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Landfill Leachate Treatment using Compost and Zeolites as Sorbent Materials

Master of Science Thesis in the Master's Programme Industrial Ecology – For a sustainable society

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Water Environment Technology
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Cover:

Landfill "El Carrasco", Bucaramanga, Colombia. Compost and zeolites as sorbent materials. Wetland scheme from http://www.unep.org/yearbook/2003/fig40.htm; Landfill Leachate Treatment Using the PACT® System, SIEMENS.

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Abstract

Landfill leachate could be a major problem for watercourses if not properly treated. The first step to successfully implement a treatment that suits the contamination problem of the leachate is to know what are the constituents of the leachate; contaminants as metals, pathogens, nutrients (phosphorus and nitrogen), organic compounds, to name a few.

In this thesis work chemical analysis of contaminants in leachates from a landfill, and batch beaker sorption test with real lechates, were carried out to give results to be used as a basis for suggestion of efficient treatment process of the landfill leachates.

The chemical analysis of contaminants in leachate at the Bucaramanga landfill site in Colombia showed very high concentrations of N, P TOC and As. Metals as Cd, Cr, Cu, Pb and Ni were also detected in high concentrations. For this type of contaminants, especially metals, low cost adsorbents such as zeolites and compost had been proved effective. The mechanisms of removal are ion exchange and adsorption due to charged surfaces of the zeolites and the compost material. In the laboratory batch test carried out with an zeolites and compost materials, high concentrations of metals as As demonstrated a high sorption capacity of the materials, but other compounds containing N, P and organic C could have interfered or obstructed the bonding sites for the other metals to be attached, and therefore decreased the efficiency.

Zeolites and compost had similar sorption efficiency for metals. The order of percentage removal for metals was $As > Cr > Ni$ for both materials with the following intervals 85–98% for As, 32–42% for Cr and 20–32% for Ni. Depending on the high differences in initial concentrations between the metals it was also necessary to compare the percentage removal with the metal uptake in $\mu g/g$; the metal uptake for both materials showed the following order, $Cr > Ni > As$.

Regarding nutrients sorption, zeolites showed better results for both N and P; for N, the zeolites sorption capacity was about twice as high, $15 - 36\%$ for zeolites and $3 - 19\%$ for compost respectively. For P, the compost material behaved randomly with sorption of $9 - 15\%$ for three measurements, and zero sorption and even a release of phosphorus in the other two; with zeolites the sorption range was $10 - 25\%$.

In order for the different options for leachate treatment to be implemented, it is necessary to improve local legislation towards strict thresholds for contaminants. Legal regulations of emissions would not only promote the implementation of adequate treatments, but also the development of new technologies.

Key words: zeolites, compost, metals, sorption.

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Preface

This paper analyzes the potential that compost and zeolites has as adsorbents for metals and nutrients, more specific, arsenic, cadmium, chromium, copper, lead, nickel, nitrogen, phosphorus and organic carbon as constituents of a landfill leachate.

The tests have been carried out from February to late May 2011 in Bucaramanga, Colombia. The leachate samples were taken at the landfill "El Carrasco". The preparation of the samples and laboratory work was performed at Universidad Pontificia Bolivariana – seccional Bucaramanga (UPB) and the chemical analysis of metals concentration in the Laboratorio químico de consultas industriales of Universidad Industrial de Santander (UIS).

It is important to mention the institutions that were part of the project as Empresa de Aseo de Bucaramanga (EMAB) who gave access to the landfill for the sampling and also gave relevant information about the landfill and Universidad Pontificia Bolivariana who provided full access to the institution facilities and also financed all the costs of the project.

I would like to thank the supervisors of the study Assistant Prof. Yuliya Kalmykova and Associate Prof. Ann-Margret Strömvall from Chalmers University of Technology and MSc. Yolanda Gamarra from UPB who went side by side and believed in the project from the beginning. Must mention as well the assistants of the project Nazira Quizena, Camilo Franco, Andres Salazar and the laboratory personnel Naydu Villamizar who I thank for their help during sampling and the laboratory work and of course the directives of UPB who supported and helped the project to develop (MSc Luis Eduardo Castillo, Dr Luis Felipe Casas, Eng Samuel Montero, PhD Maria Fernanda Serrano and Mgr Primitivo Sierra Cano).

This project could never be done without the help and guidance of the people and institutions mentioned above, for that I sincerely show my appreciation and gratitude to them.

Gothenburg June 2011

Ivan Herrera

1 Introduction

Landfills may differ in many ways, as for example with respect to the components present in the disposed waste and regulations on the types of waste that may be accepted. United States federal agency started with landfill regulation after 1984 (Federal Emergency Management Agency, 2002), in Sweden the Swedish EPA is the responsible agency which continues improvement in legislation as the one adopted in 2001 (EC Directive (99/31/EC)), and later in 2005 the Council Decision 2003/33/EC was implemented. For Colombia the first regulation adopted in 1998 (EMAB, 2010). Therefore, all kind of waste was disposed before the legislation, mixing hazardous waste, household waste, scrap, metals etc. It is also possible that early landfills were constructed with no leachate and gas collection system. This mix of wastes is and will be a problem that municipalities will have to deal with, even if new regulations and methods are now implemented, the disposal from previous years still will have an environmental impact if not treated properly.

"El Carrasco" nowadays receives approximately 700 ton/day of solid waste originating from the metropolitan area of Bucaramanga and 6 small municipalities. The landfill is built in terraces; each terrace is around 5 meter high and is covered with impermeable soil, mostly clay; around 1 liter per second of contaminated water, so called landfill leachate is released from the landfill. Due to the mixed waste leachate may contain all kind of substances.

The treatment performed, for many years and until May 2011, in the landfill "El Carrasco" was physical-chemical treatment where flocculation and sedimentation were the main removal processes.

First the leachate from the old (closed) section and from the current used section are gathered in an open pond where it is retained, then the leachate is conducted through a canal where acid and aluminumsulfate are added to help precipitation and flocculation, finally the leachate is taken to the second pond were it will be retained for about 48 hours before release to the creek "La Iglesia".

Since May 2011 the physical-chemical treatment has been replaced for aerobic bacteria treatment and a Upflow Anaerobic Sludge Blanket UASB reactor is been build downstream to complement the actual treatment, the reactor started to work in July 2011. The reactor is the final treatment for the leachate.

1.1 Aim and goals

The aim of this project is to measure the actual pollution discharge, including heavy metals, from the leachate of the landfill "El Carrasco". In addition, organic and inorganic materials will be tested for the removal of pollutants present in the leachate in order to make suggestion of economical and feasible solutions that can be implemented in a near future as a complement to the existing treatment and on other similar landfills. The sorption capacity of compost materials and zeolites will be assessed for pollutants present in the landfill leachate.

Specific Goals

- Analyze the actual treatment process for the leachate regarding the removal efficiency of metals, nitrogen, phosphorus and total organic matter (TOC).

- Assess the sorption of arsenic, cadmium, chromium, copper, lead, nickel, nitrogen, phosphorus and TOC using compost and zeolites.
- Suggest theoretical alternative to enhance the actual treatment performed in the landfill "El Carrasco".

1.2   Scope and limitations

This research is meant to assess how effective the sorption treatment with compost and zeolites can be, regarding removal of pollutants as arsenic, cadmium, chromium, copper, lead and nickel, nutrients and total organic carbon.

The basis for the adsorbent materials choice was their availability within the city area, the low price in the market and the low quantity of material needed for the treatment.

The major limitation for this study was the number of samples analyzed; only one sample for every studied concentration of adsorbent was analyzed potentially increasing the uncertainty of the results.

Previous data about concentration of the pollutants in the leachate could not be found; therefore the results of the sorption experiment had no reference to compare with. As concentration of pollutants in the leachate were not known at the design of the experiment (due to the long chemical analysis time) it was difficult to choose an adequate quantity of adsorbent.

1.3   Site and landfill description

Bucaramanga is the most important and capital city of Santander with an area of 165 km^2; if combined with Floridablanca, Girón, and Piedecuesta, municipalities that conform the metropolitan area, the population reach over one million habitants which represents the 50% of the regional population (DANE, 2005). It is an important number because "El Carrasco" is the landfill that collects the waste from the metropolitan area together with 6 additional municipalities which amounts to the disposal of more than 50% of the waste from the whole region of Santander. The average temperature of the metropolitan area is about 27°C all year long, this characteristic is due to the location, 998 meter above sea level, the so called winter are rain periods that usually takes place from April to May and September to November, but as seen in the Table 1.1 the climate characteristic are quite stable during all year.

Table 1.1 Average climate data of Bucaramanga (IDEAM, 2005)

Month	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Annual
Max daily temp (°C)	30.0	29.0	28.0	27.5	27.1	25.0	26.1	27.4	28.3	26.6	27.2	28.5	**27.6**
Min daily temp (°C)	19	20	18.4	18	16	15	16	18	17	19	19	19	**17.8**
Total precipitation (mm)	81	90	121	133	110	112	106	103	98	133	119	73	**1279**
Days with precipitations (≥ 1 mm)	10	14	14	17	18	20	24	20	19	18	14	11	**199**
Hour of sunlight	151	116	107	106	91	90	86	118	111	114	133	123	**1346**
Humidity (%)	80	80	82	83	88	89	82	82	83	84	85	83	**83.4**

Bucaramanga is located in the middle of a seismic fault, Santa Marta − Bucaramanga fault; therefore a present high seismic activity is taken into account for all kinds of constructions. Regarding soil, specifically in the landfill zone, the upper layer is mostly clay with low permeability (SIGAM, 2002; EMAB, 2010).

Colombian geographical characteristic, with high mountains across the all territory, creates a unique hydrographic behavior of its rivers and creeks, with an important number of water sources high up in the mountain crests that later on reaches or became bigger rivers. The collision of creeks and river may eventually become a problem when contaminated watercourses pollute clean rivers downstream. An example of this is Rio de Oro which upstream is an important water source for drinking and recreational water to Piedecuesta but after it reaches the municipal area the pollution of this important watercourse begins by multiple pollution sources and one of this is the creek La Iglesia which receives the leachate from the landfill "El Carrasco".

Landfill description and operation

The 10 municipalities that dispose waste to the landfill called "El Carrasco" are: Bucaramanga, Floridablanca, Girón, Piedecuesta, Lebrija, Rionegro, El Playón, Charta, Cáchira and Suratá. "El Carrasco" is regulated by the EMAB S.A. E.S.P "Empresa de Aseo de Bucaramanga" a mixed economy company (municipal and private).

