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The influence of the length of a cork column on the
removal of particles, metals and organic compounds
from rainwater runoff

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ABSTRACT

This project focuses on the removal efficiency of physical contamination, heavy metals (represented by chromium) and organic compounds (represented by anthracene) by cork columns.

Columns of 5 cm, 15 cm and 24 cm lengths are tested on their removal efficiency on the 3 kinds of pollution.

- The physical contamination involves 2 scenarios of pollution. The first scenario is considering a high pollution area; the turbidity according to this is 70 NTU. The second scenario is a normal pollution area, with a turbidity of 30 NTU. The stormwater is collected and by mixing different rainwater the correct turbidity is obtained. The first step of suspended matter removal is the pre-sedimentation step, which is carried out after the suspended matter is settled down 15 min. Secondly the stormwater is poured through each column, and the removal efficiency is calculated.
- The heavy metal removal efficiency experiments are divided into 2 parts. First the influence of suspended matter on heavy metal sorption is examined. Afterwards the removal efficiency of heavy metals by the columns is investigated by using AAS.
- For the removal of organic compounds the same procedure is followed as heavy metals. The influence of suspended matter on organic compounds sorption is determined by HPLC.

ACKNOWLEDGEMENTS

In the second year of my studies we had some presentations about final projects in Belgium, but also in foreign countries. I had some doubts to start this adventure outside Belgium, but my friend Wouter convinced me to go together.

The city we chose was Girona, we had a wonderful time in Spain and we met a lot of people who made this journey a lot more fun.

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1 INTRODUCTION

1.1 CORK

1.1.1 Occurrence

Cork is harvested from the bark of the *Quercus suber*, also called the Cork Oak. Cork is a natural, renewable and biodegradable raw material.

Cork oak forests are concentrated mainly in the Mediterranean region, in the South of Europe and in North Africa. The annual production is about 340 000 tonnes. Europe has the biggest part of the production and produces more than 80% of the world's cork. In addition, the production of cork stoppers, the annual production of cork waste is around 50 000 tonnes. Cork by-products are mainly used as an energy source due to their low economic value and high capacity to burn.



Figure 1: Oak tree

1.1.2 Harvesting

Cork can be separated from the tree without damaging it; therefore the harvest of cork is an environmental friendly process. When the tree has come to an age of 25 years, the cork can be removed for the first time. The first harvest of a tree almost always produces poor quality of cork; this is called "male cork". This is used for making floors, shoes and industrial products. The extractions usually occur at intervals of 9 years. The second time the cork is of higher quality, also known as "gentle cork". This cork is used for wine and champagne bottles.

1.1.3 Chemical composition

Cork has different properties such as high elasticity and low permeability. The cellular structure of cork wall consists of a thin lignin rich middle lamella, a thick secondary wall made up from alternating suberin and wax lamella and a thin tertiary wall of polysaccharides. There is a significant difference between wood and cork, explained in the figure below.

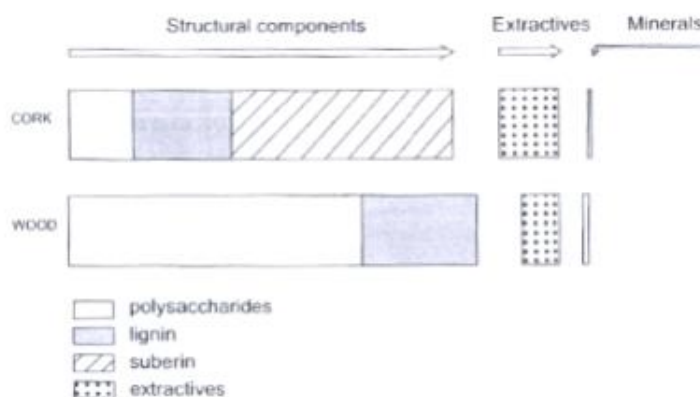


Figure 2: Schematic representation of the chemical composition of cork and wood of the cork oak (Pereira, 2007)

Some studies suggest that the secondary wall is lignified and therefore may not consist exclusively of suberin and waxes. Of this cell wall components, suberin is the most abundant (40%), lignin corresponds (22%), polysaccharides (22%) and extractives (15%).

1.1.4 Suberin

The structure of suberin in cork is not yet fully understood. It has been proposed that suberin consists of a polyester structure composed of long chain fatty acids, hydroxyl fatty and phenolic acids, connected by ester groups (International Material Reviews, Cork: properties, capabilities and applications et al 2005).

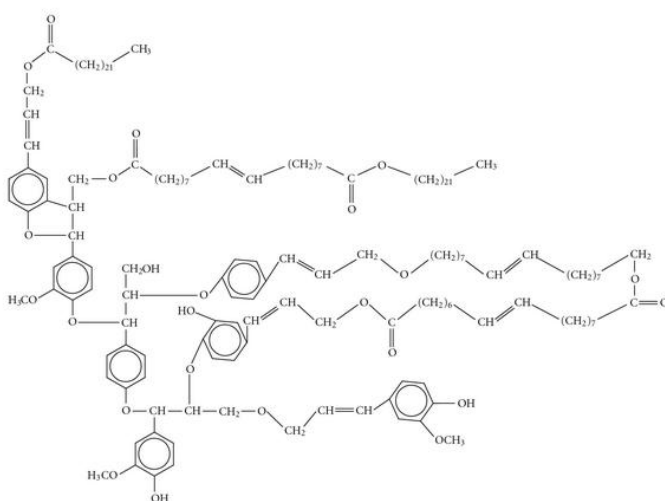


Figure 3: Chemical structure of suberin

1.1.5 Lignin

Lignin is a complex polymer of aromatic alcohols (Candolle, 1813).

The composition of lignin varies from species to species (International Material Reviews, Cork: properties, capabilities and applications et al 2005).

As a biopolymer, lignin is unusual because of its heterogeneity and lack of a defined primary structure. The differentiation between lignin and the aromatic component suberin has been difficult to establish.

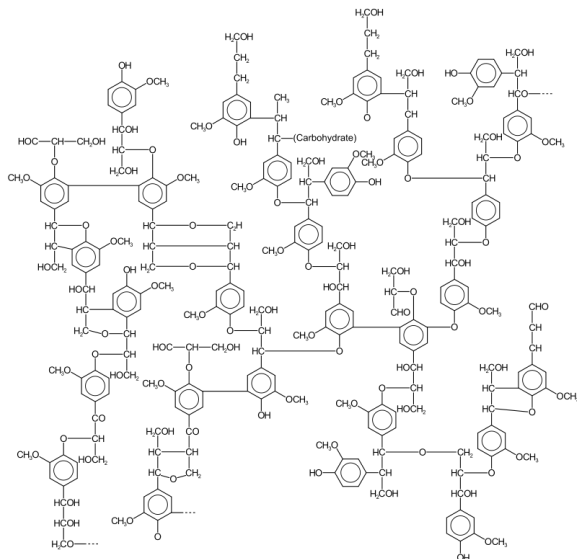


Figure 4: Chemical structure of lignin

1.1.6 Polysaccharides

Their percentage may vary from tree to tree and the concentration they can be detected depends on the method used (International Material Reviews, Cork: properties, capabilities and applications et al 2005).

The polysaccharides gave structure to cork, preventing the cork to collapse.

Polysaccharides consist of low molecular weight chains or monomers connected by glycoside linkages.

Component	Pereira ¹⁰			
	Virgin	Amadia	Gil and Moiteiro ^{7B}	Natividade ³¹
Polysaccharides, %	11–16	25–30	12–20	22
Waxes, %	17–20	13–14	3–5–7–9	2
Tannins, %			6–7	1

Table 1: Low molecular weight components of cork

1.1.7 Extractable components

Cork has some components, not chemically bonded to the main structure and easily extractable with solvents. Some of these components carry the responsibility for the organoleptic properties of wine. The 2 most important components are waxes and tannins.

Non-polar or low polarity solvents extract waxes, for example: benzene, acetate and ether.

Polar solvents such as water and ethanol extract tannins.

The concentration of the 2 components strongly depends on the composition of the cork. (Table 1)

1.1.8 Phenolic compounds

These are solvent extractable of low molecular weight. These also include the chemical families of flavonoids and tannins. These chemical groups have been differentiated on their potential biological activity.

1.2 CORK INDUSTRY

1.2.1 Wine stoppers

Wine corks can be made of a single piece of cork or can be composed of particles. Corks made of granular particles are called 'agglomerated corks'.

There was a decrease of cork wine stoppers due to the increase of cheaper synthetic alternatives, but wine stoppers are making a comeback. Today cork stoppers represent approximately 60% of all wine stoppers.

Cork has an interesting cellular structure, because of this it is easily compressed into a bottle and it will expand to form a tight seal. It is unavoidable that will come natural flaws, channels and this will make the cork crack in the bark. Because of this process the cork will become highly inconsistent.

Screw caps are seen as a cheap alternative for lower grade wines.

These alternatives have both advantages and disadvantages. For example, screw tops are considered a trichloroanisole free seal, TCA can be found in this screw caps.

They reduce the oxygen transfer almost to zero; this causes reductive quality of wine.

TCA is one of the largest causes of cork taint in wine.

Natural stoppers allow oxygen to interact with the wine, so the wine can age.

1.2.2 By-products of the cork industry

40% of the cork industry productions are by-products. Cork can be used for different by-products such as: badminton shuttlecocks, incorporation in agglomerates and briquettes, use as agricultural substrate, filling agent, source of chemicals or in the linoleum production, removal of pollutants by biosorption and production of activated carbons.

Cork's form structure and natural fire retardant make it interesting for acoustic and thermal insulation in houses, floors, ceilings and facades.

A by-product of the production is corkboard. Corkboard is gaining popularity as a non-allergenic, easy to handle and safe alternative to petrochemical-based insulation products.

Sheets of cork, also a by-product of stopper production, are used to make floor and wall tiles. Cork has a low density and so it is a suitable material for fishing floats and fishing rods.

Granules of cork can be mixed into concrete. The concrete will have a lower thermal conductivity, lower density and better energy absorption.

1.3 STORMWATER CHARACTERISTICS

1.3.1 Introduction

In European context, there is currently no European or national normative specifically defining quality standard for rainwater uses.

Some approaches do exist in countries such as France (Décret du 2 juillet 2008) or the UK (BS 815, 2009), where some standards have been proposed, although these are merely guidelines and are particularly focused on the domestic uses of rainwater.

In Spain, the reference approach is Royal Decree (RD) 1620/2007, which establishes quality standards and the possible uses for reclaimed water.

The threshold values established for urban uses in RD 1620/2007 have been taken as the reference standards for the present study.

<i>USES</i>		<i>Intes. nematode</i>	<i>E. coli</i>	<i>TSS (mg/L)</i>	<i>Turb. (UNT)</i>	<i>Other criteria</i>
<i>Urban</i>	<i>Residential</i>	<i>1 egg/10L</i>	<i>0 (UFC/ 100 mL)</i>	<i>10</i>	<i>2</i>	<i>Other pollutants^a</i>
	<i>Services</i>	<i>1 egg/10L</i>	<i>200 (UFC/ 100 mL)</i>	<i>20</i>	<i>10</i>	<i>Other pollutants^a</i>
	<i>Agricultural</i>	<i>1 egg/10L</i>	<i>100, 1000, 10000 (UFC/ 100 mL)</i>	<i>20, 35</i>	<i>10</i>	<i>Other pollutants^a</i>
	<i>Industrial</i>	<i>1 egg/10L</i>	<i>1000, 10000 (UFC/ 100 mL)</i>	<i>5,35</i>	<i>15</i>	<i>Other pollutants^a</i>
	<i>Recreational</i>	<i>1 egg/10L</i>	<i>200, 10000 (UFC/ 100 mL)</i>	<i>20, 35</i>	<i>10</i>	<i>Other pollutants^a</i>
	<i>Environmental</i>	<i>1 egg/10L</i>	<i>0,1000 (UFC/ 100 mL)</i>	<i>10, 35</i>	<i>2</i>	<i>NT: 10 mg N/L NO₃: 25 mg NO₃/L Art.257 to 259 RD 849/1986</i>
<i>Domestic uses*: toilet flushing (hand-basin toilets excepted), vehicle washing, clothes washing, surface landscape irrigation, irrigation of crops to be eaten cooked, impoundments, use in fire protection systems and commercial air conditioners</i>						<i>none</i>

^a Other pollutants such as heavy metals and PAHs contained must meet the Environmental Quality Standards (RD 60/2011).

TSS: total suspended solids

n.d.: non detectable

Table 2: Quality criteria for water reuse applications according to Spanish and United Kingdom legislations

1.3.2 Composition of rainwater

The composition of rainwater is largely due to dissolving particulate materials in the atmosphere when droplets of water nucleate with atmospheric particulates.

The compositions vary geographically. In open ocean and coastal areas they have a salt content and CO_2 as a bicarbonate anion, this creates an acidic pH. Terrestrial rain compositions vary from place to place because the composition is affected by the types of particulates in the atmosphere.

Particulate concentration can also be affected by human activities, such as industry.

And the last parameter that affects the composition is the local climate. The precipitation in one area compared to another.

