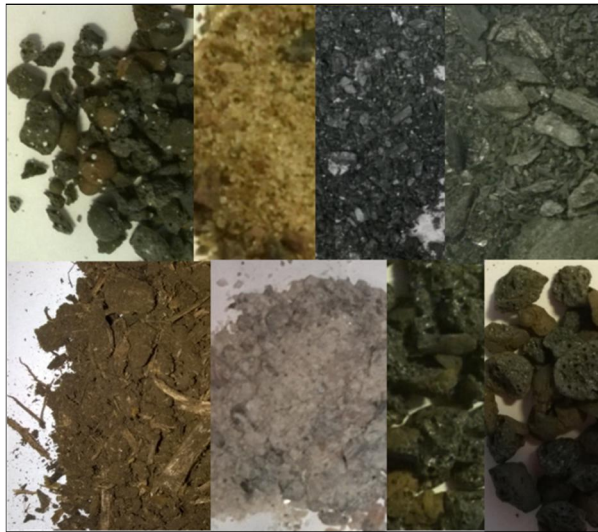


RESEARCH REPORT

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Filter material and product availability for stormwater filtration

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Summary		
<p>Most stormwater treatment technologies focus on volume control and total suspended solids removal. Simultaneous removal of all the main pollutants typically found in urban runoff is a bigger challenge. Well-characterised filter materials and filtration systems are needed for designing effective stormwater purification systems. Filter material selection should be based on the properties of the water to be treated and the target water quality.</p> <p>This report presents information on filter material and product availability. A brief summary of information about selected filter materials potentially applicable for stormwater filtration, including producers' website addresses, is presented. Primarily Finnish material producers are featured, as well as some useful research projects and their website addresses.</p> <p>The materials included are not necessarily as effective as possible for stormwater filtration without further processing or modification. A limited state-of-the-art assessment is provided herein on the production and modification of selected filter materials for use in engineered stormwater infiltration systems. The materials included are expanded clay products, biochar, peat as well as filter aggregates and natural minerals, including limestone. Information on iron oxide coating, manganese oxide coating, mixture with ferric sulphate and alkaline treatment is included.</p>		
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Preface

This is a WP1 report (D1.2) on Filter Material Availability in the Finnish StormFilter-project (Engineered Infiltration Systems for Urban Stormwater Quality and Quantity, 2015–2017). This project aims to generate new bio- and mineral-based solutions, through utilization and development of materials produced by Finnish industries, for enhanced urban stormwater management. The project promotes new technologies for clean water and a greener living environment. Integration is with smart city technologies, when using ICT and monitoring techniques to quantify quantity and quality of stormwater. The StormFilter-project is funded by TEKES (Finnish Funding Agency for Innovation) together with VTT Technical Research Centre of Finland Ltd, Aalto University, and partners covering a wide value of chain of municipalities, Finnish cities, material producer and stormwater designers.

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This report can be found on the StormFilter Web page: <http://www.vtt.fi/stormfilter>

Espoo, October 2016

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1. Introduction

Well-characterised filter materials and filtration systems are needed for designing effective stormwater purification systems. Filter material selection should be based on the properties of the water to be treated and the target water quality. It is beneficial to understand the mechanisms by which chemical and biological contaminants are removed during infiltration through the selected filter media, in order to assess the filtration system's capacity, limitations, and projected lifespan. (Korkealaakso et al. 2016). Desirable characteristics for all filter media are adequate permeability, low or no reactivity to substances in the water, high durability and resistance to compression, free of impurities and insoluble in water (EPA 1995).

For any filter material it is important to know the physical properties of the media as most media remove solids by mechanical processes. Physical properties such as media gradation will affect the flow rate of stormwater with the same amount of driving head. Similarly, the shrink-swell properties of filter materials are a critical parameter which can lead to clogging if not properly evaluated. Many types of pollutants are soluble, and can be removed only through chemical and/or biological processes. For this kind of purification there must be information on the filter material efficiency. Also information on the sorption capacity and reaction kinetics is needed for proper stormwater filter design. It is also important to know whether the filter material itself may add constituents to the treated water or alter its pH, e.g. via dissolution reactions. The long-term behaviour of the filter material during continual exposure to stormwater containing a complex mixture of different pollutants as sediments, organic matter, bacteria, nutrients, and heavy metals requires thorough investigation to understand the biogeochemical transformations occurring. Risks due to the potential for material dissolution or (bio)geochemical transformation following prolonged submergence and the onset of anaerobic conditions, such as the release of previously sorbed contaminants, must be assessed.