The landfill is split in three main sectors, or so called "cárcavas", that with time have been filled up with the waste from the same cities but the method of disposal has been quite different especially for the sector 2 as will be explained further down.

The history of "El Carrasco" starts in 1978 when it began as an open dump without any regulations, the trucks came with the solid waste and deposited it into the field that is now called sector 2 (see Figure 1.1).This practice continued until 1985 when the decision to change the place of disposal was made, because of the constants fires and the will to improve the final disposal of the waste. The new location becomes the zone 1 of sector 1. However, due to the lack of regulation still no care for the leachate and gases was taken.

Sector 1 is divided in two zones, zone 1 used between 1985 to 1998, in this zone waste was placed in terraces in a way that slopes of waste were sometimes uncovered increasing leachate production and presence of rodents, carrion birds and insects. Zone 2 is used since 1998, when the national legislation was created, until present, in this zone the waste is spread with bulldozers making terraces and covered with a plastic membrane and soil from the region, mostly clay, to avoid excess of infiltration. This sector has a total volume of 667 thousand m^3.

Sector 2 was used from the beginning in 1978 until 1985 and 500 thousand tons of waste was disposed. This sector just as zone 1 of sector 1 is now closed and covered with impervious material mostly clay, fireplaces were build to control the gases emerging from the decomposition of the organic matter.

Sector 3 is still unused and considerations have been made to use this sector as an expansion of the landfill, but the environmental organizations as CDMB proclaimed that "El Carrasco" must close by the end of 2011.It is important to mention that several times this decision has been postponed since, so far, there is no other alternative for the disposal of waste. This sector is still covered with native vegetation. Figure 1.1 shows a panoramic view of all the sectors of the landfill.

As can be seen in Figure1.1, the landfill is located in a small canyon with presence of high slopes; the vegetation is mostly grass and the type of vegetation of a dry area. There are no important underground aquifers in the zone that can be affected by the leachate and no surface watercourses apart from the surface run-off in periods of heavy rain.

Regarding the permeability of the natural soil, measurements were made by the EMAB (Espinoza 2004).The soil profile was divided in 9 layers that combined had approximately 90 meters depth. The results show that infiltration maximum value ($1x10^{-2}$cm/sec) was measured in one of the deepest layers, which means that it is a layer with gravel. The average value ($1x10^{-6}$cm/sec) especially in the upper layers show soil that is mostly clay with low permeability, these conditions prevents the infiltration of leachate into the soil. Even though the natural characteristics of the soil are in a safe margin of impermeability the bottom of the landfill was covered with a 40 mm geo-membrane of high density polyethylene (HDPE) to avoid damage and contamination of possible aquifers in the zone.

Figure 1.1 *Panoramic view of "El Carrasco" area (EMAB, 2010)*

The cover layer of the landfill has been made in two ways;

1) The daily cover: it's a layer of 20 cm, the material used is soil taken from the area; the soil has a fine content which leads to some permeability. For this reason the terraces must be interconnected so that leachate can be evacuated to the final treatment facility. The way to do this interconnection is to uncover areas of the previous terrace before the new layer of waste and soil is spread.

2) The final cover: this cover is done when the sector is no longer used. It's a layer of 60 cm with the same material (soil) as used for the daily cover, since the layer is thicker, when compaction is done the permeability value is much lower; a second layer must be set and this one is soil that allows vegetation to grow and prevent erosion.

The soil has a load capacity that allows a column of solid waste of 57 meters to be disposed. The load capacity is 40 ton/m^2.

The initial density of the disposed waste is about 300 kg/m^3 but after compaction, density can be between $0.7 - 0.8$ ton/m^3. Humidity present in the waste from the metropolitan area is high which leads to augmentation in microbiological processes. Another important data that must be included is the evapotranspiration with monthly values between 74 and 104 mm, this can influence further decisions for alternative treatment of the leachate.

As mentioned before "El Carrasco" is the place for the final disposal for several cities. It means that variation of the waste can be significant primary from the disposal of the mayor cities (Bucaramanga, Piedecuesta, Floridablanca and Girón) where commercial activities and industries are present and comprise around 90% (1'000.000 inhabitants of the total population that "uses" "El Carrasco"). It is allowed to dispose of commercial, industrial and household waste at "El Carrasco"; however, hazardous wastes must be treated in a special manner and are not treated at the landfill. Hazardous waste has three possible destinations, Cucuta, Medellin or Bogotá, this type of waste is incinerated in certified special ovens. (MinAmb, 2010)

Three different studies were performed in 1996, 2000 and 2002 with the intention to investigate what kind of material is usually disposed. Despite different analysis methods and time of measurement similar values can be seen for each kind of material. It is worth mentioning that no records of previous years are available. For the material disposed in sector 2, the components of the solid waste are shown in Table 1.2. In 2010 another study was performed but with a minor difference since this shows the waste from each economical class of the city, the results from this study are shown in Table 1.3.

In Colombia neighborhoods or city sectors are classified according to the economic situation of the people living in it, starting from Class 1 (Poorest or Low -Low) to class 6 (Richer or high). According to the document EMAB 2010[b], the following values represent, in percentage, the distribution of the population in the metropolitan area.

Class 1 (Low-Low) = 22.3%
Class 2 (Low) = 41.2%
Class 3 (Medium-Low) = 27.1%
Class 4 (Medium) = 6.3%
Class 5 (Medium-High) = 1.9%
Class 6 (High) = 1.2%

This classification regulates the taxes and the price of public services as well as health insurance and education in public schools and universities. Classes 1, 2, and for some services Class 3 are subsidized by the Classes 4, 5 and 6.

As can be seen from the Tables 1.2 and 1.3 the major composition of the waste, more than 70%, is organic or biodegradable material. Nonetheless, it must be taken into account that almost no recycling is performed at the source leading to the combination of all kind of waste.

It can be seen that household waste disposed at this particular landfill shows high similarity to the composition of municipal waste presented by Reeve 2002. The definition of non-hazardous waste in the references cited and in this document includes household, commercial and some industrial waste.

Table 1.2 *Waste distribution (EMAB, 2010)*

	Results of Different Studies (%)		
Type of waste	GEOTEC 2002	COGAN-RODRIGUEZ 2000	EPB-UIS 1996
Organic (c)	56.27	62.9	56
Plastic	7.88	14.9	19.4
Paper / carton	7.4	7.2	8.8
Sanitary (a)	2.93	4.4	2.7
Glass	1.26	3.5	4.2
Textile	5.67	2.7	4.6
Leather	4.19	1.97	1.9
Metals	1.03	1.7	2.4
Construction	4.28	0.46	
Hospitals	0.27	0.24	
Special (b)	0.15	0.08	
Tires	1.4	0.023	
Others	7.27		
Total	100	100.073	100

a: Toilet paper, tissues, diapers

b: Batteries, electronics, etc.

c: Food, garden res., wood

Table 1.3 *Waste characterisation by economical class (adapted from EMAB, 2010[b])*

	Economical Classes					
Type of waste	1	2	3	4	5	6
	%	%	%	%	%	%
Organic (a)	71	70	67	66	63.93	63.7
Paper	2	2	5.3	6	6.01	6.05
Carton	2	2	2.7	3	4.01	4.03
Plastic	12	13	17	15	15.03	15.13
Textile	6	5	3.5	4	4.01	4.03
Wood	1	2	1	0.5	1	1.01
Glass	3	3	1	2	2	2.02
Metals	1	2	1	2	2	2.02
Other	2	1	1.5	1.5	2	2.02

a: Food and garden residues.

1.4   Different stages of landfills

There are many parameters to classify landfills as for example construction methods, collection of the leachate, the gasses produced and type of accepted waste. It is hard to give one definition for the stages that a landfill goes through. One of the primary characteristic for the landfill is its age that influence type and concentrations of pollutants in the leachate as different processes undergo with time in a landfill. If based on Meeroff et al 2008 "El Carrasco" could be classified as: canyon method regarding the construction, solid waste landfill according to the type of waste

discharged and class I regarding the quantity of waste received, more than 20 ton/day. The age classification is difficult since parts of the landfill have been filled at different times and the leachate from "El Carrasco" contains characteristics of both, the young and an old landfill. Age of the landfill is more than 30 years in sector 2 that started as an open dump; however sector 1 is still in operation. The indicators for characterizing the landfills age and type are presented in Table 1.4.

In this study chemical oxygen demand (COD) and biochemical oxygen demand (BOD) were not measured but based on Castillo et al. 2003 and CDMB 2010 values, showed in Table 1.5 and Figure 1.2. It can be seen that the BOD_5/COD ratio values vary between 0.4 to 0.6 which places "El Carrasco" into a young-medium landfill. Values of pH in this and the studies mentioned above, are above pH = 8 and with an operation for more than 10 years "El Carrasco" fits into the old landfill category. When waste distribution is taken into account then the landfill maybe within "young" category due to the high content of the organic material disposed.

Table 1.4 *Landfill classification regarding leachate components (Meeroff et al 2008)*

Characteristic	Young Landfill	Medium Landfill	Old Landfill
Age (Years)	< 5	5 - 10	> 10
Type	Biodegradable	Intermediate	Stabilized
pH	< 6.5	6.5 - 7.5	> 7.5
COD (mg/L)	> 10000	5000 - 10000	< 5000
BOD5/COD ratio	> 0.5	0.1 - 0.5	< 0.1

Table 1.5 *Different parameters measured on "El Carrasco" (adapted from CDMB 2010)*

BOD_5	COD	D.O.	TSS	pH	F.C.	T.C.
mg/L	mg/L	mg/L	mg/L		MPN/100ml	MPN/100ml
1982.33	4830	0.0	9039.33	8.34	2400000	2400000
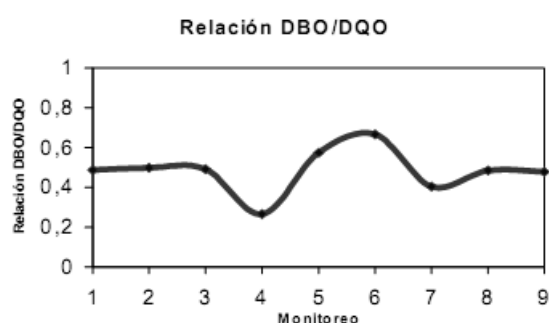
Figure 1.2 *BOD_5 / COD ratio of leachate (Castillo et al, 2003)*

Meeroff et al 2008 mention three stages of a landfill: biodegradable, intermediate and stabilized; an explanation of these stages is held in the lines below.