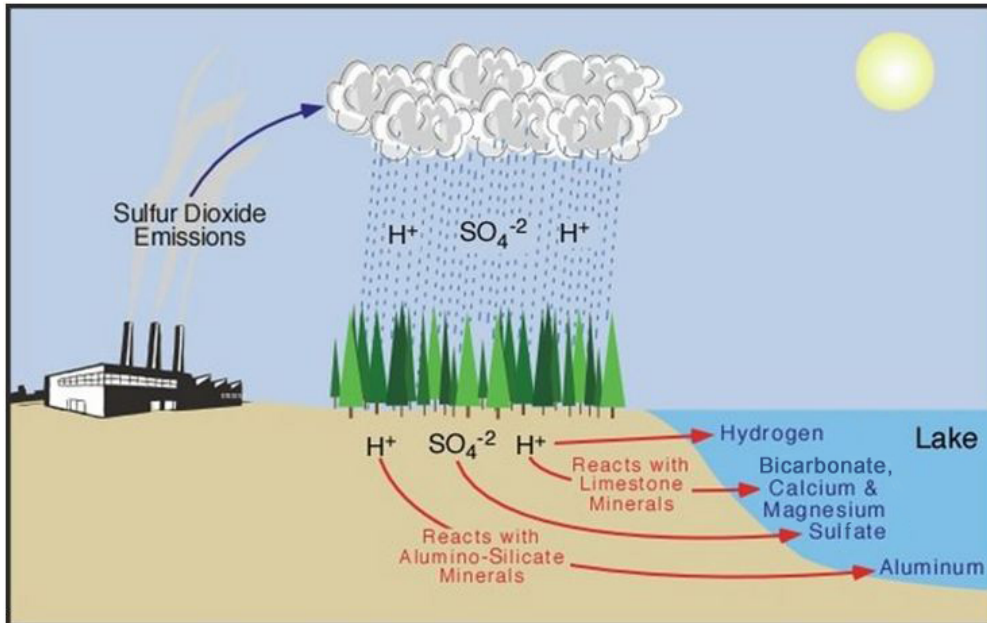


Figure 5: Acid rain due to industry

A large number of potentially toxic substances, including metals, occur in stormwater. Metals of primary concern are cadmium, copper, zinc and lead, with roughly 50% of the metal load in dissolved form. Lead concentration in the environment has declined since the 1970's, when lead in gasoline and paint was banned, but there is still substantial degrading lead paint present in the urban environment, making this a continuing concern. Large concentrations of metals can be lethal, and moderate concentrations can reduce growth, reproduction, and survival in aquatic organisms. Small concentrations of metals also have been documented to alter the behaviour and competitive advantage of invertebrates, a result that could change the balance of ecosystems.

Investigations of the toxicity of stormwater runoff from urban highway sites near Los Angeles, USA, indicated that the toxicity to water fleas was due to copper and zinc.

Once in an aquatic environment, metals can accumulate in freshwater biofilms to such an extent that the biofilm concentrations are larger than sediment metal concentrations. Fish and invertebrates feed on biofilms, as a result, the metals can be transferred through the food chain and bioaccumulation will continue to occur.

Besides metals, stormwater is contaminated with suspended solids. Sedimentation often settles to the bottom of water and can directly affect water quality. Excessive levels of sediment in water can increase the risk of infection and disease through high levels of nutrients present in the soil. These high levels of nutrients can reduce oxygen and boost algae growth. Limited native vegetation and excessive algae has the potential to disrupt the entire aquatic ecosystem due to limited light penetration, lower oxygen levels and reduced food reserves.

Excessive levels of sediment and suspended solids have the potential to damage existing infrastructure. Sedimentation can increase runoff by plugging underground injection systems; so more runoff stormwater is created. Increased sedimentation can also reduce storage behind reservoirs, this can lead to increased expenses for public agencies and it affects the quality of the water.

Stormwater is channelled into storm drains and surface waters, the natural sediment load discharged to receiving waters decreases, but the water flow and velocity increases. In fact, a typical city creates 5 times the runoff of typical woodland of the same size.

Atmospheric particulate matter has been widely studied in recent years due to its impact on human health, increasing respiratory disease or as a carrier of toxic substances, such as adsorbed PAH's. Polycyclic aromatic hydrocarbons have been intensively studied in past decades because some of these compounds are highly carcinogenic or mutagenic. PAH's are mainly emitted from incomplete combustion processes associated with anthropogenic sources and natural sources such as volcanic eruptions and forest fires. Approximately 90% of PAH's emissions are estimated to be anthropogenic sources typically including the combustion of fossil fuels, industrial processes and domestic heating systems.

Vehicular traffic is considered to be the major contributor to the urban atmosphere.

Source emissions and meteorological conditions as well as gas-particle partitioning may result in the seasonal of PAH's concentrations. For example a study in Guangzhou, China has studied the influence of meteorology on PAH's concentrations. A parameter that influence the PAH's concentrations is the wind. A negative correlations between individual PAH's with wind speed, indicates the expected dilution effect of atmospheric turbulence on pollutant concentrations. A second parameter is the temperature; the temperature is becoming less important at lower temperatures. So a breakdown in temperature dependence and wind speed has a great influence on the PAH's concentrations.

1.4 BIOSORPTION

Cork by-products are mainly used as an energy source because they have a high capacity to burn. Cork has a heterogeneous chemical composition providing numerous binding possibilities for a wide range of pollutants, for example PAH's.

One of the better technologies to remove PAH's from water is active carbon.

A disadvantage is that it has a high operational cost, so the need to search for other adsorbent increased.

Waste materials are very interesting, by using the cost of waste disposal decreased, which contributes to the environmental protection.

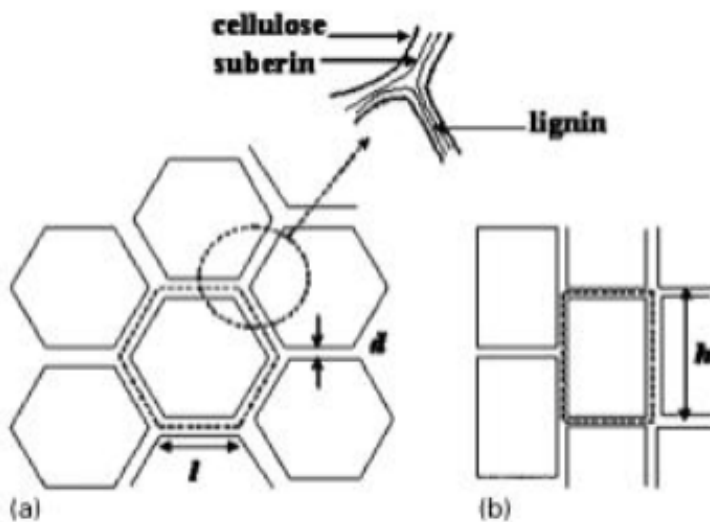


Figure 6: Microscopic structure of cork (*Cork: properties, capabilities and applications*)

The lignin–phenanthrene interaction is mostly hydrophobic in nature being largely determined by the π -stacking interaction between the aromatic groups of the interacting partners. This result justifies the observed correlations as dichloromethane extractives; being hydrophobic, compete with phenanthrene adsorption, whereas phenolic groups, as well as negatively charged groups, enhance the hydrophilic character of the sorbent surface, so hindering the adsorption of phenanthrene.

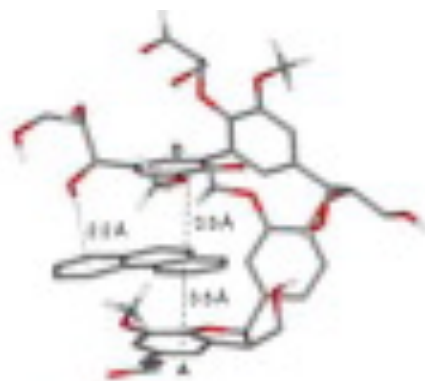


Figure 7: Molecular interaction lignin-phenanthrene (*An integrated approach to understanding the sorption mechanism of phenanthrene by cork*)

1.5 TECHNIQUES

1.5.1 Turbidity meter

Turbidimetry is the process of measuring the loss of intensity of transmitted light due to the scattering effect of particles suspended in it. Light is passed through a filter creating a light of known wavelength, which is then passed through a cuvette containing a solution. A photoelectric cell collects the light, which passes through the cuvette. A measurement is then given for the amount of adsorbed light.

The turbidity meter used in this project is one of Eutech Instruments, Portable Turbidimeter TN-100/T-100.



Figure 8: Portable turbidimeter TN-100/T-100



Figure 9: Turbidimeter with calibration standards and sample vials

1.5.2 AAS

AAS stands for Atomic Absorption Spectroscopy; it is a method for the quantitative determination of chemical elements by using the absorption of optical radiation by free atoms in the gaseous state.

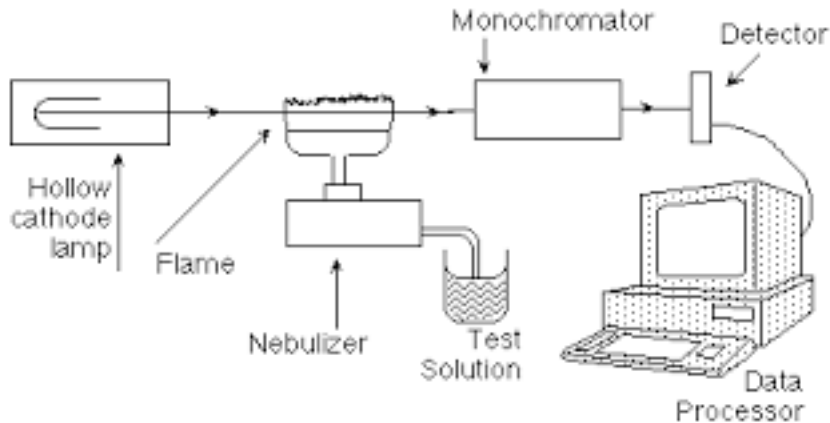


Figure 10: AAS diagram

1.5.2.1 Atomizers

There are different kinds of atomizers that can be used in AAS.

The oldest and most common one are flames, the air-acetylene flame has a temperature of 2300°C and the nitrous oxide system has a temperature of 2700°C.

When using flame atomizers the samples are mostly liquids or dissolved samples.

An analytical nebulizer, who transforms the sample into an aerosol, nebulizes the sample solution. The aerosol goes to the spray chamber, there it is mixed with the flame gases and only the smallest aerosol droplets enter the flame. Because of this, only 5% of the aspirated sample solution reaches the flame.

After the spray chamber, there is the burner. The burner produces a flame with a length of 5 of 10 cm. For optimizing the burner, the height can be adjusted and the mixture of air-acetylene. The highest sensitivity is reached when the beam passes the zone of highest atom cloud density in the flame.

In the flame, there is a process that consists of different stages:

1. Desolvation: evaporating the solvent and the dry sample particles remain
2. Vaporization: particles converted into gaseous molecules
3. Atomization: dissociating into free atoms
4. Ionization: atoms can be partial converted into gaseous ions

The second used atomizers are electro thermal atomizers, ET AAS using graphite tube atomizers. This technique also consists of 4 different stages:

1. Drying: evaporating the solvent
2. Pyrolysis: thermochemical decomposition
3. Atomization: sample to gaseous phase
4. Cleaning: residues are removed by high temperature

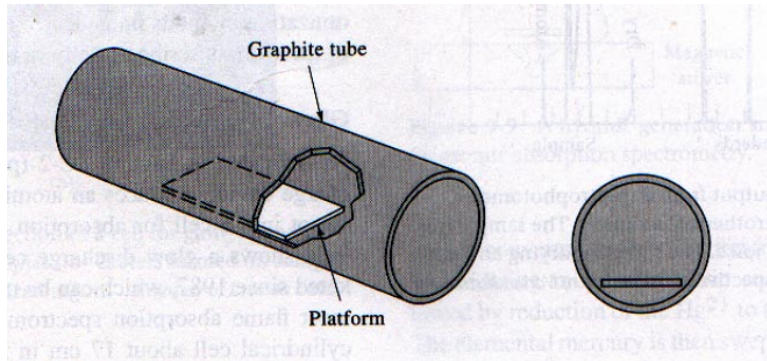


Figure 11: Graphite furnace

1.5.2.2 Radiation source

There are 2 major sources: line source (LS AAS) and continuum source (CS AAS).

In LS AAS, the high spectral resolution required for AAS is provided by the source itself. The source emits lines that are narrower than the absorption lines.

CS AAS, for example deuterium lamps, are used for background correction. The advantage of CS AAS is that it only requires a medium-resolution monochromator. The disadvantage is that a separate lamp is necessary for each element.

Hollow cathode lamps are the most common radiation source in LS AAS. The lamp is filled with neon or argon at low pressure. The lamp has an anode and a cathode. At the anode, there is the element of interest. A high voltage across the anode and cathode, results into ionization of the fill gas. Gas ions are accelerated towards the cathode. There is the impact on the cathode and sputter cathode material is excited to emit radiation.

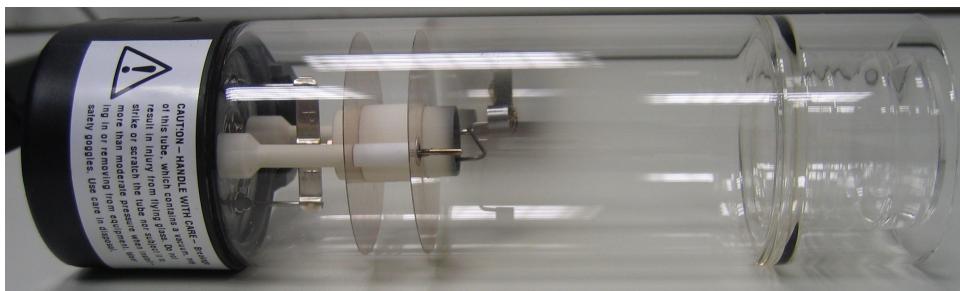


Figure 12: Hollow cathode lamp

1.5.2.3 Monochromator

A monochromator is used to select the specific wavelength of light, which is absorbed by the sample. The light selected by the monochromator is directed onto a detector that is typically a photomultiplier tube. This produces an electric signal proportional to the light intensity.

