UNIVERSITÀ DEGLI STUDI DI PADOVA

Second Cycle Degree in Environmental Engineering

ICEA Department

Master Thesis

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ATTENUATION OF HEAVY METALS IN MUNICIPAL SOLID WASTE LANDFILL LEACHATE BY DIFFERENT STATIONARY PHASES

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Academic Year:2014-2015

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EXTENDED ABSTRACT IN ITALIAN

ATTENUAZIONE DI METALLI PESANTI IN PERCOLATO DI DISCARICA DI RIFIUTI SOLIDI URBANI ATTRAVERSO DIVERSE FASI STAZIONARIE.

In questa tesi è stata studiata la speciazione di metalli pesanti in percolato proveniente da reattori di laboratorio utilizzati per la simulazione di diverse tipologie di discarica (anaerobica, aerata, con ricircolo del concentrato) per rifiuti solidi e la loro attenuazione mediante filtrazione attraverso diverse fasi stazionarie.

La speciazione dei metalli pesanti contenuti nel percolato è molto importante per valutare la loro possibile interazione con l'ambiente, specialmente con l'acquifero e il suolo in caso di emissioni incontrollate di percolato attraverso la barriera di fondo della discarica.

In letteratura gli studi riguardanti l'effetto dell'aerazione della discarica sui metalli pesanti nel percolato sono pochi e per la maggior parte delle volte limitati alla valutazione del contenuto totale, piuttosto che delle specie presenti.

Nei test descritti nella tesi sono state utilizzate diverse tecniche analitiche caratterizzate da limiti di rilevabilità differenti ma capaci di fornire un'ampia serie di informazioni sulla natura chimica delle specie contenute nel percolato come illustrato nella seguente tabella.

Nome Analisi	Principio di funzionamento	Motivo analisi	Limiti di rilevabilità
ICP-OES	Spettroscopia a emissione atomica	Misurare contenuto totale metalli	ppb
ESEM	Microscopio elettronico a scansione	Analizzare la morfologia della superficie del campione	ppm
FT-IR	Spettroscopia di assorbimento infrarosso	Identificare il tipo di legami presenti	ppb
GC-MS	Gas cromatografia e spettrometria di massa	Analizzare i componenti organici volatili	ppm
ESI-MS	Spettrometria di massa electrospray	Analizzare i componenti organici	ppm
NMR	Spettrometria di risonanaza magnetica nucleare	Analizzare i componenti organici	ppm

A causa del tipo di esperimento (in reattori di laboratorio), della conseguente limitata disponibilità di percolato e della bassa concentrazione dei metalli di interesse, tra tutte le tecniche analizzate, l'unica che ha permesso di quantificare il contenuto di metalli è stata l'ICP-OES; le altre hanno consentito di ottenere informazioni indirette, permettendo di determinare la natura delle molecole organiche e degli ioni inorganici presenti in soluzione e capaci di interagire con gli ioni metallici per coordinazione. In particolare, le misure ESEM hanno rilevato che le maggiori specie ioniche sono costituite da cationi alcalino ed alcalino terrosi (Na^+, K^+, Ca^{2+}, Mg^{2+}) e anioni diffusi nell'ambiente come cloruri e carbonati che possono coordinare centri di metalli di transizione o formare sali poco solubili (ad es. $PbCl_2$ and $PbCO_3$). Le analisi FT-IR e NMR hanno mostrato la presenza di specie organiche complesse in diverse proporzioni a seconda della tipologia di campione analizzato. Tutti i campioni contengono derivati alifatici e specie ossidrilate, la concentrazione delle quali tende a diminuire nei campioni di percolato di età maggiore. Tali specie si possono ritenere responsabili della coordinazione di più centri metallici e della conseguente formazione di sistemi macromolecolari e particelle colloidali. L'invecchiamento sembra avere invece un effetto più limitato sul contenuto in specie alifatiche.

L’analisi in ICP-OES ha evidenziato come il contenuto in metalli pesanti nei percolati di origine anaerobica è generalmente superiore a quello dei percolati da reattore aerato.

Successivamente, lo studio dell'interazione tra metalli e fasi stazionarie di natura diversa (carbone attivo o vermiculite) ha permesso di ricavare informazioni sulla relazione tra la specie dei metalli nel percolato e le condizioni in discarica (aerobiche o anaerobiche). Infatti, i risultati ottenuti mostrano interessanti differenze tra i percolati delle due diverse provenienze con un maggiore attenuazione del contenuto metallico per i percolati da reattore anaerobico (36-65%) rispetto a quelli da reattore aerato (10-34%). Le filtrazioni attraverso carbone attivo e vermiculite mostrano efficienze di rimozione molto simili suggerendo che il meccanismo di adsorbimento dei metalli pesanti presenti nel percolato possa essere simile nei due casi e coinvolgere l'interazione dei cationi metallici in soluzione con i gruppi ossigenati anionici sulla superficie delle particelle dei due materiali.

I risultati ottenuti suggeriscono che l’aerazione dei rifiuti nei reattori favorisca l’ossidazione delle specie organiche e organometalliche con conseguente liberazione di ioni metallici non coordinati in soluzione. Si può quindi ipotizzare la loro ulteriore ossidazione e/o inertizzazione mediante la formazione di composti inorganici poco solubili che quindi si separano dal percolato (idrossidi, carbonati o cloruri). Questo giustificherebbe la più bassa concentrazione di metalli rilevata nel percolato da reattori aerobici rispetto a quello da reattori anaerobici.

Lo studio della componente colloidale (sospensione stabile) del percolato è stato condotto per centrifugazione, pesata della frazione sospesa e misura del contenuto di metalli nella frazione liquida, rivelando una maggiore frazione colloidale nei percolati anaerobici e la proporzionalità tra frazione colloidale e concentrazione di metalli pesanti nel percolato. Tali specie si originano per adsorbimento degli ioni metallici su particelle microscopiche di idrossidi metallici poco solubili (in particolare di ferro) o dall'interazione delle molecole organiche ossigenate disciolte nel percolato, che sono capaci di legare più centri metallici attraverso i gruppi ossidrilici e carbossilici di cui dispongono, formando strutture macromolecolari di grandi dimensioni. Questo è di particolare importanza durante il processo di filtrazione attraverso le fasi stazionarie poiché i colloidi, data la loro dimensione, difficilmente superano la barriera fisica costituita dai materiali porosi generalmente utilizzati a tale scopo. Infatti, i percolati anaerobici, caratterizzati da una maggiore frazione colloidale, dopo il contatto con fase stazionaria denotano una attenuazione più accentuata rispetto ai percolati di origine aerobica.

1. INTRODUCTION

1.1 Environmental risk of heavy metals mobility in municipal solid waste landfill

A large amount of heavy metals are contained in the landfills and are considered a potential environmental risk for the future. Municipal landfills contain a mixture of different type of waste: household, commercial waste, industrial waste and treatment sludges. In the municipal solid waste (MSW) many substances are not stable under natural conditions and especially not when they are in contact with water (Flyhammar and Hakansson, 1999). In landfills, the anaerobic state is the situation mainly present. Under this condition, metals are prevalently immobilized as sulphides or they can form complexes with the solid organic matter or, in a minor part, precipitate out as carbonates. Since the sulphur content is not sufficient to immobilize all the metals deposited, (Ostman et al., 2008) organic materials retains a large fraction of metals in landfill. During the years, the oxygen intrusion inside the landfill increases and subsequently the oxidized material increases the risk of metals being released. In fact, the intrusion of oxygen induces an increase of the cation exchange capacity causing the immobilization of metals as sulphides and the complex formation between metals and the organic fraction (Martensson et al., 2008; Bozkurt et al., 2000). Thus consequently metal sulphides dissolve and solid organic matter content becomes depleted. Therefore, due to these reasons, municipal landfills usually produce leachate with heavy metals concentrations in the microgram per liter to milligram per liter.

Heavy metals constitute an environmental problem, if the leachate migrates into surface water or groundwater, or a treatment issue where the leachate is collected and treated prior to discharge. In fact, once they get into groundwater or soil, it becomes extremely difficult to remove them due to the complex speciation chemistry coming into play. Furthermore, heavy metals are toxic for human beings and, when they leach to aquifer, they can become bioavailable to living organisms (Hashim et al., 2011). Thus, in recent years, the authorities have required the monitoring of heavy metals in landfill leachate that has been done routinely by landfill operators (Baun and Christensen, 2004). The leachate deriving from a sanitary landfill is the wastewater most difficult and most expensive to treat due to its high content of organic and inorganic pollutants.

In landfill leachate, one of the most common groups of contaminants are heavy metals such as:

- cadmium (Cd)
- chromium (Cr)
- copper (Cu)

- lead (Pb)
- nickel (Ni)
- zinc (Zn)

Heavy metals can be contained in landfill leachate in significant concentrations (Sinan Bilgili et al., 2006).

In this context, it becomes very important to understand which parameters control heavy metal solubility. There have been a large number of studies in literature that have reported metal concentrations of landfill leachate.

Ostman et al. in 2008 aerated landfill material from combined household and industrial waste for 14 months to simulate the natural ageing processes as air slowly begins to penetrate the landfill mass. During aeration, pH of landfill material decreased from 8.6 to 8.1 and carbon content also decreased. The aim of the experiment was to study the stability of the landfilled heavy metals. They concluded that the solubility of heavy metals is mainly affected by pH, redox status and availability of organic matter. The dissolution of metals is favoured at low pH values, which is one of the characteristics of young landfill leachate. Indeed, solid wastes contain soils and organic compounds that have significant absorption capacity especially at high values of pH. The pH is a crucial parameter to determine the solubility of heavy metals, which has its minimum value when the pH is in the range of 7-10. In the study it was also deduced that the organic material plays a fundamental role on the solubility of the metals. In fact, organic fraction contributes to metal mobility by forming the complex-binding of metal ions.

Bilgili et al. (2006) studied the metals concentration of simulated aerobic and anaerobic pilot scale municipal landfill. The operational conditions used in the reactors to simulate different landfill condition are presented in the following table.

Column	Operational condition
A1	Aerobic with leachate recirculation
A2	Aerobic dry
A3	Anaerobic with leachate recirculation
A4	Traditional landfill

Table 1.1 Operational condition of the four columns.

The metal concentrations of the four leachate sample (2 aerobic and 2 anaerobic) were determined by atomic absorption spechtrophotometry. The results showed that heavy metals degradation is faster in aerobic conditions than in anaerobic conditions thanks to the aeration that increases the oxidation process. They also studied the pH variation during the landfill life. It was noticed that pH is in the acidic ranges (4-6) at the first stage of degradation for both aerobic and anaerobic landfill. Instead, in the following phases, the increase of pH is much greater in the aerobic reactors which reach a final value equal to 8-9. Considering that metal dissolution is enhanced at low pH (Kjieldsen et al., 2002) and this condition is maintained longer in the anaerobic landfill, it is possible to concluded that heavy metals content is higher in the anaerobic leachate.

In a study conducted by Jensen et al. in 1998 the distribution of heavy metals in landfill-leachate polluted groundwater was analysed. The results confirmed that the mobility of heavy metals may be enhanced by the complexing capacity of the organic matter leaching from the landfill and by the content of colloidal matter in the leachate and in the leachate-polluted groundwater.

Therefore, it is possible to say that heavy metals mobility in leachate is controlled by many factors of various type that contribute to distribute heavy metals between different species (different size-fractions, organic species and dissolved inorganic species) in the leachate.

In this context, the speciation of heavy metals is very important in order to assess the content of metals in the leachate so as to evaluate their subsequent treatments.

1.2 Speciation of heavy metals

The leachate is rich in organic matter, salts and has alkalinity. For these reasons, it is likely that heavy metals are present in different forms, for example, as fine colloidal matter or dissolved organic or inorganic complexes. In order to better understand the behaviour of the heavy metals in the environment or in a treatment plant or to establish stringent sampling procedures, it is important to address the different forms in which the heavy metals are present in the leachate (Baun and Christensen, 2004).

In fact, depending on its form, heavy metals can change its oxidation state and associate with the colloidal or dissolved fraction or form complexes of different nature. Therefore, speciation of heavy metals in landfill leachate is very important to assess the type of metals contained and their interaction with the environment (aquifer and soil). The art of speciation is relatively recent and the type and quality of results obtained are closely related to the experimental methods employed. The speciation of metals concerns the division of the total content into the different physical and chemical forms (Ure and Davidson, 1995; Stumm and Morgan, 1996). Heavy metals in aquatic environments exist as free metal ions, inorganic complexes, organic complexes and associated with colloids, where colloids are generally defined as small particles which size ranges from nm up to 1-10 µm (Gounaris et al., 1993). The factors that influence the distribution of the metals in various species are the nature of the metal and other chemical parameters such as pH, redox conditions, concentration of cations and anions and the primary type and amount of organic material and colloidal (Ure and Davidson, 1995). Metal species can vary from free metal ions with diameter less than 1 nm to large organic complexes and colloids with diameters up to several micrometers.

The speciation method can be physical or chemical. The first refers mainly to the size and molecular weight of the species.

There are several physical methods used in the analysis of aqueous samples. The most commonly used are:

- screen filtration
- ultra filtration
- dialysis

Others such as gel permeation chromatrography, centrifugation and flow field fractionation are used less frequently.

Chemical speciation refers to the chemical form of the species (presence as free ions or complexes) and composition of the colloidal matter. Chemical speciation techniques are divided into chemical speciation of suspended solids and speciation of dissolved species.

Suspended solids in aqueous samples are mainly composed by colloidal materials. These last have a large potential association with metals due to their large specific surface area. Therefore, thanks to the chemical speciation of solids, important information concerning the composition of the solids can be obtained. Thus, in this way it is possible to determine the content of heavy metals in the solids and the type of association between heavy metals and solids.

The most commonly used technique for the chemical speciation of suspended solids are:

- acid digestions,
- sequential extractions,
- X-ray techniques
- different kinds of surface techniques.

To perform the chemical speciation of the dissolved species in aqueous samples there is a wide range of techniques. The most used methods are:

- ion-exchange resin technique,
- liquid chromatography
- electro-analytical techniques such as ion-selective electrode
- voltammetry.

Although in the literature there are few studies concerning the speciation of heavy metals in landfill leachate, some useful information can still be found.

Jensen et al. (1996) studied the distribution of heavy metals between different species in leachate polluted groundwater using two samples. These latter were diluted with trace of heavy metals (Cd, Cu, Ni, Pb, Zn) in the concentrations usually found in landfill leachate (µg/l level). Then the leachate sample were divided, under anaerobic conditions, into colloidal, organic and dissolved inorganic species of heavy metals. The results of the size fractionation and anion-exchanger (table 1.2, 1.3) show that, in landfill leachate, the major part of heavy metals is associated to the colloidal fraction:

- Cd: 38-45%
- Ni: 27-56%
- Zn: 24-45%
- Cu: 86-95%

- Pb: 96-99%

	Colloids %		Dissolved %	
	Organic	Inorganic	Organic	Inorganic
Cd	30	15	55	0
Ni	46	10	30	14
Zn	10	35	25	30
Cu	55	40	5	0
Pb	66	30	4	0

Table 1.2 ``Total'' speciation of Cd, Ni, Zn, Cu and Pb in the leachate-polluted groundwater samples L1 obtained by combining the results from the size fractioning, the anion exchange and the model speciation.

	Colloids %		Dissolved %	
	Organic	Inorganic	Organic	Inorganic
Cd	38	0	62	0
Ni	27	0	0	73
Zn	4	20	11	65
Cu	80	6	12	2
Pb	99	0	0	1

Table 1.3 ``Total'' speciation of Cd, Ni, Zn, Cu and Pb in the leachate-polluted groundwater samples L2 obtained by combining the results from the size fractioning, the anion exchange and the model speciation.

Furthermore, it is showed that the heavy metals are strongly complexed by the organic matter in leachate-polluted groundwater, especially with respect to Cd, Cu and Pb. More than 60% of Cd, Cu and Pb were found to be in organic form. Although inorganic complexation in the dissolved fraction was significant, it was of little overall importance since the dissolved size fractioning was dominated by organic complexes. Therefore, it is well-founded that organic matter in landfill leachate binds heavy metals strongly and that colloidal matter has a high affinity for heavy metals.

In another study, Jensen and Christensen (1999) determined the distribution of colloids and associated heavy metals in four Danish landfill leachates by screen filtration and ultra filtration.
The leachate samples were divided into four size fractions:

- < 0.001 μm
- 0.001 – 0.40 μm
- 0.40 – 1,2 μm

- > 1.2 µm

The results show that, in spite of a low metal concentration, a relevant but highly varying fraction of heavy metals was associated with the colloidal fractions. In particular, 10-60% of total Ni and 0-95% of total Zn. Jensen and Christensen (1999) also studied the speciation of heavy metals in the dissolved fractions. It was found that a considerable part, although variable, of heavy metals in the dissolved fraction was complexed with the dissolved organic fraction (DOM). In addition, it is found that the main dissolved species with respect to Cd, Cu, Ni, Pb, and Zn were the carbonate complexes, whereas free metal ions were much less essential species (less than 30%).

Klein and Niesser (1996) examined heavy metal containing colloids in six leachate samples from a German landfill. The samples of leachate were divided into six-fractions by screen filtration and ultra filtration with subsequent determination of heavy metal content in each size-fraction. The experiment showed that the main part of heavy metals (80%) was in the colloidal fraction (> 0.001 µm), especially in the humic fraction that represent the main part of the smallest colloidal fraction. Generally, more than 80% of the colloids in the smaller fractions (< 1 µm) are found as organic particles instead the larger colloids (1-100 µm) were primarily inorganic particles, mainly constitutes of carbonates, silicates, and iron oxides. The following table showed the results in details.

	Fraction 1 0-0.001 µm	Fraction 2 0.001-0.01 µm	Fraction 3 0.01-0.1 µm	Fraction 4 0.1-1 µm	Fraction 5 1-10 µm	Fraction 6 10-100 µm
Cr	7.6	61.2	5.8	8.6	8.7	8.1
Cu	11.3	33.2	8.1	28.3	8.7	9.9
Ni	9.4	38.5	14.8	14.0	11.2	12.1
Pb	17.3	42.5	2.3	15.7	6.9	14.8
Zn	4.9	38.4	13.3	29.1	6.2	8.1

Table 1.4 Distribution of heavy metals between the six fractions in six leachate samples from one landfill (Klein and Niesser, 1996).

Therefore, also this study showed that heavy metals were mainly associated to colloidal organic material.

The many different forms of heavy metals present in landfill leachate have significant implications for the sampling, since there are no standard procedures, and for the assessment of the content of metals in the leachate so as to evaluate their subsequent treatments and the behaviour in the environment, especially acquifer and soil.

Despite the studies on speciation of heavy metals in leachate landfilll are very limited, they use different approaches and methods, and being not representative of all the types of landfilled wastes or landfill technologies, they all agree that most of the heavy metals in the leachate are associated with colloids or are present as complexes. Furthermore, the studies show that free metal ion constitutes only a small fraction (generally less than 30% and in some cases less than 10%) of the total metal content. A wide range of heavy metals exists in landifill leachate and the species other than free metal ion predominate. This is relevant because metals in leachate behave differently if they were present as free metals. The different variety of species that can be found in landfill leachate have implications for leachate sampling and for the assessment of heavy metal concentrations in leachate connected to the following treatments and to the possibility to have a pollution of the surrounding groundwater and soils.

1.3 Analysis method

As it has been said before, heavy metals contamination poses a significant threat to the ecosystem due to the effects on the environment and living organisms, even at very low concentrations. Therefore, determination of metal ions at the micro and trace level is fundamental for the prevention of the environment pollution due to the leachate migration. Their detection permits to assess the risk and subsequently use the appropriate preventive measures to avoid the pollutants diffusion. The analysis requires appropriate methods and sensitive techniques to detect heavy metals because usually they are present in trace. The detection instrument has to reach in-site, real-time and online determination of trace amounts of heavy metals.

The analytical methods available at the DII (Dipartimento di Ingegneria Industriale) chemistry laboratory which could be more suitable to study heavy metals speciation are:

- The Nuclear Magnetic Resonance Spectroscopy (NMR) is a very powerful analytical technique that allows to obtain detailed information on the molecular structure of the test compounds. It is a spectroscopic method based on the magnetic properties of the nuclei of certain atoms and isotopes. The NMR spectroscopy is a form of absorption spectrometry that measures the absorption of electromagnetic radiation in molecules immersed in a strong magnetic field.

- Infrared spectroscopy IR is a spectroscopic absorption technique normally used in the field of analytical chemistry and materials characterization, as well as in physical chemistry for the study of chemical bonds. This technique concerns the infrared region of the electromagnetic spectrum, characterized by a light with the wavelength and lower frequency than visible light and gives information about the vibration modes of chemical bonds. IR is also characterized by rapidity of execution, accuracy, precision, good sensibility and low cost.

- The ultraviolet spectroscopy visible (UV-Vis) is a spectroscopic technique of molecular absorption commonly used in analytical chemistry. This technique regards the absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region. Therefore it uses light in the visible and adjacent (near-UV) ranges.

- Gas Chromatography – Mass Spectrometry (GC/MS) is an analytical method which combines the features of gas–liquid chromatography and mass spectrometry to identify different substances within a test sample. This technique constitutes one of the most advanced analytical methods and allows the identification and quantification of organic substances in a variety of matrices. The GC-MS is one of the most used techniques in analytical chemistry.

- Electrospray ionization mass spectrometry (ESI-MS) is a desorption ionization method typically used to determine the molecular weights of proteins, peptides, and other biological macromolecules. The methods of desorption ionization can be performed on solid or liquid samples and allow the sample to be non-volatile or thermally unstable. This method is characterized by an impressive sensitivity that makes this technique able to perform accurate quantitative and qualitative analysis.

- Inductively coupled plasma optical emission spectrometry, indicated by ICP-OES, is an analytical technique based on the use of optical emission spectrometry combined with inductively coupled plasma. It is a very sensitive technique that is able to determine different metallic and nonmetallic inorganic substances present in concentrations of about one part per billion (ppb). It exploits the use of a plasma torch ICP to produce excited atoms and ions and a optical emission spectrometer to detect the ions produced.The ICP-OES technique can be used in environmental analysis of water (or other type) samples or in toxicological determinations such as detection of heavy metals concentration.

- The environmental scanning electron microscope, commonly indicated by the acronym ESEM, is a type of scanning electron microscope. It allows, unlike a scanning electron microscope which operates in vacuum, to analyze also biological, non-metallic or insulating and wet or liquid samples.The objective of ESEM analysis is to create a fluorescence spectrum, characterized by some intensity peaks related to energy (keV). Each element presents a characteristic spectrum with primary and secondary peaks. The spectrum allows qualitative and quantitative analysis of the elements in the sample.

1.4 Adsorption of heavy metals by different kind of solid liners

The presence of various pollutant species such as heavy metals in leachate constitutes a potential source of ground water and soil contamination. Therefore, actions are required to prevent and protect the area surrounding the landfill. The geological barrier of municipal solid waste landfills is a key factor for the protection and safety issue in waste disposal (Bilitewski et al., 1997; Christensen et al., 2010; Savage, 1995). In fact, the barrier aims to confine the wastes and limit the spillage of leachate during and after the lifetime of the landfill. Many researchers have reported that soils have high heavy metals sorption capacity. The soil solid phase comprises Fe, Al, Mn-oxyhydrates, carbonate, clay minerals and organic substances (Suzuki et al., 2008).

In this context, the material most suitable for the composition of geological barriers are the mineral clays thanks to their small particle size, complex porous structure and very low permeability (Sànchez-Jimenez et al., 2012).

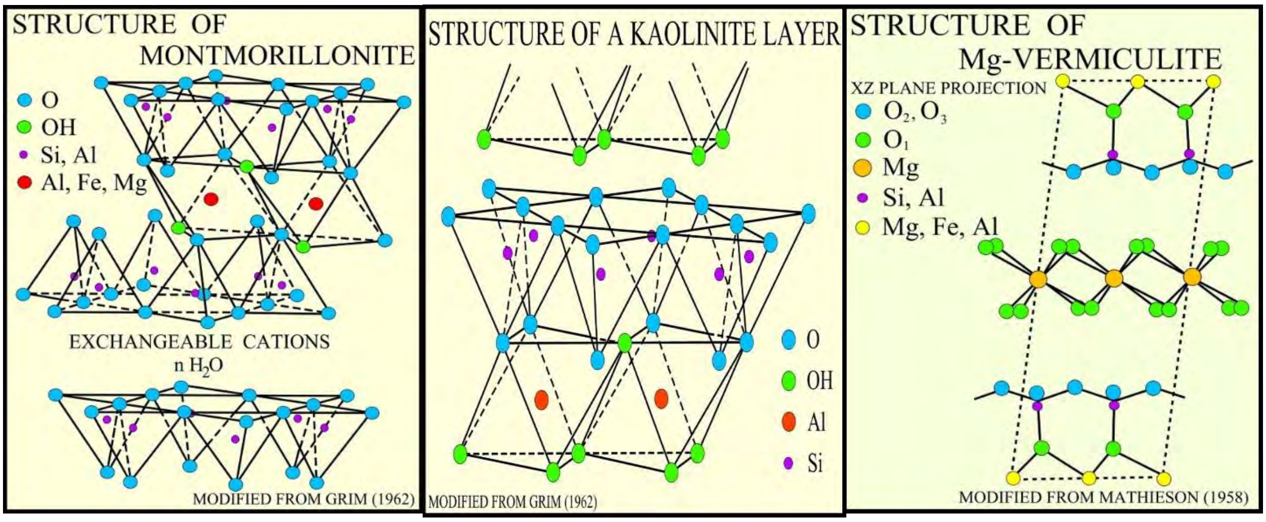


Figure 1.1 Crystalline structure of different type of clay: montmorillonite, kaolinite and vermiculite.