Landfill is in the biodegradable stage when the organic material disposed in the landfill is decomposed by aerobic microorganisms, also called aerobic stage. Decomposition leads to high internal temperatures and release of CO_2 and water which due to the carbon dioxide content is quite acidic and causes dissolution of minerals and leaching of metals.

The intermediate stage in a landfill occurs when the air inside the landfill starts to be depleted because of the earlier aerobic processes, and then anaerobic microorganisms continue with the decomposition labor, creating organic acids. Leachate pH decreases to around pH $= 5 - 6$, and metal concentrations as well as oxygen demand increase substantially, eventually gases like ammonia and carbon dioxide are produced. This can be also called the anaerobic – acid stage.

The final stage is the stabilized phase when all the biodegradable matter has been consumed and transformed by the microbial activity, BOD_5/COD ratio is low, and landfill is considered as stable. Methane gas is being produced by degradation of organic acids and due to the reaction between CO_2 and hydrogen gas; in this stage the pH starts to increase and metal concentrations consequently decrease, this stage is also called methanogenic and starts after approximately six months after the cell is covered (Meeroff, 2008; Baird and Cann, 2008).

1.5   Pollutants

Landfills can release many different types of pollutants because a mixture of wastes is disposed. Pollutants like heavy metals, ammonium, sulfate, organic compounds, persistent organic pollutant, etc. can be found in the leachate. High concentration and reactions between substances can transform them from harmless to hazardous components; in addition the process called synergy (reinforcement) can occur regarding the toxicity of the pollutants.

In this study the heavy metals are the main concern, however, the nutrients (nitrogen and phosphorus) will also be mentioned.

Nutrients as pollutants

Eutrophication is the process when nutrients as N and P cause environmental damage. Excess of nutrients leads to an extreme growth of plants and algae. Eventually vegetation, after the regular life cycle, will die and high quantities of biomass will accumulate at the bottom of the watercourses and lakes. Further, the decomposition of the biomass by microorganisms will deplete the dissolved oxygen and cause oxygen deficiency that may kill fishes and other organisms. Depending on whether it is fresh watercourses or coastal waters the limiting nutrient will vary; phosphorus is the limiting nutrient for fresh waters and nitrogen is for coastal waters (Hill, 2010).

Metals

Trace metals are often toxic to living organisms and the toxicity can vary depending on the form: dissolved in water or in the free ion form, in their organic form and even the oxidation state can show different toxic behavior (Baird and Cann, 2008; Reeve, 2002). Trace metals are characterized by bioconcentration (accumulation of a substance in a living organism, when it is unable to metabolize it or does it in a slow rate), synergism (higher toxic effect when substances combine as the effect they will have separately); partitioning to sediments through adsorption, ion exchange and precipitation and potential re-dissolution into the water column at changed environmental conditions. Metals mobility across the environment is by atmospheric pollution, surface water pollution (dissolved or as a complex), they are also naturally present in the soil. Human toxicity due to metal intake is mainly due to the effect that metal-sulfur bond has on the enzymes that regulate the speed of metabolic reactions;

the metals cations attach to the sulfhydryl group collapsing the normal behavior of the enzyme, effects of this can be fatal.

1.6   Adsorption properties of zeolites and compost

Adsorption is a process of fixation of ions or even molecules (adsorbate) to the surface of a solid (adsorbent); the adsorbate can be in a form of gas, liquid or solid phase. An adsorption phenomenon is caused by intermolecular attractions; three forms of adsorption can be named, physical, chemical and ion-exchange where Van der Waales forces, chemical bonds (usually covalent) and substitution of similar charged ions are the main characteristics respectively.

Removal of nitrogen, phosphorus and organic pollutants with adsorbent material like zeolite has been tested with good results, which means that any of the three types of adsorption will be present and competing with metals ions.

Multiple layers of adsorbate can be placed over the adsorbent surface. Once the active site or surface of the adsorbent has been occupied by physisorption, processes like chemisorption or ion-exchange can't occur.

The adsorption efficiency decreases when macromolecules and/or suspended particles are present in the solution (Inglezakis and Poulopoulos, 2006), this must be taken into consideration for further analysis of results.

Zeolites

Zeolites are naturally occurring alumino-silicate minerals. Due to their composition they have the capability of adsorption in three ways: ion-exchange, physisorption and chemisorption. The way adsorption is performed is by the substitution of cations present in the zeolites (sodium, potassium, calcium, magnesium) by metal cations present in the solution, by Van der Waals forces or covalent bonds respectively.

In zeolites a permanent negative charge is present due to Al^{3+} substitution for Si^{4+} in the mineral structure. The negatively charged surface attracts cations present in the solution (Mozgawa and Badja, 2005).

Clinoptilolite was the zeolite used in this study primarily because of its abundance and its good performance as adsorbent, containing a SiO_2/Al_2O_3 ratio, by mol, between 8 and 12.The lower the ratio the better the adsorption rate since the presence of Al promotes the adsorption properties (Rodriguez 1997). Table 1.6 gives some examples of different configurations of zeolites (Clinoptilolite) which are fairly similar; Tasajera, Piojillo and San Andres are Cuban extraction sites while West Anatolia is from Turkey.

Table1.6 Zeolite composition (adapted from Canosa et al 2000, Cabrera et al 2005 and Erdem et al 2004)

Composition (wt %)	Clinoptilolite named by excavation site				
	Tasajera (a)	Piojillo	San Andres	Tasajera (b)	West Anatolia
SiO_2	66.6	64.3	63.2	62.4	69.3
Al_2O_3	12.2	9.43	12.5	13.1	13.1
Fe_2O_3	2.08	2.18	0.81	1.63	1.31
CaO	3.19	3.24	2.36	2.72	2.07
MgO	0.77	0.81	0.69	1.22	1.13
Na_2O	1.53	2.08	1.20	3.99	0.52
K_2O	1.20	1.00	2.31	1.20	2.83
Other	11.0	15.1	15.5	13.2	6.98
Total	98.6	98.1	98.5	99.4	97.3
SiO_2/Al_2O_3 (mol)	9.29	11.6	8.61	8.05	8.97

Zeolites adsorption of metals and other substances is recognized which leads to the question, why is it not used in more extent for contaminated water treatment? A possible reason is that knowledge about performance of the zeolites in liquid with multiple substances or pollutants is limited so no accurate behavior can be predicted, some isotherms, i.e. mathematical models that shows how much adsorbate will be attached to the adsorbent, have been developed but still no mathematical model can be adopted for this purpose.

Some characteristics that suggest utilization of zeolites for wastewater or leachate treatment are, abundance and easy extraction which leads to fairly low price in the market (100 USD/ton), stability to chemical and thermal processes which allows the reutilization of it.

Compost

Compost can be defined as organic material that has been decomposed by bacteria, fungi and worms. The surface of the decomposed organic material contains broken cell walls that are negatively charged which provide good conditions for cations, such as metal ions, to bond either by adsorption or ion-exchange. Humic substances from the organic material are the major sorption agents (sites) (Seelsaen et al., 2007).

It is known that living biomass also traps metals as they are "consumed" by plants through the roots or just attached to them by the bacteria and microorganisms living in the roots (Baird and Cann, 2010). In such a way the biomass may be toxic when ingested as fruits, seeds etc (Bailey et al., 1998).

One of the obvious advantages for compost use as a filter material is the availability since organic waste (garden, household, restaurants etc) can be found in every place also it is considered as that, waste. This means that price for the adsorbent material will not be a major concern.

Previous studies with compost concentration of 1 – 10 g/L has shown important results for adsorption of heavy metals with removal values up to 97% with metal initial concentration of 100 mg/L (Seelsaen et al., 2007).

1.7 Freundlich isotherm

The sorption isotherm represents the amount of sorbate in a solid phase (bound at the surface of the adsorbent) as a function of the material still in the solution. The equation used in this study was the Freundlich isotherm as it fits better for the characteristics of the material used, such as heterogeneity of adsorption sites (Kalmykova 2009).

Freundlich equation can be written in two ways, exponential or linear as follows:

Exponential

$q = K_f * C^n$

Or

Linear

$\text{Log } q = \text{Log } K_f + n * \text{Log } C$

Where

q: Concentration of adsorbate per unit of adsorbent ($\mu g/g$).

K_f: Freundlich unit capacity coefficient ($\mu g/g$)

C: Concentration of adsorbate in solution ($\mu g/l$)

n: Adsorption exponent ($\mu g/l$)

The isotherm will be more accurate as the regression coefficient (R^2) is closed to 1, the calculation of n and K_f is given by the slope of the graph and the value of Y when X is zero or to mention in other way, when the plot line intercept the Y axis.

2 Experimental procedure

This chapter explains the research procedure; preparation for sampling, sampling and field work, laboratory work and laboratory methods and analyses.

Different references were taken as guidelines for the experimental procedure as stirring time, adsorbent quantity, material of the bottles, etc.

2.1 Preparation for sampling

Preparation for sampling requires cleaning of all containers that are going to be in contact with the sample; the purpose is to avoid any contamination that would alter the result values of the substances analyzed. Plastic containers of 4 L capacity were used for the collection of the leachate on the landfill. All the plastic bottles were filled with 10% HCl and left for 24 hours and thereafter rinsed multiple times with deionised water; plastic bottles were chosen to avoid contamination of metals coming from the bottles itself (Reeve, 2002; Erdem et al, 2004). Amber coloured bottles, 120 ml, were used for the TOC analysis to prevent photocatalytic decomposition of the organic material.

Figure 2.1 Sample bottles.

2.2 Sampling and field work

Samples were taken directly from the leachate treatment facility located on the territory of the landfill; four points were chosen for sampling. Table 2.1 and Figure 2.2 give an explanation for the location of these points.