1.5.3 HPLC (Parmentier, 2011)

High performance liquid chromatography is a technique used to separate the components in a mixture that includes the injection of a volume of liquid sample into a column packed with particles, called the stationary phase. The individual components present in the sample move through the packed column with a liquid (mobile phase) that is forced through the column by high pressure delivered by a pump. The separation of the components involves various chemical interactions between the molecules of the components and the packing particles. After the separation, the components are detected at the exit of the column by a flow through device that measures the amount. The result of HPLC is a chromatogram. (Vansteenland, Role of chemical components of cork on sorption of pesticides)

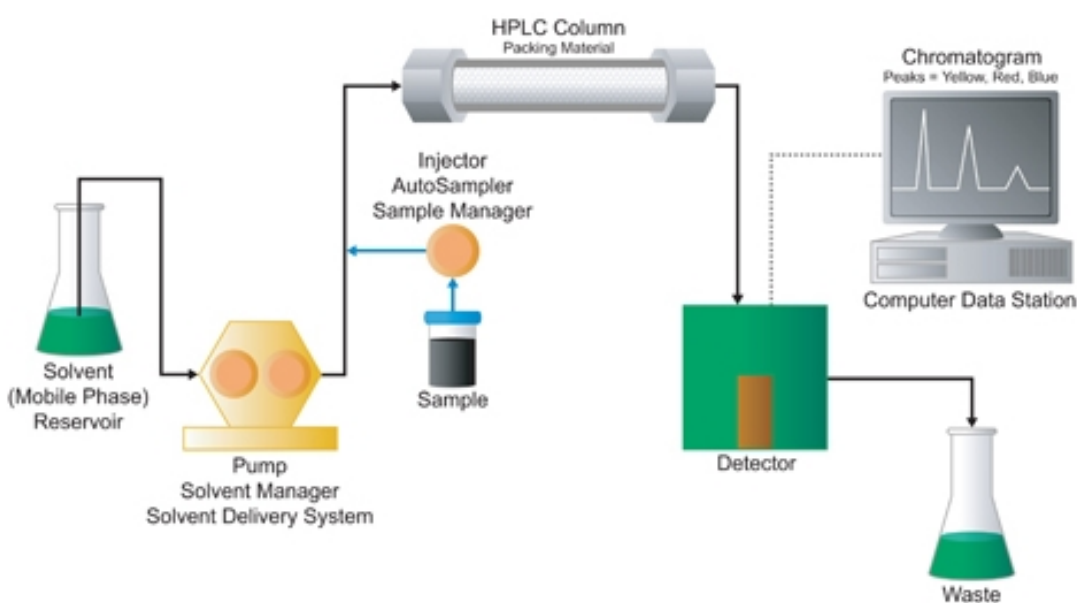


Figure 13: HPLC diagram

1.5.3.1 Normal phase HPLC

The column is filled with tiny silica particles and the solvent is non-polar, for example hexane. A typical column has an internal diameter of 4,6mm and a length of 150 to 250mm. Polar compounds in the mixture passing through the column will stick longer to the polar silica than non-polar compounds.

1.5.3.2 Reverse phase HPLC

The silica is modified to non-polar by attaching long hydrocarbon chains to its surface. A polar solvent is used, for example a mixture of water and alcohol such as methanol. There will be a strong attraction between the polar solvent and polar molecules in the mixture being passed through the column. Polar molecules will therefore spend most of their time moving with the solvent.

1.5.3.3 Solvent reservoir

The reservoir contains the mobile phase; mostly consist of water and organic solvents. Before using the eluent, a degassing is carried out to remove bubbles, which can damage the pump. To prevent other damage, the solvent is aspirated through a filter with a porosity of 20 μm .

1.5.3.4 Pump

A high-pressure pump is needed because of the resistance flow liquid in the column. A typical pump can reach a pressure in the range of 400 – 600 bar. During the experiment, the pump gives a constant mobile phase composition (isocratic) or an increasing phase composition (gradient).

1.5.3.5 Injector

A 'six way plug' is used to introduce the sample in the column. The injector can resist the high pressure of the system. The injected volume is reducible and is about 5 – 20 μL .

1.5.3.6 Retention time

The time necessary for a particular compounds to travel through the column to the detector is known as the retention time. This time is measured from the time at which the sample is injected to the point at which the display shows a maximum peak height for that compound. Different compounds have different retention times. For a particular compound, the retention time will vary depending on:

- Pressure: this affects the flow rate of the solvent
- Nature of the stationary phase: the material and particle size
- Exact composition of the solvent
- Temperature of the column

The conditions for HPLC have to be carefully controlled.

1.5.3.7 Detector

The detector detects the individual molecules that elute from the column by using a UV absorption technique. Then the detector provides an output to the recorder or computer, which results in a liquid chromatogram.

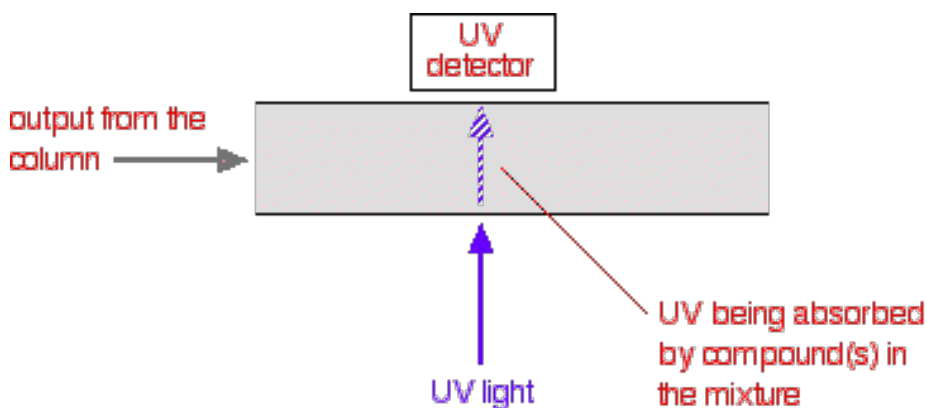


Figure 14: UV detector

1.5.3.8 Computer

The computer records the signals of the detector and calculates the retention time of the sample components and the amount of the sample.

2 BACKGROUND

Cork is the bark of the cork oak tree, *Quercus suber*. It is a natural, renewable and biodegradable raw bio resource that is harvested every 9 to 12 years.

It is mostly associated with the production of wine stoppers, 60% of the cork market. The cork industry generates a large amount of cork waste every year during the manufacturing of cork stoppers.

Previous research data indicates that cork has a great potential as a biosorbent for organic pollutants. Cork is composed of structural and non-structural components. Structural components include lignin and suberin and polysaccharides. Non-structural components include the extractives, which are mainly aliphatic and phenolic compounds.

This chemical composition of cork provides numerous binding possibilities for a wide range of pollutants.

Water reuse is a critical element for managing the water resources. Through water conservation and water recycling, the environmental needs can be satisfied and a sustainable development can be achieved.

As to rainwater applications, there are 2 aspects to take into account: water quality requirements and potential uses. The quality standards are usually fixed according to the potential uses of the water, specifically to the analysis of potential health risks. Some approaches exist in countries such as France (Décret du juillet 2008) or UK (BS 815, 2009), where some standards have been proposed, although these are only focused for domestic uses. In Spain the approach is Royal Decree 1620/2007, which establishes different quality standards, and potential uses for water reuse.

Stormwater contains different pollutants such as physical and chemical contaminants. The physical pollutants that are examined are dissolved and suspended matter. For the chemical contamination Cr(III) is used, as a heavy metal and anthracene as a PAH.

This research is aimed at evaluating the removal of the main physical and chemical contamination present in stormwater using cork columns with the final purpose to be reused.

3 OBJECTIVES

The general purpose of this research is to evaluate the removal efficiency of suspended matter, metals and organic compounds by 3 different lengths of cork columns.

The lengths of the cork columns are 5 cm, 15 cm and 24 cm.

All 3 columns are divided into 2 parts; a part with cork particles of the size 6,30 mm - 3,15 mm and a part with particle size 3,15 mm – 1 mm.

To achieve this purpose the following steps will be carried out:

1. Prepare columns.
2. Collect the stormwater.
3. Evaluate the removal efficiency of physical contamination by the 3 cork columns.
4. Investigate the Cr(III) and anthracene removal efficiency.
5. Search the optimal length of cork column.

4 EXPERIMENT

4.1 BIOSORBENT SAMPLES

The used cork is granulated cork. This cork is a mixture of the belly and the cork and is considered as a by-product of the cork industry.



Figure 15: Cork stoppers

The particle size of the cork is divided into 2 different sizes.

The filter of 2 mm to separate the cork particles was not available, as replacement the filter with a sieve size of 3,15 mm is used.

The smallest size is 1–3,15 mm. The biggest particles are 3,15-6,30mm.

4.1.1 Design of the three cork columns

A previous study has shown that the best length for the cork column is 25 cm, it is possible higher columns are better, but this is not yet tested. (Group MiMa)

This column is divided into 2 parts, explained in the table below.

Particle size (mm)	Length (cm)
6,3-2	6
2-1	19

Table 3: Proportion of cork particle sizes for column of 25 cm

In this project, 3 columns with different Lengths are used. The length of each particle size is calculated on this proportion of 6/25 and 19/25.

	Length _{6,3-3,15mm} (cm)	Length _{3,15-1mm} (cm)
5 cm	1,2	3,8
15 cm	3,6	11,4
24 cm	5,8	18,2

Table 4: Calculated proportion of cork particle sizes for 3 lengths of columns

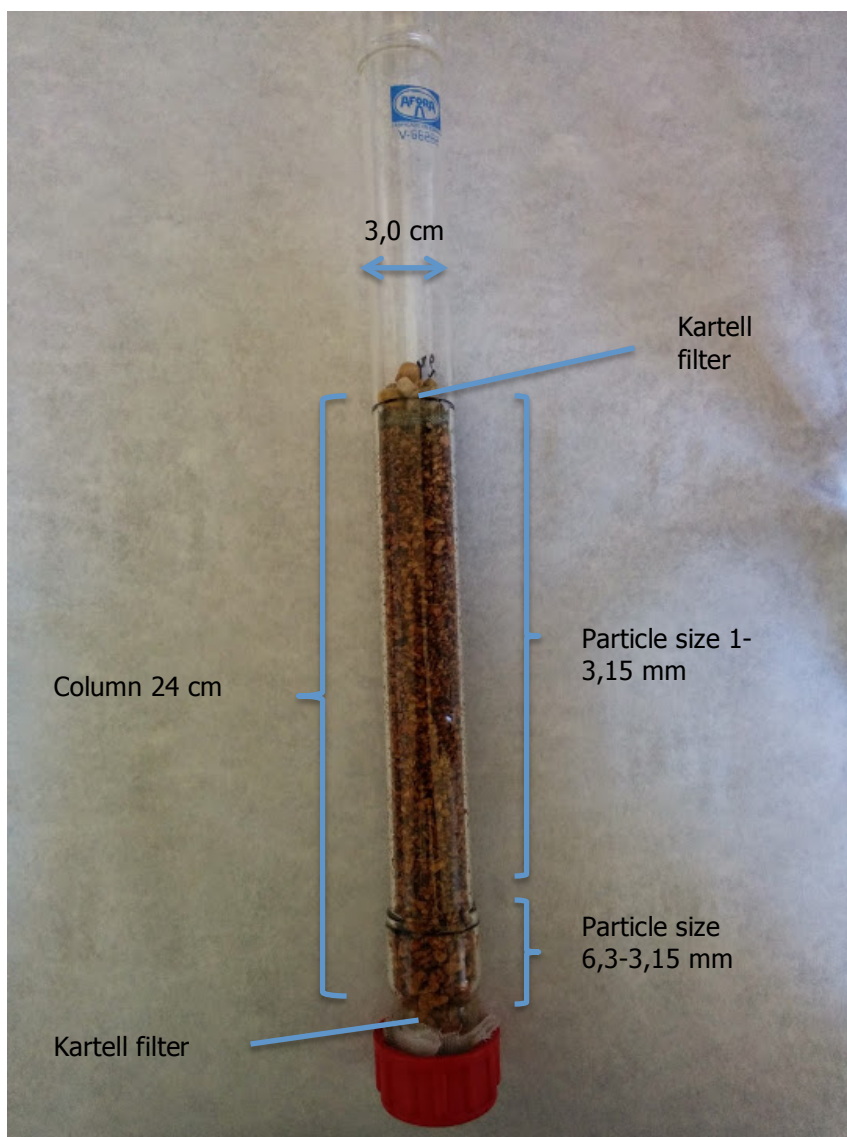


Figure 16: Design of cork column

4.2 COLLECTION OF STORMWATER

The stormwater used for this project is collected at the University of Girona. It is collected by simply a funnel and a flask and collected from a roof runoff.