Thanks to its high specific surface area, the clay is characterized by a strong chemical and physical interaction with fluids and dissolved species that are subject to electrostatic repulsion, absorption or specific cation exchange reactions. These interactions allow to retain leachate components such as metallic cation in the barrier (Churchman et al. 2006). Another important characteristics of clay minerals that make it the most used material for the barrier construction are the high availability and the low cost (Bailey et al., 1999). In order to guarantee the longevity of the mineral barrier an increased cation exchange capacity and a low permeability of the geological barrierare desirable. These features can be provided by the smectite-type minerals in its small amounts (2-10%) maintaining a structural stability of the barrier. In fact, it provides a low permeability to natural soils and increases the cation exchange capacity of the geological barrier allowing the retention of certain polluting agents contained in the leachate (Gautier et al., 2010).

Clay linings are generally composed by bentonite and, in particular, montmorillonite. This latter can adsorb heavy metals in two different mechanism:

- Cation exchange in the interlayers resulting from the interactions between ions and negative permanent charges;
- Formation of inner sphere complexes through Si-O^- and Al-O^- groups at the clay particle edges (Abollino et al., 2003).

Another useful material to remove heavy metals is activated carbon (Modin et al., 2011). This material is largely used because of its high specific surface area, chemical stability and durability. Therefore adsorption by activated carbon has become a preferred choice due to its simplicity, cheap, easy to scale-up and most importantly able to remove low concentration substance even at part per million levels with high efficiency (Zaini et al., 2010).Heavy metals sorption by activated carbon is based on the surface acidity and on the special surface functionality. On it the removal mechanisms comprise of ion-exchange, basal plane cation interaction and coordination to functional groups (Sato et al., 2007). Its efficiency in the removal of metal from solution has been widely demonstrated but few studies have described heavy metals removal from landfill leachate using activated carbon (Foo et al., 2009). Heavy metals sorption by activated carbon is mainly affected by pH solution and acidic/basic character of the carbon surface (Huang et al., 1987). Usually the sorption is attributed to acidic sites (Sato et al., 2007). In that case, the sorption mechanism is via ion exchange with H^+ or complex formation with negatively charged sites as illustrated below:

$$xCOH + M^{2+} \rightarrow (CO)_xM^{2-x} + xH^+$$
$$xCO^- + M^{2+} \rightarrow (CO)_xM^{2-x}$$

where M stands for any metal removed (Rao et al., 2008).

Hence, it is very important to study the interactions between the pollutants and the material used to compose the landfill barrier in order to choose the suitable material to protect and preserve the surrounding area. In this context, heavy metals are one of the most important pollutants in the leachate that must be retain by the geological barrier.

Leachate composition strongly varies depending on the landfill and waste type. Furthemore, the composition of the leachate and of the heavy metals inside it changes according to the evolution process of waste degradation which is strongly linked to the biological and chemical-physical processes occurring in the landfill lifetime (Ghorbel-Abid et al., 2011).

In fact, there are three main categories of landfill type: aerobic, anaerobic, semi-aerobic. For each of these, there is a specific waste degradation process and a consequent exiting leachate with different qualitative characteristics. Finally, the nature of the metals in the leachate is also affected by the landfill age.

Heavy metals behaviour and bioavailability depend on the absorption and precipitation/dissolution process between solid and liquid phases (Alloway, 1995).To assess the risk of contamination of the surrounding environment is important to characterize the geochemical mechanism that govern the vertical migration of heavy metals. It is commanded by the mechanism of adsorption. The factors that mainly characterize the amount of heavy metals absorbed by the solid phase are the nature and concentration of the metals, the contact time, the temperature and the pH (Du and Hayashi, 2006). Solid phase can retain cations in the surface thanks to electrostatic attractions or specific adsorption by the formation of complexes. The process of transfer between the solid and liquid phases and the subsequent transport of metals is allowed thanks to the formation and rupture of complexes. (Aharoni et al., 1991).Therefore, it is important to know the landfill type from which the leachate is originated in order to understand the interaction between heavy metals and the material used as liners in the barrier. In fact, the leachate varies depending on the landfill type and consequently also the mechanism of absorption of the metals contained in it by the solid liners.

In order to understand more clearly the adsorption of heavy metals by solid liners many studies have been conducted. Sànchez-Jimenez et al. (2012) studied the interaction of clayey materials with heavy metals to evaluate their suitability as geological barrier of landfills. For the experiment five different types of clays have been used. The study has been conducted using solutions that simulate the characteristics and conditions of leachate from municipal solid waste landfills in acetogenic (young leachate) and methanogenic (old leachate) stage. In particular, they studied interactions between zinc(II), lead(II), cadmium(II) and chromium(III) ions and clayey materials. The results (figure 1.2) showed greater retention for zinc(II) and chromium(III) and low sorption capacity for cadmium (II). Moreover, all the clayey displayed lower metal sorption capacity in the young leachate conditions as it is possible to see in the figure below.

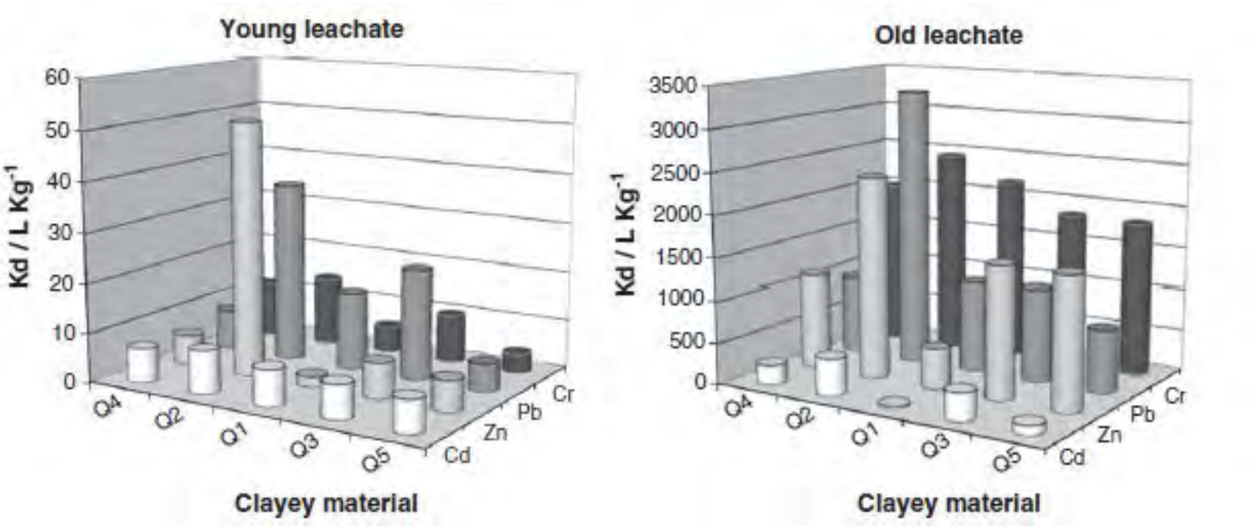


Figure 1.2 Distribution coefficient (Kd) for Cadmium (II), zinc (II), lead (II) and chromium (III) at five clayey materials, in competitive conditions, using the young (left) leachate and old (right) synthetic leachate (Sànchez-Jimenez et al., 2012).

The parameter that mainly control the metal retention capacity of clayey material are abundance of clay minerals, carbonate content, specific surface area and the presence of smectite control. Therefore, the study confirmed that clayey materials are suitable as components of the multibarrier in controlled urban landfills.

Ghorbel-Abid and Trabelsi-Ayadi in 2011 investigated the interaction between Cr(III) and Cd(II) ions in solution with the local landfill clay located in Tunis. The experiment was carried out using aqueous solutions rich in chromium and cadmium, studying the absorption properties of natural clay and the Na-purified clay using a batch technique. The equations describing the interaction between heavy metals and clay are:

$$xCr^{3+}{}_{(s)} + 3M^{x+}{}_{(c)} \longrightarrow xCr^{3+}{}_{(c)} + 3M^{x+}{}_{(s)}$$

$$yCd^{2+}{}_{(s)} + 2M^{y+}{}_{(c)} \longrightarrow yCd^{2+}{}_{(c)} + 2M^{y+}{}_{(s)}$$

where x and y are the exchangeable cations valence M (Na, K, Ca, Mg, Mn) and subscripts (s) and (c) denote solution and clay phases. The results showed that the uptake of the purified clay is faster than the natural clay. Moreover, the study confirmed that the adsorption capacity for the both clay is 174.5 mg/g for the chromium and 42.5 mg/g for the cadmium. Finally also this investigation support that clay is an important agent to retain heavy metals pollutants in the landfill barrier.

Other experiment conducted by Abollino et al. in 2003 studied the adsorption of metals by clays (especially montmorillonite). In particular the sorption of seven different type of heavy metals on

Na-montmorillonite. The results showed that the adsorption strongly varies both as a function of pH and of the ligand present in solution as it is possible to notice in the figure below.

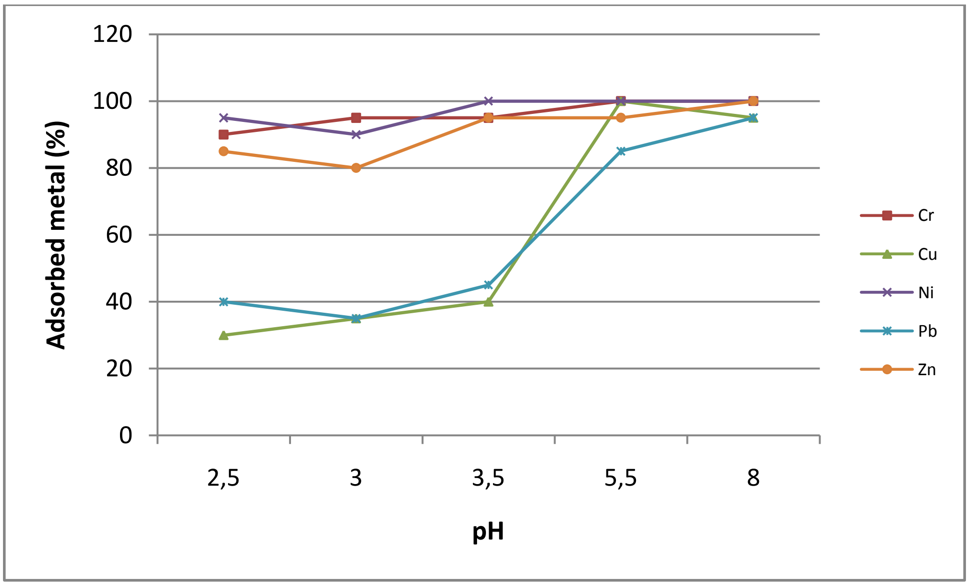


Figure 1.3Adsorption of Cd, Cr, Cu, Mn, Ni, Pb, and Zn on Na-montmorillonite as a function of pH (initial concentration of metals 1.0 x 10^{-4} M).

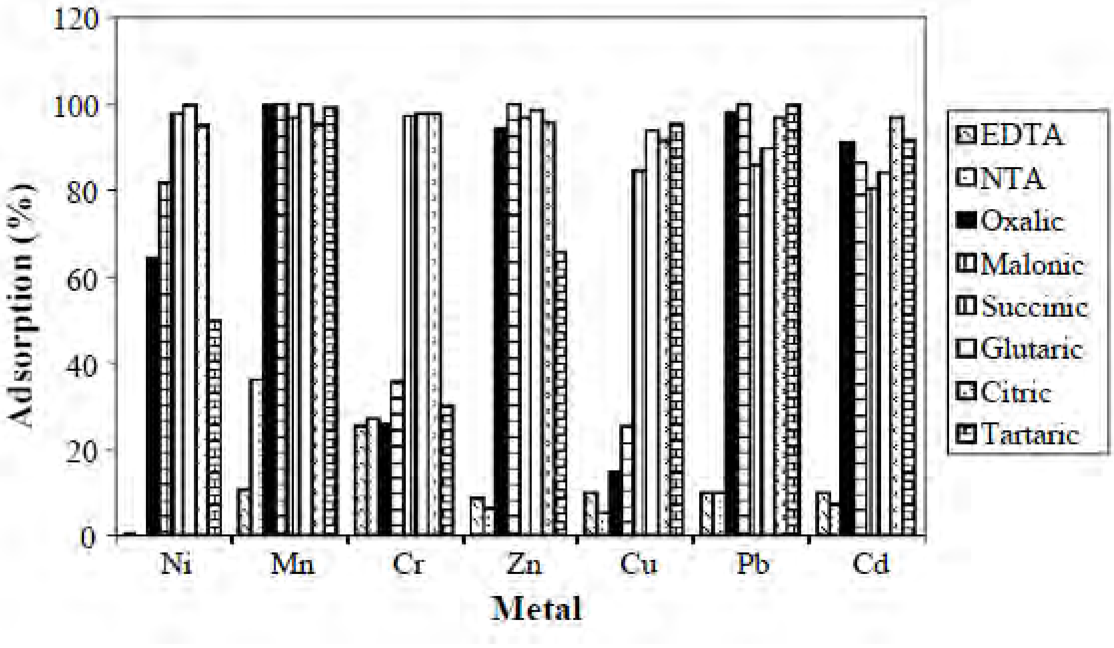
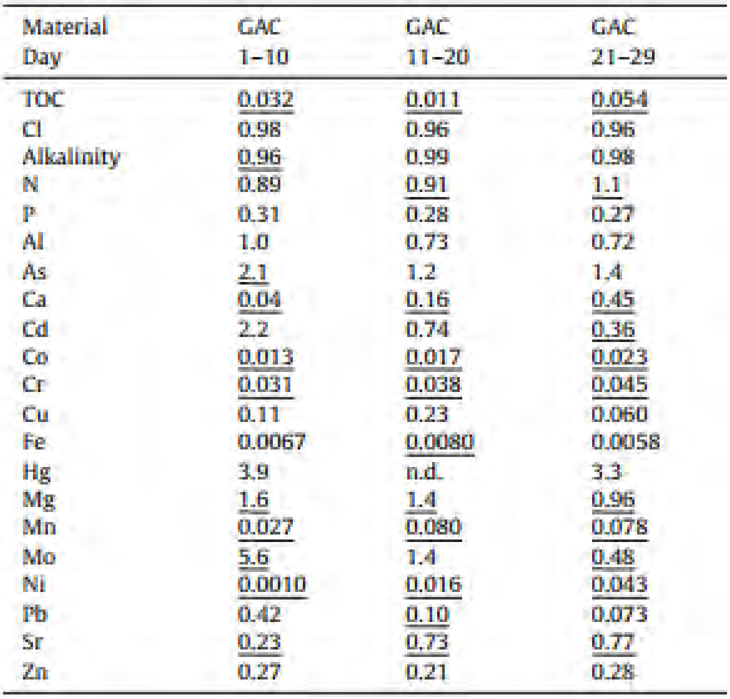


Figure 1.4 Metal adsorption on montmorillonite in the presence of different ligands (pH 5.5; metal concentration 1.0 x 10^{-4} M; ligands concentrations 1.0 x 10^{-3} M) (Abollino et al., 2003).

Therefore, it is necessary to take into account these two factors in designing a barrier system to retain heavy metals.

Modin et al. in the 2011 conducted a study to evaluate the efficiency of sorption filters based on granular activated carbon for the removal of metals from landfill leachate. For this experiment granular activated carbon (GAC) with a particle size of 0.25-1 mm was used. PVC columns filled with the filter material in a quantity equal to 500 g weight and the leachate was pumped through the column at an initially flow rate of 1 m/day. The experiment lasted 29 days. The columns with GAC removed heavy metals with efficiency. In particular more than 90% of Co, Cr, Fe, Mn, and Ni were removed.Ca, Cu, Pb, Sr, and Zn were removed, in all samples but not at the same percentage and finally As, Cd, Hg, Mg and Mo were released from the filters in one or more samples as it is possible to notice in the following table.



Material Day	GAC 1–10	GAC 11–20	GAC 21–29
TOC	0.032	0.011	0.054
Cl	0.98	0.96	0.96
Alkalinity	0.96	0.99	0.98
N	0.89	0.91	1.1
P	0.31	0.28	0.27
Al	1.0	0.73	0.72
As	2.1	1.2	1.4
Ca	0.04	0.16	0.45
Cd	2.2	0.74	0.36
Co	0.013	0.017	0.023
Cr	0.031	0.038	0.045
Cu	0.11	0.23	0.060
Fe	0.0067	0.0080	0.0058
Hg	3.9	n.d.	3.3
Mg	1.6	1.4	0.96
Mn	0.027	0.080	0.078
Mo	5.6	1.4	0.48
Ni	0.0010	0.016	0.043
Pb	0.42	0.10	0.073
Sr	0.23	0.73	0.77
Zn	0.27	0.21	0.28

Table 1.5 Removal efficiencies by filtration in columns filled with granular activated carbon (GAC). Numbers represent effluent concentration/influent concentration (C/C_0). Significant differences between C and C_0 are underlined (Modin et al., 2011).

The main parameters governing the sorption of metals to activated carbon are the pH of the solution and the acidic/basic character of the carbon surface. During this experiment, leachate pH increased from 7.2 to 9 suggesting basic character of the GAC. In this study, dominating heavy metals mechanism seem to have been cation interaction with basic surface sites and immobilization of metals together with organic matter since more than 90% of organic matter was removed in the columns and heavy metals in landfill leachate are thought to form complexes with organic matter.

Therefore, this experiment confirmed that granular activated carbon (GAC) is a very effective material with regard to removal of metals even if sometimes there is the risk of As release.
Another interesting study was conducted by Wasay et al. in 1999. They tested granular activated carbon (GAC), granular activated alumina (GAA) and ferric chloride solution (FCS) for the treatment of leachate contaminated by heavy metals (Cd(II), Cu(II), Cr(III), Hg, Mn(II), Pb(II), and Zn(II)). The results showed that only GAC removed efficiently heavy metals. 97% of Hg was removed at optimum pH ranging from 5.4 to 6.9, while 78 to 96% of Cd, Cu, Mn, Pb and Zn were removed at optimum pH ranging from 6.9 to 7.7. Hence, these studies confirmed that GAC is efficiently for heavy metals removal from leachate.

Finally, it can be confirmed that the knowledge of the interaction between heavy metals and solid liners is a fundamental notion to understand how efficiently the material removes the pollutant. Therefore, this topic must be analysed in depth in order to choose the suitable material for the construction of a geological barrier.

2. THESIS OBJECTIVE

The speciation of heavy metals in leachate polluted groundwater is not well known because very few observations have been made on relevant field samples. The literature contains relatively few studies suggesting that they should be regarded as good indications rather than final conclusions. Therefore, the results of the speciation of heavy metals in landfill leachate should be seen in the light of still limited database available. This indicates that the knowledge concerning metal species in landfill leachate is still approximate (Baun and Christensen, 2004).

In this context, the aim of our work is to study the behaviour of the heavy metals in landfill leachate produced in aerobic and anaerobic conditions, identify the most suitable method for their speciation studies, and the study of the relationship between the leachate source and the effectiveness of different solid liners.

In particular, the thesis objective is to investigate on transition metals speciation in ionic or coordinated form, performing different kind of analytical analysis on several leachate samples derived from landfill of various type. In this way, it will be possible to study heavy metals speciation and assess the quality and accuracy of different analytical methods tested. Our investigation is of great importance to environmental protection as it helps to elucidate the possible form in which heavy metals are present in leachate and consequently to evaluate their possible interaction with the aquifer and the soil. In fact, depending on the form type, metals can change their oxidation state and associate to the colloidal or dissolved fraction or form complexes. Hence, identifying the most accurate method of analysis, it will be possible to evaluate the metals behaviour in the environment and consequently take the suitable preventive measures so as to avoid pollution of the area surrounding the landfill. Therefore, this work aims to improve the knowledge in the field of heavy metals speciation so as to evaluate their potential environmental contamination.

After evaluating the best method of heavy metals analysis, the goal of the thesis focuses on the study of the attenuation of heavy metals in municipal solid waste landfill leachate by different stationary phases (active carbon and vermiculite). In particular, we intend to analyse the heavy metals speciation in six different type of leachate (3 aerobic and 3anaerobic) using as an indirect method the passage through a particular solid liner. In fact, the functional groups and adsorption sites on solid liners of different type (clay and carbon) can give interesting information about the metals species produced in aerobic or anaerobic conditions through their interaction. This could give useful information about the effect of the landfill treatment on the fate of heavy metals in the leachate percolating through the landfill barrier.

This investigation can also help to assess the metals behaviour in the environment, especially in aquifer and soil. In this way, the study aims to improve the field of heavy metals speciation in landfill leachate with respect to its treatment, toxicity to surface and risk to groundwater. This investigation will be very important because literature studies and knowledge regarding this topic are very limited.

Furthermore, this study is a starting point for a future study on the adsorption efficiency of heavy metals by solid liners and the mechanism by which this adsorption takes place.

Finally, one of the goals of this thesis will be to suggest the possible development of the study of heavy metals speciation in different municipal municipal solid waste landfill leachate (aerobic and anaerobic) through analytical techniques in order to characterize their potential pollution in the environment.

3. MATERIALS AND METHODS

3.1 Samples origin

In our study we decided to analyze leachate from different treatments (aerobic and anaerobic) and ageing. For this purpose we used leachate derived from a simulated landfill reactors managed in –SANA” mode and from a simulated landfill reactors managed in –Concentrato” mode. In the following sections the origin of the leachate samples is illustrated.

3.1.1 Leachate Samples from SANA management

The samples of young leachate, used for our experiment, derived from a test conducted by the Department of Industrial Engineering (DII) at LISA (Laboratorio di Ingegneria Sanitaria Ambientale). The experiment is to simulate a landfill with six columns filled with waste. These last were taken from the landfill in "Lo Scapigliato" in the town of Rosignano Marittima, in the province of Livorno, Tuscany. The total amounts to a quantity of 200 kg. It is Municipal Solid Waste characterized by high content of putrescible substance. Since the wastes were very heterogeneous and large size, they were sieved at 80 mm and it was taken undersieve. The amount used for the test has thus been reduced to 112 kg, compared to 200 kg initial.

The waste is then inserted into the column at a density equal to 0.5t/m^3.

Merceological analysis showed the following results.

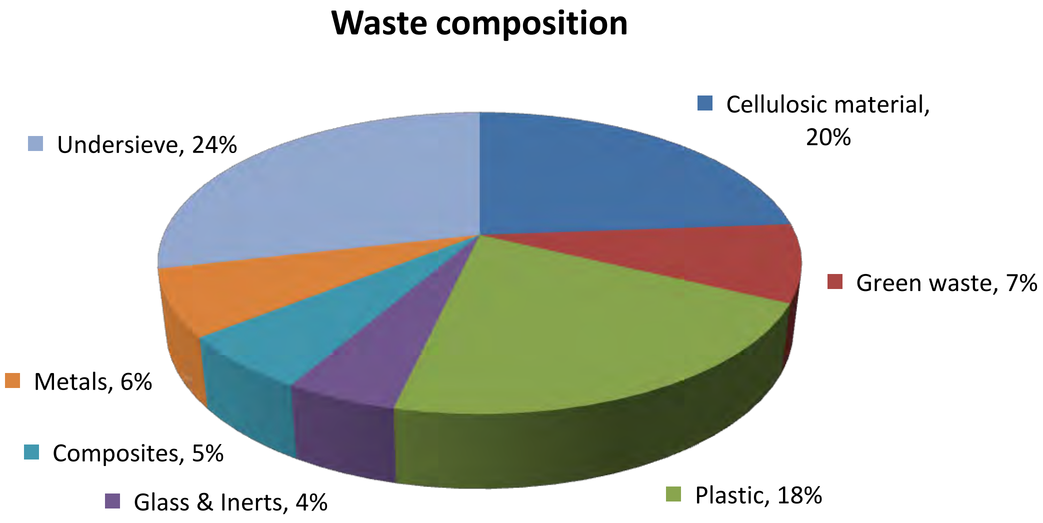


Figure 3.1 Waste composition for SANA experiment.

The test conducted at LISA laboratory simulates the landfill with six columns filled with this waste. Four of them are managed in SANA mode while the other two remain in anaerobic conditions for control purpose.

