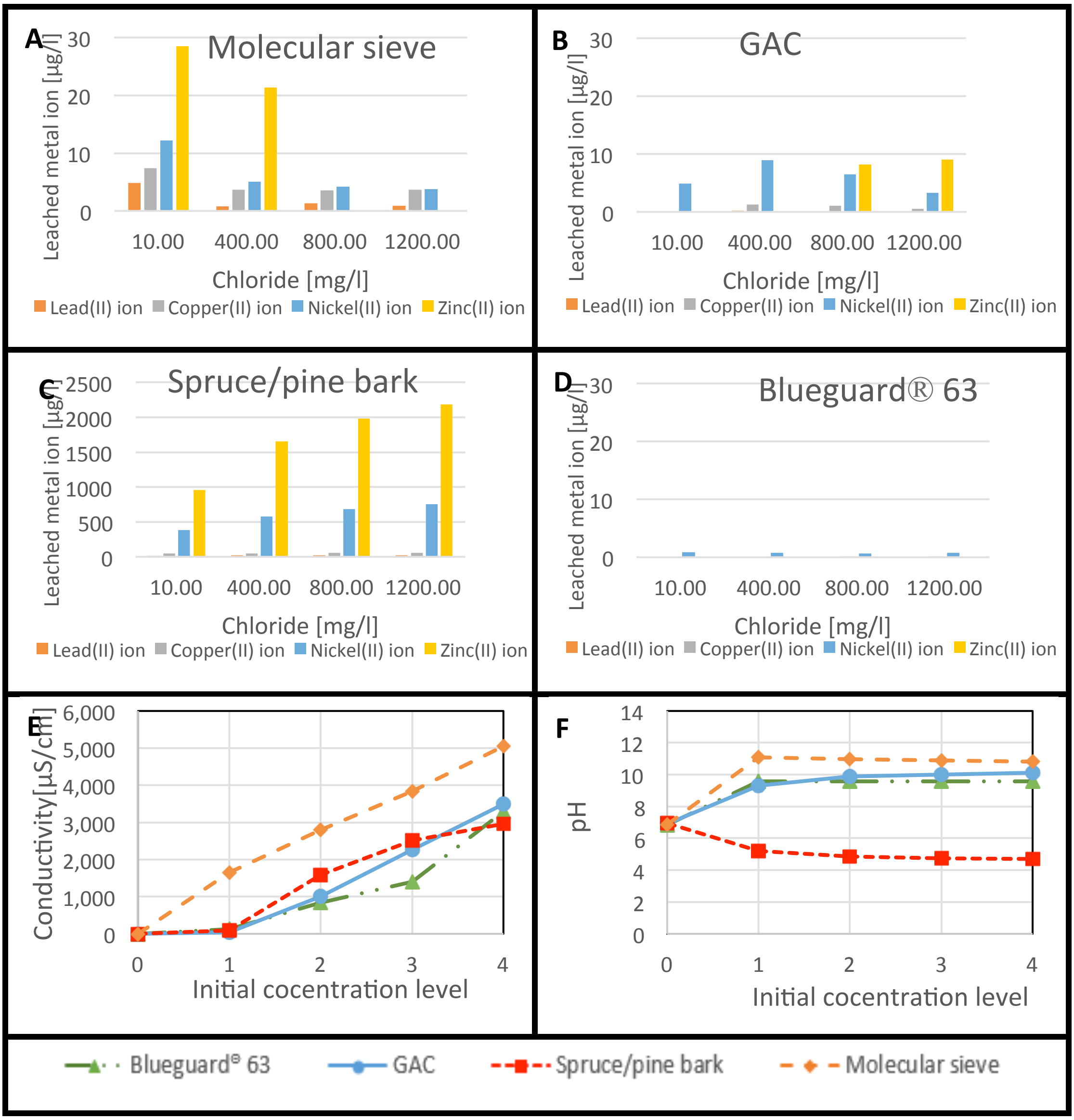

Figure 22 Leaching ability of Blueguard® 63, GAC, spruce/pine bark and molecular sieve in a saline solution for copper (II) (A), lead (II) (B), nickel (II) (C) and zinc (II) (D), in addition their conductivity (E) and pH (F).

Table 24 Leached metals in saline solution

	Copper leaching (µg/l)	Lead leaching (µg/l)	Nickel leaching (µg/l)	Zinc leaching (µg/l)	pH	Conductivity (µS/cm)
Blueguard 63 ®	0.0	0.0	0.6 – 0.9	0.0	9.6	119 – 3,300
GAC	0.1 – 1.3	0.0 – 0.2	3.3 – 9.0	0.0 – 9.1	9.3 – 10.1	35.5 – 3,490
Spruce/pine bark	12.7 – 21.8	4.0 – 7.9	144.3 – 190	407 – 543	4.7 – 5.2	94 – 2,960
Zeolite molecular sieve	3.6 – 7.4	0.7 – 4.9	3.8 – 12.2	0.0 – 28.5	10.8 – 11.1	1,653 – 5,050

The leaching test shows that for 3 out of 4 sorbents, the ability to keep the heavy metals in a saline solution is not or only slightly affected. Blueguard ®, GAC and molecular sieve show heavy metal release of less than 30 µg/l. Thereby bark shows a deficit in a saline solution to keep the adsorbed metals. This could be because of the acidic pH of bark, in which the heavy metals occur in their cationic form. Therefore it is possible that chloride attract for the adsorbed heavy metal ions. The higher amount of adsorbed nickel and zinc ions, could be one explanation for the higher leaching of those metals.

5 Conclusions and recommendations

The batch test shown for several sorbents high removal efficiency in synthetic stormwater, whereat the most sorbent/sand mixtures were not able to convience with their removal capacity. Only for bottom ash and Blueguard ® G 1-3 mixed with sand were also very good results obtained. The pure sorbents which assured with their heavy metal uptake were the Blueguard ® products, spruce/pine bark, GAC and zeolite molecular sieve.

For the further use of the sorbents as a filter media, their pH values should be questioned. Which values are acceptable for the flora and fauna? Therefor it should be considered to look for possibilities in the column study to neutralize the pH again. To raise the pH from a acid pH a layer of liming materials and to lower it sulfat could be considered.

GAC, pine/spruce bark, molecular sieve and Blueguard ® 63 were also tested in a saline solution, but only the bark sorbent was affected by the high amounts of salt. The removal efficiency decreased with increasing chloride concentration and the bark also leached in the saline solution.

The comercial products and molecular sieve had very high heavy metal uptake, whereby GAC and Blueguard ® 63 should be prefered due to their lower pH compared to molecular sieve. It could also be considered to use the waste products pine/spruce bark or the bottom ash/ sand mixture because of their cost effieciency compared to the commercial products. It could be considered if there are treatments to improve the pine/spruce bark ability to keep the heavy metals ions in a saline solution. The advantange of the bark sorbent would be the acidic pH, in which the heavy metals do not form hydroxides and are not precipitated and also its unexpensivness.

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