4.3 PREPARATION AND FILTRATION OF THE STORMWATER

Stormwater can contain a lot of pollutants, but the main pollution of stormwater is due to suspended matter, heavy metals and organic compounds (Llopart et al, 2010).

4.3.1 Physical contamination

The average rainfall in Barcelona is 640 millimetres, measured for 55 days, shown by a previous study (Agencia Estatal De Meteorologia). The average Spanish roof has a surface of 30 m². The 2l used in all experiments is extrapolated on the surface of the cork column.

The preparation of the stormwater is separated into 2 scenarios. The first scenario is a period of heavy rainfall, a turbidity of 70 NTU. The second one is a dry period; a turbidity of 30 NTU, this turbidity is based on a previous paper (Analysis of rainwater quality, Novatech Sostaqua Project et al 2010).

While the stormwater is passing the cork columns, the flow rate is measured. Every minute the volume that passed the column is measured with a graduated cylinder.

The stormwater is prepared (6l) and the initial turbidity is measured while the water is agitating, the suspended matter is measured 9 times.

The second step is the removal of the suspended matter that is settled down after 15 min. For this removal a Masterflex pulsating system is used, this system vacuum cleans the surface and removes the suspended matter that is settled down together with a volume of stormwater of 200 ml.

Again the turbidity is measured 9 times, this is the concentration suspended matter after removing the down layer.

The volume of 6l stormwater is divided into 3 times 2l; there is 2l stormwater for each cork column.

The stormwater is poured through each column and is collected. While agitating the turbidity is measured 9 times after passing the columns.

This final measurement can determine the suspended matter removal by the cork columns.

These actions are repeated for 30 NTU.

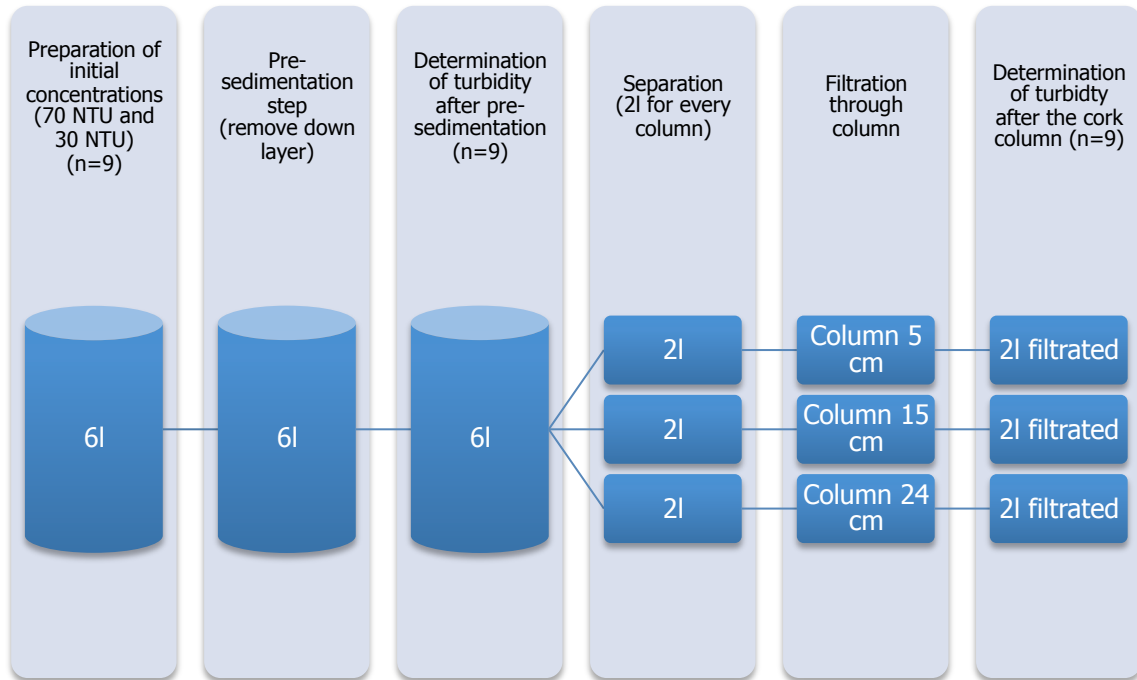


Figure 17: Schematic representation of stormwater handlings

4.3.2 Heavy metals

To investigate the removal of heavy metals by the columns, a previous step is necessary. First the influence of suspended matter on the sorption of heavy metals is examined. This investigation is divided into 2 parts:

- 1) Interaction between the suspended matter and chromium
- 2) The removal of chromium by the cork columns

To examine the interaction between the suspended matter and Cr(III), 3 tests are necessary:

- 1) Tapwater + [Cr(III)] 20 mg/l
- 2) Stormwater without particles + [Cr(III)] 20 mg/l
- 3) Stormwater with particles + [Cr(III)] 20 mg/l

Stormwater with a turbidity of 30 NTU is used for all the experiments concluding heavy metals. For the interaction between suspended matter and Cr(III), 2l of each water is needed.

An amount of 4l of stormwater is prepared with a turbidity of 30 NTU; 2l of this volume is filtrated and is used as stormwater without particles.

For the filtration process a Whatman filter with a sieve size of 0,45 μm is used.

In each 2l, a concentration of 20,0 mg/l chromium is added.

$$2000 \text{ ml} \cdot 20 \frac{\text{mg}}{\text{l}} = c \cdot 10,0 \text{ ml}$$

$$c = 4000 \frac{\text{mg}}{\text{l}} = 4,000 \frac{\text{g}}{\text{l}} \text{Cr} = 1,000 \frac{\text{g}}{250,0\text{ml}} \text{Cr}$$

$$n = \frac{m}{M} = \frac{1,000\text{g}}{52,0\text{g/mol}} = 0,01923 \text{ mol Cr} \xrightarrow{\cdot 2} 0,009615 \text{ mol } K_2Cr_2O_7$$

$$m = n \cdot M = 0,009615 \text{ mol} \cdot 294,2 \frac{\text{g}}{\text{mol}} = 2,8287 \text{ g } K_2Cr_2O_7 \text{ in } 250,0 \text{ ml}$$

A volume of 10,0 ml of the solution $K_2Cr_2O_7$ is added in 2l to obtain the concentration Cr(III).

When the Cr(III) is added, a sample is taken after 1 min. The 3 types of water are agitated for 24 hours. The second sample is taken after 1 hour and the last sample is taken after 24 hours.

These samples are saved in the fridge, to have no decrease in chromium concentration.

While waiting 24 hours, standard solutions are made to measure the chromium with AAS.

After the experiment the standard solutions are measured, as the samples.

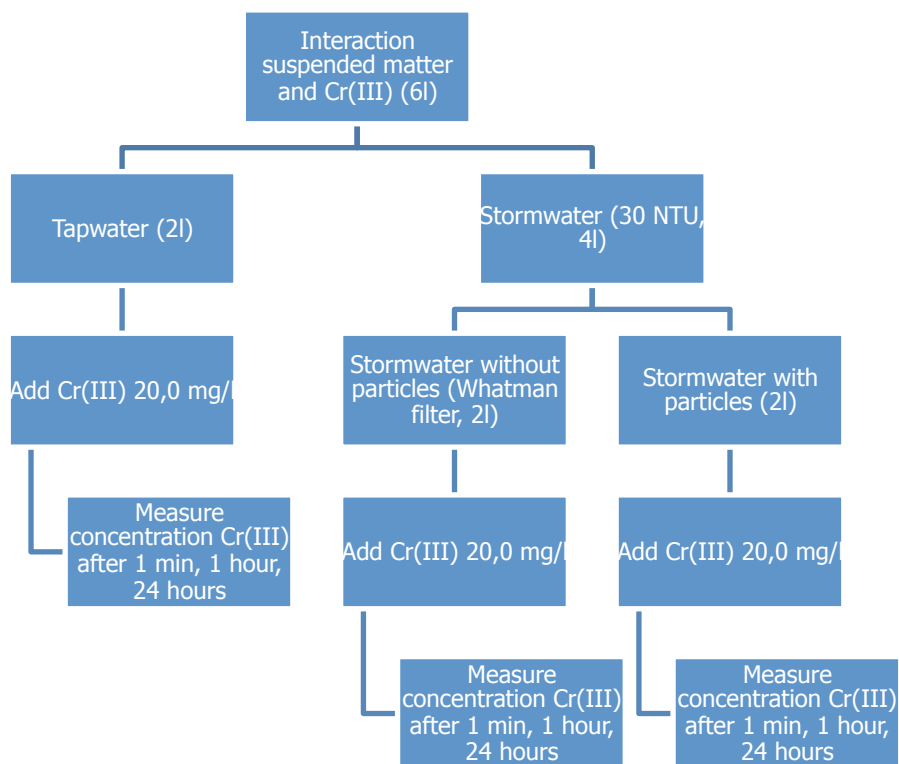


Figure 18: Schematic representation of interaction suspended matter and Cr(III)

The second part of heavy metals is the removal efficiency by the cork columns. An amount of 6l tapwater is prepared and a volume of 12l stormwater with a turbidity of 30 NTU. Half of the volume stormwater is filtrated with a Whatman filter with a sieve size of 0,45 μm . In each 6l, a concentration of 20,0 mg/l chromium is added. A sample is taken after 1 min, to determine the initial concentration chromium.

A volume of 2l of each type of water is poured through each column and is collected. After all experiments the samples are measured with AAS, the same standard solutions are used.

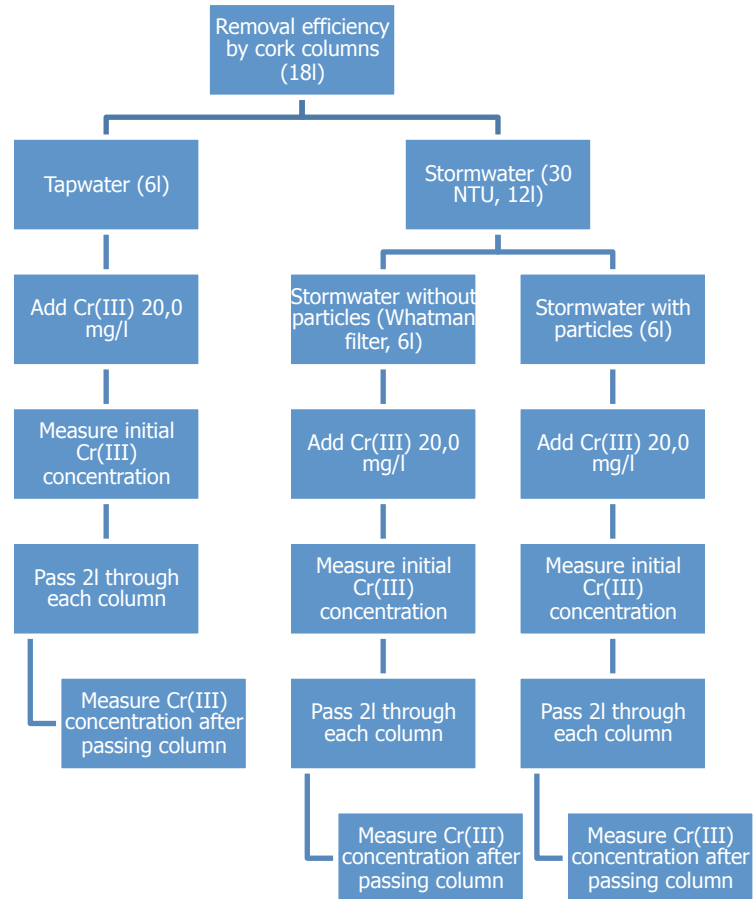


Figure 19: Schematic representation of removal efficiency of heavy metals by cork columns

4.3.3 PAH's

To investigate the removal of organic compounds by the columns, a previous step is necessary. First the influence of suspended matter on the sorption of organic compounds is examined. This investigation is divided into 2 parts:

- 1) Interaction between the suspended matter and anthracene
- 2) The removal of anthracene by the cork columns

To examine the interaction between the suspended matter and anthracene, 2 tests are necessary:

- 1) Stormwater without particles + [anthracene] 50 µg/ml
- 2) Stormwater with particles + [anthracene] 50 µg/ml

Stormwater with a turbidity of 30 NTU is used for all experiments concluding organic compounds. For the interaction between suspended matter and anthracene, 2l of each matrix is needed.

A volume of 4l stormwater is prepared and 2l of this amount is filtrated using a Whatman filter with a sieve size of 0,45 µm.

In each matrix a concentration of 50 µg/ml anthracene is added.

$$c = \frac{1,000g \text{ anthracene}}{100,0 ml \text{ dichloromethane}} = 0,01000 \frac{g}{ml} \text{ anthracene} = 10,00 \cdot 10^3 \frac{\mu g}{ml} \text{ anthracene}$$

$$2000ml \cdot 50 \frac{\mu g}{ml} = 10,00 \cdot 10^3 \frac{\mu g}{ml} \cdot V$$

$$V = 10,0ml$$

A volume of 10,0 ml of the stock solution of anthracene is added to the 2l of stormwater with particles and to the stormwater without particles to obtain a concentration of 50 µg/ml.

A sample is taken after 1 min. The 2 matrixes are agitated for 24 hours. The second sample is taken after 1 hour and the last sample after 24 hours.

These samples are saved in the fridge, to have no decrease in anthracene concentration.

After 24 hours the samples are measured with HPLC.