The SANA management is divided into three steps:

1. Semi-aerobic
2. Anaerobic
3. Aerobic

In the semi-aerobic phase, the columns are aerated with an average air flow equal to 50 l/d. In the anaerobic phase instead ventilation is stopped out. The leachate that comes out daily is completely recirculated.

The goal is to demonstrate the effectiveness of management mode SANA and the more biogas production compared to traditionally managed columns.

Figure 3.2 The six columns that simulate the landfill.

During the experiment, the leachate samples are daily collected and analyzed.

The following parameters are analyzed:

- pH
- TOC
- COD
- BOD_5
- TKN
- NH_3
- SO_4^{2-}
- Cl^-
- Alkalinity
- Volatile Fat Acids

Figure 3.3 Leachate samples collected.

The leachate SANA samples utilized for our experiment are characterized by the following parameters. It is important to underline that these samples are characterized by a young age.

Sample characteristics			
Sample name	S1	S2	S3
Sample data	04/07	08/09	27/10
Column	1	1	1
Phase	Semi-aerobic	Semi-aerobic	Anaerobic
pH	5.35	6.36	7.81
TOC [mgC/l]	9130.00	12100.00	4840.00
COD [mgO_2/l]	30000.00	34778.40	7736.00
BOD_5 [mgO_2/l]	27431.00	26982.00	-
TKN [mgN/l]	866.34	2019.00	1973.44
NH_3 [mgN/l]	402.36	1596.80	1531.32
SO_4^{2-} [mg/l]	2261.70	1394.40	1011.90
Cl^- [mgO_2/l]	3.139.36	3321.66	2414.62
Alkalinity [mg$CaCO_3$/l]	448.00	4163.00	7394.00
VFA [mgCH_3COOH/l]	2212.80	5287	745.20

Table 3.1SANA Leachate samples characteristics.

Figure 3.4 SANA leachate sample.

3.1.2 Leachate samples from Concentrato management

Leachate samples of medium-old leachate derived from a test conducted by the DII (Dipartimento di Ingegneria Industriale) at LISA laboratory. The purpose of the experiment is to evaluate the effects of the RO concentrate reinjection into landfill body, focusing on the chemical and hydraulic point of view. Have been used six laboratory columns filled with pretreated municipal solid waste, in which were injected different volumes of concentrate.

The RO concentrate sample was taken from the landfill of Sarcedo (VI) that is an old landfill type of special non dangerous waste assimilated to urban waste.

The waste used for the experiment coming from Sanremo and is equal to an amount of 100 kg of pretreated waste. Its characterization is presented in figure below.

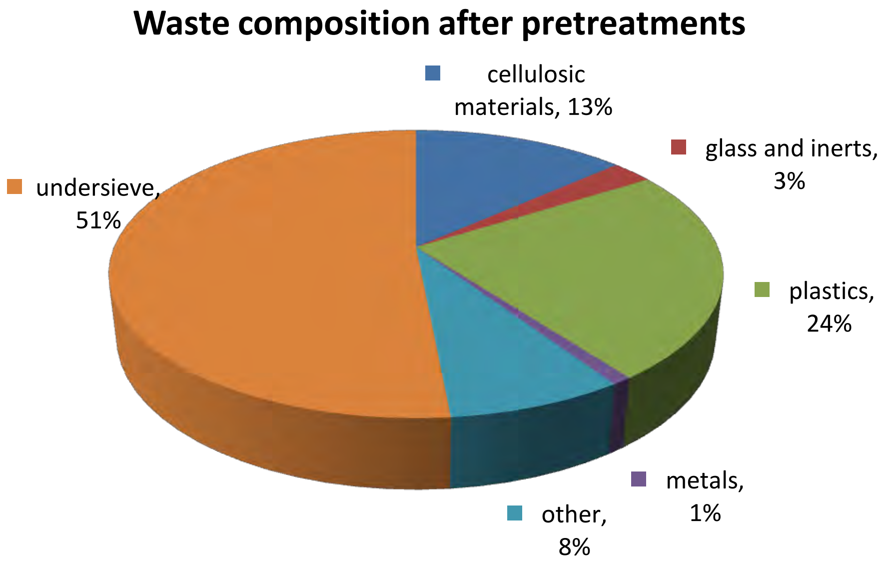


Figure 3.5 Waste composition after pretreatments for Concentrato experiment.

For the test have been used six plexiglas columns filled with 14.7 kg of waste each one. Then it is placed above the gravel layers and compacted manually up to reach a density of 0.5 t/m^3. The gas produced is collected in bags for quantify the volume and the composition. While the extraction of the leachate is done thanks to a drainage valve placed at the bottom of the column. The figure 3.6illustrates a schematic representation of the column used in the test.

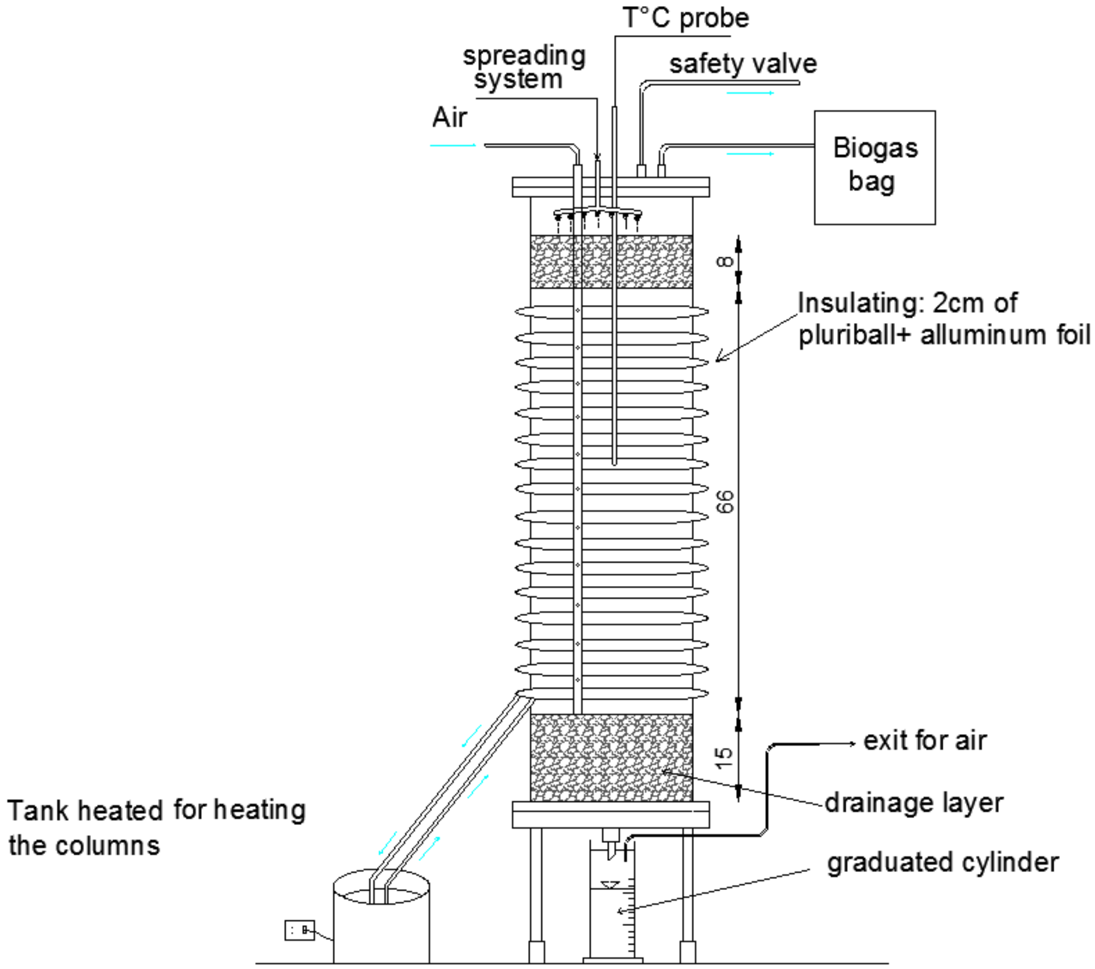


Figure 3.6 Schematic representation of the columns used in the experiment.

The first operation for the management of the columns consist on raise the moisture of the waste mass from 33% to 50% adding gradually 5 liters of deionized water to ensuring the formation of at least 1-2 liters of leachate. The concentrated and the deionezed water were injected manually every Monday (once a week) with a total sum volume equal to 1 l/d and a composition that change for each column. Three columns were aerobic and three anaerobic. The aeration of the aerobic columns was average of 50 l/d. The proportion between water and concentrated is reported in the table 3.2. The leachate is manually recirculated every day. The figure 3.7 illustrates the management columns scheme.

		INPUT (1 l/week)	AERATION (l/d)
ANAEROBIC	**C1**	100% RO concentrate	-
	C2	50% RO concentrate +50% water	-
	C3	100% water	-
AEROBIC	**C4**	100% RO concentrate	50
	C5	50% RO concentrate +50% water	50
	C6	100% water	50

Table 3.2 Management of the columns. The table shows the proportion of water and concentrate injected in every columns, and reports the daily air flowrate.

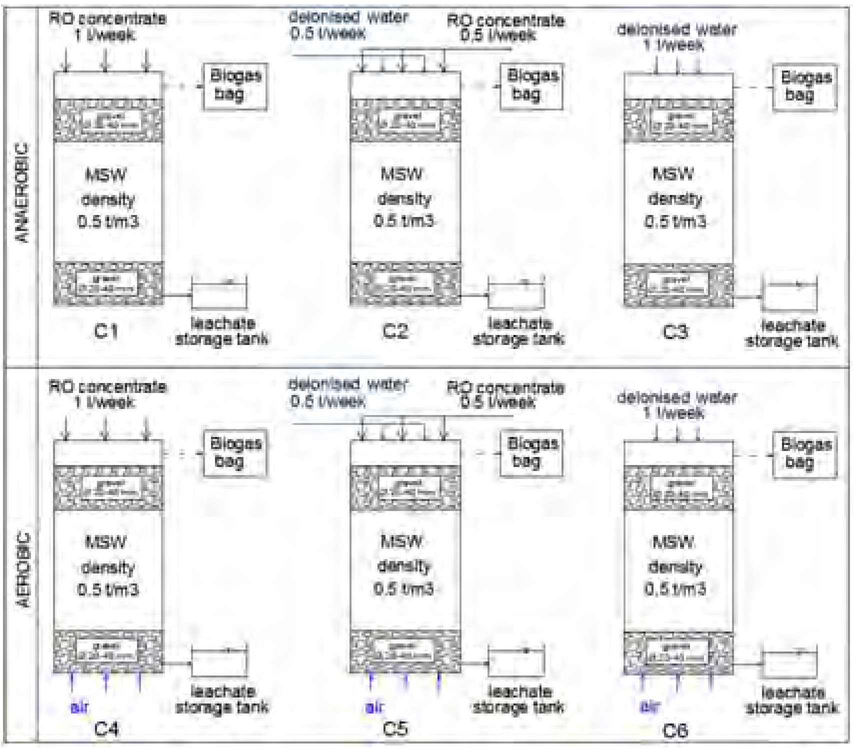


Figure 3.7 Management columns scheme.

Significative leachate samples were collected every week. On them are performed the following analysis:

- pH
- Liquid solid ratio
- COD
- NH_4
- Cl^-

The Concentrato leachate samples utilized for our experiment are characterized by the following parameters. It is important to underline that these samples are characterized by an old age.

Sample characteristics						
Sample data	26/01	26/01	26/01	02/02	02/02	02/02
Sample name	C1	C2	C3	C4	C5	C6
Column	1	2	3	4	5	6
Phase	Anaerobic	Anaerobic	Anaerobic	Aerobic	Aerobic	Aerobic
pH	8.28	8.31	7.86	7.78	7.69	7.95
L/S (l/Kg)	1.085	1.107	1.023	1.059	1.086	1.045
COD [mgO_2/l]	8343	6180	3562	3290	5176	7490
NH_4 [mgN/l]	2843	1707	605	542	469	940
Cl^- [mgO_2/l]	2533	1535	688	1324	1413	1661

Table 3.3 Concentrato leachate samples characteristics.

Figure 3.8 Concentrato leachate samples.

3.2 Sample Preparation

Due to the particular characteristics of the analytical technique performed on the samples we performed delicate sample preparation which will be reported separately in the following paragraphs.

3.2.1 Sample preparation for ESEM and FT-IR analysis

This technique needs solid samples. For this reason, it is necessary to separate the solid fraction. This procedure is performed by vacuum drying a definite amount of leachate at room temperature. In a typical preparation, 50 ml of leachate was placed in a 250 ml round bottom flask connected to a vacuum line.

A liquid nitrogen trap has been used in order to collect the vapours. This is important in case the sample contains substances that cannot be discharged in the atmosphere. The process was constantly monitored because bubbling could easily produce foams.

Figure 3.9 Vacuum drying of leachate sample.

At the end of the process the dry residue was scraped off with a scraper, weighed and collected in vials (figure 3.10) for storage. This part represents the total solid fraction of the sample.

Figure 3.10 Total solid fraction of the sample.

A small fraction of the solid sample was placed on a carbon coated holder for the ESEM analysis and introduced in the analysis chamber without further treatment. To perform the FT-IR analysis, it was necessary to prepare the sample using an infrared transparent matrix. It consists of a tablet composed for the 10% by the solid sample and for the 90% by KBr (Potassium Bromide).

In the figure below illustrates the instruments to create the tablet.

Figure 3.11 Instruments for the preparation of the tablet for the FT-IR analysis.

3.2.2 Sample preparation for ESI and GC-MS analysis

Sample preparation for ESI and GC-MS analysis consisted in a preparation of a solution of the leachate in a proper solvent and subsequent filtration to remove any suspended matter. According to the technique and the polarity of the fraction under analysis, solvents can be methanol (CH_3OH, protic polar solvent), acetonitrile (CH_3CN, aprotic polar solvent), acetone (CH_3COCH_3, aprotic polar solvent) or dichloromethane (CH_2Cl_2, aprotic slightly polar solvent). In general, the solution was prepared by diluting 1 ml of leachate to 5 ml with the solvent followed by filtration on glass fibre plug.

3.2.3 Sample preparation for NMR analysis

Samples for NMR analysis need to be perfectly homogeneous so a separation of any suspended matter was necessary. For the ^{13}C-NMR analysis, about 10 ml of leachate samples were centrifuged.

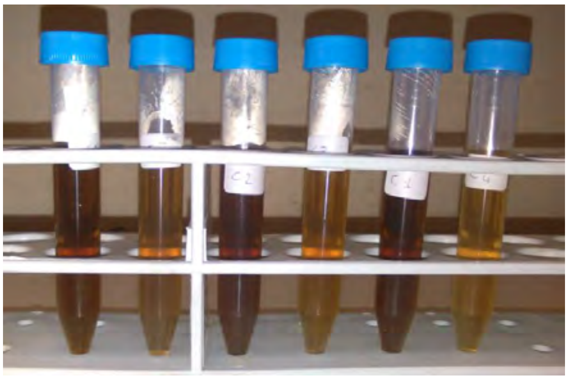


Figure 3.12 Sample preparation for NMR analysis

Centrifugation was performed at 10000 rpm for 10 minutes in order to separate by gravity the colloidal fraction from the dissolved fraction. The instrument utilized to perform the centrifugation was the Awel MF 20-R non refrigerated centrifuge (figure 3.13).

Figure 3.13 Awel MF refrigerated centrifuge.

The colloidal fraction (> 0.001 μm) was weighed in order to perform a physical fractionating on the sample. The dissolved fraction instead was utilized for NMR analysis. 400 microliters of the dissolved fraction were put in an NMR tube with 100μl of deuterium oxide (D_2O).

For the ^{1}H-NMR analysis, the sample was subject to vacuum drying in order to remove the water. The solid fraction was weighed and25 mg of it was treated with 0.5 ml of deuterium oxide or deuterated chloroform and then filtrated.

Filtration was performed using a Pasteur pipette (figure 3.14), equipped with a glass wool plug, that discharges into a NMR tube.

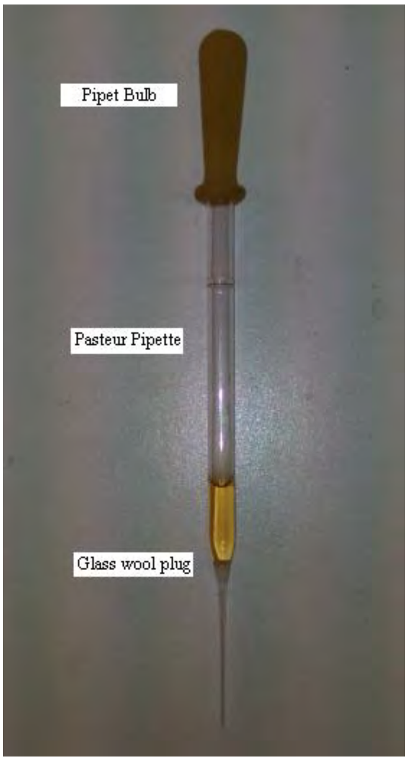


Figura 3.14 Pasteur pipette equipped with glass wool plug.

The purpose of filtration is to remove any undissolved sample and particulates from the solution because they may adversely affect the resolution and the line shape of the NMR spectrum.

3.2.4 Sample preparation for ICP analysis

Samples preparation for ICP analysis was performed according to US EPA method 3050B. This method titled "Acid digestion of sediments, sludges and soils" provides two separate digestion procedures, one for the preparation of samples for analysis by flame atomic absorption spectrometry (FLAA) or inductively coupled plasma optical emission spectrometry (ICP-OES) and the other for analysis of samples by Graphite Furnace Atomic Adsorption (GFAA) or inductively coupled plasma mass spectrometry (ICP-MS). This method is a very strong acid digestion that will dissolve almost all elements that could be environmentally available.

The preparation procedure for each sample is composed by the following steps:

- At the beginning, 30 ml of leachate sample was transferred in a two necks 250 ml round bottom flask.
- For the digestion, the samples were mixed with 10 ml of 1:1 HNO_3 covering with a watch glass or vapour recovery device. The samples were then heated to 95°C ± 5°C and refluxed for 10 to 15 minutes without boiling (figure 3.15).

Figure 3.15 Leachate sample heated to 95°C ± 5°C and refluxed during preparation for ICP analysis.

- Subsequently, the samples were allowed to cool at room temperature, 5 ml of concentrated HNO_3were added and they were refluxed for 30 minutes. If brown fumes were generated, indicating oxidation of the sample by HNO_3, step was repeated over and over until no brown fumes were given off by the sample indicating the complete reaction with HNO_3.

- Then the solution was evaporated to approximately 5 ml by heating at 95°C ± 5°C without boiling. The evaporation was enhanced by using a water pump (figure 3.16).

Figure 3.16 Evaporation of the solution thanks to the water pump during preparation for ICP analysis.

- After the last step was completed and the samples were cooled, 2 ml of water and 30 ml of 30% H_2O_2were added. The balloon was covered with a watch glass and warmed to start the peroxide reaction. In this step, care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. The sample was heated until effervescence subsided and then was allowed to cool.
- Then 30% H_2O_2 in 1 ml aliquots was continuously added with caution until the effervescence was minimal or until the general sample appearance was unchanged. The maximum amount H_2O_2 solution was less than 10 ml.

- After that, the sample was heated at 95°C ± 5°C without boiling and evaporated thanks to a water pump until the volume of the acid-peroxide digestate was reduced to approximately 5 ml.
- In the last step, the sample was allowed to cool and then was diluted to 100 ml with deionized water. Particulates in the digestate were removed by filtration with a 0.45 µm filter. The sample is therefore ready for analysis by ICP (figure 3.17).

Figure 3.17 Sample collected ready for ICP analysis.

In general, the filtration is performed to eliminate undissolved particulate, which is mainly composed of silicate particles. In our case, all the solutions were clear before filtration indicating no or a very little presence of silicate components.

3.3Analysis

In this section, all the analysis performed on SANA and Concentrato leachate samples are reported. ESI-MS, FT-IR, GC-MS and NMR analysis were performed at DII (Dipartimento di Ingegneria Industriale) chemical laboratory, ICP-OES at LISA laboratory in Voltabarozzo and ESEM at CUGAS (Centro Universitario Grandi Apparecchiature Scientifiche) laboratory in Padova.

The initial analysis was conducted in order to study heavy metals speciation in landfill leachate and to identify the most suitable technique to adopt in heavy metals speciation studies. Subsequently Concentrato sample were subjected to ICP-OES analysis before and after filtration by different stationary phases (active carbon and vermiculite) in order to study the interaction of metals in landfill leachate with different solid liners. The table 3.4 summarizes the analysis performed. In particular, for each sample it reports if the analysis is performed on the liquid or solid fraction.

	S1		S2		S3		C1		C2		C3		C4		C5		C6	
	L	S	L	S	L	S	L	S	L	S	L	S	L	S	L	S	L	S
ESEM		x		x		x												
ESI-MS	x		x		x		x		x		x		x		x		x	
FT-IR		x		x		x												
GC-MS	x		x		x		x		x		x		x		x		x	
ICP-OES	x		x		x		x		x		x		x		x		x	
NMR	x		x		x		x		x		x		x		x		x	

Table 3.4 Analysis performed on the sample. For each sample is indicated if the analysis is conducted on the liquid fraction(L) or on the solid fraction (S).

3.3.1 ESEM: Environmental scanning electron microscope

The solid samples obtained by vacuum drying have been analysed with environmental scanning electron microscope (ESEM) in order to evaluate their morphology, composition and to quantify the concentration of different elements in the sample. The analysis was performed onS1, S2 and S3 leachate samples originated from SANA management.

The scanning electron microscope (SEM) is a type of microscope that hits the sample with parallel beams of electrons to evaluate its composition. The samples have to be clean, dry and electrically conductive. Nonconductive specimens have to be coated with a conductive film to avoid specimen charging. The electrons interact with the sample in three ways: some are reflected (elastic diffusion), others penetrate the surface of the samples, others are absorbed by the atoms of the sample producing electrically excited ions. These ions, returning to their fundamental states, emit secondary electrons, Auger electrons or photons at a high spectral X energy (fluorescence).

Handling the emissions of photons is possible to extrapolate the morphology information (measure of the angle between the incidental beam of secondary electrons and the surface of the sample) and composition of the surface of the sample (measure of the atomic number of elements in the sample) and therefore finally is possible to create an image of the sample (measure of the electrons backscattered).

In the PC monitors two images appear: the first one is related to the diameter of the electron beam, the smaller is the diameter the higher is the resolution; the second one is related to the energy of the electron beam, the higher is the energy, the deeper the beam will penetrate the sample surface and the higher will be the volume of backscattered electrons. This image allows to distinguish the heavier elements (lighter) from the lighter element (darker).

The SEM's primary limitations, as a general imaging and analytical technique, were the restrictions that are imposed on samples by requiring a high vacuum sample environment.

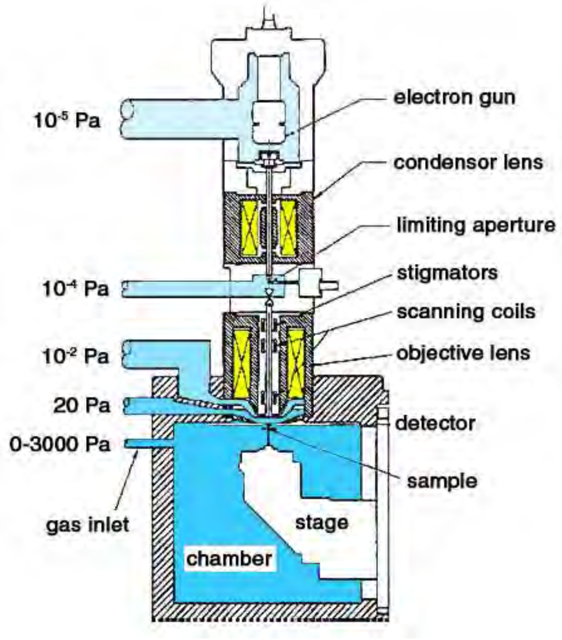


Figure 3.18 schematic illustration of ESEM system.

The Environmental scanning electron microscope (ESEM) retains all of the performance advantages of a conventional SEM, but removes the high vacuum constraint on the sample environment. Wet, oily, dirty, non-conductive samples may be examined in their natural state without modification or preparation. The objective of ESEM analysis is to create a fluorescence spectrum, characterized by some intensity peaks related to energy (keV). Each element presents a characteristic spectrum with primary and secondary peaks. The spectrum allows qualitative analysis of the elements of the sample. The intensity of the peaks is linked to the abundance of the atoms of the particular specie in the sample volume. The area subtended under the peaks-curve is proportional to the concentration of the different species. Every manufacturer company gives the correction parameters end errors for these types of tools.

In this thesis work, to perform the analysis it has been utilized the microscope ESEM, model XL30 Philips.