Table 2.1 Description of sample location

Name	Description of location
P1	Pure leachate at drainage pipe outlets (Before enter pond 1 - No treatment)
P2	Connection canal after pond 1, before addition of the chemicals
P3	Connection canal (After addition of HCl, before addition of aluminum sulfate)
P4	Outlet of pond 2 (Treated leachate)

Figure 2.2 *Sample locations*

Pond 1 gathers leachate coming from two different points of the same landfill; one pipe discharges the leachate from sector 2 and another one from sector 1.The procedure for taking the leachate from these pipes were to fill half bottle from each pipe, this condition can be applied due to the fact that the flows coming from both pipes are similar, 0.67 l/s and 0.84 l/s for sector 2 and 1 respectively.

2.3   Laboratory work

After leachate was gathered the laboratory work was divided in two major steps:

1. Preparation of samples for substances concentration analysis of untreated leachate.
2. Preparation of samples for substances concentration analysis of leachate treated in sorption beaker tests with compost and zeolites.

Samples without treatment

For this step, four samples, for every point (P1, P2, P3, P4), were put in the clean bottles and sent to the accredited laboratory "Laboratorio Químico de Consultas Industriales, UIS" for analysis of metals, nutrients and TOC; the samples were not pretreated with filtration or sedimentation.

Vacuum filtration, with 0.45μm cellulose acetate filters, to another set of samples from P1 and P4 was intended to be performed for dissolved metals analysis. The filters clogged almost immediately, probably because of a high quantity of particles, organic material and colloids, for this reason sedimentation of the leachate was chosen instead as follows:

1. Decantation of the initial sample.
2. The original sample was split in three bottles and time was given for sedimentation.
3. With a pipette leachate was taken from the three bottles to the plastic bottles, taking equal quantity of each one.

4. Finally samples were acidified with concentrate nitric acid (1% v/v) to avoid precipitation and adsorption to the bottle walls (Hui et al, 2005).

The samples were named P1 Sed and P4 Sed.

Sorption beaker tests with zeolites and compost

Small quantities of sorbent material, compost and zeolites, was used in the experiments according to the laboratory protocol by Kalmykova 2009.

The treatment of the leachate with adsorbents has been conducted as following:

1. Leachates from points P1 Sed and P4 Sed, with no preservation, were added into the beakers along with the zeolites, five different concentrations of adsorbent were used(0.1, 0.25, 0.5, 1.0 and 2.0 grams of adsorbent for 500ml of leachate)
2. All five beakers were stirred for 24 hours at 181 rpm; E&Q Floculador was used. Previous studies report 24 hours as equilibrium time for the stabilization of the adsorption process (Mozgawa and Bajda, 2005; Seelsaen et al, 2006).
3. After stirring, samples were allowed to settle for 30 minutes.
4. With a pipette treated leachate was carefully placed to a new bottle.

Treated P4 Sed samples for nutrients and TOC measurements were taken directly to the laboratory for the analysis; samples for metal analysis were acidified and kept in the fridge. Note that nitrogen, phosphorus and TOC were not measured for treated P1 Sed leachate; explanation for this will be given in the Results and Discussion chapter.

The same procedure 1-4 was performed when compost was used as adsorbent material.
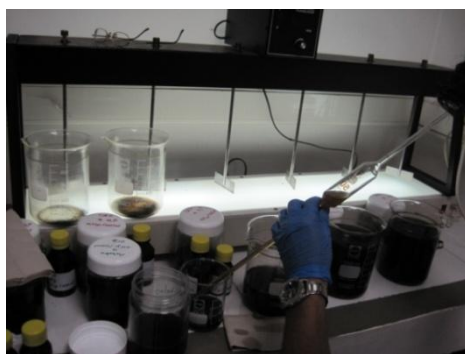

Figure 2.3 *Sorption Beaker Test*

Figure 2.4 *Treated leachate has been transferred to measurement Bottles with a pipette.*

On the beakers placed on top of the flocculation stirrer machine the sediments left behind can be seen.

Composition of the sorption materials

Selected zeolites

The zeolites used for the study comes from Ecuador and has been purchased through the Colombian company Isapinher Ltda. This zeolite is called clinoptilolite and is part of the zeolite group of Heulandites.

The diameter of the particle size chosen was 1-3 mm; its density is 1.71 g/cm^3 and an ion exchange capacity of 2.54 meq/g.

The chemical composition of this kind of zeolite is hydrous sodiumaluminium-silicate.The chemical distribution given by the company is SiO_2, Al_2O_3, $TiO2$, Fe_2O_3, Na_2O, although, no percentages of each component were provided.

If clinoptilolite is dehydrated it will easily adsorb H_2O, NH_3, N_2, O_2 and CO_2 (Morante, 2004).

Specific areas of the selected granulometry are:

- $5.8 \; cm^2/g$ for 1 mm particle size,
- $2.9 \; cm^2/g$ for 2 mm particle size and
- $1.9 \; cm^2/g$ for 3 mm particle size

Selected compost material

For this study the compost was gathered from garden waste of the UPB and has been in decomposition for about 6 months. The compost was air-dried for a period of approximately 72 hours before the experiments.

The compost was grinded and particle size was about 1 to 3mm.

Chemical analysis

The chemical analysis methods used by the analysis laboratory are:

Table 2.2 Chemical analysis methods

Analysis demanded	Units	Method
Total Nitrogen	mg N/L	Kjeldhal-Titrimetric
Total Phosphorus	mg P/L	Spectrophotometric
Arsenic	mg as/L	Atomic absorption/Hydride generation
Cadmium	mg Cd/L	Atomic absorption
Chromium	mg Cr/L	Atomic absorption
Copper	mg Cu/L	Atomic absorption
Lead	mg Pb/L	Atomic absorption
Nickel	mg Ni/L	Atomic absorption

3   Results and discussion

In this chapter results will be presented regarding concentrations of pollutants in untreated samples (further - "initial concentration"), after adsorption using organic and inorganic materials and comparison to guidelines for metals, total N, total P and TOC.

After initial concentration results were analyzed, the decision of which sample should be used for the sorption experiment was taken. The criteria to choose the samples is to find a material suitable for adsorption of substances contained in the leachate, because the values of P1 Sed are higher than P4 Sed, P1 was chosen regarding metals.

No measurement data for N, P and TOC has been available at the moment of the design of the experiment. As storage of samples may change the properties of the leachate, decision has been taken without consideration of the concentrations (laboratory analysis takes two or three weeks). If sorption treatment will be implemented on the landfill it will be placed after the current treatment, so for this and the reason above the sample chosen for the test was P4 Sed.

The initial concentrations of metals, nutrients and organic carbon were compared with five guidelines; two from the Swedish EPA, one from the CCME and two from the Colombian local authorities RAS and Decree 1594.The reason to use five guidelines is to gather information that involves all the substances analyzed as not all the regulations provides guidelines for every one of them; it is also important to compare how legislations can differ from country to country.

Table 3.1 pH and turbidity of leachate from "El Carrasco"

Test	Unit	P1	P2	P3	P4
pH		8.31	8.8	7.9	8.14
Turbidity	NTU	325	238	257	331

Turbidity values communicate that the leachate contains elevated quantity of particulate material which can be organic or inorganic. Turbidity was measured in the laboratory before sedimentation of the samples. It can be suggested that the major content of the particles is organic because inorganic matter has higher density and settles faster (SEPA, 2000). Measured turbidity is high according to SEPA, where high turbidity is consider being above 7 FNU or NTU.

The samples for metals analysis were P1 and P4; the concentrations found in all the samples exceeded all the guidelines except for the local guidelines of RAS and Decree 1594 where threshold values are extremely high (Table 3.2).

If values are compared with the SEPA Environmental Quality Criteria – Lakes and Watercourses, all the concentrations of metals will be between class 4 and 5 with high biological acute and chronic risk, as quote in the mentioned report *"Class 4 and 5. A growing risk of biological effects. Metal concentrations in class 5 affect the survival of aquatic organisms even where exposure is short-term."*(SEPA, 2000).

In Table 3.2 and 3.3 it is shown that the concentration of metals in the leachate samples exceeds by far the guideline values. Even if As values are higher in P1 Sed than P1 normal it is within the error interval. For Cd and Pb an interval is showed because results from the lab where under detection limit, still the detection limit is high enough to be "extremely serious" as quote in the guideline values. The Cr concentrations have to be mentioned as they are extremely high. The point P4 represents the leachate that is released to the creek La Iglesia.

As for nutrients and organic carbon, samples for measurements were four, P1, P2, P3 and P4, and results showed a similar behaviour as metals, i.e. high values compared to every guideline. As a matter of fact, the pollution with nutrients and TOC is even relatively higher than the metal pollution of the leachate, see Table 3.4.

Table 3.2 Metals concentration in leachate

Substance	Units	P1 normal	P1 Sed	P4 normal	P4 Sed
As	μg/l	35	38	23	20
Cd	μg/l	<D.L.	<D.L.	<D.L.	<D.L.
Cu	μg/l	40	20	10	10
Cr	μg/l	800	820	640	630
Pb	μg/l	<D.L.	<D.L.	<D.L.	<D.L.
Ni	μg/l	250	250	260	250

<D.L.: Below detection limit set by the laboratory. Cd = 14 μg Cd/l - Pb= 260 μg Pb/l

Table 3.3 Guideline values for metal pollutants

Substance	Units	P1 Sed	P4 normal	Guideline (a1)	Guideline (a2)	Guideline (b)	Guideline (c)
As	μg/l	38	23	<50	15 - 45	500	5
Cd	μg/l	0 - 14	0 – 14	>0,1	>3	100	0,017
Cu	μg/l	20	10	12 - 40	9 - 30	3000	2 - 4
Cr	μg/l	820	640	>200	>150	500	(8.9 / 1.0) *
Pb	μg/l	0 - 260	0 – 260	>10	>30	500	1 - 7
Ni	μg/l	250	260	150 - 450	140 - 450	2000	22 - 150

a1: Swedish EPA - Methods for Inventories of Contaminated Sites; Based on Canadian water quality criteria for protection of aquatic life (Cr val es are for Cr (III))

a2: Swedish EPA - Methods for Inventories of Contaminated Sites; Based on "Environmental Quality Criteria for Lakes and Watercourses"

b: Colombian - Decree 1594 de 1984 (Art 74)Law for discharge into a watercourse (Converted to mg/l)

c: Canadian Water Quality Guideline (Protection of Aquatic Life); * Cr (III) and Cr (VI) respectively.