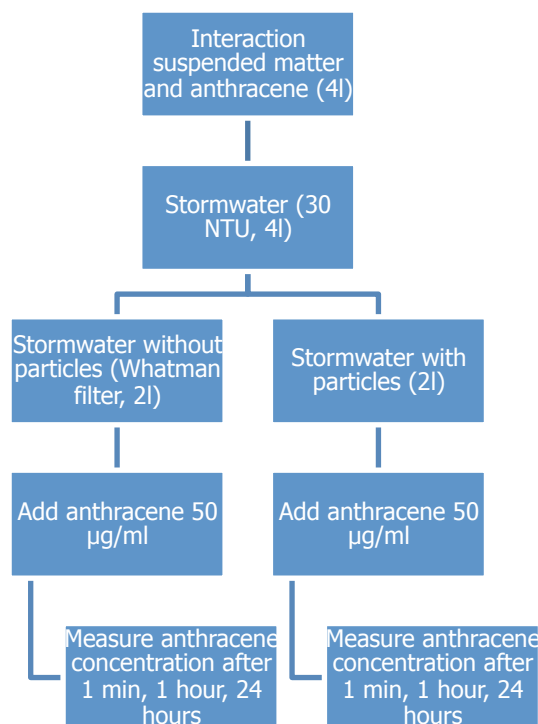


Figure 20: Schematic representation of interaction suspended matter and anthracene

The second part of organic compounds is the removal efficiency by the cork columns.

A volume of 12l stormwater with a turbidity of 30 NTU is prepared and 6l is filtrated with a Whatman filter with a sieve size of 0,45 μm to obtain stormwater without particles.

A concentration of 50 $\mu\text{g}/\text{ml}$ is added to each matrix. A sample is taken after 1 min, to determine the initial concentration anthracene.

An amount of 2l of each matrix is poured through each column and is collected.

All samples are measured with HPLC.

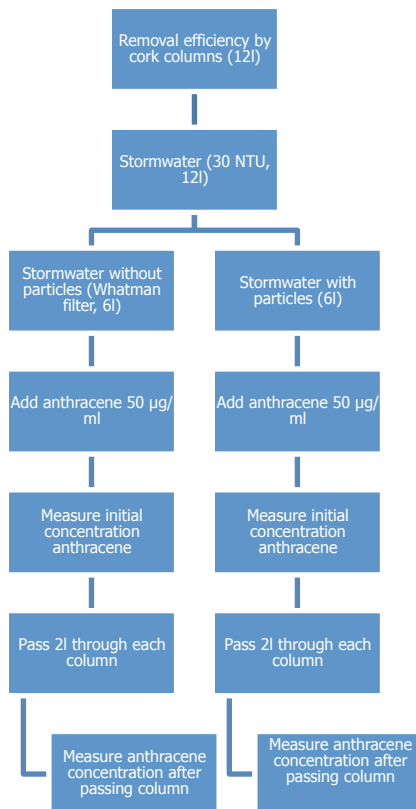


Figure 21: Schematic representation of removal efficiency of PAH's by cork columns

5 RESULTS AND DISCUSSION

5.1 PHYSICAL CONTAMINATION

5.1.1 Flow rate

The first step was measuring the volume of stormwater passing through the 3 cork columns versus the time to evaluate their flow rate.

The flow rate of tapwater is measured every litre using a graduated cylinder. The experiment is repeated 3 times.

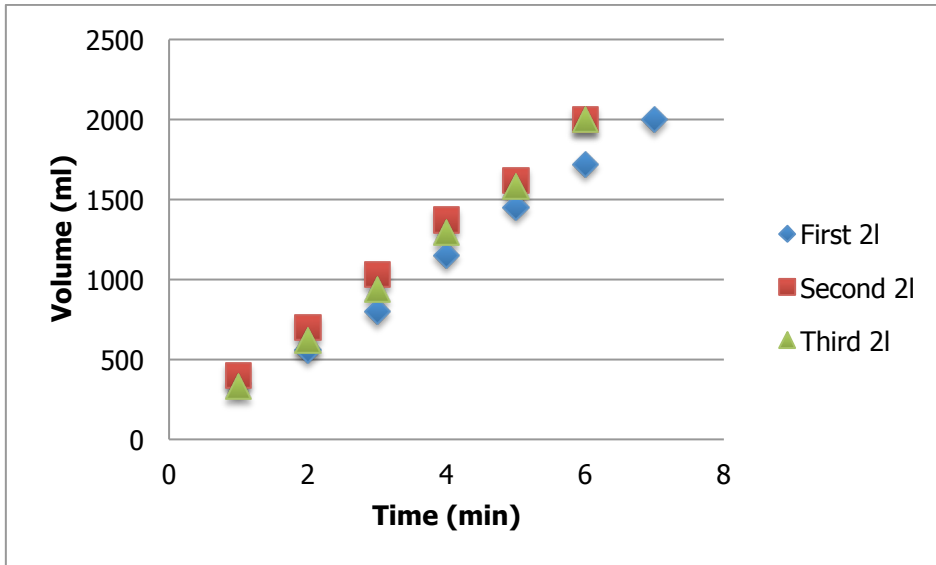


Figure 22: Flow rate of column 5 cm

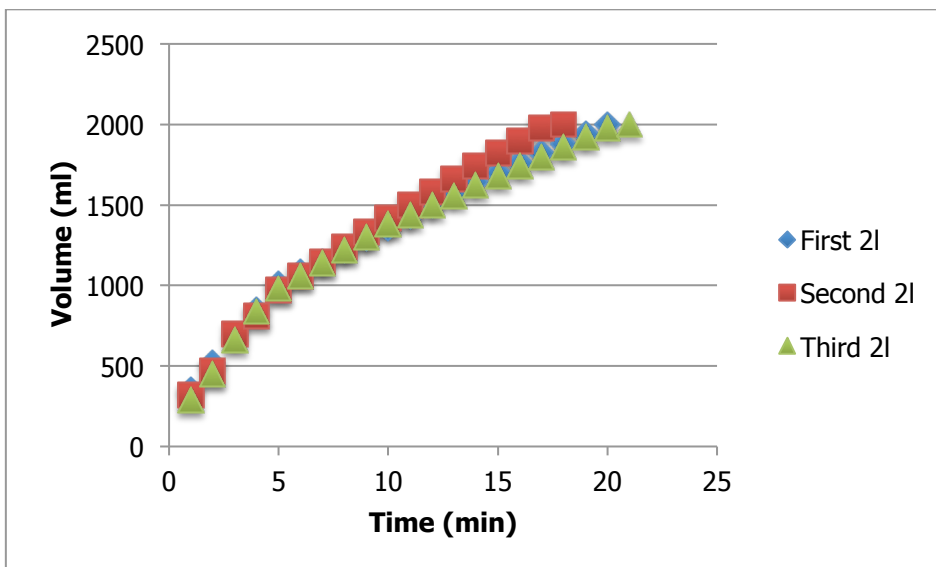


Figure 23: Flow rate of column 15 cm

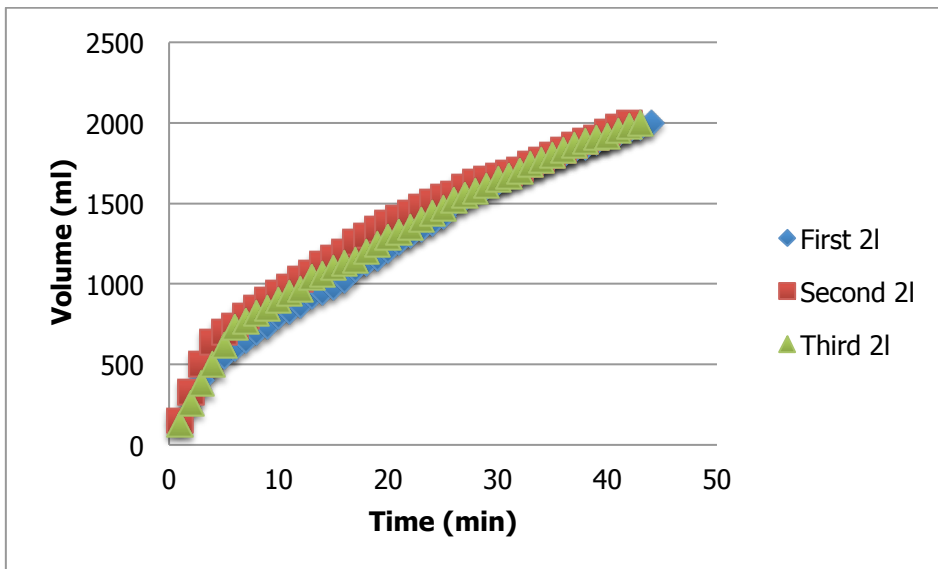


Figure 24: Flow rate of column 24 cm

As observed in the figures, after 5 min the column of 5 cm has passed 1500 ml, the column of 15 cm has passed 1000 ml and the column of 24 cm has passed 700 ml. For passing the total volume of 2l stormwater the column of 5 cm needed 7 min, the column of 15 cm 21 min and the column of 24 cm 45 min.

Accordingly to these data the flow rate is calculated.

The flow rate of the smallest column is 286 ml/min, the column of 15 cm 95 ml/min en the highest column had a flow rate of 44 ml/min.

Following on these calculations the higher the column, the slower the flow rate.

5.1.2 Measurement of the removal efficiency of suspended matter

In European context, there is currently no European or national normative specifically defining quality standard for rainwater uses.

Some approaches do exist in countries such as France (Décret du 2 juillet 2008) or the UK (BS 815, 2009), where some standards have been proposed, although these are merely guidelines and are particularly focused on the domestic uses of rainwater.

In Spain, the reference approach is Royal Decree (RD) 1620/2007, which establishes quality standards and the possible uses for reclaimed water.

The threshold values established for urban uses in RD 1620/2007 have been taken as the reference standards for the present study.

Table 5 shows different applications for re-used stormwater, according to Spanish legislations. The values for turbidity are used to determine which applications are possible for the stormwater.

USES		<i>Intes. nematode</i>	<i>E. coli</i>	<i>TSS (mg/L)</i>	<i>Turb. (UNT)</i>	<i>Other criteria</i>
<i>Urban</i>	<i>Residential</i>	1 egg/10L	0 (UFC/ 100 mL)	10	2	<i>Other pollutants[§]</i>
	<i>Services</i>	1 egg/10L	200 (UFC/ 100 mL)	20	10	<i>Other pollutants[§]</i>
	<i>Agricultural</i>	1 egg/10L	100, 1000, 10000 (UFC/ 100 mL)	20, 35	10	<i>Other pollutants[§]</i>
	<i>Industrial</i>	1 egg/10L	1000, 10000 (UFC/ 100 mL)	5,35	15	<i>Other pollutants[§]</i>
	<i>Recreational</i>	1 egg/10L	200, 10000 (UFC/ 100 mL)	20, 35	10	<i>Other pollutants[§]</i>
	<i>Environmental</i>	1 egg/10L	0,1000 (UFC/ 100 mL)	10, 35	2	NT: 10 mg N/L NO ₃ : 25 mg NO ₃ /L Art.257 to 259 RD 849/1986
<i>Domestic uses*: toilet flushing (hand-basin toilets excepted), vehicle washing, clothes washing, surface landscape irrigation, irrigation of crops to be eaten cooked, impoundments, use in fire protection systems and commercial air conditioners</i>						<i>none</i>

[§]Other pollutants such as heavy metals and PAHs contained must meet the Environmental Quality Standards (RD 60/2011).

TSS: total suspended solids

n.d.: non detectable

Table 5: Quality criteria for water reuse applications according to Spanish and United Kingdom legislations

Two scenarios of pollution were considered. 70 NTU corresponding to a extremely high polluted area and 30 NTU, which is the range of the turbidity in big cities like Barcelona. (Llopart et al, 2010)

5.1.2.1 Water contaminated with 70 NTU

2 steps are involved in the decontamination of suspended matter:

- 1) Removal efficiency by decantation
- 2) Removal efficiency by filtration

5.1.2.1.1 Removal efficiency by pre-sedimentation

The volume of stormwater is 6l, this amount is prepared and pre-sedimentated by using a decantation system. The experiment has been repeated 3 times.

This is an experiment without the cork columns.