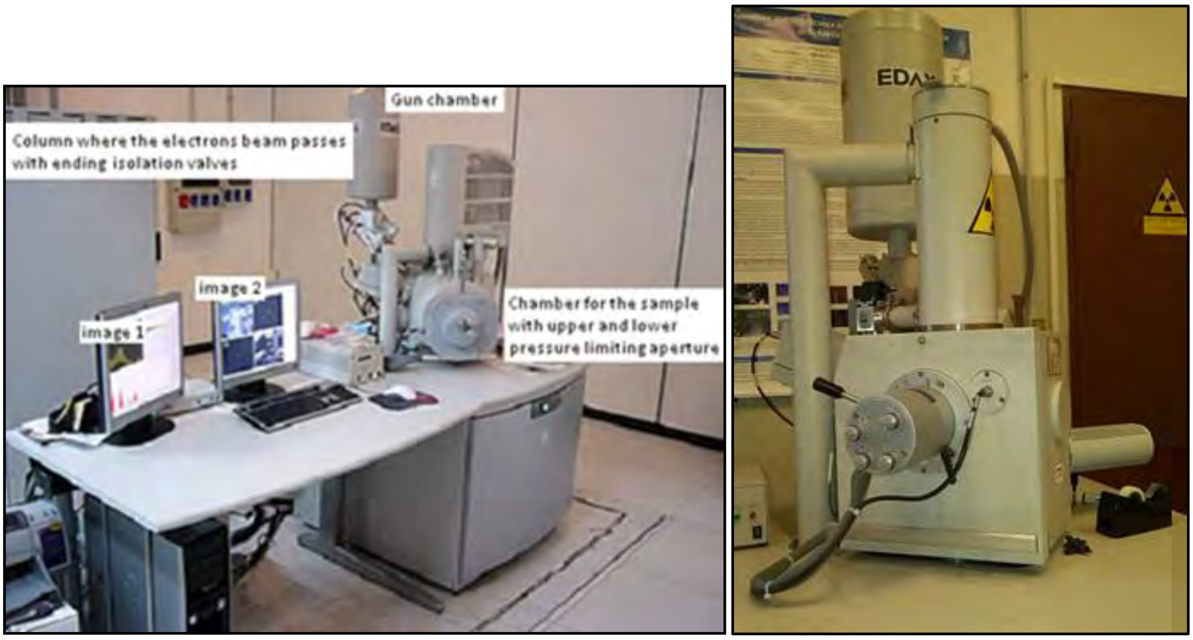


Figure 3.19 ESEM device.

3.3.2 ESI-MS: Electrospray ionization mass spectrometry

The ESI-MS analysis was performed on both SANA and Concentrato samples diluted with suitable solvents (methanol or acetonitrile) and filtered.

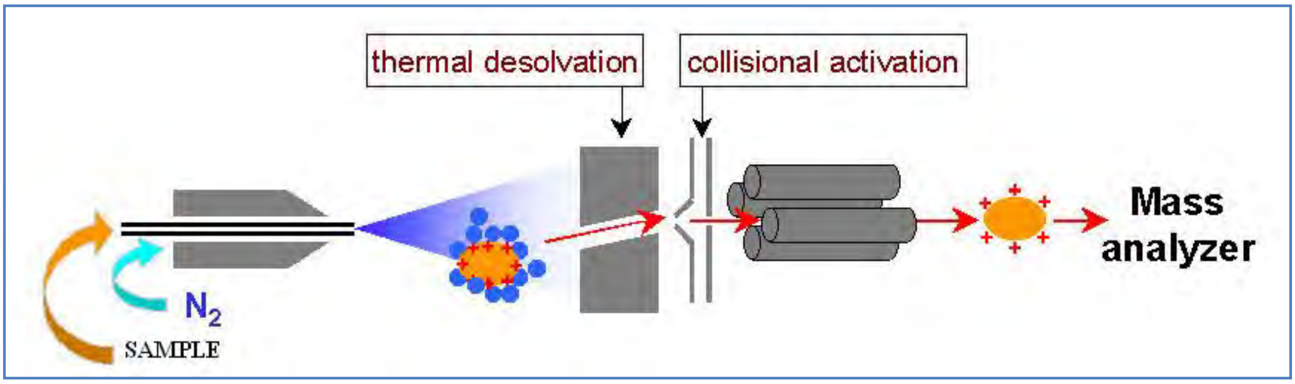


Figure 3.20 ESI MS operational scheme.

Electrospray ionization (ESI) is an ionization method for the determination of the mass and isotopic distribution of fragments generated by large molecules such as peptides, proteins, organometallics, and polymers. A sample solution is injected with a syringe into a strong electric field in the presence of a flow of warm nitrogen to assist desolvation. The droplets formed evaporate in a region maintained at a vacuum of several torr causing a decrease in their volume and a subsequent increase in their charge density. The multiply charged ions then enter the analyzer. In the obtained ESI spectrum, the ions carry multiple charges, which reduce their mass-to-charge ratio compared to a singly charged species. This allows to obtain the mass spectra for large molecules. In this work, the ESI analysis was performed on a Finningam LCQ-DUO instrument with Xcalibur software (figure 3.21) for data elaboration.

Figure 3.21 Finningam LC duo instrument used for ESI analysis.

3.3.3 FT-IR: Fourier transform infrared spectrometer

The solid fraction of the samples, obtained after vacuum drying, were also analysed by FT-IR to study the metals speciation inside the leachate. In this case, the samples analysed are the S1, S2 and S3 of the leachate deriving from SANA management.

The FT-IR spectroscopy is an absorption spectroscopy technique that allows to obtain a qualitative analysis about the characteristics of the functional groups of a molecule through their adsorption properties of infrared radiation. This method exploits the fact that when a IR beam with a certain wavelength hit a molecule, causes a change in the vibrational energy level by modifying the length of the chemical bonds (stretching), or deforming the bond angle(bending).Each functional group has a specific absorption that allows to gain qualitative information.

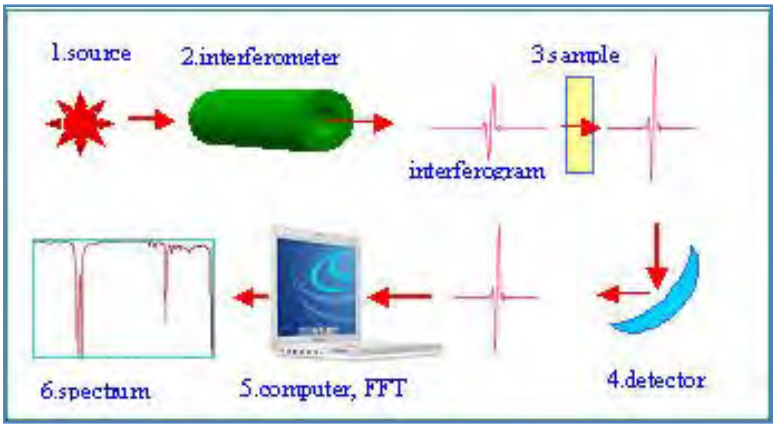


Figure 3.22 Schematic illustration of FT-IR system.

Thanks to this technique, it is therefore possible to obtain information about the functional groups present in the molecules of the sample and thus indirectly on the molecules structure. The instrument used for the analysis is the FT-IR PerkinElmer Spectrum100 and the results are then adapted with OMNIC software (figure 3.23).

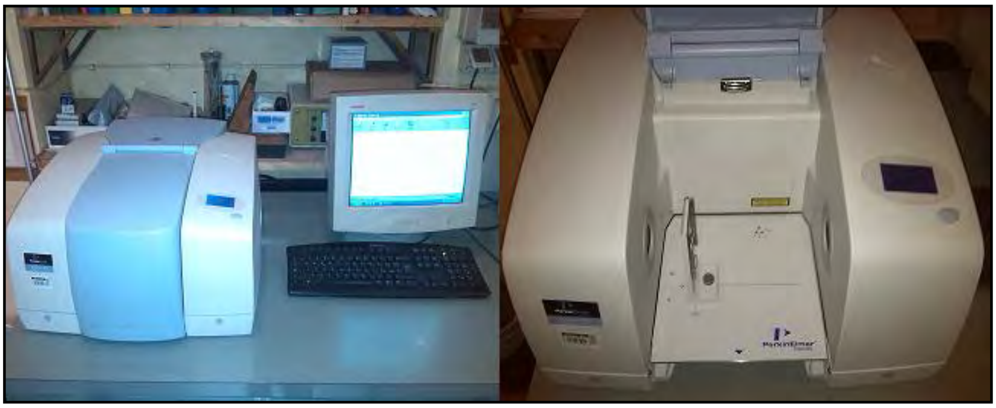
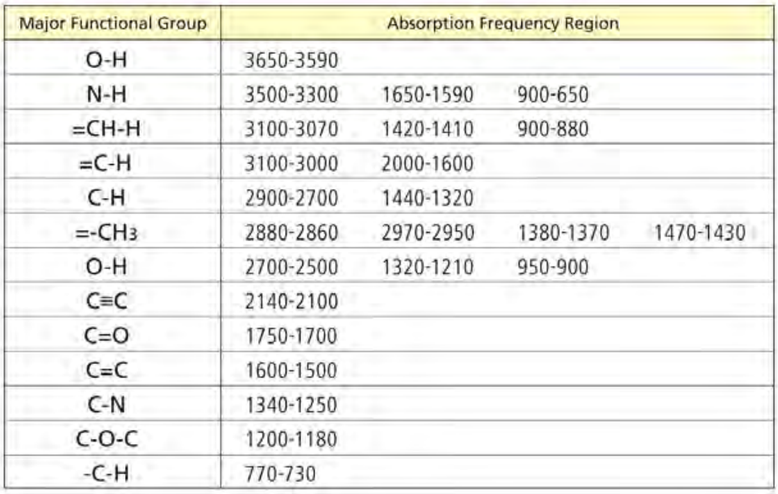


Figure 3.23 FT-IR PerkinElmer Spectrum100 utilized for the analysis.

The IR spectrum in the abscissa reports the wave number (in cm^{-1}, more often used than the frequency) and in the ordinate the percentage of radiation transmitted. Figure 3.24 presents the absorption frequency region of the major functional groups.



Major Functional Group	Absorption Frequency Region			
O-H	3650-3590			
N-H	3500-3300	1650-1590	900-650	
=CH-H	3100-3070	1420-1410	900-880	
=C-H	3100-3000	2000-1600		
C-H	2900-2700	1440-1320		
=-CH_3	2880-2860	2970-2950	1380-1370	1470-1430
O-H	2700-2500	1320-1210	950-900	
C≡C	2140-2100			
C=O	1750-1700			
C=C	1600-1500			
C-N	1340-1250			
C-O-C	1200-1180			
-C-H	770-730			

Figure 3.24 Absorption frequency region of the major functional group.

3.3.4 GC-MS: Gas chromatogram - Mass spectrometry

The GC-MC analysis has been performed on SANA and Concentrato samples by diluting the liquid fraction with a suitable solvents (methanol, acetone) to analyse the volatile fraction of the leachates. GC-MS is an analytical technique that allows to identify and quantify substances in a variety of matrices. The gas chromatograph separates the compounds present in the sample and the mass spectrometer acts as a detector.

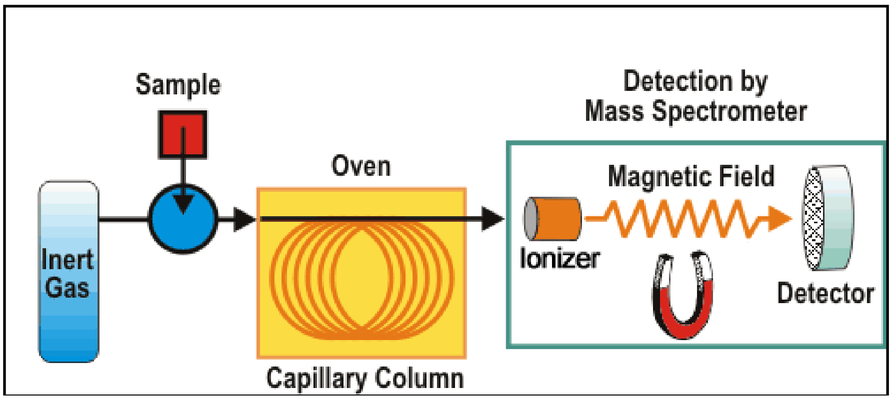
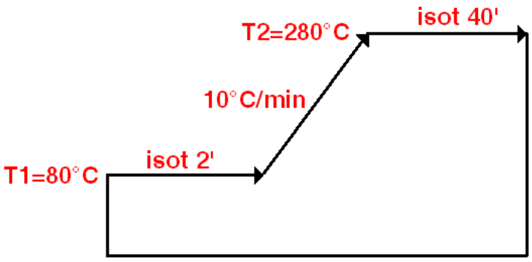


Figure 3.25 GC-MS schematic illustration.

Initially the sample undergoes the gas chromatography (GC) separation, in which it is separated in its different components according to their chemical properties (polarity) and their relative affinity for the stationary phase of the column during its permanence within the column. The molecules obtained are retained by the column and then eluted off from it at different times (called retention time, RT). This allows to the mass spectrometer (MS) downstream to capture, ionize, accelerate, deflect, and detect the ionized molecules separately given information on their mass/charge ratio and fragmentation.

To perform the analysis a Carlo Erba Instruments AUTO/HRGC/MS 1000 MS, as gas chromatograph equipped with a DB-5 Agilent J&W column and coupled to a mass spectrometer detector Carlo Erba Instruments MS QMD 1000 was used (figure 3.26). The temperature program of the chromatographic analysis is reported in the scheme below.



The interpretation of the chromatogram was performed using the provided program management of the device it is performed.

Figure 3.26 Carlo Erba GC-MS device.

3.3.5 ICP-OES: Inductively coupled plasma optical emission spectrometry

Inductively coupled plasma optical emission spectrometry was performed on SANA sample and on Concentrato sample before and after the filtration process by active carbon and vermiculite in order to study the interaction between the metals in the landfill leachate and the stationary phases. ICP-OES analysis was performed at LISA laboratory.

ICP-OES is a type of emission spectrometry, which is capable of identifying metallic and non-metallic inorganic substances in very low concentrations (part per billion, ppb). This technique performed through an initial ionization of the sample with an inductively coupled plasma torch and a subsequent quantification of the ions produced using an emission spectrometer.

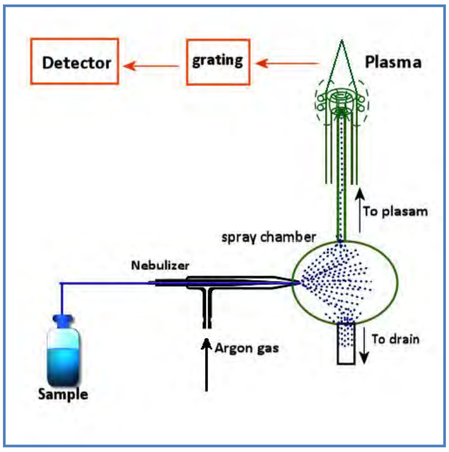


Figure 3.27 ICP-OES general operational scheme.

The nebulized sample is introduced from the central tube of the torch through the flow of argon, which acts as a carrier. The analyte is thus subjected to evaporation of the liquid phase and a subsequent vaporization and atomization of the species present. Then the atomic elements produced undergo the loss of their associated electron with lower force, and recombine repeatedly in the plasma, giving off radiation at the characteristic wavelengths of the elements involved. Then the spectral composition of the light emitted from the source is analysed using a monochromator (diffraction grating), which splits the incoming light in the spectra that are intercepted by a photomultiplier. Thanks to this last is possible to measure the intensities of all the wavelengths and therefore to identify and quantify the specific trace metals by using an external standard calibration reference.

The ICP-OES technique can be used in environmental analysis of different type of samples (water, solids, etc.) and the toxicological determinations of heavy metals prior the complete dissolution of the analyte. The instrument utilized to perform the analysis is the Perkin Elmer Optima 4200 DV ICP-OES as illustrated in the figure below.

Figure 3.28 Perkin Elmer Optima 4200 DV ICP-OES.

3.3.6 NMR: Nuclear Magnetic Resonance Spectroscopy

The NMR analysis was performed on SANA and Concentrato sample. NMR is a strong and rapid technique to identify reaction products or organic compounds. The NMR spectroscopy is a form of absorption spectrometry that measures the absorption of electromagnetic radiation in molecules immersed in a strong magnetic field. Under appropriate conditions a sample immersed in a magnetic field can absorb the electromagnetic radiation in the region of the radio frequency (rf) and the characteristics of the sample determine the frequencies absorbed. The absorption is determined by the presence of certain nuclei of the molecule (usually carbon-13 and hydrogen-1) with a nuclear magnetic momentum. A graph of the peak intensity against the frequencies of the absorption peaks constitutes the NMR spectrum.

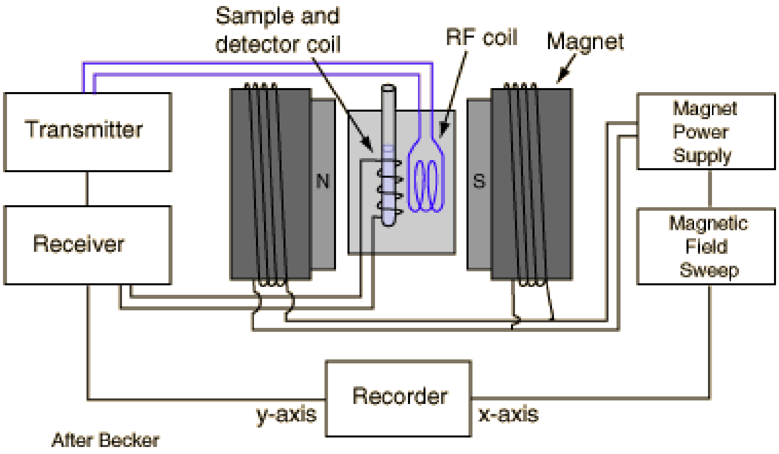


Figure 3.29 NMR spectroscopy operational scheme.

^{1}H and ^{13}C {^{1}H}NMR spectra were run at 298K, on a Bruker 200 AC spectrometer (figure 3.30) operating at 200.13 and 50.32 MHz, respectively; δ (chemical shift) values are given in ppm. Peak positions are relative to Me_4Si and were calibrated against residual solvent resonance (^1H) or deuterate solvent multiplet (^{13}C).

Figure 3.30 Bruker 200 AC NMR spectrometer.

3.4. Filtration Process

Interesting information about the nature of the metal species in the leachate can be produced by its interaction with a solid phase with adsorbing properties. For this reason, some experiments on the filtration of the leachate samples through different liners have been performed and the filtrate analysed to detect the heavy metals content.

3.4.1 Characterization of the solid liners

In this part, it is explained in detail the characteristics of solid liners used in the study. Two different type of materials have been selected: activated carbon and vermiculite due to their different chemical composition and adsorption behaviour. Moreover, the filtration time has been taken into account to produce a method that can be easily set up and reproduced.

3.4.1.1 Activated Carbon

The activated carbon (figure 3.31) selected for the experiment is the 207EA type. It is a mineral granular carbon with high activation grade, studied in particularly for application in liquid phase. The 207EA finds prevailing employment in the municipal waters, drain, and wastewaters treatments, in beverage and beer industry and in process and industry waters treatments.

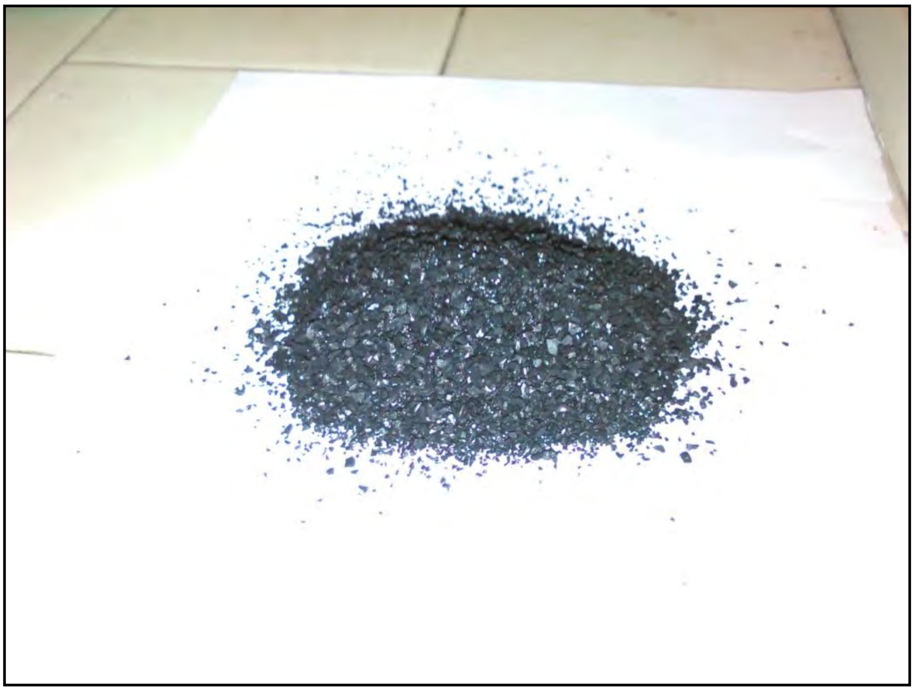


Figure 3.31 Active Carbon 207EA.

The main applications of the 207EA are the following:

- dechorination;
- deozonation;
- removal of taste and odour;
- removing micropollutants and pesticide;
- protection of reverse osmosis membranes and resins.

The properties and the design information of the material are summarized in the following tables (tab. 3.5, 3.6).

207EA Properties		
Surface area (BET method)	m^2/g	950-1050
Moisture content, as packed	%	<5
Density	g/cm^3	0.48-0.52
Backwashed and drained bed density	g/cm^3	0.42-0.48
Hardness	%	93-96
Iodine number	mg/g	900-1050
Abrasion number,	min	75
Methylene blue index	mg/g	180-230
Soluble ashes in water	-	<1
pH	-	7-8
Effective size	mm	2.36-0.60

Table 3.5 207EA carbon properties.

207EA Design information		
Empty bed contact time	min	10-20
Bed depth	m	1.5-3
Linear velocity	m/h	10-20
Backwash bed expansion	%	20

Table 3.6 207EA design information.

Other important characteristics of a solid liner are the pressure drop and the bed expansion. In the following two figures (fig. 3.32, 3.33) their values for 207EA are represented in dependence with the linear velocity.

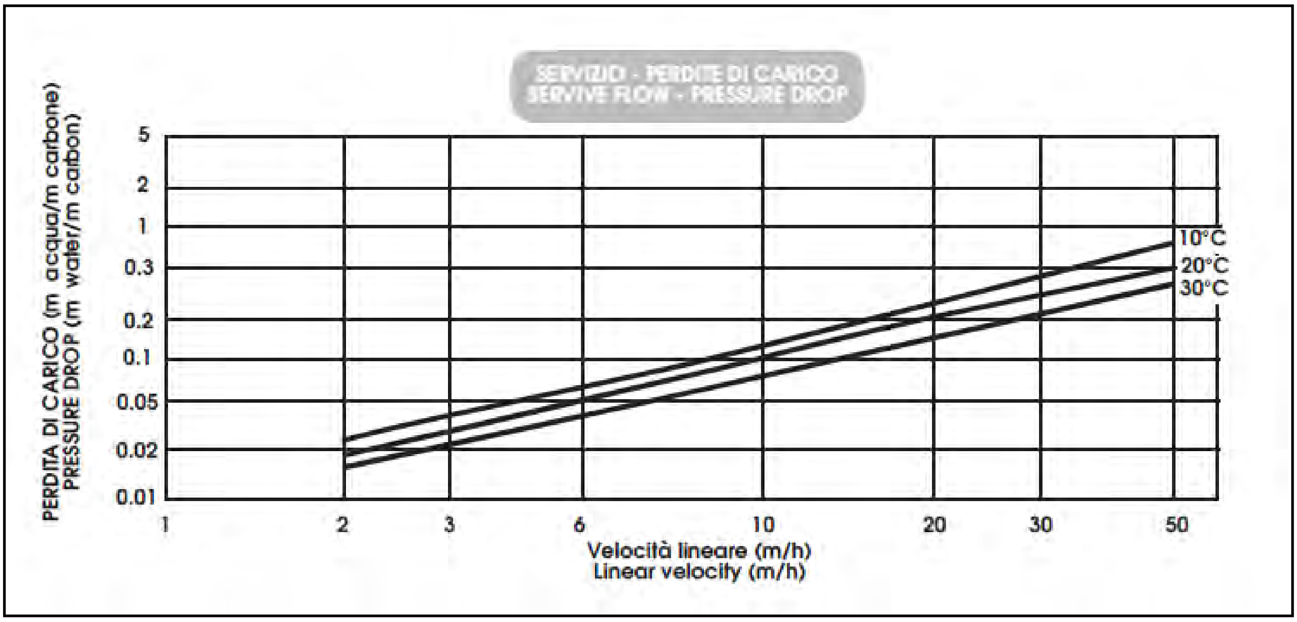


Figure 3.32 Pressure drop of the 207 EA carbon.