Designers of water filtration systems need a filter material that meets their particular specifications. As most runoff contains a range of different pollutant constituents, it is unlikely that a single filter material will adequately remove all contaminants to yield water of the desired quality. Thus, filtration systems containing mixtures of multiple materials may provide the best solution. An understanding of individual geomaterials' pollutant removal capabilities and the interactions between different materials provides ample knowledge for the design of fit-for-purpose stormwater filtration systems using optimised mixtures of reactive geomaterials to achieve the required water quality objective.

Additional considerations include material cost and availability, as well as specific handling requirements or safety considerations. Some materials may be readily modified to improve their physical or chemical characteristics with respect to pollutant removal. Thus, knowledge of the available and feasible processes and methods for material production or derivatisation to increase the efficiency of stormwater purification is important.

This report includes collected information on filter materials especially to be used in Finland, i.e. Finnish companies producing potentially applicable materials. These materials are not necessarily applicable to stormwater filtration without further processing or modification. Limited information on the production flow and modification possibilities for filter material enhancement is included herein.

Information on the filter materials' detailed technical properties, e.g. information on stormwater pollutant removal efficiencies, is not included in this report, but should be available by request from the identified suppliers.

2. Filter materials

Table 1 includes a brief summary of information about selected filter materials potentially applicable to stormwater filtration, including producers' website addresses. Primarily Finnish material producers are featured. Table 2 includes information on some valuable research activities, with website addresses.

More information on different types of filter materials for stormwater treatment is included in Korkealaakso et al. 2016.

Table 1. Information on bio- and mineral based filter materials.

Producer/ possibilities	Www addresses	Information
Washed sand		
Sibelco	http://www.sibelco.eu/water-treatment	Quartz sand is produced in Nilsä; 0.7–1.2 mm, 1–2 mm, 3–5 mm
Viasveden Hiekka- ja Kuljetusliike Oy	http://www.viasvesihiekka.fi/tuotteet.html#suodatinhiekka	Quartz sand is produced in Pori; 1–2 mm; 0.8–1.2 mm
Seepsula Oy	http://seepsula.fi/tuotteet/	Tuusula; 0.2–2 mm
Processing Oy Finland/Sweden	http://www.processingwater.com/fi	Various filter materials in stock e.g. different kinds of sand
Finnsementti Oy	http://www.finnsementti.fi/en/products/crushed-aggregates	Crushed: limestone, granite, gabro, kyanite, dolomite, quarts
Crushed and/or sieved natural aggregate products		
Rudus Oy	http://www.rudus.fi/tuotteet/kiviaineks-et	SSr 0–16 mm, sieved natural Finnish gravel; KaM 0–5 mm, crushed and sieved Finnish rock
Activated carbon		
KW-Filter Oy	http://www.kwfilter.fi/sivut/adsorbointia-ineet_akhi.html	Wide selection of activated carbon products
Haarla Oy	http://www.haarla.fi/?lang=en	Range of activated carbon products for e.g. water treatment
Akva Filter Oy	http://www.akvafilter.fi/site/	Importation of different kind of water treatment materials e.g. activated carbon
Processing Oy Finland/Sweden	http://www.processingwater.com/fi	Different filter materials in stock e.g. activated carbon
Polynova/ sales rep for the Jacobi Carbons AB	http://www.polynova.fi/Aktiivihiiili	Activated carbon designed for water treatment
Biochar		
RPK-Hiili Oy	http://www.rpkhiili.fi/biohiili	Producing biochar for several purposes e.g. for soil amendment (biochar producing temperature over 350 °C)
Biolan Oy	www.biolan.fi	Producing biochar for their gardening topsoil blends. Also studied as a greywater filter material (Basnet 2015).
Porous expanded aggregate		
Saint Gobain Rakennustuotteet Oy/ Leca	http://www.e-weber.fi/index.php?id=345	<ul style="list-style-type: none"> • Leca 0–3 mm crushed • Leca 2–4 mm round • Leca 3–8 mm crushed • + other fractions available
Saint-Gobain Weber Oy	Filtralite® http://www.filtralite.com/products	Different kinds of filter materials produced from expanded clay
Perlite		
Nordisk Perlite ApS, Denmark	http://www.perlite.dk/finnish/finnish.htm	Perlite for different purposes; produced in Denmark, importer Nutriforte Oy
Zeolite		
Processing Oy Finland/Sweden	http://www.processingwater.com/fi	Different filter materials in stock e.g. zeolite
Suomen Ympäristö-Pro Zeolit Ky	http://www.zeolit-ego.com/	Product Zeolit-Ego TM (50% calcium carbonate CaCO ₃ , 50% zeolite)
Crushed Autoclaved Aerated Concrete (CAAC)		
Xella Suomi	http://www.ytong.fi/ytong_flachsturz.php	Ytong, CAAC, 0.2–4 mm
Rudus Oy	http://www.rudus.fi/tuotteet/kierratys/b	Betoroc contains CAAC but also bricks, mortar