	First 2l	Second 2l	Third 2l
Initial turbidity (NTU)	67,2 (7,81)	65,4 (2,62)	67,4 (2,39)
Turbidity after pre-sedimentation (NTU)	43,2 (5,02)	29,0 (3,94)	29,6 (3,64)
% Removed by pre-sedimentation	35,7	55,7	56,1

Table 6: Turbidity measurements 70 NTU and removal percentages (Averages, standard deviations between brackets, n=9)

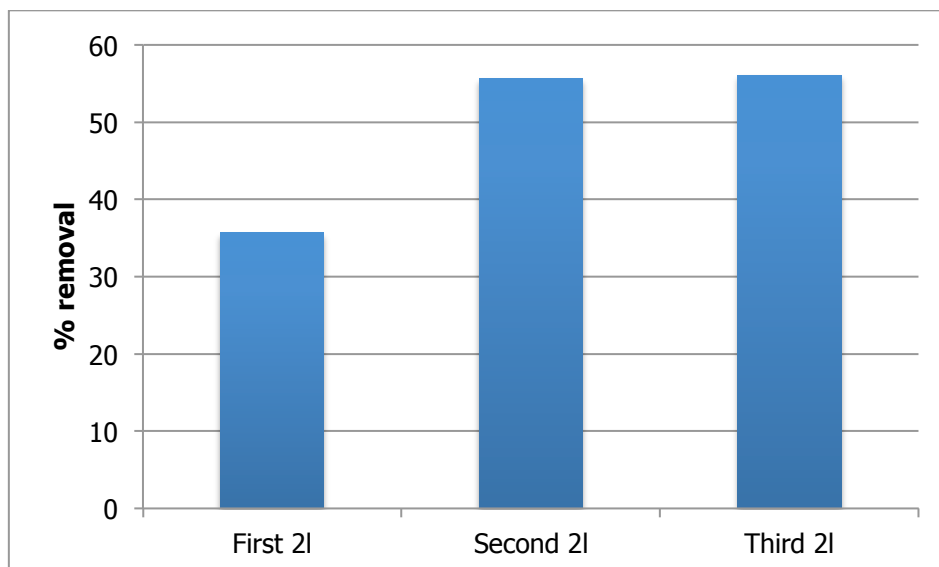
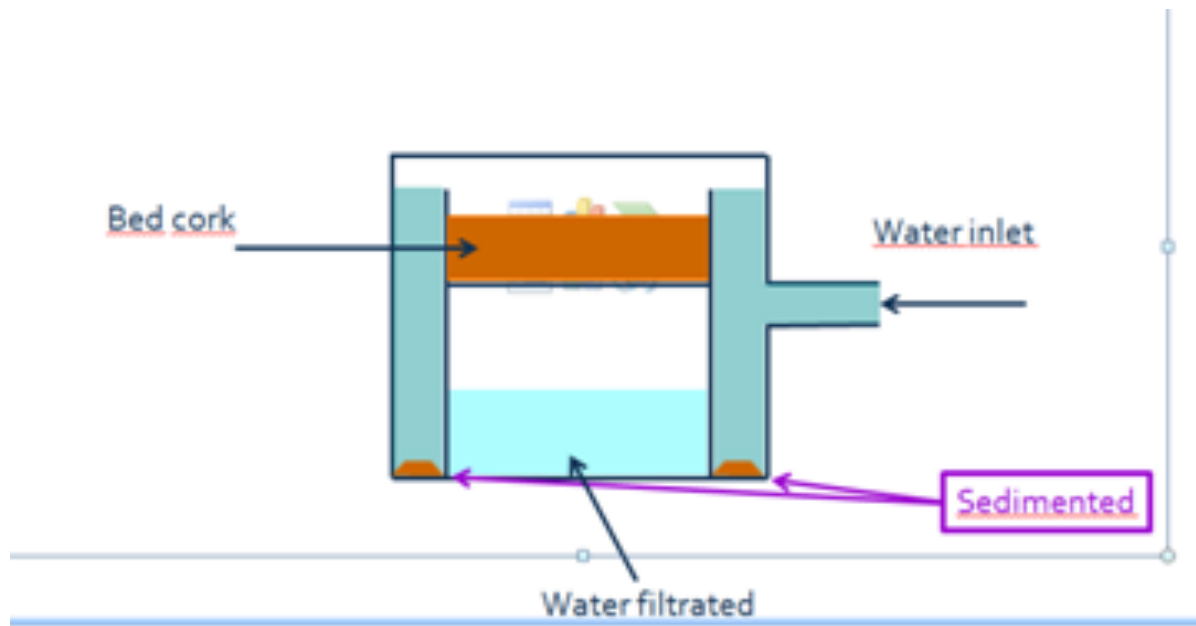


Figure 25: Percentage removal by pre-sedimentation for 70 NTU stormwater

As observed in the figure 25, the use of a pre-sedimentation step before filtering through cork column is efficient to significantly reduce the physical contamination: an average of 49% is removed by using a simple previous decantation. In addition, this method is an easy, efficient and cost-effective way, which permits a significant removal of suspended solids before filtering. According to this, the design of the tank is given in Fig 26.

However, if the stormwater would only be pre-sedimentated, it has no further water reuse applications (Table 5) because turbidity is still too high (> 30 NTU).



afanir notes

Figure 26: Design of the tank containing the bed cork filter

5.1.2.1.2 Removal efficiency by filtration

The volume of stormwater is 6l, it is prepared previously, the initial turbidity is measured and also a measurement after pre-sedimentation. An amount of 2l of water after being pre-sedimentated is passed through each column; the experiment has been repeated 3 times.

	First 2l	Second 2l	Third 2l
Initial turbidity (NTU)	67,2 (7,81)	65,4 (2,62)	67,4 (2,39)
Turbidity after removing down layer (NTU)	43,2 (5,02)	29,0 (3,94)	29,6 (3,64)

Turbidity after passing column:

	First 2l	Second 2l	Third 2l
5 cm (NTU)	33,7 (2,36)	21,84 (2,25)	26,17 (1,80)
15 cm (NTU)	21,6 (1,93)	16,64 (0,76)	17,62 (1,08)
24 cm (NTU)	14,88 (2,47)	8,50 (0,51)	8,35 (0,33)

Table 7: Turbidity measurements 70 NTU (Averages, standard deviations between brackets, n=9)

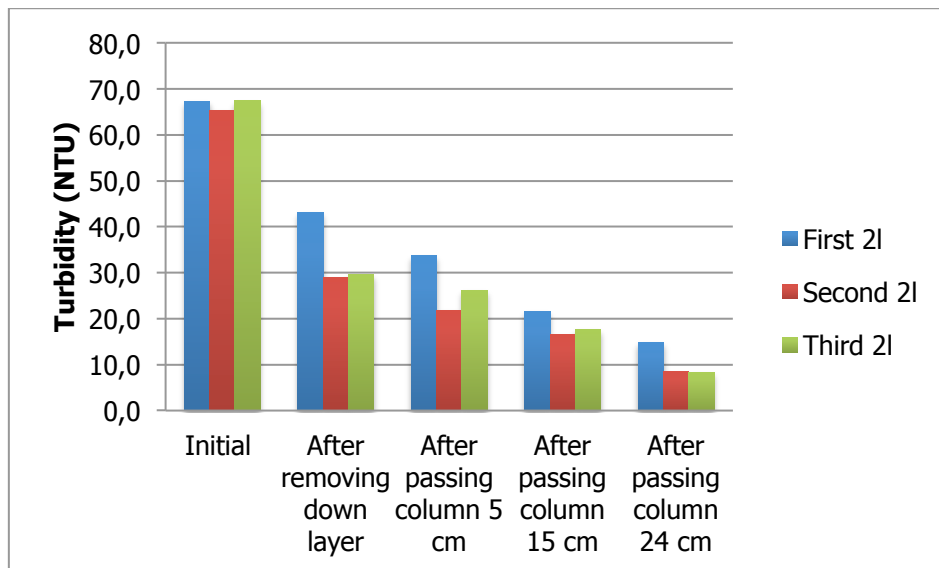


Figure 27: Course of turbidity during volume stormwater for 70 NTU

The experiments for 70 NTU has shown that the column of 5 cm isn't useful for any water reuses, the filtrated stormwater contains too many suspended matter. (Table 5)

When the column has a length of 15 cm and the stormwater is filtrated, it can reach a value of 15 NTU. This water can be used for industrial uses. (Table 5)

The highest column of 24 cm can decrease the turbidity from 33,9 NTU to approximately 10,6 NTU. These values are averages of table 7. The suspended matter is low enough to reuse the water for: urban services, agricultural, industrial and recreational uses. (Table 5)

	First 2l	Second 2l	Third 2l
Removal column 5 cm (%)	21,99	24,69	11,59
Removal column 15 cm (%)	50,00	42,62	40,47
Removal column 24 cm (%)	78,16	70,69	71,79

Table 8: Removal percentages by column for 70 NTU

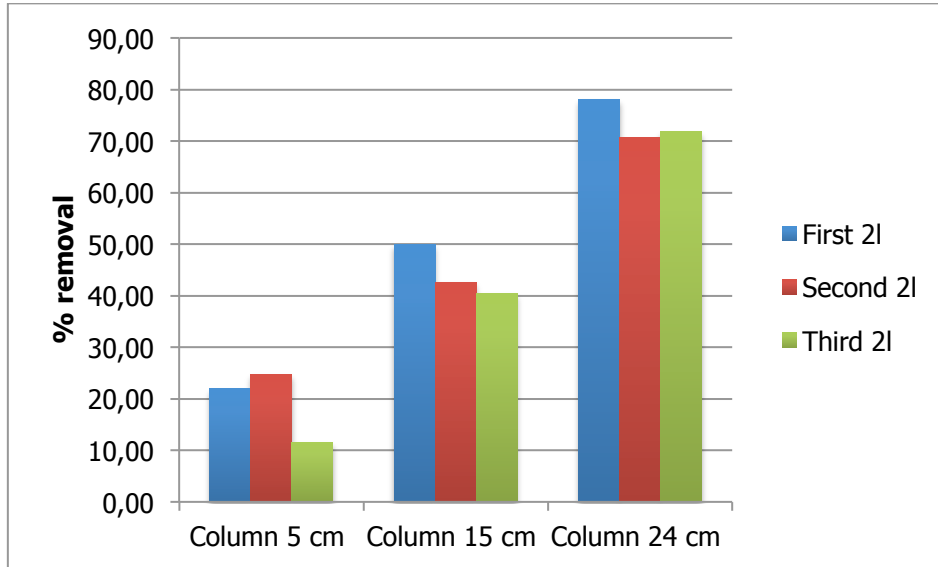


Figure 28: Percentage removal only by filtration for 70 NTU

In figure 28 the removal of suspended matter is only due to filtration, these are values calculated from the turbidity after removing the down layer.

% Removal by column of			
	5 cm	15 cm	24 cm
	21,99	50,00	78,16
	24,69	42,62	70,69
	11,59	40,47	71,79
Average	19,42	44,36	73,55

Table 9: Average removal percentages by column (Averages calculated with table 8)

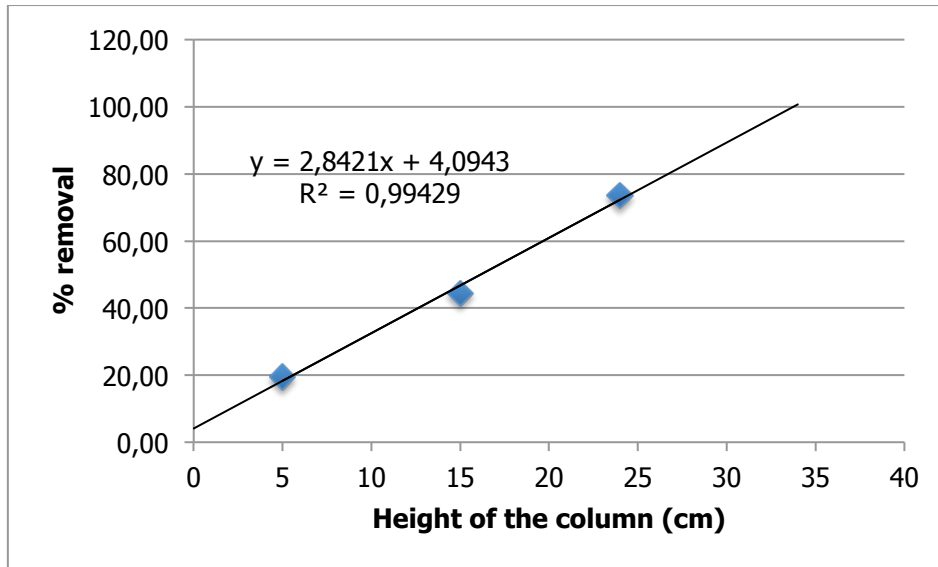


Figure 29: Average reductions by columns (filtration) for 70 NTU

The column of 5 cm has an average of reducing stormwater of 70 NTU by 19,42%, for the column of 15 cm this is 44,36% and for 24 cm it is 73,55%.

If the column is higher, it can decrease the suspended matter more.

With figure 29 predictions are possible; for example if the turbidity needs to decrease 60%, the length of the column should be 19,67 cm.

If the all the suspended matter needed to be reduced (100%), the length of the column should be 33,74 cm. This is only calculated with graph 29, this graph only exists out of 3 points, and so the outcome can be different.

As shown in table 5 the maximum turbidity the reuse the stormwater for all applications is 2 NTU.

The average percentage removed by pre-sedimentation is 49%. This removal in respect to stormwater of 70 NTU, the stormwater has a turbidity of 35,7 NTU after pre-sedimentation. If the stormwater has to be used for all applications the maximum turbidity is 2 NTU, according to table 5. This is a removal of 94,4%. For this removal a cork column of 31,8 cm is necessary based on the equation in figure 29.

5.1.2.2 Water contaminated with 30 NTU

2 steps are involved in the decontamination of suspended matter:

- 1) Removal efficiency by decantation
- 2) Removal efficiency by filtration

5.1.2.2.1 Removal efficiency by pre-sedimentation

The volume of stormwater is 6l, this is prepared and pre-sedimentated, the experiment has been repeated 3 times.

This is an experiment without the cork columns.