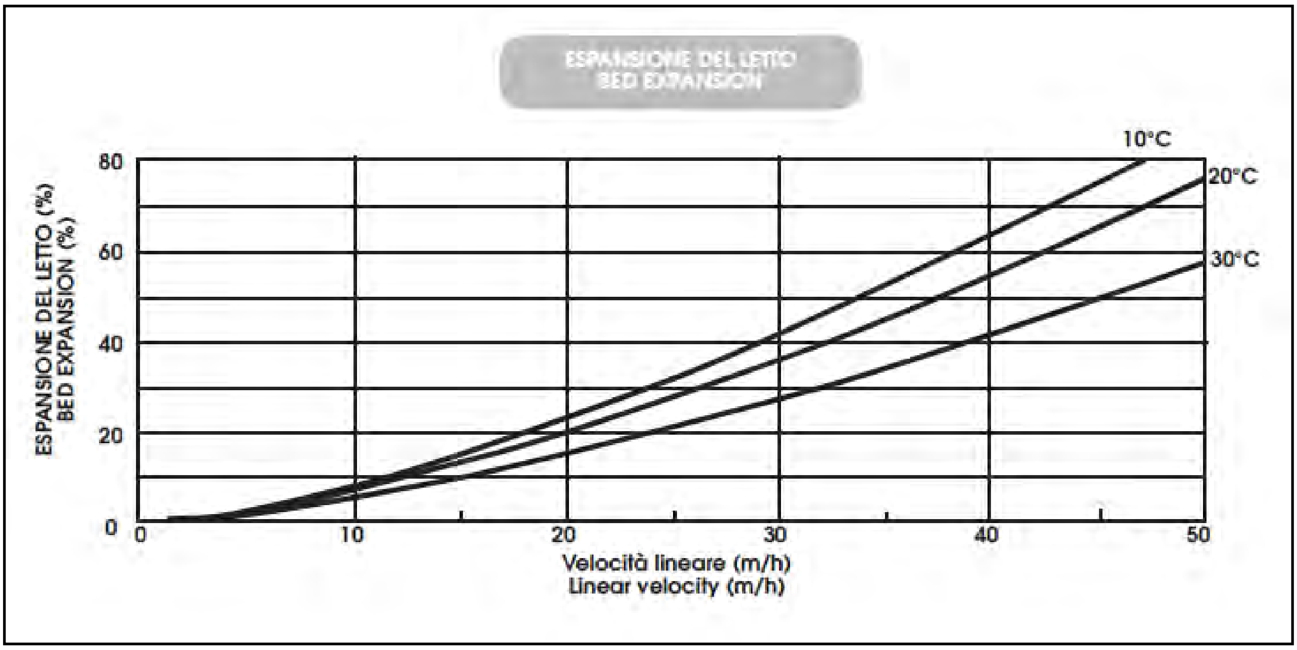


Figure 3.33 Bed expansion of 207 EA carbon.

3.4.1.2 Vermiculite

Vermiculite (figure 3.34) is the geological name given to a group of hydrated laminar minerals of the clay family, which are aluminium-iron-magnesium silicates, resembling mica in appearance. Crude vermiculite consists of thin, flat flakes containing microscopic layers of water. Rock and other impurities are removed from the crude ore, which is then crushed and sorted into sizes. Vermiculite is a safe inert material and is light in colour. When heated it expands (exfoliates) up to 30 times its original volume. The exfoliation process converts the dense flakes of the ore into lightweight porous granules containing innumerable minute air layers. Exfoliated (expanded) vermiculite is light and clean to handle, has a high insulation value, acoustic-insulating properties and will absorb and hold a wide range of liquids.

Figure 3.34 Vermiculite.

These granules are non-combustible, and are insoluble in water and all organic solvents. Expanded vermiculite is easily poured, is light, clean, highly absorbent and provides baffle against impact shock when used for packaging.

In particular, thanks to its layered structure and surface characteristics, vermiculite is utilised in products such as:

- treatment of toxic waste,
- air-freight packaging of hazardous goods,
- intumescent coatings and gaskets.

Other applications of exfoliated vermiculite are:

- friction brake linings market,
- high temperature insulation,
- loft insulation,
- various construction products,
- animal feeds,
- horticulture and many other industrial applications.

The table 3.7 and 3.8 present the physical and chemical properties of the Vermiculite utilized in the experiment.

Physical Properties	
Mineral Name	Vermiculite
CTCN Number	680620 90 0 00
Melting Point (°C)	1330
Specific Heat (1kJ/kg.K)	1.08
Specific Gravity (Crude)	2.5
Specific Gravity	2.8
Mohs Hardness (Crude)	1 - 2
pH (ISO 787-9)	7 - 8
% Loss at 105°C (Expanded Product)	< 0.5
% Loss at 1000°C (Expanded Product)	< 6

Table 3.7 Physical properties of the vermiculite.

Chemical Analysis	
Silicon (SiO_2)	39.4%
Magnesium (MgO)	25.2%
Aluminium (Al_2O_3)	8.8%
Potassium (K_2O)	4.5%
Iron (Fe_2O_3)	4.0%
Calcium (CaO)	1.8%
Carbonate (CO_2)	1.4%
Titanium (TiO_2)	0.8%
Fluorine (F)	0.5%

Table 3.8 Chemical analysis of the vermiculite.

For the vermiculite bed expansion and drop pressure diagram were not available.

3.4.2 Filtration system

Filtration experiments were conducted on Concentrato samples in the DII laboratory with the aim to study the interaction of heavy metals in municipal solid waste landfill leachate by different stationary phases and their adsorption efficiency. Each sample was filtrated by a solid bed composed of active carbon, in one case, and vermiculite in another as it is shown in the following table.

Leachate sample	Type	Solid liners
C1	Anaerobic	Active carbon
		Vermiculite
C2	Anaerobic	Active carbon
		Vermiculite
C3	Anaerobic	Active carbon
		Vermiculite
C4	Aerobic	Active carbon
		Vermiculite
C5	Aerobic	Active Carbon
		Vermiculite
C6	Aerobic	Active Carbon
		Vermiculite

Table 3.9 Concentrato leachates sample filtration by different stationary phases (active carbon and vermiculite).

For the experiment it was used a syringe column of 60 ml with a 1-2 mm thick cotton filter at the bottom in order to prevent the exiting of particulate transported by the outgoing leachate. In a typical experiment, 15 ml of solid liner (active carbon or vermiculite) was settled at the bottom of the syringe and slightly pressed in place while 45 ml of leachate sample was poured on the top and let percolate through the solid liner by gravity at room temperature (20°C). Outgoing leachate was collected in a baker and then filtered with a filter of glass wool in order to remove any possible particulate of active carbon or clay.30 ml of each of the 12 exiting leachate samples were then subjected to digestion treatment for ICP analysis in order to determine the effect of the solid liners on the concentration of heavy metals in the leachate. This method was chosen because it better simulates the conditions that occur in a real landfill barrier.

In the figure 3.35 and 3.36 it is possible to see the filtration device during the leachate filtration by active carbon and vermiculite.

Figure 3.35 Leachate filtration by activated carbon.

Figure 3.36 Leachate filtration by vermiculite.

4. RESULTS AND DISCUSSION

4.1 Heavy metals speciation analysis on leachate samples

These analyses were performed in order to study heavy metal speciation in landfill leachate and to identify which is the most suitable technique in this among those available. The following paragraphs illustrates in detail the results obtained.

4.1.1 ESEM

The results of the ESEM analysis performed by Dr. Claudio Furlan at CUGAS laboratory on leachate samples derived from SANA management are represented by the microscopic images the fluorescence spectra of elements and composition in term of atomic and mass percent concentration in the following figures and tables.

- **Sample S1**:

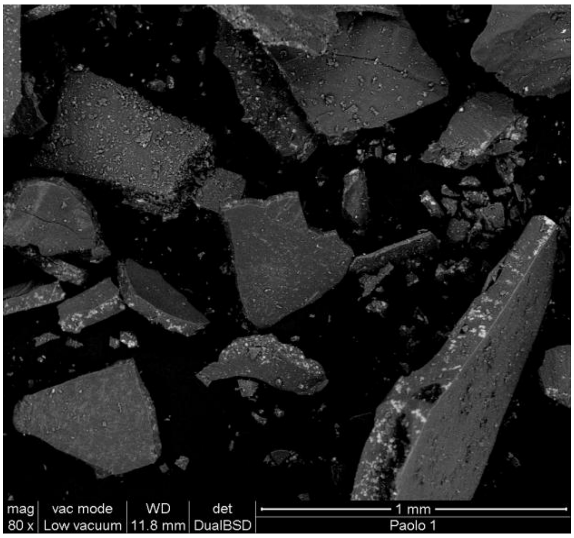


Figure 4.1 ESEM of S1 Sample.

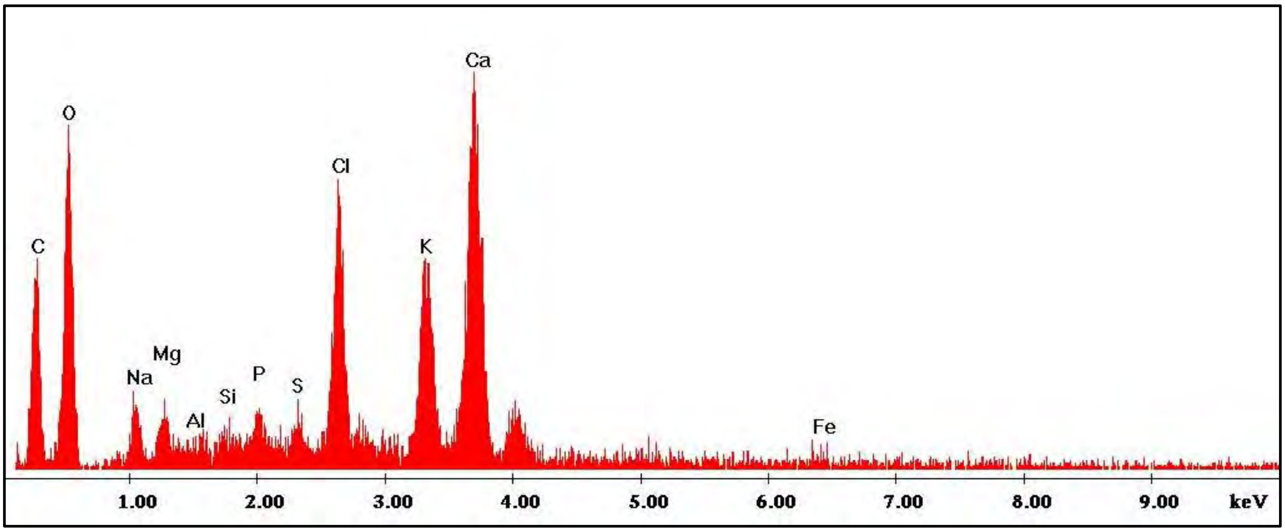


Figure 4.2 Spectra of elements in S1 sample by ESEM.

S1 Sample						
Element	**Wt %**	**At%**	**K-Ratio**	**Z**	**A**	**F**
C	30.54	44.28	0.0791	1.0586	0.2447	1.0004
O	36.36	39.57	0.0564	1.0240	0.1515	1.0001
Na	2.38	1.80	0.0083	0.9447	0.3680	1.0010
Mg	1.37	0.98	0.0067	0.9635	0.5050	1.0017
Al	0.42	0.27	0.0025	0.9311	0.6394	1.0033
Si	0.48	0.30	0.0035	0.9547	0.7586	1.0061
P	0.83	0.47	0.0065	0.9200	0.8466	1.0105
S	0.70	0.38	0.0061	0.9411	0.9050	1.0174
Cl	6.11	3.00	0.0527	0.8973	0.9450	1.0178
K	6.17	2.75	0.0548	0.8975	0.9641	1.0269
Ca	13.35	5.80	0.1166	0.9158	0.9530	1.0007
Fe	1.30	0.40	0.0106	0.8217	0.9907	1.0000
Total	100.00	100.00				

Table 4.1 Quantification of elements in S1 sample by ESEM

- **Sample S2:**

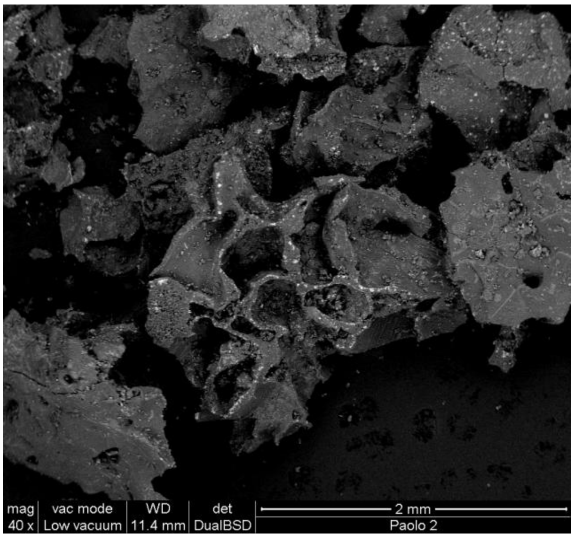


Figure 4.3 ESEM of S2 Sample.

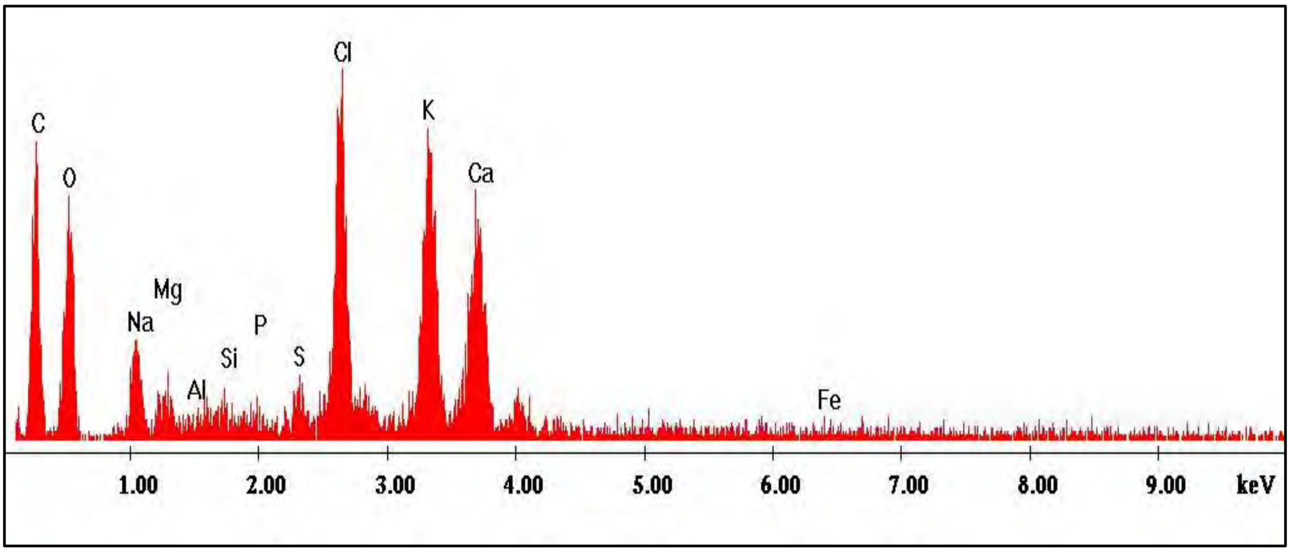


Figure 4.4 Spectra of elements in S2 sample by ESEM.

Sample 08/09						
Element	**Wt %**	**At%**	**K-Ratio**	**Z**	**A**	**F**
C	40.71	55.95	0.1017	1.0528	0.2372	1.0003
O	28.69	29.60	0.0409	1.0185	0.1399	1.0001
Na	3.46	2.49	0.0128	0.9337	0.3913	1.0009
Mg	1.02	0.69	0.0051	0.9583	0.5198	1.0016
Al	0.08	0.05	0.0005	0.9261	0.6576	1.0033
Si	0.19	0.11	0.0014	0.9496	0.7785	1.0063
P	0.00	0.00	0.0000	0.9151	0.8662	1.0117
S	0.52	0.27	0.0046	0.9361	0.9282	1.0200
Cl	8.07	3.76	0.0706	0.8924	0.9645	1.0164
K	8.72	3.68	0.0761	0.8926	0.9639	1.0145
Ca	7.59	3.13	0.0650	0.9017	0.9395	1.0005
Fe	0.96	0.28	0.0078	0.8168	0.9950	1.0000
Total	100.00	100.00				

Table 4.2 Quantification of elements in S2 sample by ESEM.

- **Sample S3:**

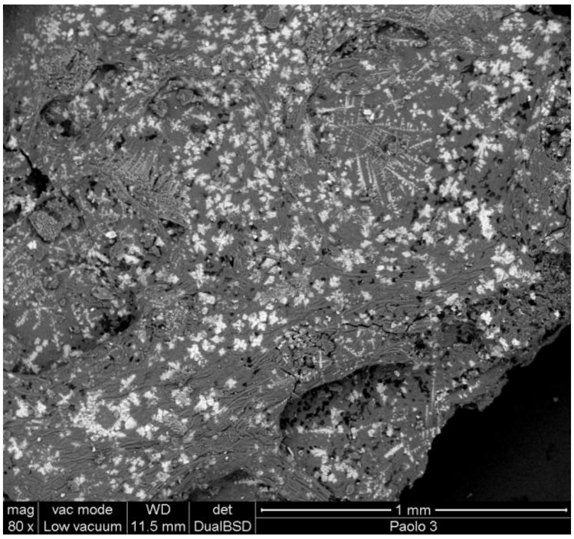


Figure 4.5 ESEM of S3 Sample.

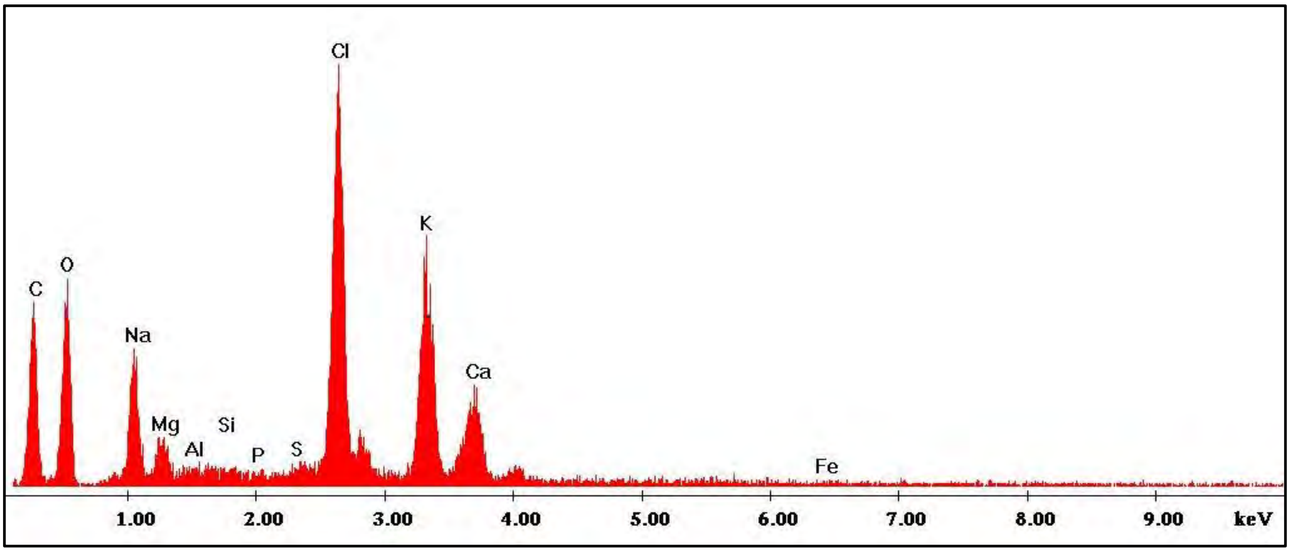


Figure 4.6 Spectra of elements in S3 sample by ESEM.

Sample 27/10						
Element	**Wt %**	**At%**	**K-Ratio**	**Z**	**A**	**F**
C	41.00	56.25	0.0804	1.0540	0.1861	1.0002
O	26.85	27.66	0.0399	1.0197	0.1455	1.0002
Na	5.32	3.81	0.0209	0.9408	0.4174	1.0012
Mg	1.44	0.98	0.0073	0.9595	0.5281	1.0019
Al	0.41	0.25	0.0025	0.9272	0.6603	1.0037
Si	0.24	0.14	0.0018	0.9507	0.7766	1.0070
P	0.18	0.10	0.0015	0.9162	0.8635	1.0128
S	0.32	0.17	0.0029	0.9372	0.9239	1.0221
Cl	11.74	5.46	0.1021	0.8935	0.9625	1.0119
K	8.48	3.57	0.0720	0.8937	0.9440	1.0064
Ca	3.69	1.52	0.0312	0.9118	0.9264	1.0002
Fe	0.32	0.09	0.0026	0.8176	0.9971	1.0000
Total	99.99	100.00				

Table 4.3 Quantification of elements in S3 sample by ESEM.

From the morphological point of view, all the SANA series samples show an irregular aspect in the solid phase with some main features such as: platelets (e.g. in fig.4.1), corrugated sheets (e.g. in fig 4.3), and crystalline efflorescence (e.g. fig.4.5) suggesting the presence of organic materials including inorganic salts. The elemental analysis produced by fluorescence spectra show for all the samples the preponderance of alkaline and alkaline earth metals chlorides along with oxygenated carbon species. Iron and heavy metals signals are too small to be visible due to their very low concentration compared to the main components of the leachate. Therefore, ESEM analysis, even if not sensitive enough to reveal traces elements, gives some useful information on the ions both positive (Na^+, K^+, Ca^{2+}, Mg^{2+}) negative (Cl^- and probably CO_3^{2-})that can influence the form in which heavy metals are present and/or interact with solid liners.

4.1.2 ESI-MS

As stated before ESI-MS technique can give information on the mass and isotopic distribution of analyte in solution through a built-in vaporization/ionization system allowing to detect charged fragments (both positive and negative) with a mass to charge ratio in the range 150-2000 m/z. During the experiments the samples of both SANA and Concentrato series have been analysed with several types of co-solvents in different combinations.

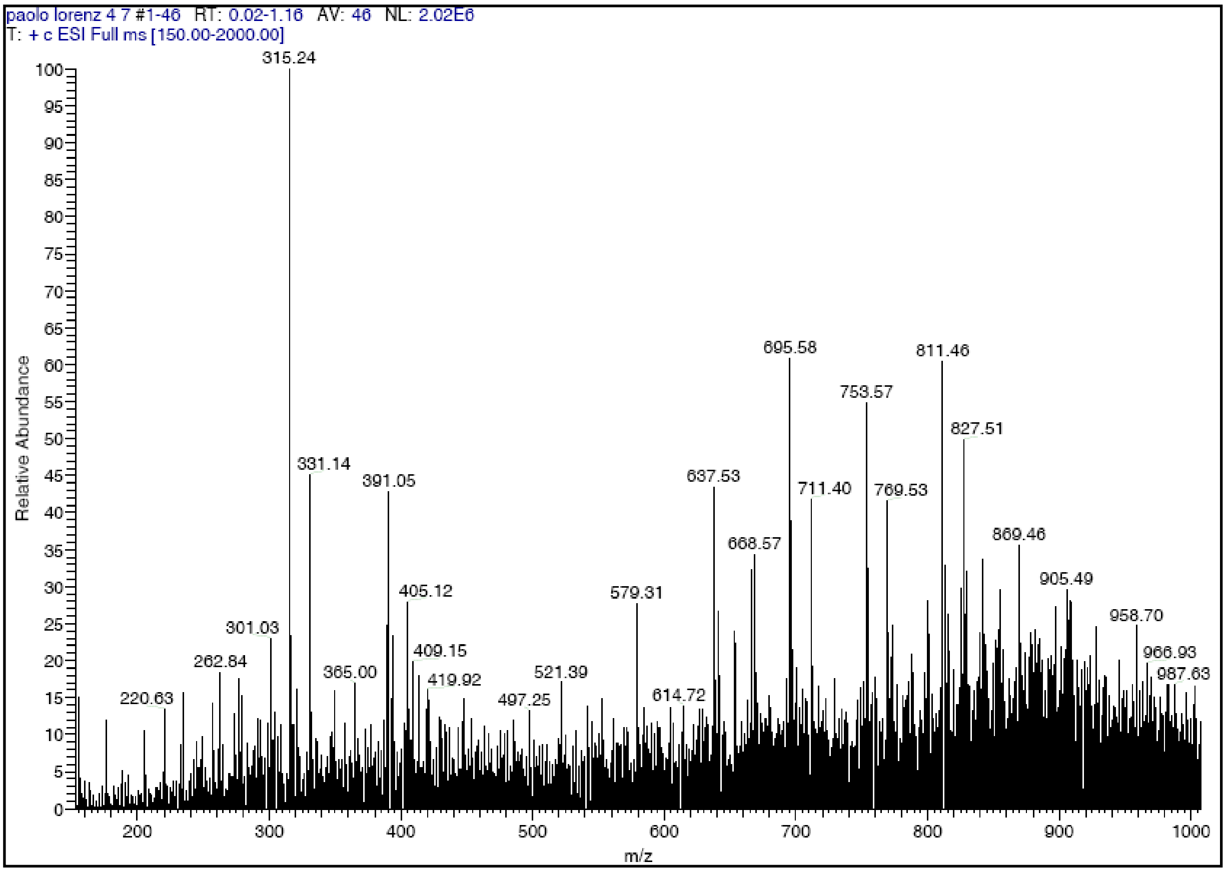


Figure 4.7 ESI-MS analysis with methanol on S1 leachate sample.