Producer/possibilities	Www addresses	Information
	etonimurske	and concrete
Wollastonite		
Nordkalk	http://www.nordkalk.fi/tuotteet/wollastoniitti/	Lappeenranta; mainly micro-sized wollastonite for ceramics and plastic/rubber applications
Slag		
Tapojärvi Oy	http://www.tapojarvi.com/en/services/factory-services/valorisation-of-stainless-steel-slag.html	Rock material is produced from the slag in the 6alorization plant (Tornio)
Finnsementti Oy	http://www.finnsementti.fi/en/products/additives	Ground granulated blast-furnace slag KJ400
Peat		
Vapo Oy	http://www.vapo.fi/	Range of peat based products
Turveruukki Oy	https://www.oulunenergia.fi/asiointi/ota-yhteytta/turveruukki	Various peat products
Several small/local producers	http://www.suomenturvetuottajat.fi/	Peat produced mainly for energy
Oxide Minerals		
Haldor Topsøe A/S (HQ)	http://www.topsoe.com/products/ck-395	Product CK-395 manganese oxide + alumina, spherical 3–5 mm diameter catalyst material
Kemwater ProChemie Ltd.	http://www.prochemie.cz/chemikalie.htm	Ferric oxo-hydroxide filtration products CFH 12 and CFH 0818
GEH Wasserchemie GmbH & Co. KG	http://www.geh-wasserchemie.de/index.php?article_id=2&clang=1	Range of e.g. granular ferric hydroxide products
LANXESS Deutschland GmbH	http://lanxess.com/en/megatrends-und-applications/water-treatment/	Bayoxide® E33 ferric oxide water filtration media
Other low cost materials		
		E.g. bark, sawdust, clay, moss; easy availability; the physical and chemical properties of the materials are not standardized for water treatment
Lime products		
Nordkalk Oy	Fostop®: http://www.nordkalk.com/products/limestone-powder/nordkalk-fostop-structure/ Filtra A: http://nordkalk.vipinfo.info/Filtra	Filtra P (production has ended), Fostop®, Filtra A; Fostop® is a lime filter designed for reducing phosphorus leaching; used in the filter drain, sand filter or filter well
Biofiltration substrate/ biological soil		
Enregis GmbH Haveno Oy (importer)	Enregis/Biocalith MR-F1: http://www.enregis.de/pdf/downloads/Biocalith_13_GB.pdf http://haveno.fi/	Biofiltration substrate, fully biological soil filter

Table 2. Information on research activities, including research on materials applicable for stormwater filtration.

Project	Www addresses	Information
Desentralized biorefineries (UEF, Karelia University of Applied Sciences)	http://www.forestenergy.org/service_center/hajautetut_biojalostamot/	E.g. possibilities to produce activated carbon.
HighBio and HighBio2 (University of Jyväskylä, University of Oulu, Chydenius, Centria, Luleå University of Technology)	https://www.chydenius.fi/tutkimus/soveltava-kemia/projektit/highbio2/HighBio2%20posterit%20A0%20EN%20March%202012.pdf https://www.chydenius.fi/tutkimus/soveltava-kemia/projektit/highbio2	E.g. possibilities to produce activated carbon.
Mobile Flip (e.g. VTT, Raussin Energia Oy)	http://www.mobileflip.eu/project.htm	Developing mobile and flexible industrial processing of biomass; e.g. for producing biochar and activated carbon.
Biotuli (different partners in South-East Finland)	http://www.biotuli-hanke.fi/	Technology and business related to biochar production.
Active research e.g. in University of Helsinki, LUT, UEF, Natural Resources Institute Finland (MTT)	http://biochar-hy.blogspot.fi/p/university-of-helsinki-biochar-team.html http://www.lut.fi/web/en/cooperation-and-services-for-the-media/lut-experts http://www2.uef.fi/en/carbon https://www.luke.fi/en/	<ul style="list-style-type: none"> • Biochar group in University of Helsinki • Lappeenranta University of Technology (LUT) Experts • 'Ecosystem Ecology Group' in University of Eastern Finland (UEF) • MTT AgriFood Research Finland
Research project: Helsinki Metropolia	https://www.theseus.fi/bitstream/handle/10024/88083/Basnet_Mukeh.pdf?sequence=1	Ferric Enriched Biochar (FEB)