Colors stand for:		Slightly serious	Moderately serious	Very serious	Extremely serious

Table 3.4 Nitrogen, Phosphorus and TOC concentrations in leachate

Substance	Units	P1 normal	P2 normal	P3 normal	P4 normal	P1 Sed	P4 sed	G.L. (a)
N (total)	mg N/l	2059	1979,4	1959	1826	1400	1372	>5
P (total)	mg P/l	22	26.5	21	23.5	16.7	16.1	> 0.1
TOC	mg C/l	646	658	681	701	652	589	>0.016

G.L. (a): Swedish EPA - Environmental Quality Criteria - Lakes and Watercourses,					Color Stand for:		Ext High

The existing treatment which is based on flocculation, coagulation and sedimentation show good results for As and Cu with removal values of 34% to 50% for As and 50% to 75% for Cu; Cr concentrations were reduced by only 20% but it must be remembered that initial concentration is extremely high. For nickel, nutrients and organic carbon the removal capacity is close to zero. Negative values of the percentage calculation can be due to the margin of error from the laboratory analysis, in such a case the efficiency can be assumed as 0 %.

The results show that actual treatment is not enough to treat the leachate and additional treatment must be considered.

Table 3.5 Efficiency of the existing treatment

Substance	Units	P1 normal	P4 normal	P1 Sed	P4 Sed
N (total)	mg N/l	2059	1826	1400	1372
Treatment Efficiency %			11.3%		2.0%
P (total)	mg P/l	22	23.5	16.7	16.1
Treatment Efficiency %			-6.8%		3.6%
TOC	mg C/l	646	701	652	589
Treatment Efficiency %			-8.5%		9.7%
As	μg As/l	35	23	38	20
Treatment Efficiency %			34.3%		47.4%
Cu	mg Cu/l	0.04	0.01	0.02	0.01
Treatment Efficiency %			75%		50%
Cr	mg Cr/l	0.8	0.64	0.82	0.63
Treatment Efficiency %			20.0%		23.2%
Ni	mg Ni/l	0.25	0.26	0.25	0.25
Treatment Efficiency %			-4%		0%

Table 3.6 Chemical composition of leachate from different landfills (AvfallSverige, D2007; Baun and Christensen, 2003)

Substance	Units	Concentration Intervals								
		Carrasco	Sweden	Germany	Denmark	USA	United kingdom	Hong Kong	Netherlands	France
As	μg/l	20 - 38	0 - 41	0.005 - 1.6	0.0005 - 0.13	N.A.	< 0.001 - 0.049	N.A.	N.A.	N.A.
Cd	mg/l	0 - 0.014	0 - 0.003	0.0005 - 0.14	0.00002 - 0.03	0.001 - 0.130	< 0.01 - 0.03	< 0.01 - 0.02	0.0001 - 0.002	N.A.
Cu	mg/l	0.01 - 0.04	0.0016 - 0.080	0.004 - 1.4	0.0005 - 0.67	0.18 - 1.3	< 0.02 - 0.16	0.01 - 0.13	0.008 - 0.085	N.A.
Cr	mg/l	0.63 - 0.82	0 - 0.161	0.03 - 1.6	0.0005 - 1.3	0.05 - 1.05	< 0.04 - 0.56	0.02 - 0.23	0.002 - 0.17	N.A.
Pb	mg/l	0 - 0.26	0 - 0.045	0.008 - 1.02	0.0005 - 1.5	< 0.1 - 1.40	< 0.04 - 0.28	0.03 - 0.12	0.001 - 0.015	N.A.
Ni	mg/l	0.25 - 0.26	N.A.	0.02 - 2.05	0.001 - 3.2	0.10 - 1.20	< 0.03 - 0.33	0.04 - 0.18	0.005 - 0.12	N.A.
pH		7.9 - 8.8	N.A.	4.5 - 9.0	4.5 - 8.6	4.5 - 8.2	6.4 - 8.0	7.2 - 8.4	5.9 - 7.0	7.8 - 8.4
N (total)	mg/l	1372 - 2059	15 - 870	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
P (Total)	mg/l	16.1 - 23.5	N.A.	N.A.	N.A.	N.A.	N.A.	**N.A.**	N.A.	N.A.
TOC	mg/l	589 - 701	N.A.	N.A.	1 - 160	N.A.	2.8 - 5690	N.A.	30 - 1700	100 - 2700
Color stand for:		Max value in El Carrasco is Below min		Into Interval	Min value El Carrasco is Above max					

If the concentrations measured in this project are compared to the values in Table 3.6, similarity in some results can be found as almost all metal concentration values from El Carrasco are in the interval of the different landfills. Comparing with landfills from Germany, Denmark and USA, the concentration values from El Carrasco are within the intervals with exception of arsenic for Germany and Denmark and Cu for USA. Arsenic and Cr concentrations in El Carrasco exceeds for several times the values in the intervals of the other landfills. For N the only point of comparison is with the Swedish landfills and concentration values of El Carrasco exceed the Swedish values several times; regarding the pH the only landfill with similar values is the one from France.

Cadmium and Pb are below detection limit of analysis at El Carrasco. However, the detection limits set at the UIS laboratory lab was more than 4 and 5 times higher respectively than the highest limits of the Swedish landfills, and 7 and 17 times higher respectively, than the highest limits of the Dutch landfill. Therefore, it is possible that Cd and Pb may be present at elevated concentrations. The measurements show that "El Carrasco" has both characteristics of a young and an old landfill since it shows high concentration of metals and nutrients in the leachate.

Landfills has different components present in the leachate and the adsorption rates of substances can be affected (Baun and Christensen, 2003), and this is the reason why measurement of the adsorbent capacity of a material for a site specific landfill is important. Table 3.6 shows how wide intervals of concentration for each substance can be found in landfills leachates from different countries.

As mentioned in Chapter 1.6 adsorption rate can be affected by other elements or compounds present in the leachate and the high concentration of N, P and TOC is a matter that must be taking into consideration for the analysis of the adsorption results.

3.1 Sorption of metals

The following Tables 3.7 and 3.8 present the results of the adsorption in microgram per liter and percentage using compost and zeolites respectively as sorption materials.

Table 3.7 *Metals adsorption using organic material (compost)*

Substance	Units	P1 Sed Initial	Point 1 Sed (Organic adsorbent material g/500ml)				
			0.1gr	0.25gr	0.5gr	1.0gr	2.0gr
			Final concentration				
As	μg As/l	38	5.58	1.48	4.73	0.52	1.64
Difference in	μg As/l		32.42	36.52	33.27	37.48	36.36
% Removal			85.3%	96.1%	87.6%	98.6%	95.7%
Cu	μg Cu/l	20	70	<D.L.	<D.L.	<D.L.	100
Cr	μg Cr/l	820	560	480	500	490	680
Difference in	μg Cr/l		260	340	320	330	140
% Removal			31.7%	41.5%	39.0%	40.2%	17.1%
Ni	μg Ni/l	250	190	170	170	170	250
Difference in	μg Ni/l		60	80	80	80	0
% Removal			24.0%	32.0%	32.0%	32.0%	0.0%
<D.L. : Below detection limit set by laboratory Cu = 50ug Cu/l							

Table 3.8 *Metals adsorption using zeolite.*

Substance	Units	P1 Sed	Point 1 Sed (Zeolite adsorbent material g/500ml)				
			0.1gr	0.25gr	0.5gr	1.0gr	2.0gr
As	μg As/l	38	2.94	2.37	1.83	7.11	1.16
Difference in μg As/l			35.06	35.63	36.17	30.89	36.84
% Removal			92.3%	93.8%	95.2%	81.3%	96.9%
Cu	μg Cu/l	20	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.
Cr	μg Cr/l	820	560	520	580	630	540
Difference in μg Cr/l			260	300	240	190	280
% Removal			31.7%	36.6%	29.3%	23.2%	34.1%
Ni	μg Ni/l	250	210	190	220	240	200
Difference in μg Ni/l			40	60	30	10	50
% Removal			16.0%	24.0%	12.0%	4.0%	20.0%
<D.L.: Below detection limit set by laboratory. Cu = 50ug Cu/l							

The calculations for sorption efficiency (%) was done with the equation based on Seesaen, 2007:

% sorption efficiency = [(Ci-Cf)/Ci] * 100

Where:

C_i = initial concentration of metal ion in the solution (mg/L)

C_f = final concentration of metal ion in the solution (mg/L)

Figures 3.1 and 3.2 summarize the metal uptake on the sorbent phase in μg/g, of As, Cr and Ni using compost and zeolites respectvely. Since adsorption efficiency can not be concluded from the percentage values, interpretation of these must be done in a analitical way. Outside data values will not be analyzed as represents measurement or sampling mistakes, e.g. 4.0% removal of Ni using 0.1 g of zeolite.

The analysis will be given in parallel for both adsorbent materials.

Starting with quantity of metal adsorbed per gram of compost and zeolite it can be seen that the trend for both materials is Cr > Ni > As. This order follows the concentration order i.e. 820 μg Cr/l > 250 μg Ni/l> 38 μg As/l. It suggests that the higher load of the metal results in the higher gradient (pressure) on the adsorption sites and more ions become adsorbed.