	First 2l	Second 2l	Third 2l
Initial turbidity (NTU)	35,3 (3,0)	35,6 (2,7)	38,6 (2,5)
Turbidity after pre-sedimentation (NTU)	13,3 (2,09)	17,2 (1,64)	21,4 (0,94)
% Removed by pre-sedimentation	62,3	51,7	44,6

Table 10: Turbidity measurements 30 NTU and removal percentages (Averages, standard deviations between brackets, $n=9$)

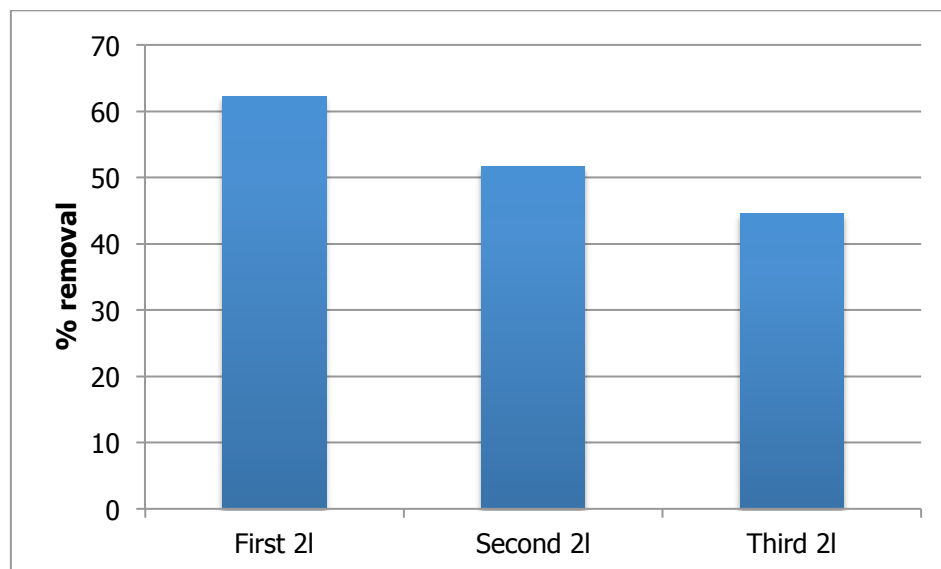


Figure 30: Percentage removal by pre-sedimentation for 30 NTU stormwater

As shown in figure 30, pre-sedimentation can remove 52,9% of the contamination before filtering. As mentioned above, this is a simple and effective method to remove most of the suspended matter and it is a cheap method.

Stormwater of 30 NTU can be pre-sedimentated to the lowest turbidity of 13,3 NTU; it can be used for industrial uses. (Table 5)

5.1.2.2.2 Removal efficiency by filtration

The amount of stormwater is 6l, this volume is prepared previously, the initial turbidity is measured and also a measurement after pre-sedimentation. 2l passed through each column, the experiment has been repeated 3 times.

	First 2l	Second 2l	Third 2l
Initial turbidity (NTU)	35,3 (3,0)	35,6 (2,7)	38,6 (2,5)
Turbidity after removing down layer (NTU)	13,3 (2,09)	17,2 (1,64)	21,4 (0,94)

Turbidity after passing column:

	First 2l	Second 2l	Third 2l
5 cm (NTU)	9,52 (0,60)	14,51 (1,44)	16,72 (0,59)
15 cm (NTU)	5,66 (0,64)	11,92 (0,90)	14,52 (0,93)
24 cm (NTU)	2,16 (0,15)	6,09 (0,43)	5,99 (0,25)

Table 11: Turbidity measurements 30 NTU (Averages, standard deviations between brackets, n=9)

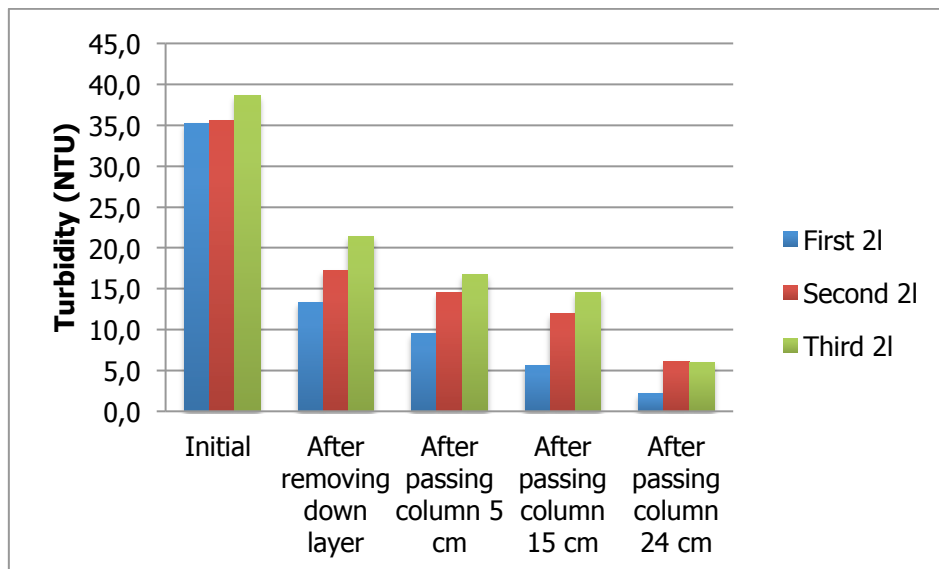


Figure 31: Course of turbidity during volume stormwater for 30 NTU

The column of 5 cm can reduce the suspended matter to 10 NTU. This stormwater can be reused for urban services, agricultural, industrial and recreational uses. (Table 5)

When the length of the column is 15 cm, it has the potential to reduce the turbidity to 5,66 NTU. This value is low enough to reuse the stormwater for urban services, agricultural, industrial and recreational uses. (Table 5)

The column of 24 cm achieves the best reduction of turbidity; this column has the potential to remove suspended matter to 2 NTU. This stormwater can be reused for all applications. (Table 5)

	First 2l	Second 2l	Third 2l
Removal column 5 cm (%)	28,42	15,64	21,87
Removal column 15 cm (%)	57,44	30,70	32,15
Removal column 24 cm (%)	83,76	64,59	72,01

Table 12: Removal percentage by column for 30 NTU

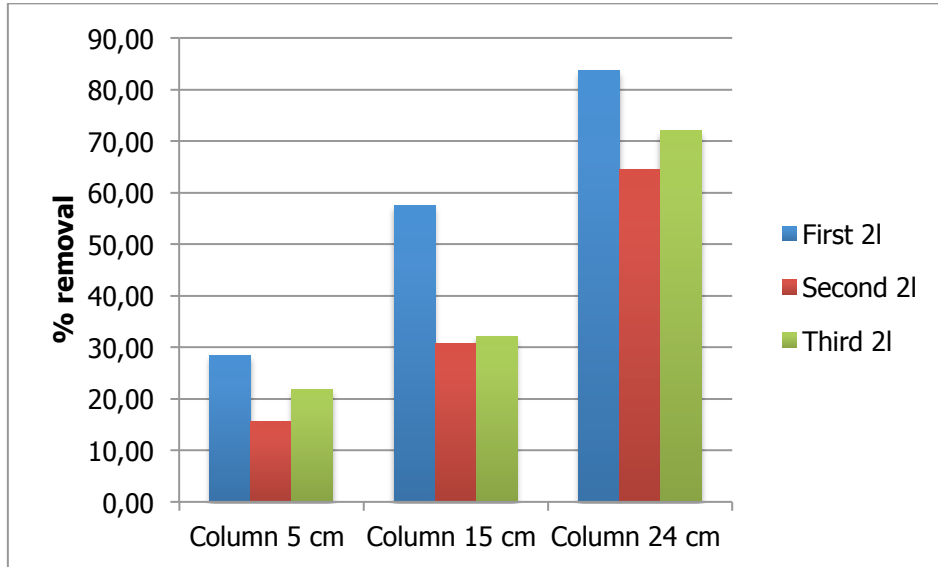


Figure 32: Percentage removal only by filtration for 30 NTU

In figure 32 the removal of suspended matter is only due to filtration, these are values calculated from the turbidity after removing the down layer.

	% Removal by column of		
	5 cm	15 cm	24 cm
	28,42	57,44	83,76
	15,64	30,70	64,59
	21,87	32,15	72,01
Average	21,98	40,10	73,45

Table 13: Average removal percentages by column (Averages calculated with table 12)

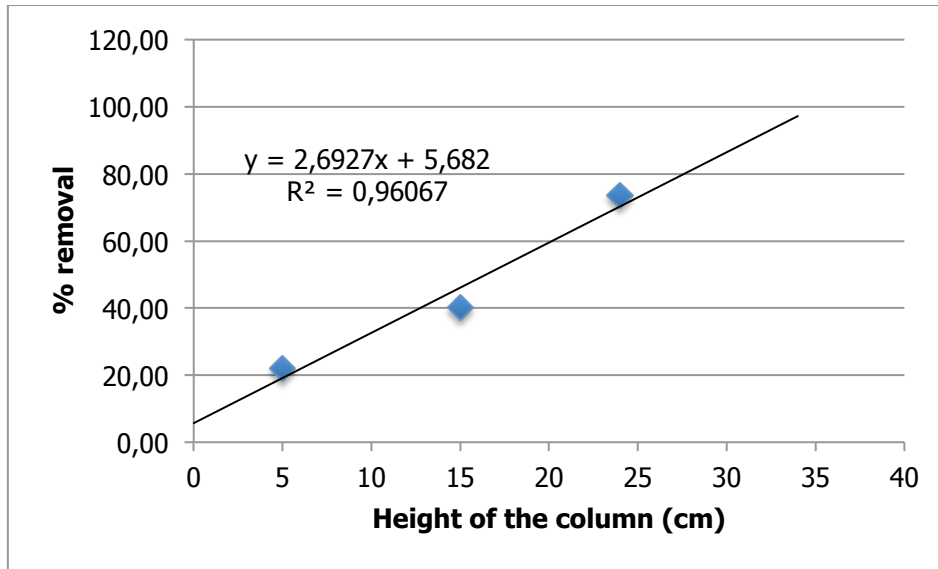


Figure 33: Average reductions by column (filtration) for 30 NTU

Stormwater with a turbidity of 30 NTU can be reduced 21,98% by a column of 5 cm, 40,10% by a column of 15 cm and 73,45% with a column of 24 cm.

With graph 33, it is possible to do predictions; if the suspended matter has to be reduced with 85%, the length of the column should be 29,46 cm.

As shown in table 5 the maximum turbidity the reuse the stormwater for all applications is 2 NTU.

The average percentage removed by pre-sedimentation is 53%. This removal in respect to stormwater of 30 NTU, the stormwater has a turbidity of 14,1 NTU after pre-sedimentation. If the stormwater has to be used for all applications the maximum turbidity is 2 NTU, according to table 5. This is a removal of 85,8%. For this removal a cork column of 29,8 cm is necessary based on the equation in figure 33.

5.2 HEAVY METALS

The investigation of heavy metals is divided into 2 different steps:

- 1) Influence of the matrix (i.e. particulate matter and suspended matter) on the sorption of heavy metals
- 2) Removal efficiency of heavy metals by the cork columns

Several experiments are carried out in each step. Three matrixes are prepared:

- 1) Tapwater + [Cr(III)] 20 mg/l
- 2) Stormwater without particles + [Cr(III)] 20 mg/l
- 3) Stormwater with particles + [Cr(III)] 20 mg/l

5.2.1 Interaction suspended matter and Cr(III)

5.2.1.1 Stock and standard solutions

Standards are prepared to determine the concentration Cr(III) in the samples with AAS.

Stock 1: 1000 mg/l Cr (III)

Stock 2: 100 mg/l Cr (III)

Stock 3: 10 mg/l Cr (III)

Number	Concentration (mg/l Cr ³⁺)	Volume stock 3 (ml)	MQ water
1	0,1	1,0	Dilute until 100,0 ml
2	0,5	5,0	
3	1,0	10,0	
4	2,0	20,0	
5	10,0		

Table 14: Standard solutions Cr(III), interaction suspended matter

5.2.1.2 Analysis of Cr(III) using AAS

These experiments are performed without using the cork columns. Samples are taken after 1 min, after 1 hour and after 24 hours that Cr(III) is in contact with the different solutions (i.e. tapwater, dissolved matter and stormwater).

An initial concentration of 20 mg/l Cr(III) is added to all three solutions.

	Conc Cr ³⁺ _{tapwater} (mg/l)	Conc Cr ³⁺ _{stormwater without particles (dissolved matter)} (mg/l)	Conc Cr ³⁺ _{stormwater with particles} (mg/l)
After 1 min	18,16	16,72	16,64
After 1 hour	19,04	16,72	16,88
After 24 hours	18,88	16,80	16,84

Table 15: Analysis of Cr(III), interaction suspended matter on sorption heavy metals

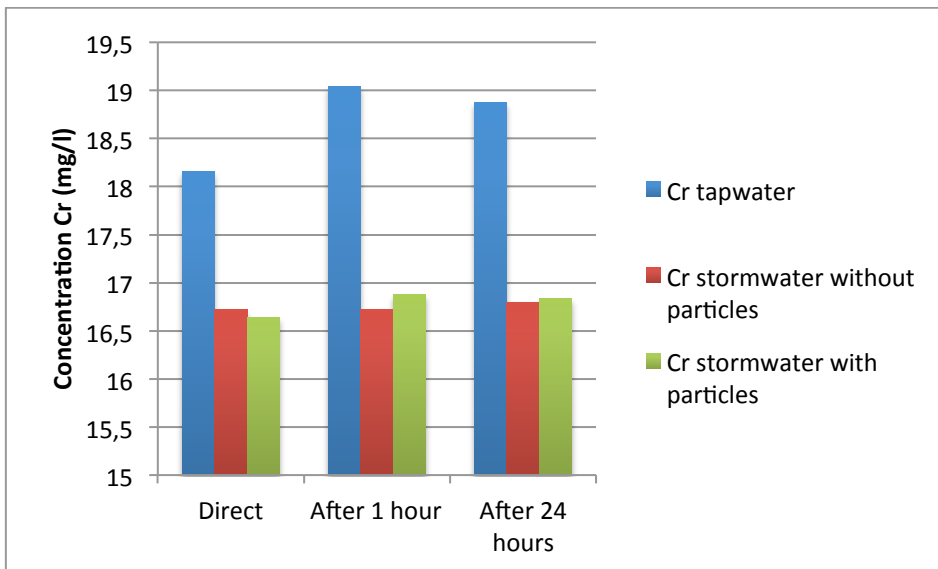


Figure 34: Analysis of Cr(III), interaction suspended matter on sorption heavy metals

As shown in table 15, Cr(III) concentrations remain almost the same at the 3 different times. This indicates that there is no significant difference of concentration in function of the time.