3. Filter material production and modification

3.1 Introduction

A brief overview is provided herein on the production and modification of selected filter materials for use in engineered stormwater infiltration systems. The materials included are expanded clay products (Leca), biochar, peat and filter aggregates and natural minerals, including limestone.

Additional state-of-the-art information on filter materials, as well as their efficiency in stormwater purification, is presented in Korkealaakso et al. 2016.

3.2 Filter material production flow

Expanded clay products, Leca

Lightweight expanded clay aggregates (i.e. Leca products) are produced from pure clay in a rotating kiln at 1150–1200 °C. Clays expand in the kiln to the final aggregate shape and form. Expanded clay particles have a porous structure, and when crushed, a large surface area is exposed. Dry particle densities are in the range 500–1600 kg/m³, and aggregate sizes in the range 0–20 mm can be produced and tailored for different applications. Expanded clay does not release harmful substances, and the acid solubility is minimal. A typical external porosity of a 4–8 mm grading is in the range of 45%, which allows for significant retention

and temporary storage of runoff water in green roofs and other water management systems (Saint-Gobain 2010).

Biochar

Biochar is produced by pyrolysis, wherein biomass is heated under low oxygen conditions and it breaks down into simpler substances. Pyrolysis releases combustible vapours from biomass that can be captured to produce renewable energy. The biomass remaining after pyrolysis becomes a fine-grained, highly porous charcoal-like material that is rich in carbon. In general, there are two types of pyrolysis: fast and slow. Slow pyrolysis permits wood of various sizes, moisture levels and nature's anomalies to be slowly processed into consistent, high quality biochar. Biochar's high degree of porosity gives the material exceptionally high surface area per unit mass, often exceeding 400 m²/g, making biochar a highly adsorbent material. Low mineralizable carbon content makes biochar highly resistant to decomposition, with biological decomposition of total biochar C in the range of ca. 1–10% over a five-year period (BiocharNow 2016, PPRC 2015, Singh et al. 2012).

Numerous agricultural and forestry by-products have been investigated as feedstock for biochar production. Whilst the physicochemical characteristics of the resultant char vary as a function of both feedstock and the thermochemical conversion process used, lignocellulosic or wood-derived biomass typically yields the greatest quantity of biochar from a given amount of biomass. Early applications of biochar focused primarily on agricultural use as a soil amendment; however, there is increasing evidence to support biochar use in engineering applications, including environmental remediation (Xie et al. 2015). To date, the widespread use of bio-based materials has been limited by poor production efficiencies, fluctuating availability of high-lignin biomass, limited geographical distribution of agricultural residues for biochar production, and/or challenges associated with operation of biomass-only power plants (Xie et al. 2015).

Optimisation of feedstock selection and thermochemical processes for fit-for-purpose biochar production concomitant with performance validation of bio-based char materials for treatment of urban stormwater runoff will expand the existing market for bio-based materials, specifically creating a new market for high-value, fit-for-purpose biochar and/or biochar derivatives for remediation of urban and peri-urban stormwater runoff. This outcome supports global expansion of the bio-based economy focused on materials recycling and conservation of ecosystems. Market expansion for bio-based materials provides direct benefits to and enhances the long-term sustainability of agro-forestry and forest products-related industries.

Peat

Another bio-based material, peat, is formed by inhibited decomposition of trees and plant species in wetland bogs, marshes and swamps. The major constituents of peat are lignin and cellulose, which can be involved in chemical bonding. Peat is a highly porous material which contains organic matter in various stages of decomposition, with lignin, cellulose, and humic substances as major constituents. These constituents have numerous reactive functional groups which can interact with metal ions via various mechanisms, including the formation of chemical bonds. These reactive functional groups are responsible for the cation-exchange properties of peat (Bulgariu et al. 2011). Peat is a relatively inexpensive and widely available adsorbent.