In order to find the metal uptake on the sorbent phase the following equation is used (Seesaen, 2007):

q_f= V(Ci-Cf)/m

Where:

q_f = metal uptake on the sorbent phase (μg/g)

V = volume of the solution (L)

m = dry weight of the sorbent (g)

e.g. for Cr 820 μg/l is the initial concentration; with 0.1 g/500ml of sorbent (compost) the metal uptake will be 1300μg/g and with 0.25g/500ml the metal uptake will be 680μg/g. It can be seen that lower adsorbent concentration (dose) results in higher

uptake per unit of adsorbent i.e. µg/g as the adsorbent surface is more effectively used.
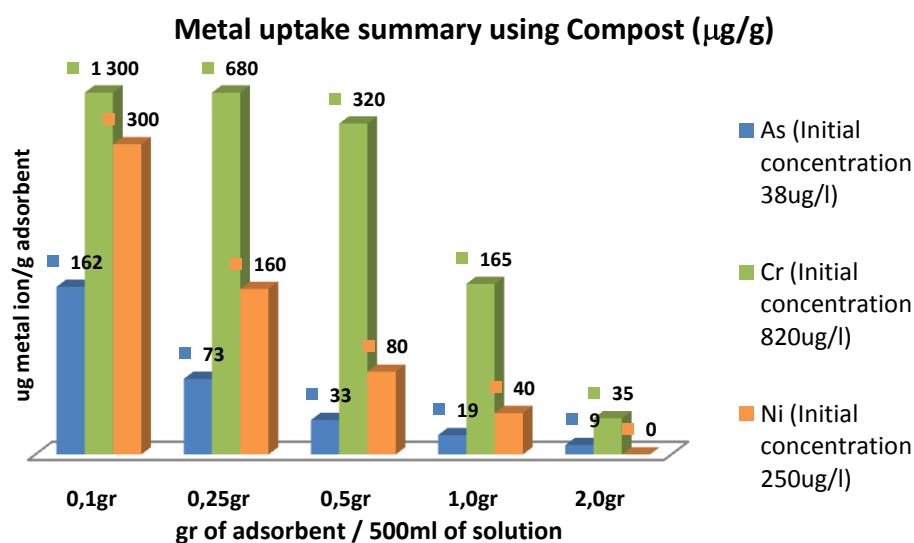

Figure 3.1Metal uptake on the sorbent phase using Compost Sorption Material (As, Cr & Ni)
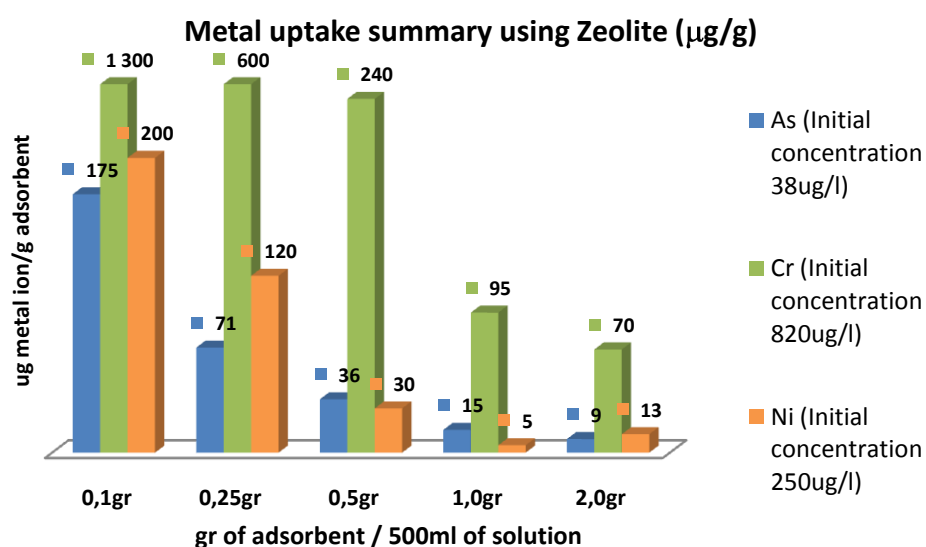

Figure 3.2 Metal uptake on the sorbent phase using a zeolite sorption material (As, Cr & Ni)

Some of the obtained data do not follow the expected trend that more adsorbent mass would result in higher percentage of adsorption; these can be explained by the following:

▪ The leachate could not be filtered and the procedure was instead sedimentation for half an hour followed by the extraction of the treated leachate with a pipette. Adsorbent and/or organic matter could have followed the aqueous sample analysed for the estimation of sorption capacity. The metal ions adsorbed are then dissolved back to the water when samples were acidified for preservation and further digested with acid in the lab, as mention in the lab

procedure, Chapter 3.1. –Therefore, they would appear as not have been adsorbed.

- Substances, apart from those analysed in this study, could interfere with the metal adsorption.
- Suspended metals in the sample could be dissolved during acid digestion.

3.1.1 Arsenic

Concentration results suggest that As may be dissolved in the leachate because values of P1 and P1 Sed and also P4 and P4 Sed are similar. If As is dissolved it may be in the form of As (III) because the reduced As is frequently present in aqueous solutions, (Baird and Cann, 2008). Arsenic (III) is more toxic than As(V), and As(III) can change into As(V) and vice versa by oxidation and reduction (Baird and Cann, 2008)

Arsenic concentration after current treatment in the landfill shows high removal values, 34% and 47%, see Table 3.5. However, additional treatment is needed because As concentration in the treated leachate is above 20μg/l, and not acceptable for any of the guidelines consulted in this study, except for the Colombian regulation, see Figure 3.3.
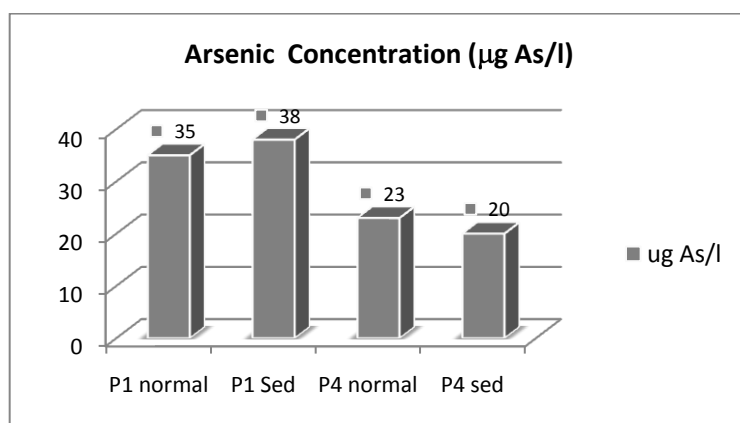

Figure 3.3 *Arsenic concentration without sorption treatment (μg/l)*

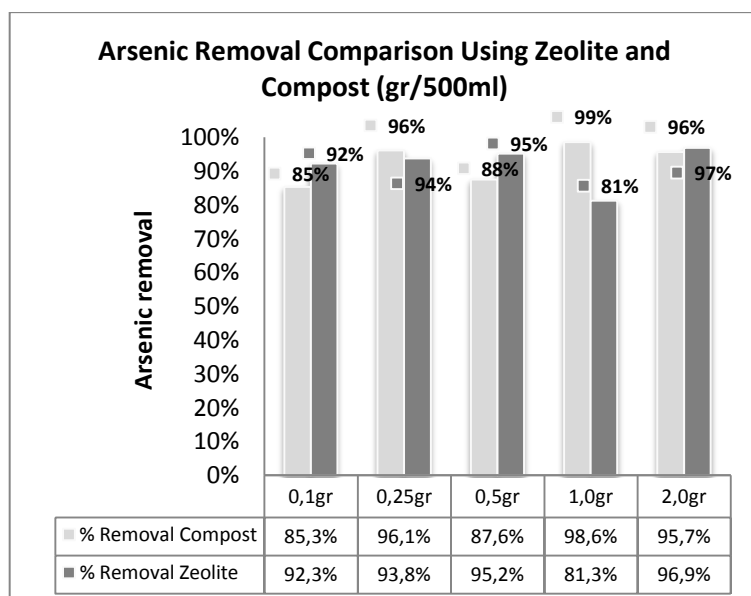|	0,1gr	0,25gr	0,5gr	1,0gr	2,0gr
% Removal Compost	85,3%	96,1%	87,6%	98,6%	95,7%
% Removal Zeolite	92,3%	93,8%	95,2%	81,3%	96,9%

Figure 3.4 *Arsenic adsorption comparison in % (Zeolite vs Compost)*

Effective removal can be seen in Figure 3.4, with removal percentage up to 97% for the zeolite and 98% with organic material. According to Mozgawa and Badja 2005, trivalent cations, as As (III), are more likely to be absorbed by chemisorption.

In general the arsenic concentration after adsorption treatment decrease to less than 5 mg/l and therefore fulfil the guideline requirements for the Canadian guideline, the most strict guideline for this substance of the ones used in this study.

Freundlich isotherms were calculated but only values for the zeolite experiment were suitable as shown below in Figure 3.5.
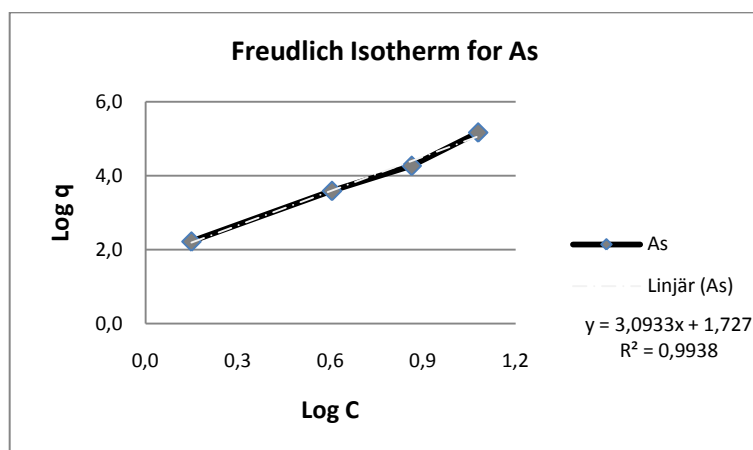

Figure 3.5*Arsenic adsorption isotherm of the zeolite described by Freundlich equation*

In Figure 3.5 it can be seen the accuracy of the isotherm since the linear plot represents almost a straight line which is represented by the R^2 value that is close to 1. Table 3.9 will show a summary of relevant data about arsenic removal with the zeolite; unfortunately isotherms for the other metals could not be calculated.

Table 3.9 *Isotherm constants for As adsorption with zeolites*

q = μg/g	Removal Efficiency %	Adsorption constants		
		K_f (μg/g)	n (μg/l)	R^2
175	97	5.624	3.0933	0.993

3.1.2 Cadmium and lead

For these metals initial concentration analysis was performed, but as shown in Table 3.2 concentration values are below the detection limit, although the detection limit set by the laboratory is high enough to be considered as an environmental risk. The detection limits for Cd and Pb were 14 and 260 μg/l respectively, and compared to guidelines where recommended values are around 0.01 μg/l for Cd and 1 μg/l for Pb it may not be concluded that pollution by these metals is not present.

Different authors (Babel and Kurniawan, 2003; Erdem, 2004; Beyazit and Peker, 2003; Mozgawa and Badja 2005) had done studies on Pb and Cd adsorption with zeolites and dead biomass with high adsorption values. Mozgawa and Badja found that chemisorption is the form of adsorption that predominates when zeolite is used as an adsorbent.

Another important finding is that the adsorption rate of Pb and Cd is reduced when Cr (VI) ions are present in the solution (Babel and Kurniawan, 2003).