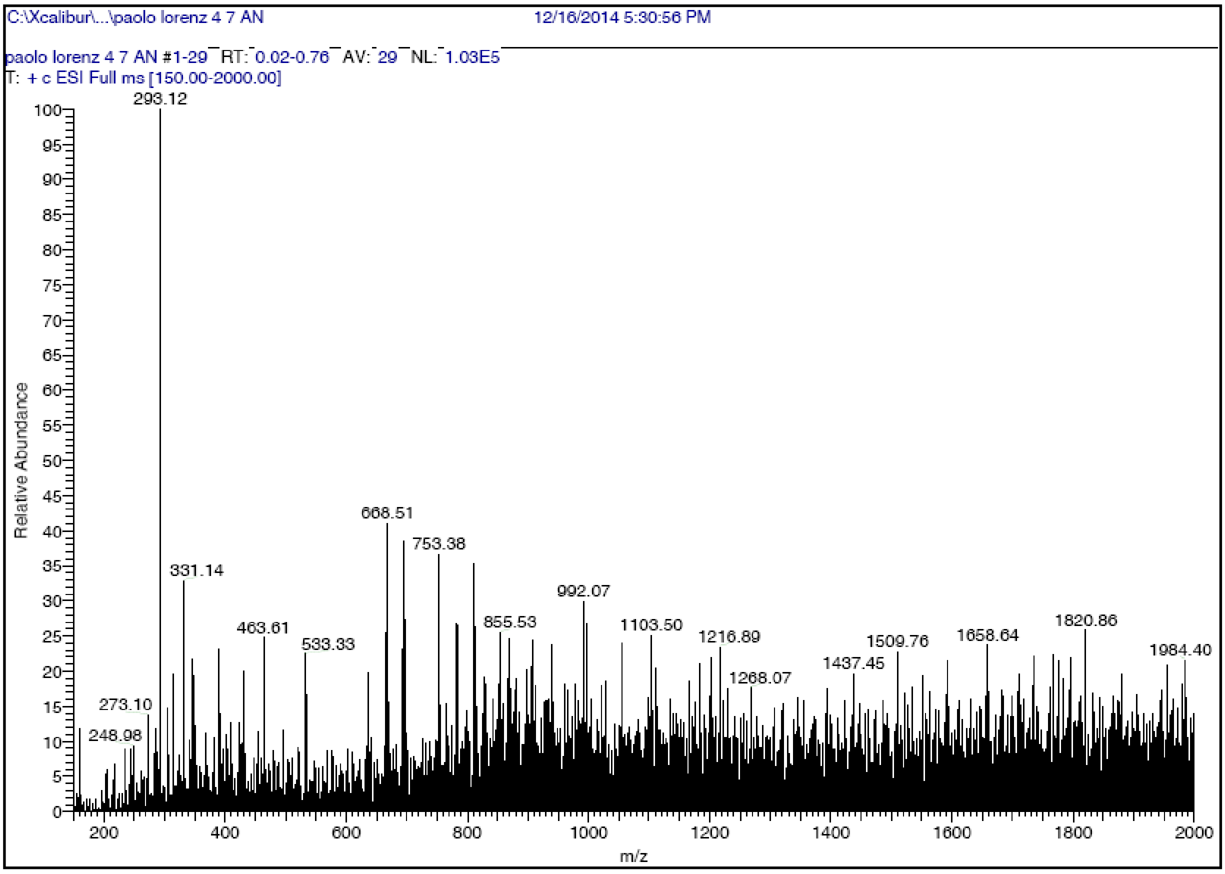


Figure 4.8 ESI-MS analysis with acetonitrile on S1 leachate sample.

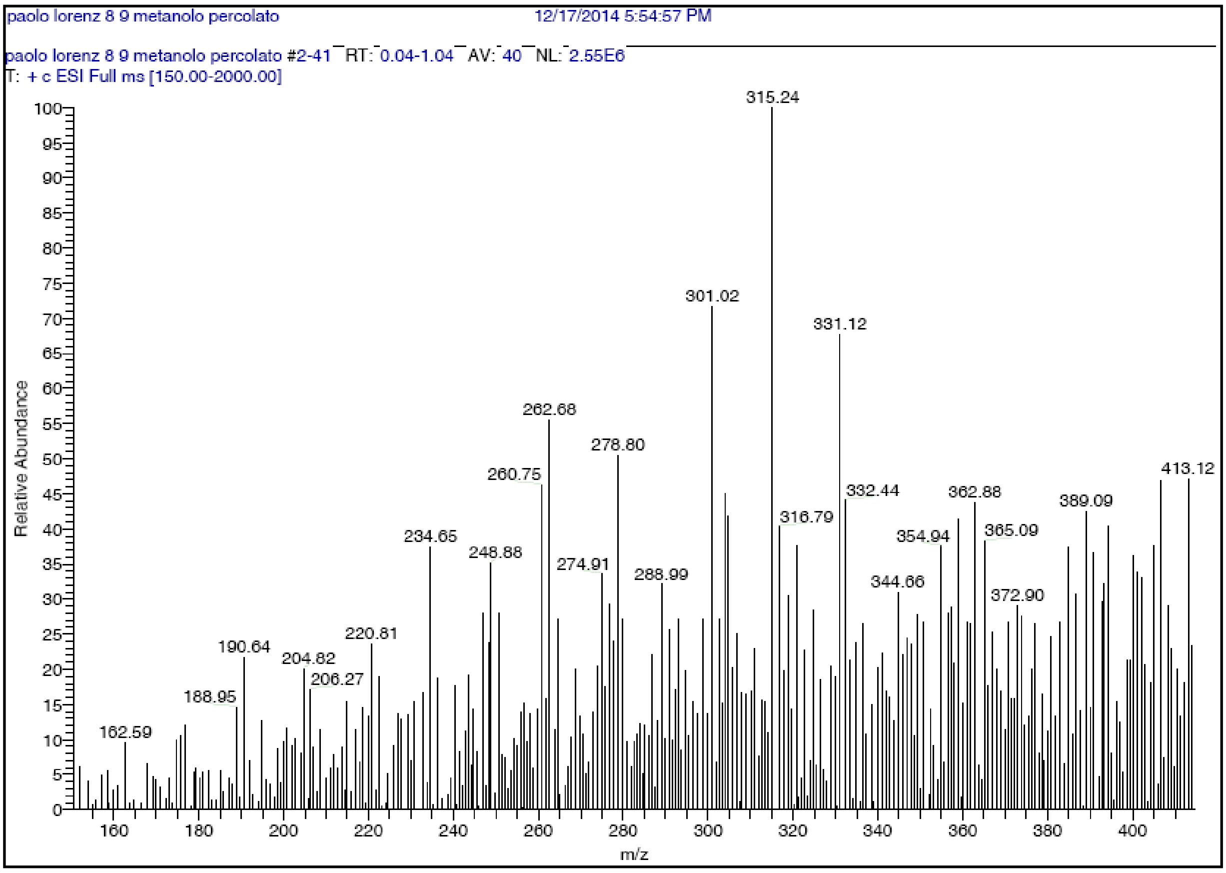


Figure 4.9 ESI-MS analysis with methanol on S2 leachate sample.

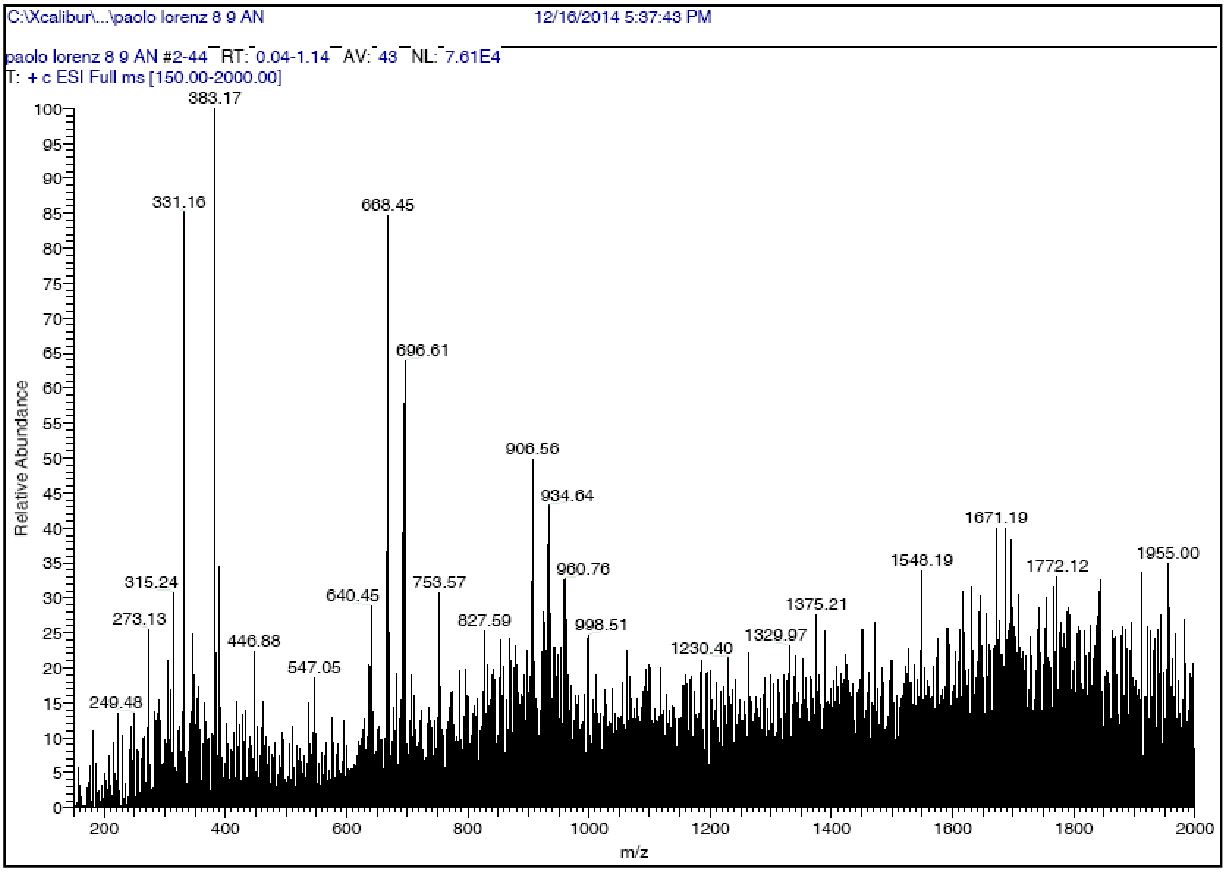


Figure 4.10 ESI-MS analysis with acetonitrile on S2 leachate sample.

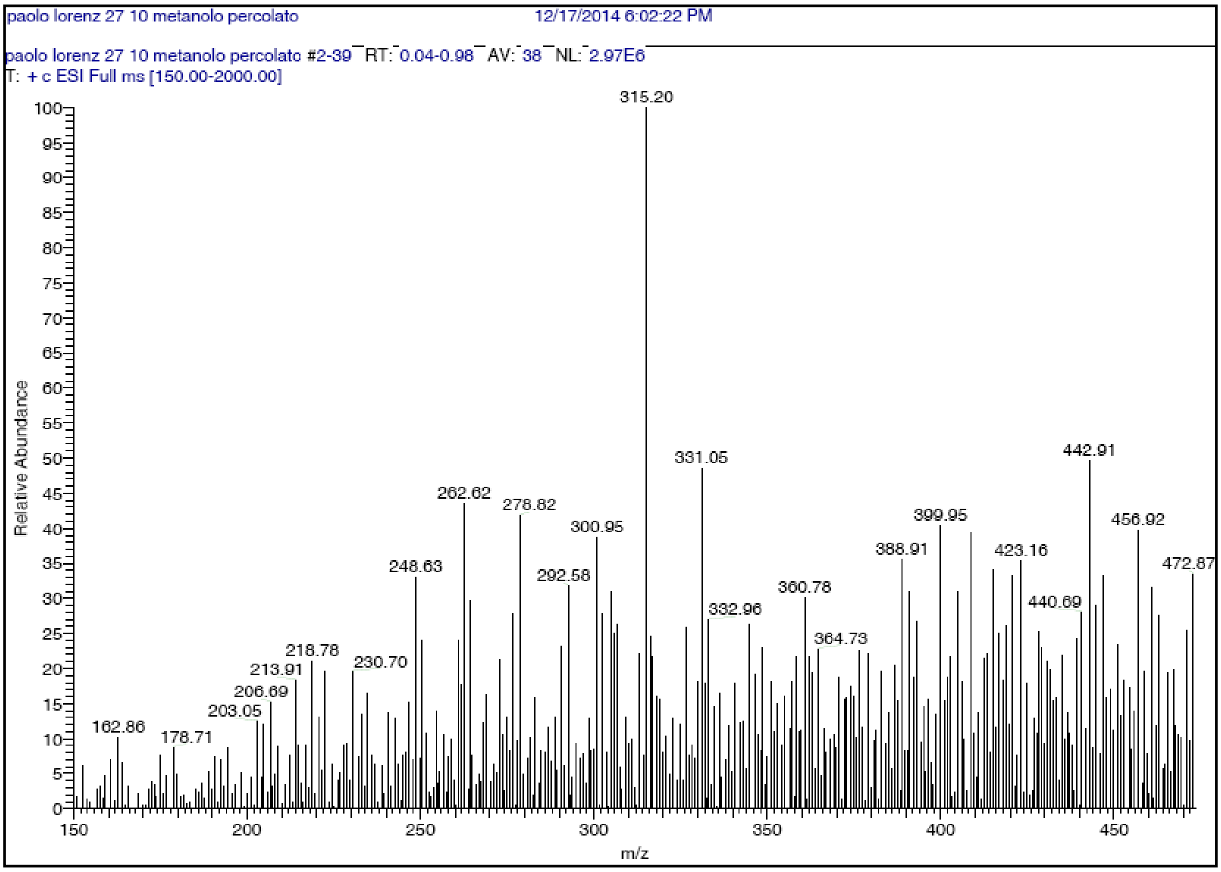


Figure 4.11 ESI-MS analysis with methanol on S3 leachate sample.

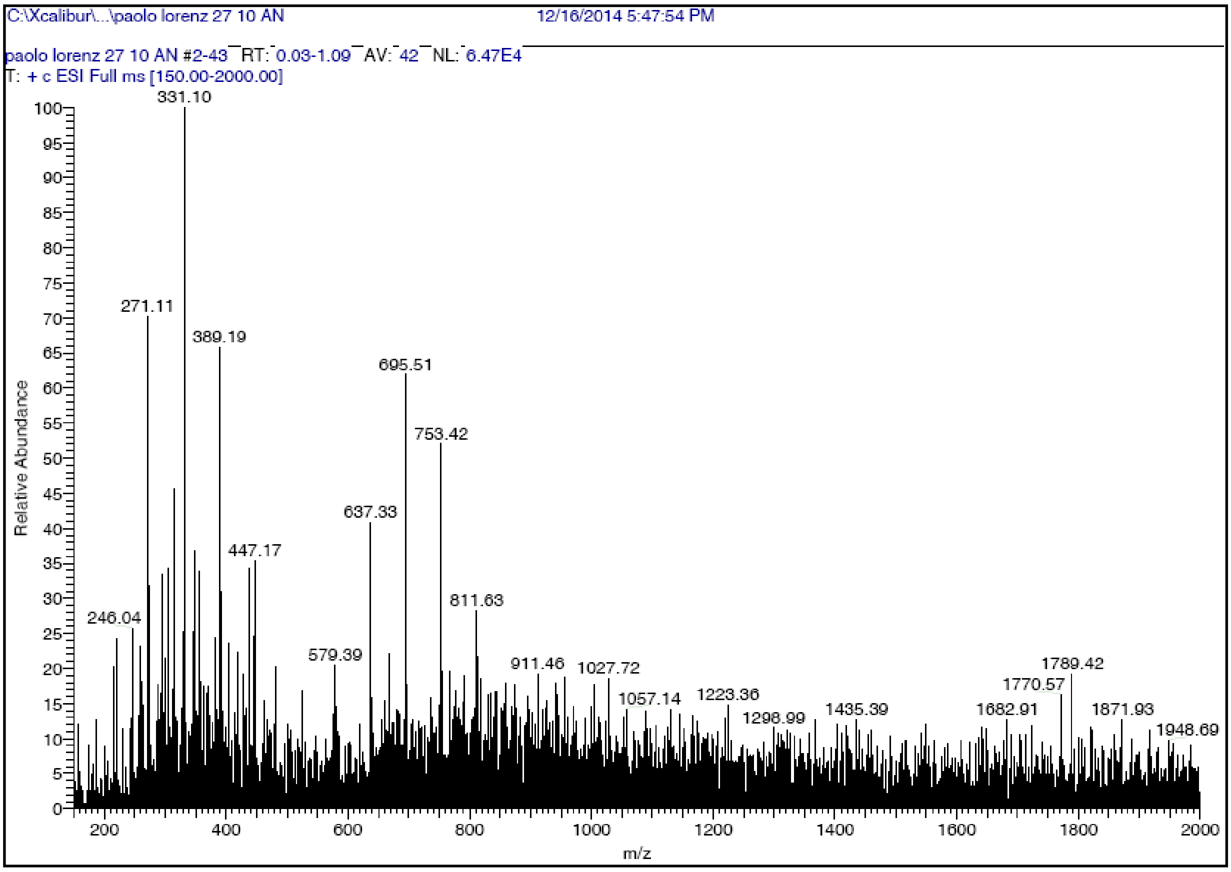


Figure 4.12 ESI-MS analysis with acetonitrile on S3 leachate sample.

In general, the ESI spectra of the SANA series prove to be quite complex but some observations can be made:

- even though the ion count is low (in the range 10^{-5}-10^{-7}) indicating a low concentration of charge species reaching the detector those obtained with methanol solutions are generally higher probably due to its polarity and protic nature (ability to transfer protons to analytes).
- The spectra show series of signus at fractional mass to charge ratio indicating the presence of multiple charged species of higher molecular mass. This is consistent with the presence of organic macromolecules originated by the oxidation process in the landfill.
- Comparing the spectra in similar solvents of S1, S2, S3 we observe a decreasing in the mass of the main charged fragments in accordance with the different ages of the leachates and the progression of the composition of the organic matter.

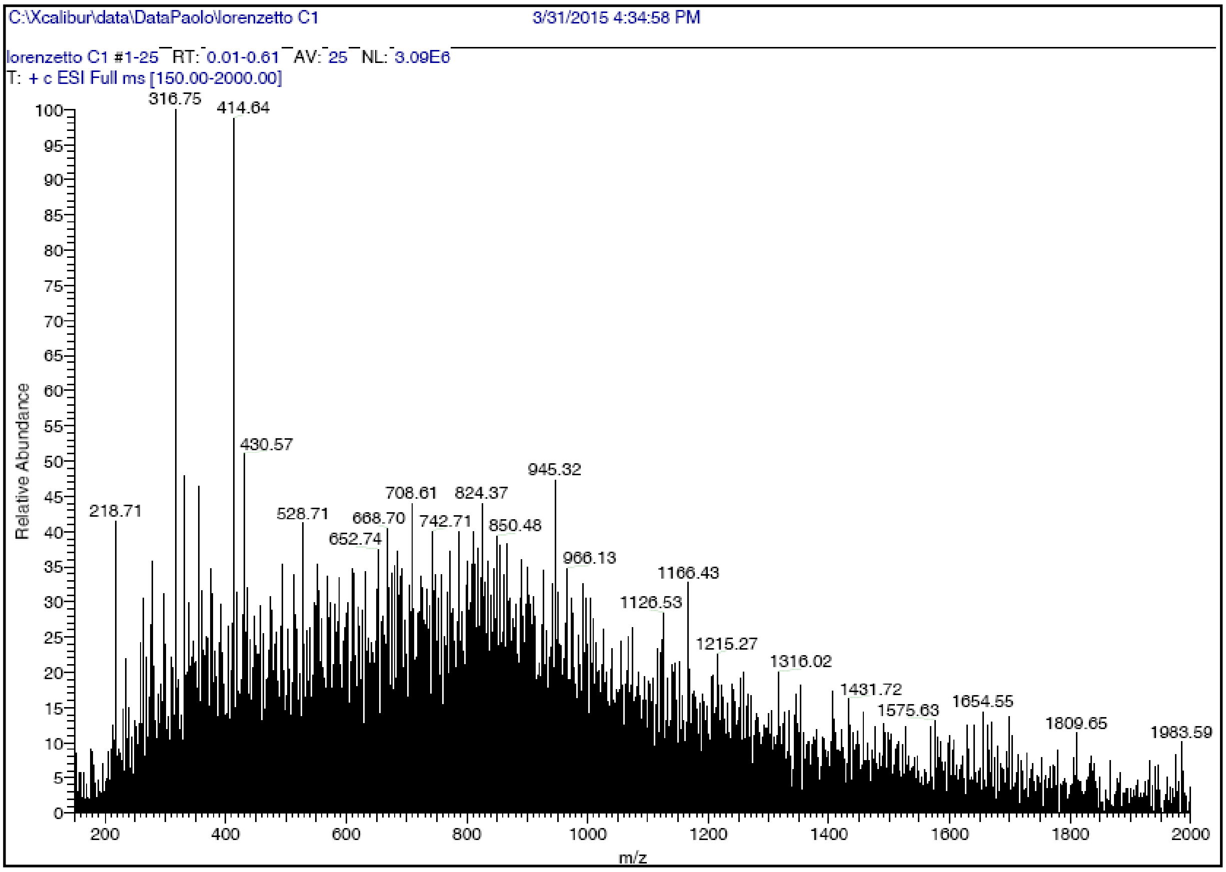


Figure 4.13 ESI-MS analysis with methanol on C1 leachate sample.

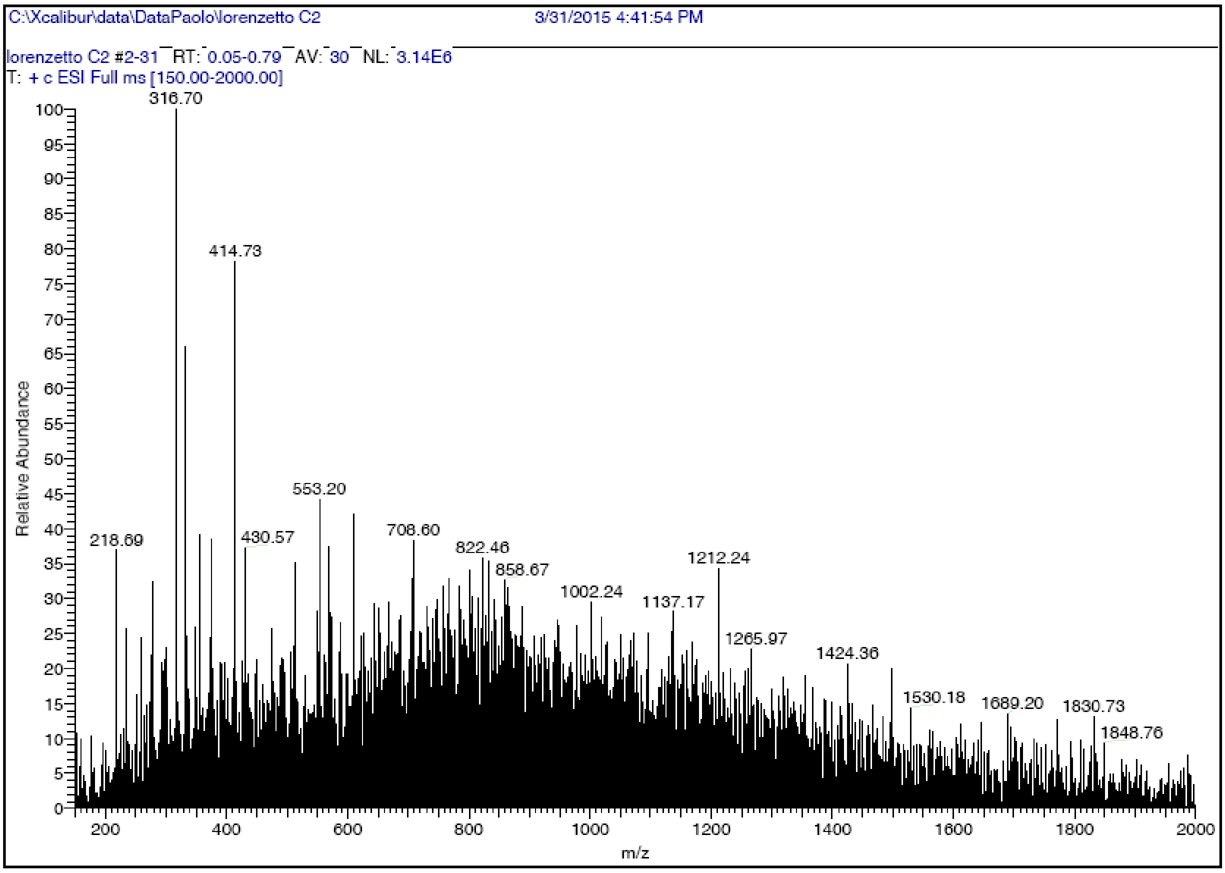


Figure 4.14 ESI-MS analysis with methanol on C2 leachate sample.