Raw peat has a high affinity for water and a low mechanical strength. Essentially, when mixed with water, it makes an impermeable mud. American Peat Technologies (APT) has developed a process to convert loose peat into hardened pellets called APTsorbTM. In this process, low temperature carbonization is used to convert natural peat into a hardened ion-exchange material. Peat pellets of approximately 9.5 mm diameter are produced first, then are crushed to form a low-cost ion exchange media, peat granules. Since the product is crushed to a uniform size, water readily passes through the peat granules. The estimated

conductivity of the peat granules is in excess of 1×10^{-2} m/s (Eger 2009, Eger et al. 2008, Green 2014).

Filter aggregates and natural minerals

Filter aggregates generally consist of crushed rock, sand or gravel. Manufactured aggregates are also occasionally used (e.g. blast furnace slags).

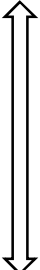
A clean, washed, well-graded sand with an appropriate hydraulic conductivity should be used as the filter medium. If available, crushed rock may be preferable to sand as the crushed rock is less likely to be contaminated with pathogens or organic material. In addition, crushed rock grains fit well together. Rounded grains of uniform particle size distribution do not produce sufficiently small pore spaces for effective filtration.

Aggregate must be sorted by sieving. Ideally the effective size (often characterized by the d_{10} size fraction %) should be just small enough to ensure a good quality outflow and prevent penetration of clogging matter to such depth that it cannot be removed by surface scraping. This is experimentally determined and is often in the range 0.15–0.35 mm, but both finer- and coarser- textured materials have been found to work satisfactorily in practice. The final selection typically depends on the available materials. It is possible to combine two or more types of stock sand to bring the effective size of the mixture closer to the ideal (EPA 1995).

Some natural minerals are not inert but rather possess characteristics which confer potential benefit as amendments to neutralise acidity, or to attenuate nutrients or trace metals. The physical and chemical breakdown of minerals, or weathering, is a mechanism through which minerals react with aqueous solution. During the mineral weathering process silicate, carbonate and hydroxide minerals consume hydrogen ions, thereby increasing the pH of solution in contact with weathering surfaces. Calcite (CaCO_3), the dominant mineral constituent of limestone, is arguably the most significant acid neutralising mineral due to its relative abundance and its rapid reaction rate (susceptibility to weathering) compared to other minerals. Calcite dissolution occurs most rapidly in an open system where the aqueous phase is in contact with a gas phase and carbon dioxide (CO_2) is available for gas exchange. Dissolution of calcite can also occur under saturated conditions; however, calcite is less soluble in the absence of carbon dioxide.

The rate at which minerals weather is an important consideration when assessing the longevity of a given filtration system and the reactivity of geomaterials therein. Physical and chemical characteristics of the mineral such as composition, crystal shape, size and degree of crystallinity, and surface area affect weathering rate, as well as solution characteristics such as pH, dissolved CO_2 content, and the extent to which the solution is in contact with the mineral surface. Environmental parameters such as temperature and redox conditions are equally influential. Mineral reactivities range from 1.00 for minerals which dissolve in moderately acidic solution (e.g. calcite) to 0.004 or virtually inert for pure quartz (SiO_2). The silicate minerals which comprise much of the aggregate used in Finland exhibit moderate (intermediate to slow) weathering rates, and generate secondary mineral products with low reactivity such as quartz, feldspar, and mica minerals.

Table 3. Relative reactivity of minerals at pH 5 (modified from Wendling and Douglas 2009).

Classification	Relative reactivity (pH 5)		Examples of typical minerals
Dissolving	1.00		Calcite (limestone), dolomite, magnesite, brucite,
Fast weathering	0.60		Anorthite, olivine, garnet, jadeite, leucite, diopside, wollastonite
Intermediate weathering	0.40	 Granites	Ortho and ring silicates, chain silicates (hornblende, glaucophane, tremolite, actinolite, anthophyllite), sheet silicates (serpentine, chrysotile, chlorite, biotite, talc)
Slow weathering	0.02		Framework silicates (albite, oligoclase, labradorite), sheet silicates (vermiculite, montmorillonite, kaolinite), gibbsite
Very slow weathering	0.01		K-feldspar, muscovite (mica)
Inert	0.004		Quartz, rutile, zircon