In Table 3.10 reported adsorption capacities in mg/g for zeolites and dead biomass are presented.

Table 3.10 *Reported adsorption capacities mg/g*

Material	Source	Cd	Pb
Bio mass	Bailey et al, 1998	11.14 - 28	9.74 - 116
Zeolite	Bailey et al, 1998	84.3	155.4
Zeolite	Babel &Kurniawan, 2003	1.20 – 70.0	1.6 - 62

3.1.3 Copper

Copper concentrations measured at "El Carrasco" are high but within the average interval for landfill leachates. The removal with the actual treatment showed removal efficiency between 50 to 70%, still the concentration discharged is high enough to be classified as environmental hazard. However, as mentioned before the Colombian legislation allows very high thresholds as for copper it is 3 mg/l.
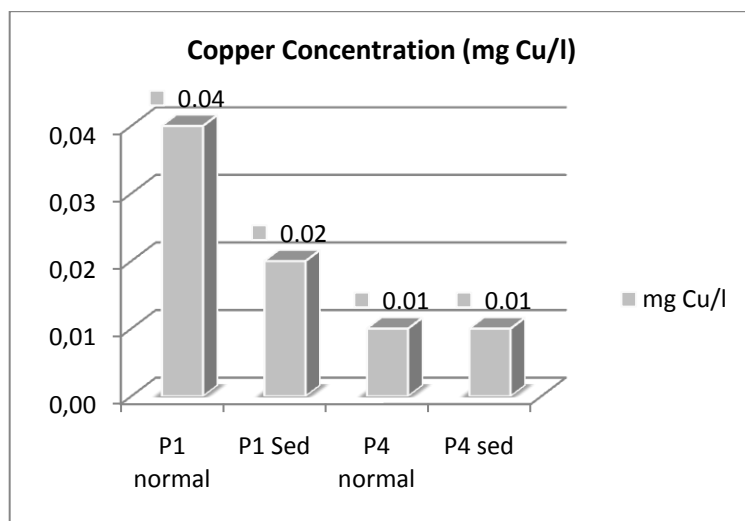

Figure 3.6 *Copper concentrations without sorption treatment (mg/l)*

It can be seen in Figure 3.6 that 50% of the Cu may be in dissolve phase when P1 normal and P1 Sed are compared.

For the samples treated with the adsorbent, the laboratory set a higher detection limit. The results were below the new detection limit, and the reason given by the laboratory was:

"…concentrations values were send to the IDEAM for the accreditation; but values can be instrumental noise or stray radiation".

The laboratory and IDEAM set the new detection limit in 0.05 mg/l and only two values were above that limit (0.07 and 0.1) this could be due to acid digestion of remaining adsorbent and/or organic material as explained in Chapter 2, Section 2.3.2.

The statement done by the laboratory can also mean that the accuracy of the first results, untreated samples, can be questioned.

3.1.4 Chromium

Concentrations of Cr in untreated samples are extremely high, over 800 ppb or µg/l, see Table 3.2. The current treatment removes chromium by around 20%. Values of P1 and P1 Sed are almost equal, as well as for P4 and P4 Sed, as can be seen in Figure 3.7, that suggests all of the Cr is dissolved and therefore in Cr (VI) form which is highly soluble in water in contrast to the Cr (III) form that is insoluble in water.

In addition, Cr could be in the form of Cr (IV) or (III) depending on oxidation (aerobic) or reducing (anaerobic) conditions respectively (Baird and Cann, 2008). Based on dissolved oxygen concentrations and the pH value, Table 1.2, it is expected that high percentage of the chromium present in the leachate is Cr (III).
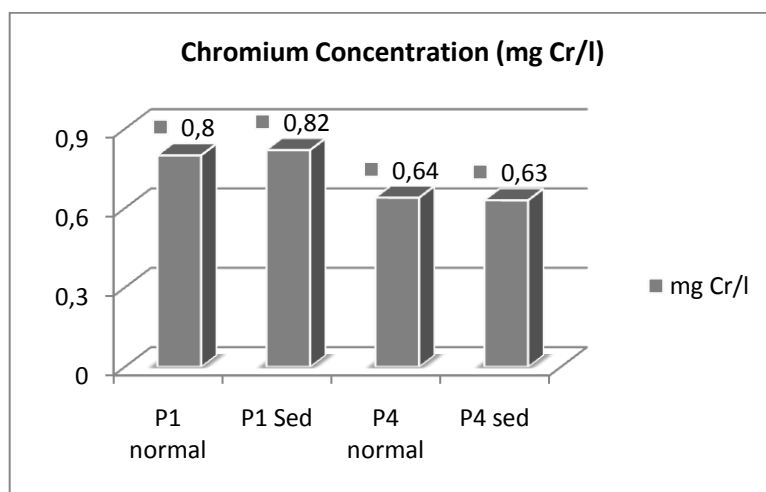

Figure 3.7 *Chromium concentrations without sorption treatment (mg/l)*

Chromium (III) is widely used in leather tanning to improve quality of the material, making it resistant to water, heat and bacteria; this activity might be one of the biggest sources of Cr since Bucaramanga is known as a city with high quantity of shoe leather factories.

Once the samples were treated with the adsorbent, chromium removal was in the order of 30 to 40% that is not so high efficiency if compared to arsenic removal and only 10 to 20% higher than the normal treatment in the landfill.

A common method to remove chromium from water is by precipitation but it must then be in Cr (III) form, because Cr (VI) does not precipitate (Bailey et al, 1998). Chromium (VI) will not be removed by zeolites as it does not exist as a cation but as an oxyanion.

Chromium adsorption in different studies report a fairly good adsorption rate and chemisorption prevail with Cr (III) (Mozgawa and Badja 2005).This means that once it is attached to the adsorbent the bonds created keep Cr immobilized in the structure.
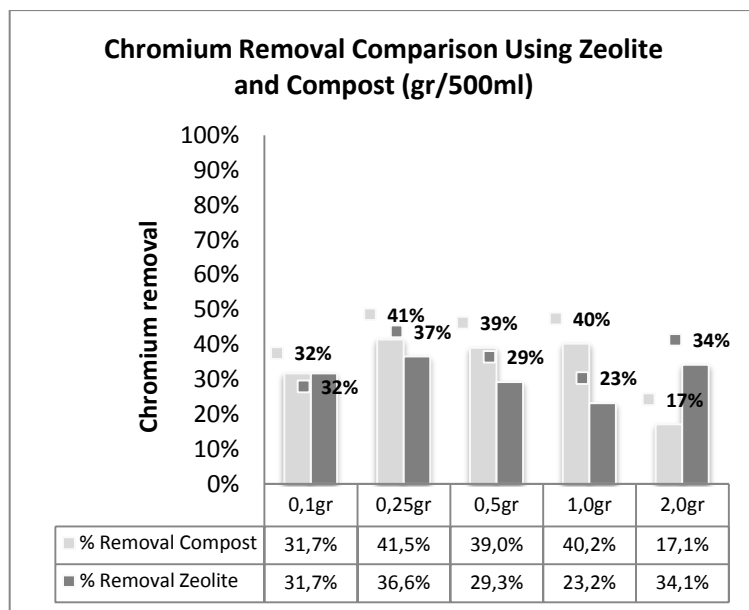
Chromium Removal Comparison Using Zeolite and Compost (gr/500ml)

	0,1gr	0,25gr	0,5gr	1,0gr	2,0gr
▪ % Removal Compost	31,7%	41,5%	39,0%	40,2%	17,1%
▪ % Removal Zeolite	31,7%	36,6%	29,3%	23,2%	34,1%

Figure 3.8 Chromium adsorption comparison in % (Zeolite vs Compost)

It can be seen from Figure 3.8 that Cr adsorption is similar between the two adsorbents, outsider values must not be considered in order to be able of analyze the figure. Adsorption with 2 gram and adsorption with 1 gram are the values considered as outsiders for organic and zeolite respectively.

It was not possible to model an isotherm for this metal that suggests that other processes besides adsorption were occurring. Still compost adsorbent is more efficient than zeolite probably because it is able to adsorb the oxyanion Cr (VI). (Babel et al, 2003; Bailey et al, 1998)

3.1.5 Nickel

The case of Ni is presented in Figure 3.9 where two main conclusions can be made:

1. Nickel is present as a dissolved metal, and
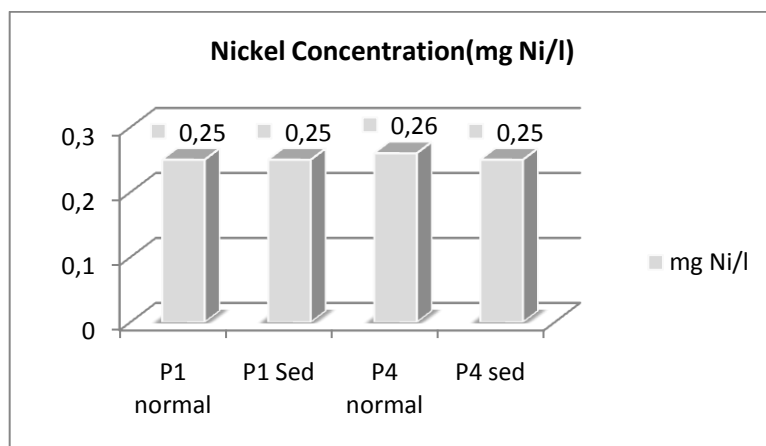2. No removal is achieved by the current treatment.