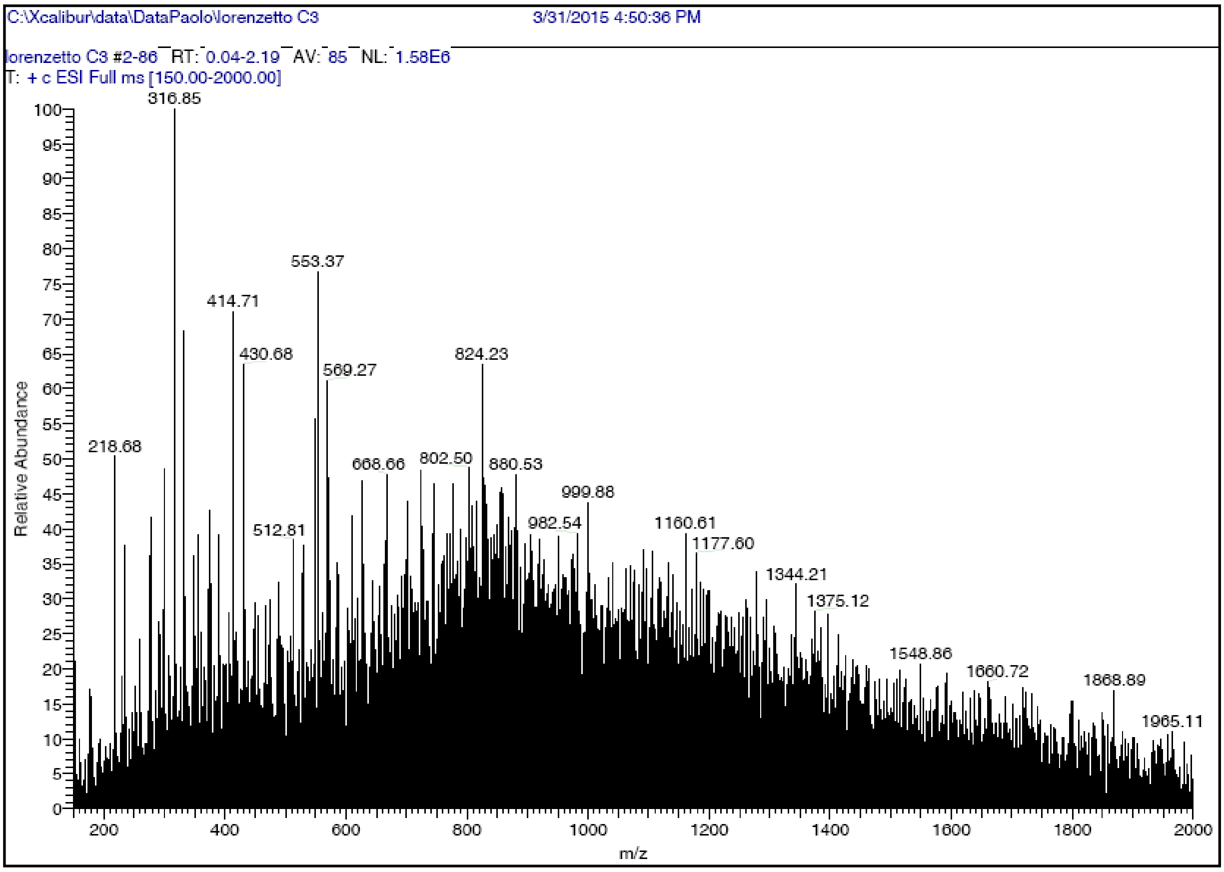


Figure 4.15 ESI-MS analysis with methanol on C3 leachate sample.

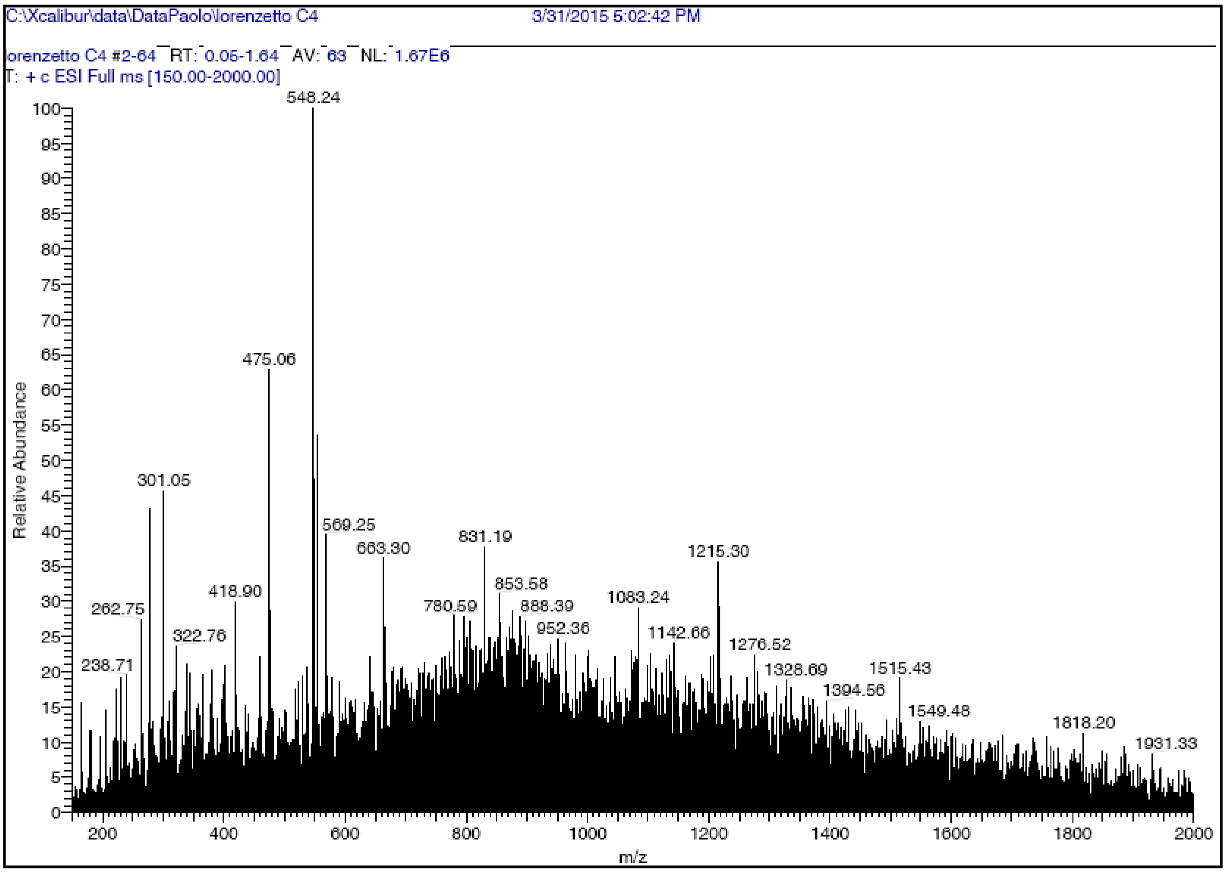


Figure 4.16 ESI-MS analysis with methanol on C4 leachate sample.

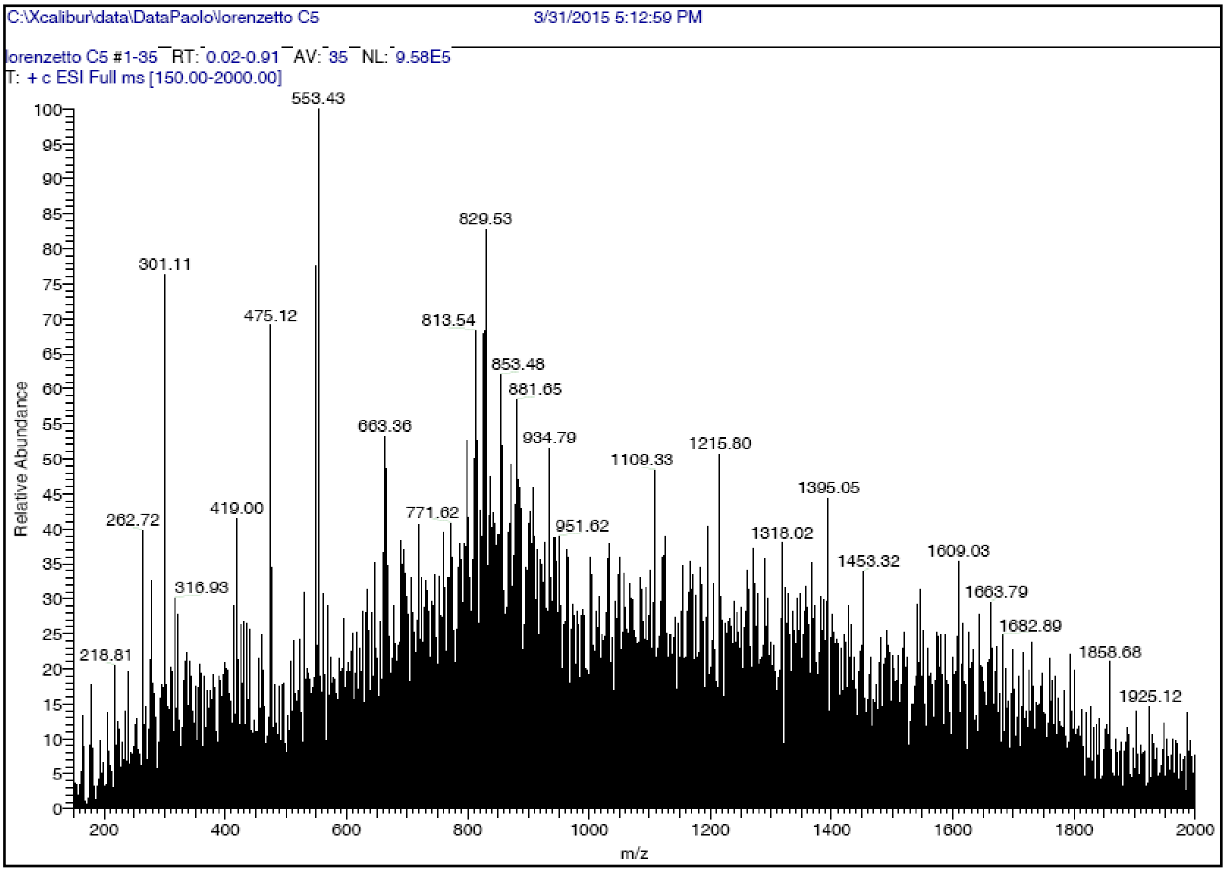


Figure 4.17 ESI-MS analysis with methanol on C5 leachate sample.

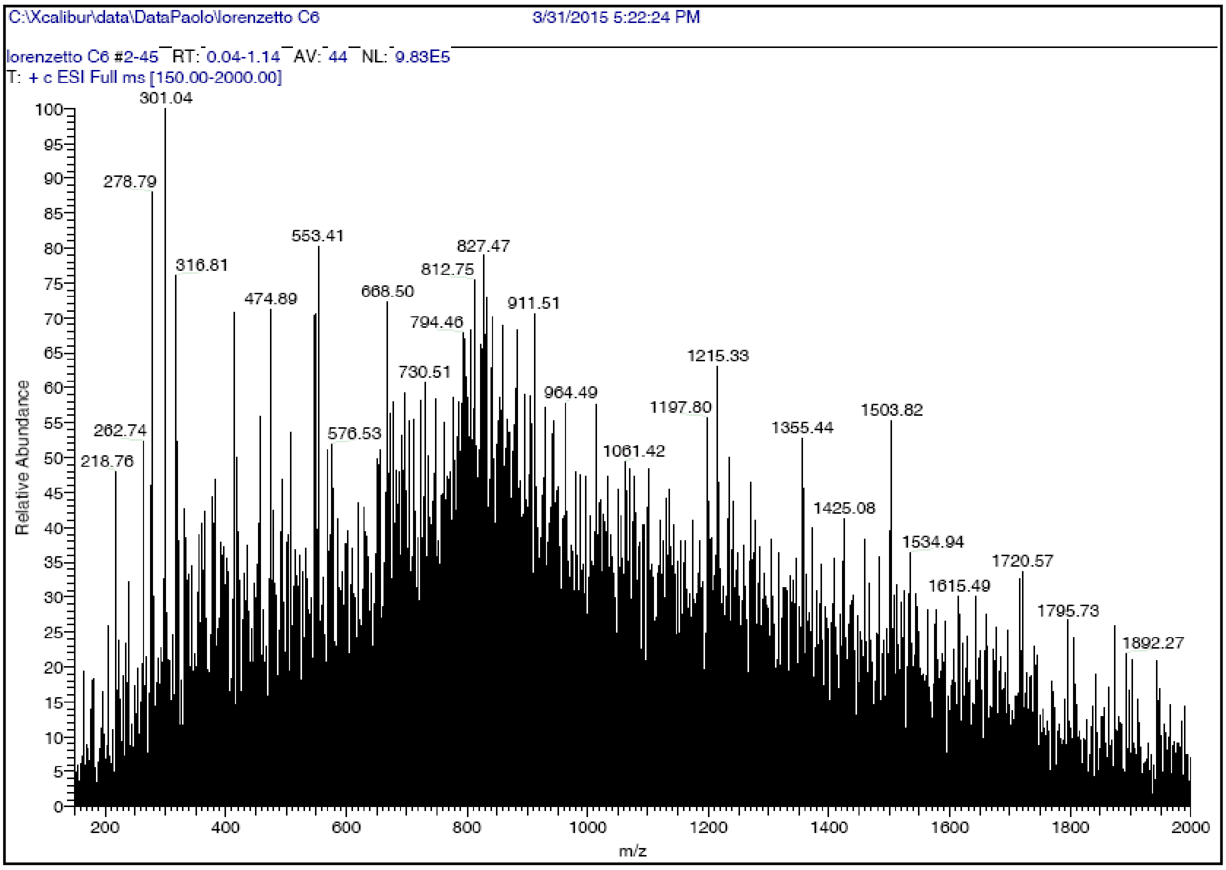


Figure 4.18 ESI-MS analysis with methanol on C6 leachate sample.

The results of ESI-MS analysis on Concentrato series samples denote an extremely small ionic concentration (in the order of 10^{-5}average) even in methanol. As for the SANA series it is not possible to discern typical isotopic patterns attributable to particular metal species. In general, a bell-shape background that can be associated to the presence of complex organic compounds in the solution (humic acids, carbohydrates, etc.) as already observed by Piccolo and Spiteller (2003).

Comparison of the main signals with SDBS MS database suggests the presence of complex cyclic and hydroxylated organic molecules, which can act as coordinating agents towards transition metals ions.

4.1.3 FT-IR

The FT-IR analysis has been performed on SANA samples in solid state within KBr solid matrix as reported in the materials and method section. The transmission spectra of samples S1, S2 and S3 are reported below.

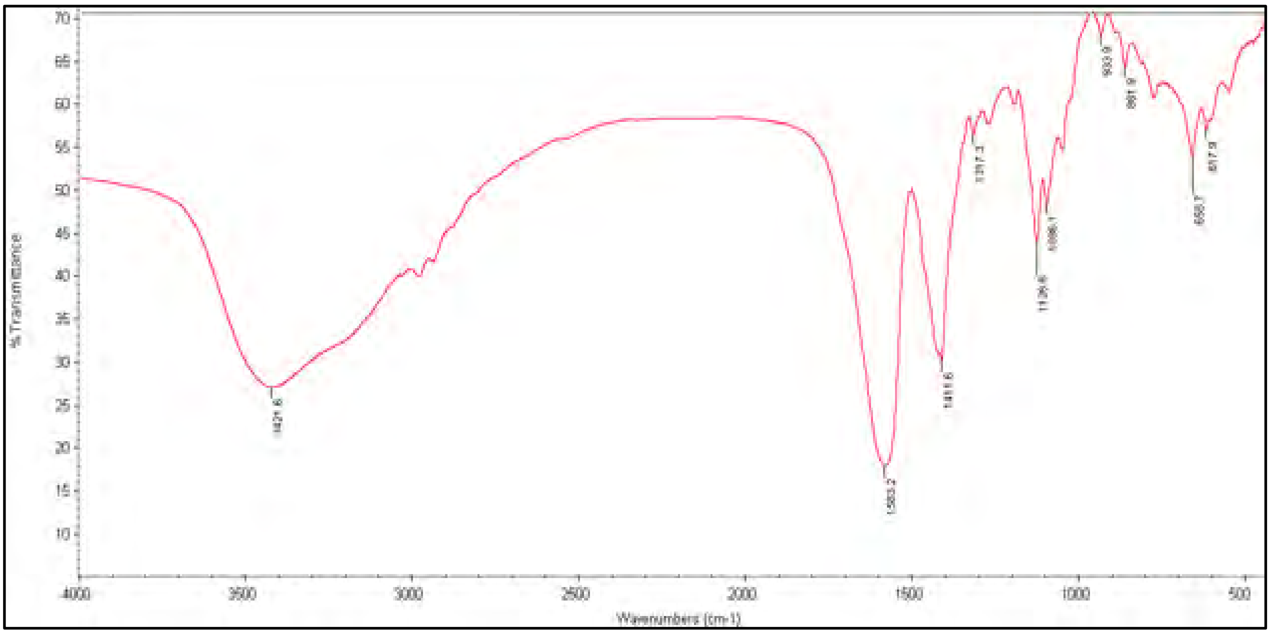


Figure 4.19 FT-IR spectra of S1 sample.

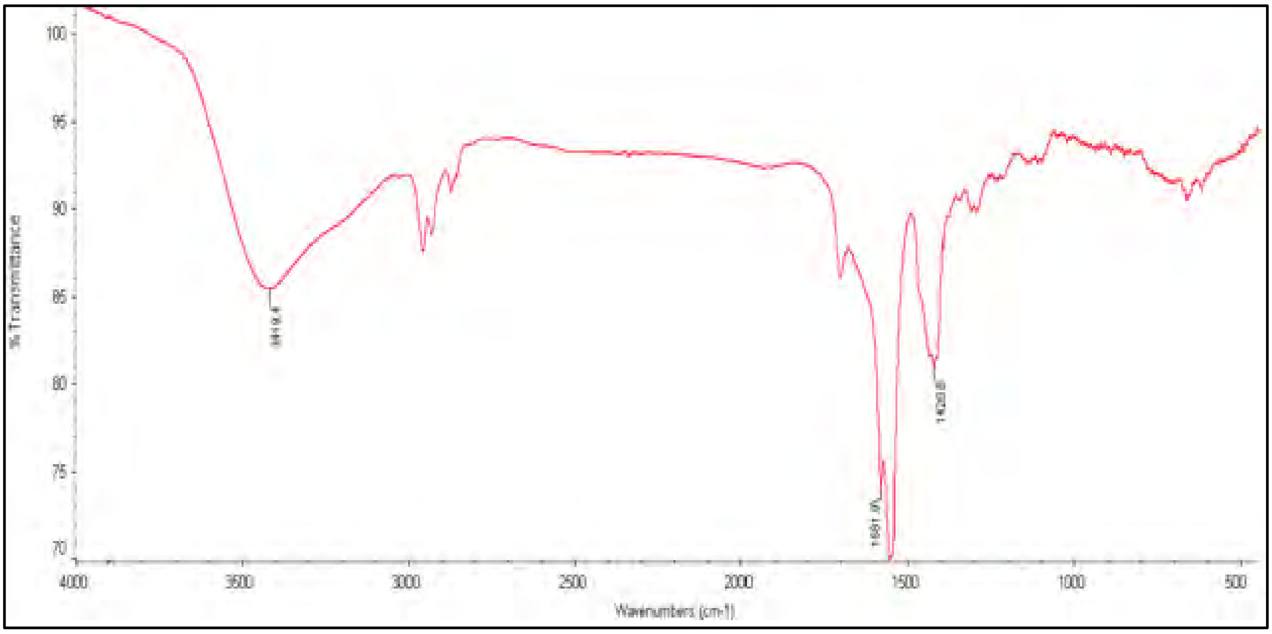


Figure 4.20 FT-IR spectra of S2 sample.

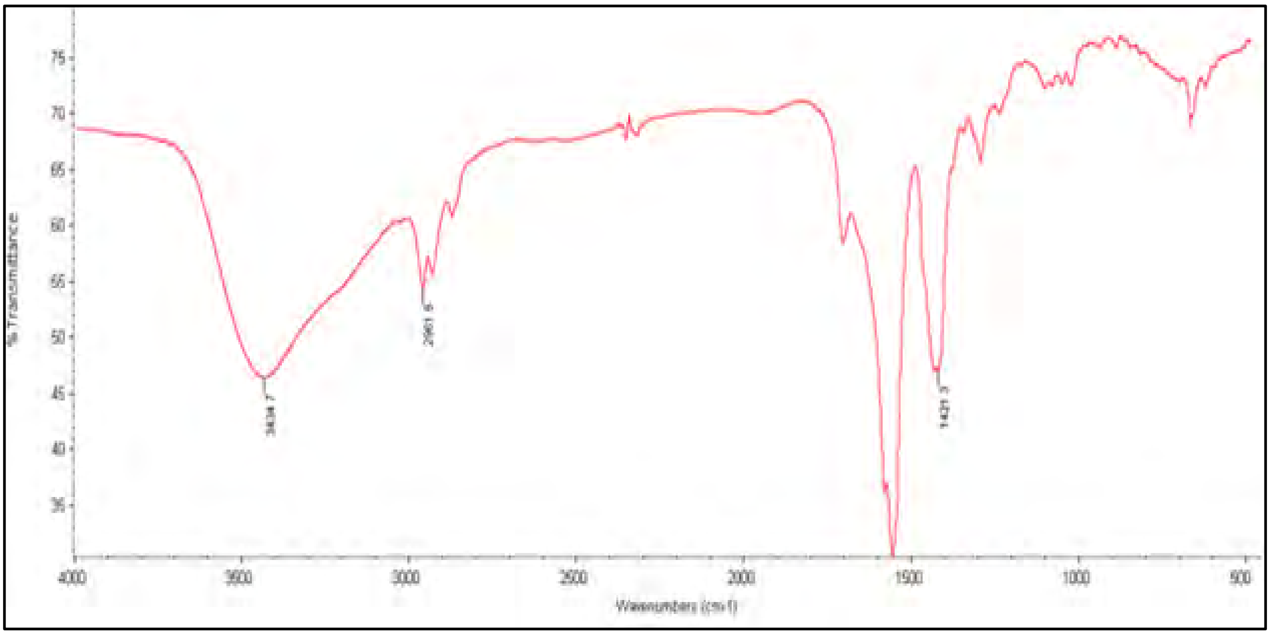


Figure 4.21 FT-IR of S3 sample.

The FT-IR results indicate the presence of traces of aliphatic organic compounds through the stretching of the CH bonds around 2900 cm^{-1} which are close to the broad and very strong signal of hydroxy bond stretching (OH) at 3420 cm^{-1} confirmed the presence of hydroxylated species in the leachate. The signals in the range of 1400-1600 cm^{-1}can be attributed to esters and carboxylate species. The S1 spectrum show signals in the range 1000-1200 cm^{-1} relative to single CO bond stretching in ethers and alcohols species.

I.R. Frequency range [cm^{-1}]	Group	Assignment
3200-2900	Aliphatic CH$_3$, CH$_2$, CH	stretching
3600-3000	OH, NH	stretching
1700-1400	Estereal and carboxylic	stretching
1000-1200	Ethereal and alcoholic	stretching

Table 4.4 Frequency of the functional groups detected in FT-IR analysis.