The sedimentary rock commonly referred to as limestone is comprised primarily of calcite and is frequently used as a soil and/or surface water amendment to neutralise acidity. The increase in solution pH can be sufficient to elicit precipitation of metals, depending on the pH at which the solution is buffered. Limestone dissolves in water at pH <6.4 to form dissolved CO₂ (denoted H₂CO₃*). The H₂CO₃* continues to react with the limestone to produce calcium and bicarbonate alkalinity. Metal ions in solution may be immobilised in the presence of CaCO₃ through either precipitation reactions as the solution pH becomes more alkaline, or by sorption to the limestone mineral surface. If solution pH increases >9.5, carbonate alkalinity (CO₃²⁻) may also become significant; however, as caustic alkalinity (OH⁻) is converted to bicarbonate alkalinity (HCO₃⁻) the pH declines to between 6 and 8. This is generally sufficient to remove trivalent metals (eg Al³⁺) as hydroxides, but insufficient to facilitate the precipitation of many divalent metal ions which may require a higher pH.

The reported order of selectivity for divalent metal sorption to the CaCO₃ mineral surface is Cd²⁺ > Zn²⁺ > Mn²⁺ > Co²⁺ > Ni²⁺ >> Ba²⁺ = Sr²⁺ (Zachara et al. 1991). Based on documented average stormwater composition (e.g. Göbel et al. 2007, Al-Anbari et al. 2008), and the sorption selectivity for divalent cations reported by Zachara et al. (1991), limestone is well suited for use in mixtures of reactive media to attenuate metals in stormwater. Treatment systems utilising limestone or similar materials to increase solution alkalinity should be carefully designed to ensure that the pH of discharged water is not excessively alkaline (e.g. >9.0).

The reactivity of limestone and its efficacy in pH buffering and/or metal attenuation is frequently reduced by coating of the limestone mineral surface by precipitated Fe-oxhydroxides in a process known as armouring. Considerable study has been devoted to overcoming the problem of Fe armouring. The most frequent solution is the use of limestone under anaerobic conditions to reduce ferric iron (Fe³⁺) to its ferrous (Fe²⁺) state.

3.3 Filter material modification

Iron oxide coating

Iron oxide coated materials can be used for removing cationic metals (Cu, Cd, Pb, Ni, Zn) as well as some oxyanions (PO₄, SeO₃, AsO₃). The specifics of the coating procedure vary with

the study but the principal is the same. The coated material, e.g. sand, is first acid-washed, rinsed with distilled water and dried. The source of iron in the coating is usually ferric nitrate ($\text{Fe}(\text{NO}_3)_3$) or ferric chloride (FeCl_3). An iron containing solution is prepared from the iron source and put into contact with the washed material to be coated. The solution is made alkaline with concentrated base to precipitate the iron from the solution. Iron is partly precipitated as a coating onto the material. The material is washed until the washing water is clear and the iron oxide coating is left on the surface of the material. The precipitation and washing steps can be repeated several times to increase the amount of coating in the final product. In the end, the coated material is dried at 105 °C and stored in capped bottles (Benjamin et al. 1996, Lai & Chen 2001, Gupta et al. 2005).

Manganese oxide coating

Manganese oxide coated materials can be used for removing dissolved metals, e.g., Ar, Pb, Cu, Cr from waste water. Several methods for the coating procedure have been developed but the general idea is as follows. The coated material is usually prepared by acid washing, rinsing by distilled water and drying in the oven. The manganese oxide coating is achieved by precipitation from a manganese containing solution. Permanganate can be reduced or manganese ion oxidized to precipitate the manganese oxide. The coated product is finally washed with distilled water until the runoff is clear, then dried in an oven at 105 °C and stored in capped bottles (Bajpai & Chaudhur 1999, Han et al. 2006, Guha et al. 2001).

Mixture with ferric sulphate

Sand or biochar can be mixed with ferric sulphate ($\text{Fe}_2(\text{SO}_4)_3$) to increase the mixtures N and P retention capacity. Dry and wet methods are used where ferric sulphate is added and mixed either as a solid or as a solution. Both methods are capable of increasing the N and P retention capacity of sand or biochar mixtures (Basnet 2015).

Alkaline treatment

Alkaline treatment for peat can be used to increase its retention capacity for Pb, Co and Ni. First, the peat is dried in air for 48 hours. Then the material is ground and sieved to less than 1–2 mm particle size. The alkaline treatment is done with an aqueous solution of NaOH. After treatment of 24 hours, the material is washed and dried in air (Bulgariu et al. 2011).

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