Nickel Concentration(mg Ni/l)

Figure 3.9 Nickel concentrations without sorption treatment (mg/l)

As for removal efficiency for metal adsorption, the values reach a maximum of 32% and 24% of removal when compost and zeolite were used respectively; still important quantity of Ni was removed. Results can be seen in Figure 3.10
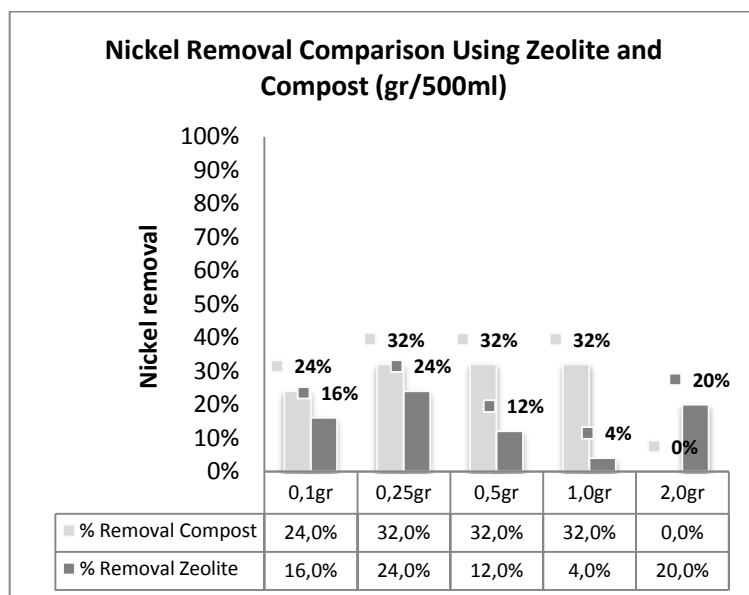

Nickel Removal Comparison Using Zeolite and Compost (gr/500ml)

	0,1gr	0,25gr	0,5gr	1,0gr	2,0gr
% Removal Compost	24,0%	32,0%	32,0%	32,0%	0,0%
% Removal Zeolite	16,0%	24,0%	12,0%	4,0%	20,0%

Figure 3.10 Nickel adsorption comparison in % (Zeolite vs Compost)

The adsorption behaviour of Ni to zeolite and compost can be caused by processes of ion exchange, adsorption method predominant for Ni (Mozgawa and Badja, 2005). Over time Ni can be displaced by other cation like NH_4^+ and return to the water solution as an ion. Previous studies have shown nickel ions affinity to be intermediate compared to other cations for adsorption by zeolites and compost.

From Tables 3.7 and 3.8 it can be seen that after 60 to 80 µg of nickel adsorption the removal process stops even if more adsorbent is present.

3.2   Sorption of nutrients and TOC

Nitrogen, phosphorus and organic carbon compete with metal ions for active sites in the adsorbents (Inglezakis and Poulopoulos, 2006), and their high concentration found in the leachate may explain to some extent the relatively low adsorption of metal ions.

Competition for active sites is not the only way to interfere metal adsorption, as mentioned in Chapter 1 organic material and macromolecules can cover the adsorbent surfaces preventing the sorption of other substances.

The maximum removal obtained for N was 19% and 36% for the compost and the zeolite respectively. Despite the relatively low fraction in % substantial amounts of N were removed as N initial concentration was extremely high.
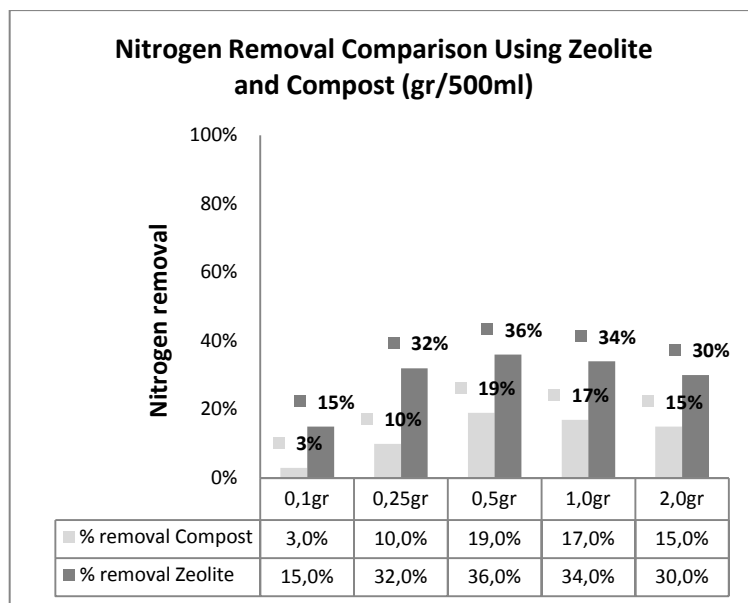
Figure 3.11 *Nitrogen removal by zeolites and compost (g/500ml)*

	0,1gr	0,25gr	0,5gr	1,0gr	2,0gr
% removal Compost	3,0%	10,0%	19,0%	17,0%	15,0%
% removal Zeolite	15,0%	32,0%	36,0%	34,0%	30,0%

Apart from sorption, nitrogen can be removed by bacterial activity transforming the molecules into gas form that then escapes to the air from the leachate.

Also for P removal efficiency was relatively low and as a maximum 15% and 25% for the compost and the zeolite respectively. In addition, when low amounts of compost were used i.e. 0.1 g and 0.25 g, some P was released from the compost (Figure 3.12). It may suggest that there were no sorption sites available for the P due to the competition with other pollutants. Moreover some of P has been released as a result of the ion or ligand exchange of the compost and the pollutants.
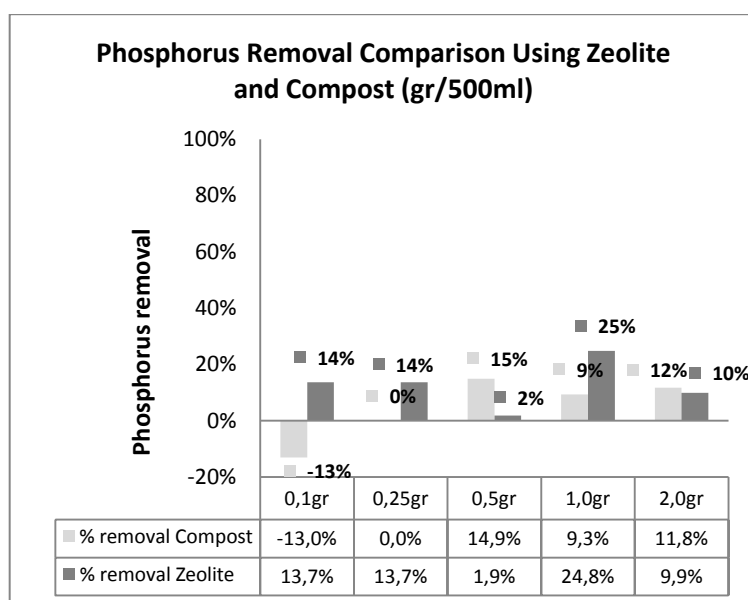

	0,1gr	0,25gr	0,5gr	1,0gr	2,0gr
% removal Compost	-13,0%	0,0%	14,9%	9,3%	11,8%
% removal Zeolite	13,7%	13,7%	1,9%	24,8%	9,9%

Figure 3.12 *Phosphorus removal by zeolites and compost (g/500ml)*

No reduction in the TOC concentration has been obtained by either material. Both the compost and the TOC acquire predominantly negative charge at neutral to basic pH (Bailey et al. 1998) and therefore repel. However, some parts of the TOC may be hydrophobic and could have been adsorbed by the physical adsorption. The fact of the absent TOC adsorption in presence of compost may suggest that TOC is

predominantly hydrophilic. However, the results can also be caused by the experimental error. As has been mentioned in Chapter 3 Section 3.1 due to the problems with filtration the adsorbents and the solution have been separated by sedimentation after the completed adsorption tests. It is probable that small adsorbent particles have been included in the analysed leachate together with the pollutants adsorbed to them.

4 Conclusions

Compost and zeolites showed moderate removal efficiency for metals and nutrients. Higher efficiencies have been previously reported by other authors for the synthetic solutions or less polluted waters. The probable factors causing lower than expected removal are:

- High concentrations of pollutants increase the competition for active sites.
- Presence of molecules that interfere with the sorption by clogging the active sites.
- Colloids and small or floating particles could have been transferred to the water samples due to the fact that filtration could not have been performed. Therefore, the pollutants attached to them appeared as not being adsorbed.

In order to improve metal sorption a pre-treatment must be implemented, effective for particles and nutrients removal; some suggestions are given in the Chapter 5.

Further and continuous analysis should be conducted in order to create a database of the pollutants present in the leachate and their seasonal variation. It is also important to monitor other pollutants than those measured in this study as for example other toxic metals and persistent organic pollutants (POP).

It is imperative to improve the Colombian legislations regarding polluted water discharges and for pollutants monitoring; it is also important to stimulate waste recycling.

The applied landfilling procedure through terraces with impermeable bottom and cover most probably provides the necessary protection of the groundwater resources. However, an efficient landfill leachate treatment is also required to protect the surface waters. As has been previously mentioned in this report a new treatment is currently been tested and a UASB reactor is been constructed on the landfill site.

5 Alternative Treatment

As mentioned in the conclusions, pre-treatment is suggested in order to reduce the concentration of nutrients and TOC and in such a way decrease the competition of pollutants for the adsorption sites and improve metals sorption in particular.

A constructed wetland is recommended as a pre-treatment for the leachate for two reasons. Wetlands provide efficient nutrients and particle removal (Zemanová et al, 2010). In addition the climate of the studied location is suitable for a constructed wetland.

Zemanová et al, 2010 reported efficiency of this treatment for more than 100 constructed wetlands only in the Czech Republic and other locations in Europe. A removal of 79% has been reported for TOC and over 70% for nitrogen and phosphorus. This efficiency could have been achieved despite the fact of the changing seasons in Europe when colder conditions suppress vegetation and microorganisms important for the pollutants removal.

The climate conditions are more favourable in Bucaramanga with an average annual temperature of 25°C and many days of sunshine. This enables all year around vegetation period for the wetland plants and microorganisms. Due to this conditions even greater than in Europe treatment efficiencies in the wetland can be expected.

As has been shown by the previous studies that high oxygen content of the leachate improves carbon and nitrogen removal in the constructed wetlands through nitrification. However, the removal is still occurring at poor or absent oxygen conditions due to anaerobic microorganisms.

It has not been the objective of this study to design a wetland for the treatment of the leachate at the el Carrasco landfill. Some common standards for constructed wetlands can be found with small differences in length and width and the usual dimension are 20 to 25 m with a depth of vegetated bed of 1 m (Zemanová et al, 2010). The important factor that must be considered is that the flow has to be evenly spread through the cross section (wide) of the wetland while the ratio of length and width can be between 1:1 to 1:10 (Davis, 2011).

The metal adsorption efficiency of zeolite and organic compost can probably be improved by the proposed pre-treatment. Extremely high content of nutrients and organic matter is the major problem with the studied leachate. The combination of the newly installed bacterial treatment (UASB reactor), a wetland and an adsorption filter would treat the leachate to the quality acceptable for release to the La Iglesia creek.

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