An initial concentration of 20,0 mg/l Cr(III) is added, as shown in table 15, the direct sample taken has an average of 17,17 mg/l. The Cr(III) concentration decreases with an average of 14% in respect to the added initial concentration. This can be due to the time the sample is taken and the sample is measured.

It was also observed that there is no significant difference in Cr(III) concentration for stormwater with or without particles. This means that there is no significant influence of the suspended matter on the sorption of Cr(III). In contrast, we observed that dissolved matter (particles less than 0,45 μm) has influence on sorption of Cr(III) because Cr(III) concentration decreases 10,38% after being in contact with this matrix.

5.2.2 Cr(III) removal by columns

5.2.2.1 Stock and standard solutions

Standards are prepared to measure the removal efficiency of Cr(III) by the cork columns with AAS.

Stock 1: 1000 mg/l Cr (III)

Stock 2: 100 mg/l Cr (III)

Number	Concentration (mg/l Cr ³⁺)	Volume stock 2 (ml)	MQ water
1	5,0	5,0	Dilute until 100,0 ml
2	10,0	10,0	
3	15,0	15,0	
4	20,0	20,0	
5	25,0	25,0	

Table 16: Standard solutions Cr(III), removal by columns

5.2.2.2 Analysis of Cr(III) using AAS

The removal efficiency of Cr(III) by the cork columns is examined, as above, with the same 3 matrixes. Cr(III) is added with a concentration of 20 mg/l, a sample is taken after 1 min, to determine the initial concentration.

After adding the Cr(III), the solutions are poured through each column and samples are taken after this step. The removal efficiency is measured using AAS.

	Initial concentration Cr ³⁺ (mg/l)	Concentration Cr ³⁺ after passing column 5 cm (mg/l)	Concentration Cr ³⁺ after passing column 15 cm (mg/l)	Concentration Cr ³⁺ after passing column 24 cm (mg/l)
Tapwater	23,30	22,56	21,52	18,58
Stormwater without particles	15,95	15,14	14,80	12,68
Stormwater with particles	15,44	15,48	14,99	12,99

Table 17: Analysis of Cr(III), removal by columns

As shown in table 17, the initial concentrations are almost the same in the matrixes of stormwater without particles and with particles and higher in tapwater. This confirms the fact that dissolved matter, more than particulate matter, has more influence on sorption of Cr(III).

	Removal Cr ³⁺ after passing column 5 cm (%)	Removal Cr ³⁺ after passing column 15 cm (%)	Removal Cr ³⁺ after passing column 24 cm (%)
Tapwater	3,18	7,64	20,26
Stormwater without particles	5,08	7,21	20,50
Stormwater with particles	0,00	2,91	15,87

Table 18: Removal percentage of Cr(III) by columns

For the column of 5 cm there is almost no difference between the initial concentration and the concentration after passing the column in all three matrixes tested.

The column of 15 cm can remove an average of 5,9% Cr(III). The highest removal (7,64%) is when tap water passed through the column. Slightly lower removal (7,21%) was observed when stormwater without particles pass through the column. The lowest removal (2,91%) was obtained when particulate matter is present in the matrix (i.e. real stormwater). These results indicate that the type of matrix has influence on the sorption of Cr(III). The same trend was observed for the cork column of 24 cm.

The highest column (24 cm) is able to reduce the Cr(III) concentration with an average of 18,9%. This column has the highest removal (20,50%) when stormwater without particles passed the column. Almost the same removal (20,26%) is obtained when tapwater is passing the column. The lowest removal (15,87%) is measured when stormwater with particles (i.e. real stormwater) is poured through the cork column of 24 cm.

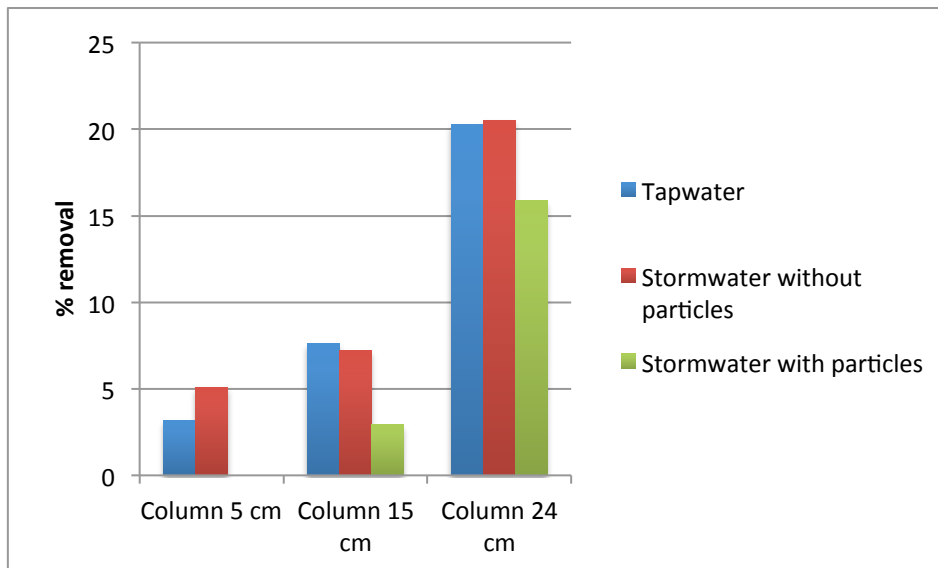


Figure 35: Removal percentage of Cr(III) by columns

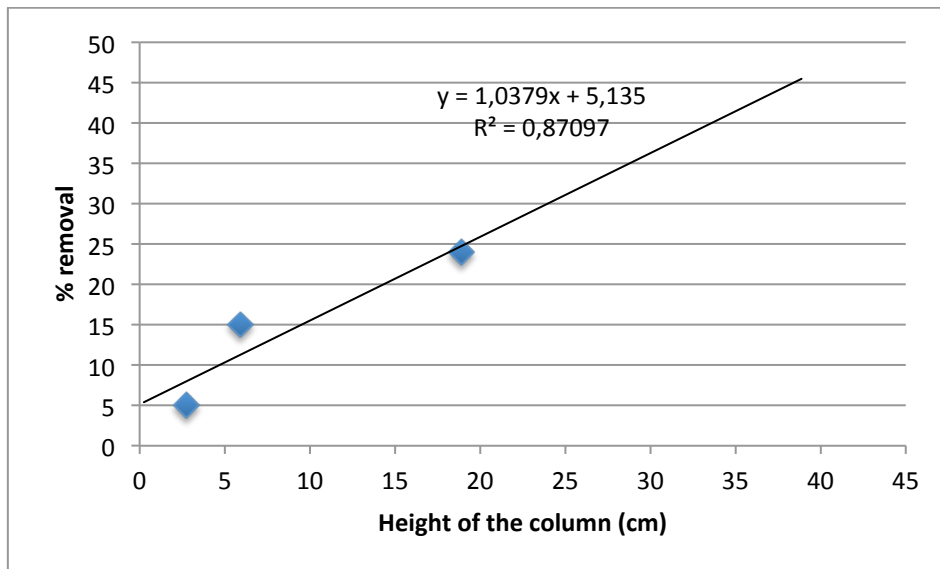


Figure 36: Average removal percentage of Cr(III) by columns

With figure 36, predictions are possible; if the Cr(III) concentration has to be reduced 100%, the length of the cork column has to be 91,4 cm. This calculation only applies on Cr(III) concentration of 20,0 mg/l or lower.

Figure 36 is a graph with only 3 points and the standard deviation isn't good, so the outcome can be different.

5.3 PAH'S

Several experiments are carried out in each step. Two matrixes are prepared:

- 1) Stormwater without particles + [anthracene] 50 µg/ml
- 2) Stormwater with particles + [Cr(III)] 50 µg/ml

5.3.1 Interaction suspended matter and anthracene

These experiments are carried out without using the cork columns. Samples are taken after 1 min, 1 hour and 24 hours that anthracene is in contact with the different solutions (i.e. stormwater without and without particles).

An initial concentration of 50 µg/ml is added to the 2 solutions.

	Area [An] _{aqueous phase, stormwater without particles (dissolved matter)}	Area [An] _{aqueous phase, stormwater with particles}
After 1 min	61 (3,189)	54 (3,199)

Table 19: Analysis of anthracene, interaction suspended matter on sorption PAH's (Ret. Time between brackets)

As shown in table 19, there is a decrease in [An] in the stormwater with particles of 11,5% in the sample taken after 1 min. This can indicate that there is an influence of the suspended matter on the sorption of anthracene.

6 CONCLUSIONS

After studying the removal efficiency of physical contamination, heavy metals and PAH's by 3 different cork columns, the following conclusions were drawn:

- The height of the column has an influence on the flow rate of the stormwater that passes the cork column. The cork column of 5 cm has a flow rate of 286 ml/min, the medium height column has a flow rate of 95 ml/min and the highest column 44 ml/min. We can conclude the higher the column, the lower the flow rate.
- A pre-sedimentation step, as well for stormwater with a turbidity of 70 NTU as for 30 NTU, can reduce the physical contamination with an average of 51%. This is a simple previous decantation that is easy, efficient and cost-effective.
- After the pre-sedimentation step and for the first scenario of pollution of 70 NTU:
 - The cork column of 5 cm can reduce the suspended matter to 19,42%, this water has no reuse applications.
 - The cork column of 15 cm can decrease the physical contamination to 44,36%, this water can be used for industrial uses.
 - The cork column of 24 cm can reduce the stormwater to 73,50%, this water has applications such as: urban services, agricultural, industrial and recreational uses.
- After the pre-sedimentation step and for the second scenario of pollution of 30 NTU:
 - The cork column of 5 cm can decrease the stormwater to 21,98%, this water has applications such as: urban services, agricultural, industrial and recreational uses.
 - The cork column of 15 cm is able to reduce the suspended matter to 40,10%. This stormwater can be used for urban services, agricultural, industrial and recreational uses.
 - The cork column of 24 cm can decrease the physical contamination to 73,45%, this water can be used for all applications.
- For the experiments with Cr(III) there is no significant interaction between the suspended matter on the sorption of Cr(III) in function of time. In contrast to these results, we observed an interaction between the dissolved matter and the Cr(III). The heavy metal (Cr(III)) removal efficiency for the column of 5 cm is 2,75%, the column of 15 cm decreases the [Cr(III)] with an average of 5,92%. The highest percentage removal is observed with the column of 24 cm, this column is able to reduce the [Cr(III)] to 18,88%.

Instruction Manual **TN-100/T-100** Portable Turbidimeter

Overview

Keys and Functions

CAL: calibration mode of the meter. When pressed, the meter is set to accept the first calibration standard. It is also used to exit the calibration mode.

READ/ENTER:

- Single-shot measurements: Press short, the display will blink for 10 times and display the measured value.
- Continuous measurements: Press and hold the key, the instrument will perform a continuous measurement.

ARROW UP/DOWN: only during calibration mode.

Turbidity Calibration

Calibration Standards

CAL 1: 800 NTU
CAL 2: 100 NTU
CAL 3: 20,0 NTU
CAL 4: 0,02 NTU

Align the mark on the vial with the mark on the meter.

Calibration Procedure

Follow the steps below at each change of solution.

- No scratches or marks on the glass vial.
- Invert the calibration standard plastic bottle 5 times. But do not shake.
- Rinse a clean vial with 3-4 mLs. Invert the vial 5 times.
- Repeat the rinsing steps and dispose of the rinsate.
- Fill the vial with the primary standard to the fill line en cap the vial.
- Clean the exterior of the vial with a cloth.
- Repeat steps 1-6 to prepare the other 3 standard solutions.

The standard reading should not drift more than 10% of the standard's NTU value. If it does, it should be replaced.

Turbidity Measurement

Preparation of Sample Vial

- Obtain a clean and dry sample vial.
- Take care to handle the sample vial by the top.
- Rinse it with 10 ml of the sample water. Repeat this for 2 times.
- Fill the rinsed vial with the sample and cap it.
- Wipe the vial with the cloth. The outside should be dry and clean.
- Apply a thin film of silicone oil on the vial.
- Wipe with the cloth.
- The vial is ready to be inserted.

Measurement Procedure

- Place the meter on a flat and level surface.
- Place the vial inside the meter. The vial's index mark must be aligned with the meter's index mark.
- Cover the vial with the light shield cap.
- Turn the meter ON.
- Press READ/ENTER.
- The measured value will appear.

Annex 1: Instruction manual: Portable Turbidimeter

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