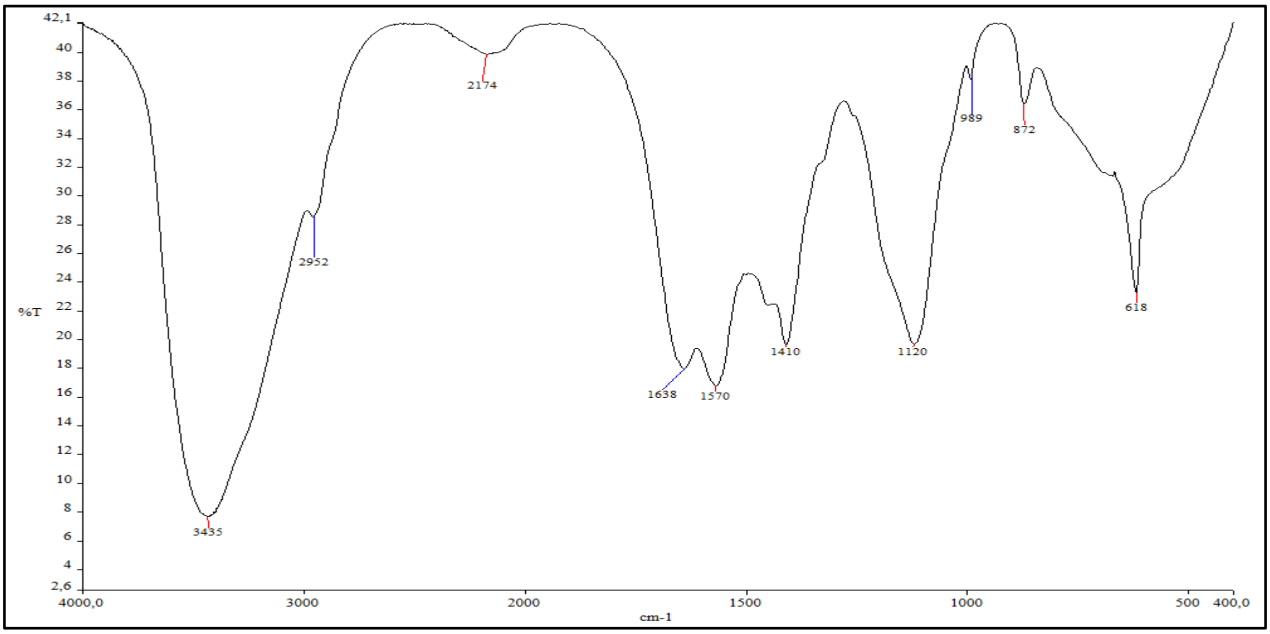


Figure 4.22 FT-IR of C1 sample.

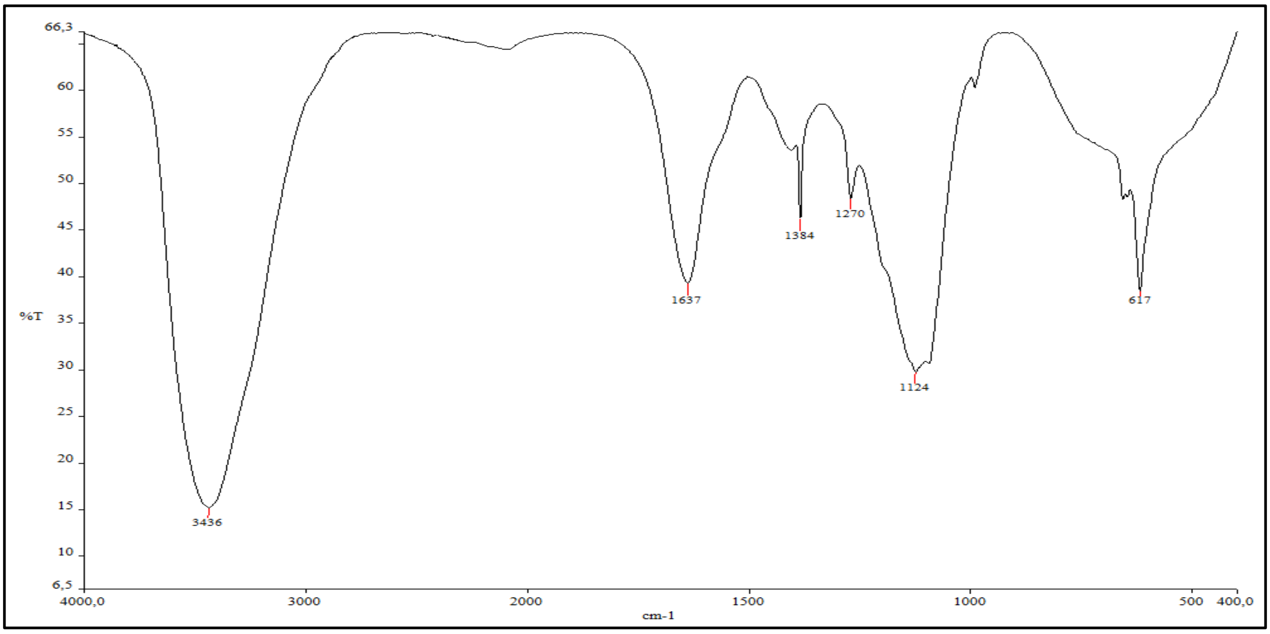


Figure 4.23 FT-IR of C4 sample.

In the Concentrato series spectra we can still recognize the signals of organic compounds CH, CO and OH bonds stretching along with broader bands in the range 1300-1500 cm^{-1} typical of inorganic carbonate salts (e.g. sodium and magnesium).

Unfortunately, this type of analysis is characterized by large signals that can hide weaker peaks such as those relative to traces as heavy metals species in very low concentration. Therefore, the results confirm that FT-IR can give information just on the main components of the nature leachate with the possible implications on heavy metals speciation.

4.1.4 GC-MS

The GC-MS analysis was performed on SANA and Concentrato series samples. The aim of the analysis was the determination of any volatile organic or organometallic species present in the leachates. For sake of completeness, the results of the analysis conducted on S1 sample with different solvents are reported, showing no signals apart from that of the eluent. This indicates the absence of volatile species or the presence of molecules that are either too small to be separated from the eluent or too complex and polar to exit the chromatographic column in reasonable time.

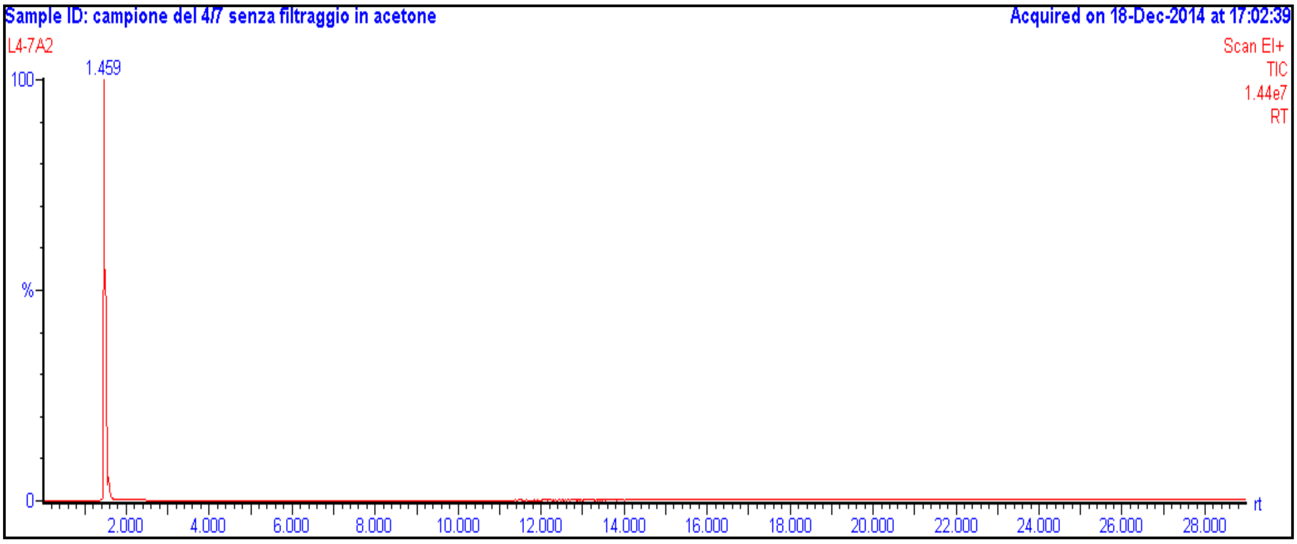


Figure 4.24 GC-MS chromatograms with acetone on S1 sample without filtering.

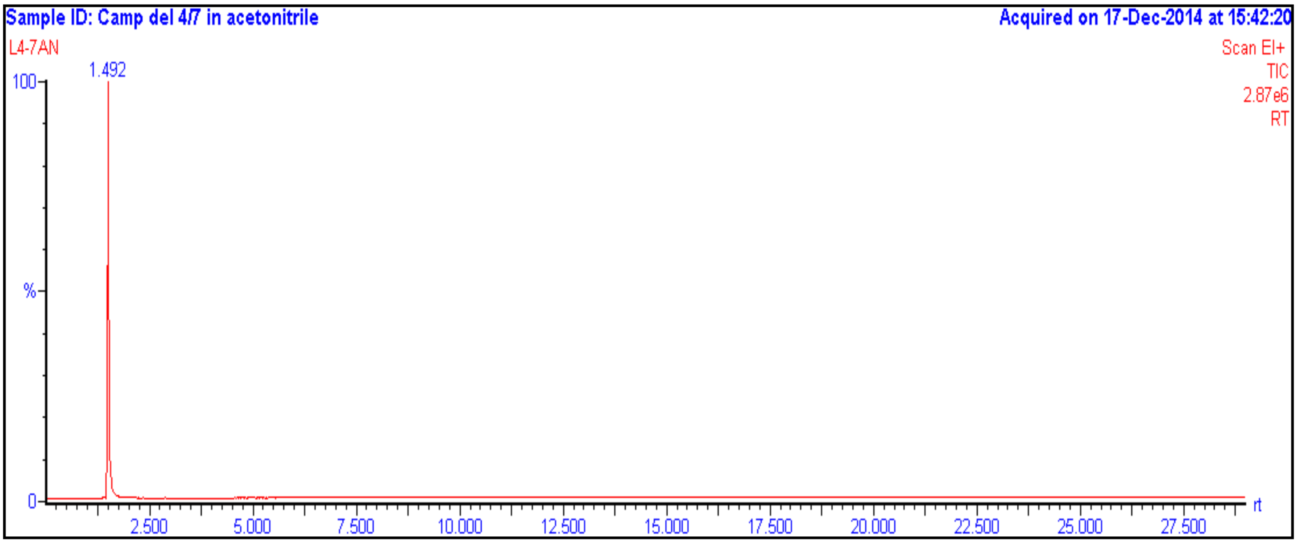


Figure 4.25 GC-MS chromatograms with acetonitrile on S1 sample.

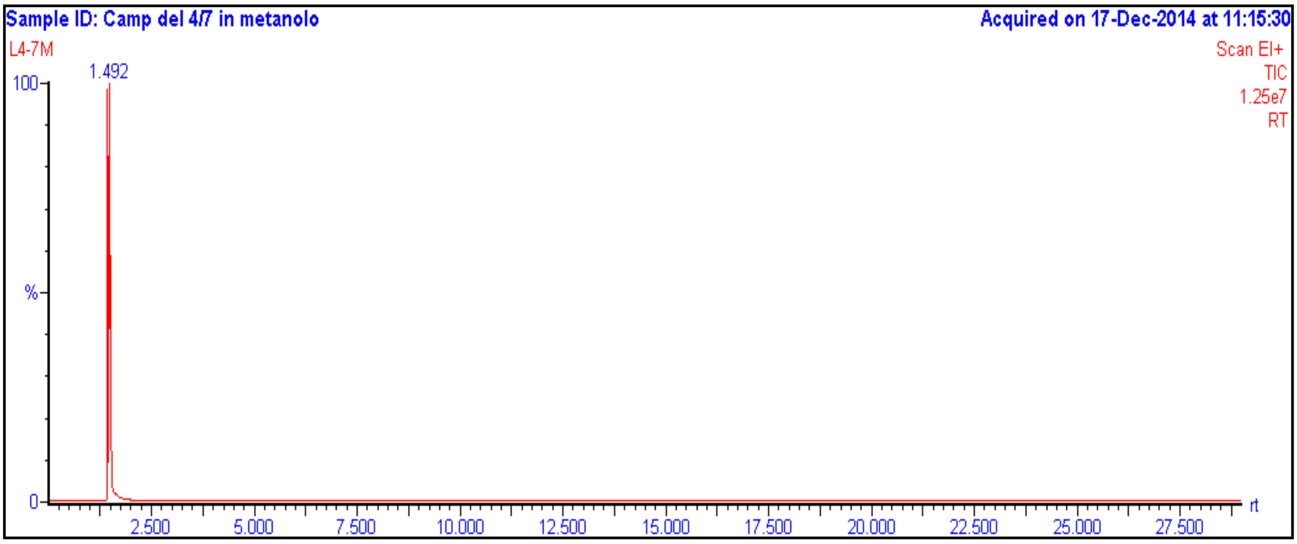


Figure 4.26 GC-MS chromatograms with methanol on S1 sample.

4.1.5 NMR

All the samples have been studied through proton and carbon-13 NMR in solution. The ^{1}H NMR spectra of SANA leachates was collected on the solid residues extract in deuterated chloroform ($CDCl_3$) and deuterium oxide (D_2O).

In general, the ^{1}H NMR spectra of the samples in chloroform show little information about the organic fraction in solution. As an example we report the spectrum relative to leachate S1 which shows the presence of some alkyl derivatives (CH_3 and CH_2 signals at 1.0-1.3 and 2.3-2.5 ppm) superimposed to the broad signal of residual water (1.90 ppm).

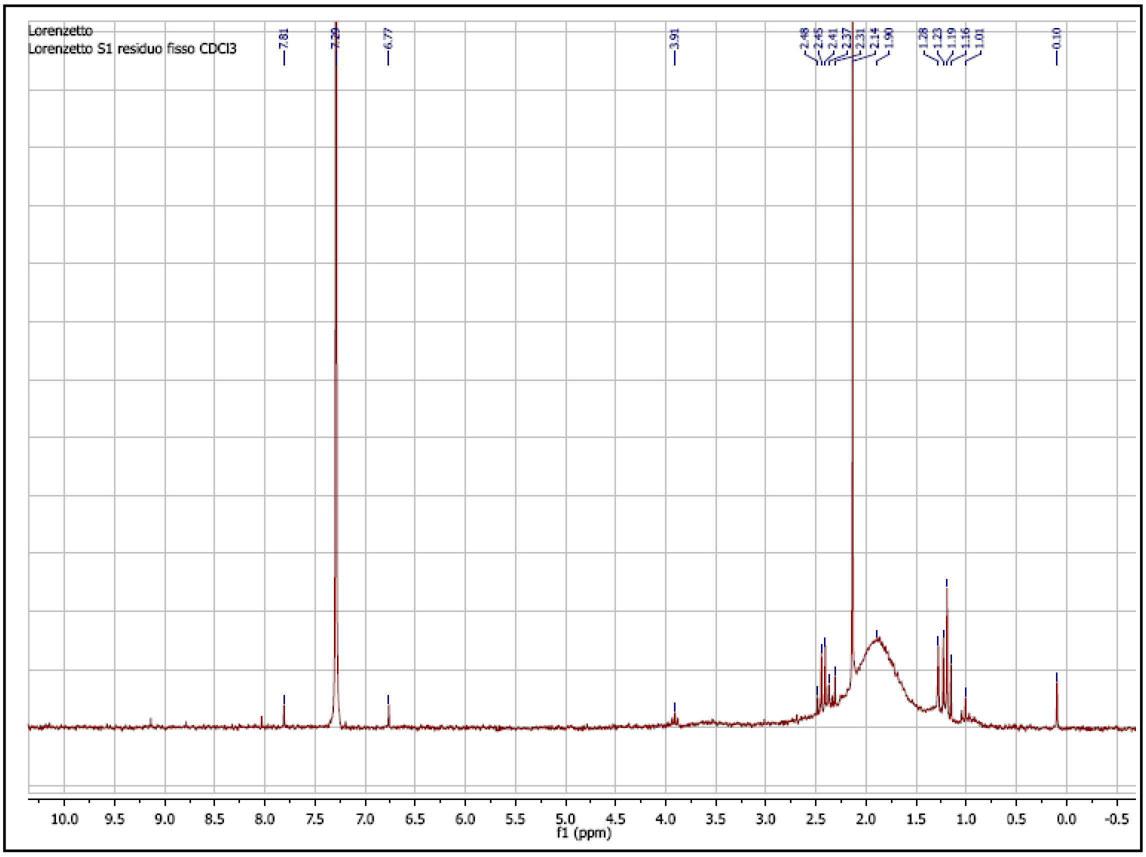


Figure 4.27 ^{1}H NMR spectrum of S1 dry residue recorded onCDCl$_3$ solution.

All the spectra of the fractions extracted with D_2O show a higher concentration of organic species which are therefore hydrophilic in nature and able to interact directly with dissolved metallic ions.

In particular, the S1 sample shows as main component of the organic species the aliphatic derivatives with signals in the range 0.5-2.2 ppm. These are typically ascribable to small alkyl chains or groups such as ethyl fragments (*e.g.*CH_3 at 0.95 ppm and CH_2 at 2.04 ppm) and methyl fragments bound to carbonyl or carboxyl groups (*e.g.* CH_3 at 1.80 ppm).

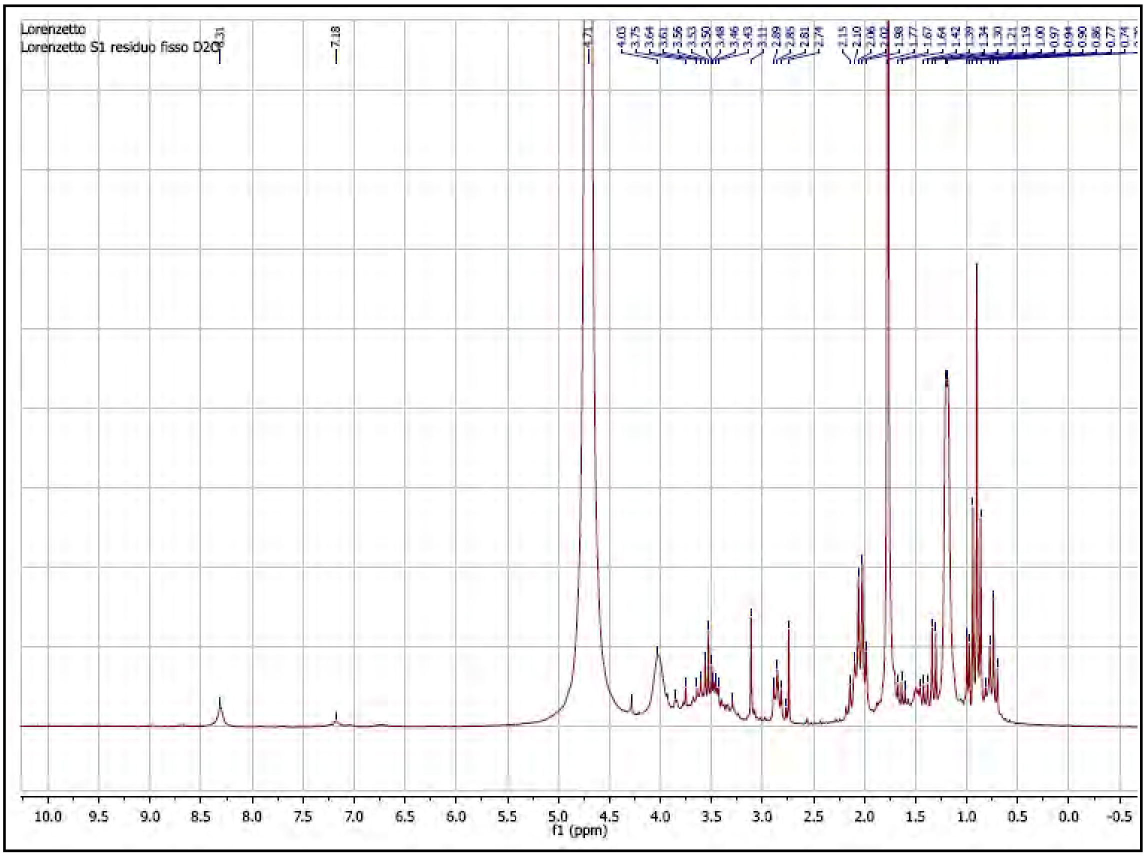


Figure 4.28 ^{1}H NMR spectrum of S1 dry residue recorded on D_2O solution.

In the range 2.6-4.3 ppm we can find the signals due to protons bound to carbon atoms directly attached to oxygen (carbohydrates, methoxyl groups, proteins, etc.) and derived from the partial oxidation of biologically derived materials (wood, paper, plastics, etc.).

Finally, in the range 6.5-8.5 we can see some very weak signal for aromatic protons (7.19 ppm) and hydroxyl groups (8.31 ppm).

The ageing of the leachate in aerobic condition has the effect of reducing the amount of oxygenated species proved by the attenuation of the signals in the range 2.5-4.5 and the disappearance of the signal at 8.30 ppm in the spectrum of sample S2 compared to the previous one. This could be related to a higher degree of degradation or to the coordination to the metal centers available in solution to form macromolecular agglomerates (colloidal species) separated in the filtration process.

The aliphatic protons signals between 0.5-2.5 ppm and the aromatic ones at 7.18 ppm show just some small change in their relative intensity and integration (proportional to the amount of different protons present in the sample).

The comparison between the spectra of samples S2 and S3 proves that the content in organic species is very similar, suggesting that the subsequent anaerobic treatment doesn't affect the soluble organic components of the leachate.

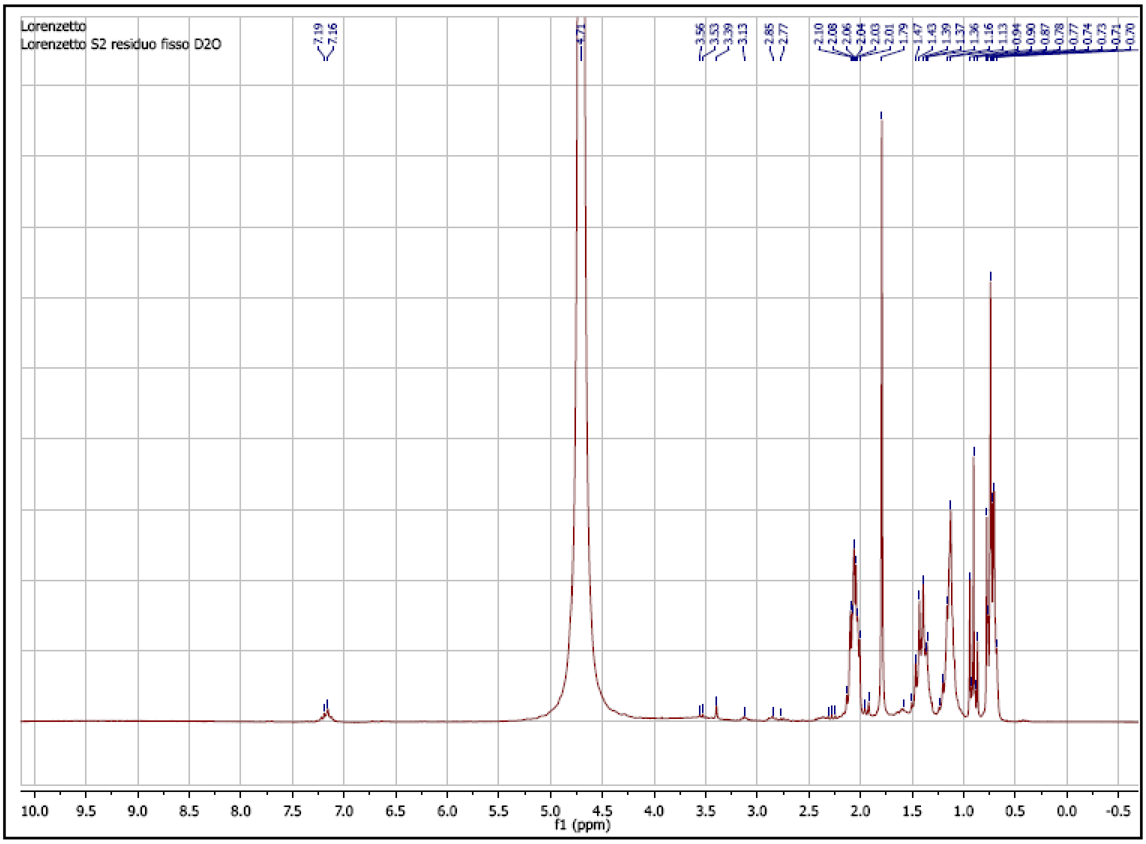


Figure 4.29 ^{1}**H NMR spectrum of S2dry residue recorded on** D_2O **solution.**

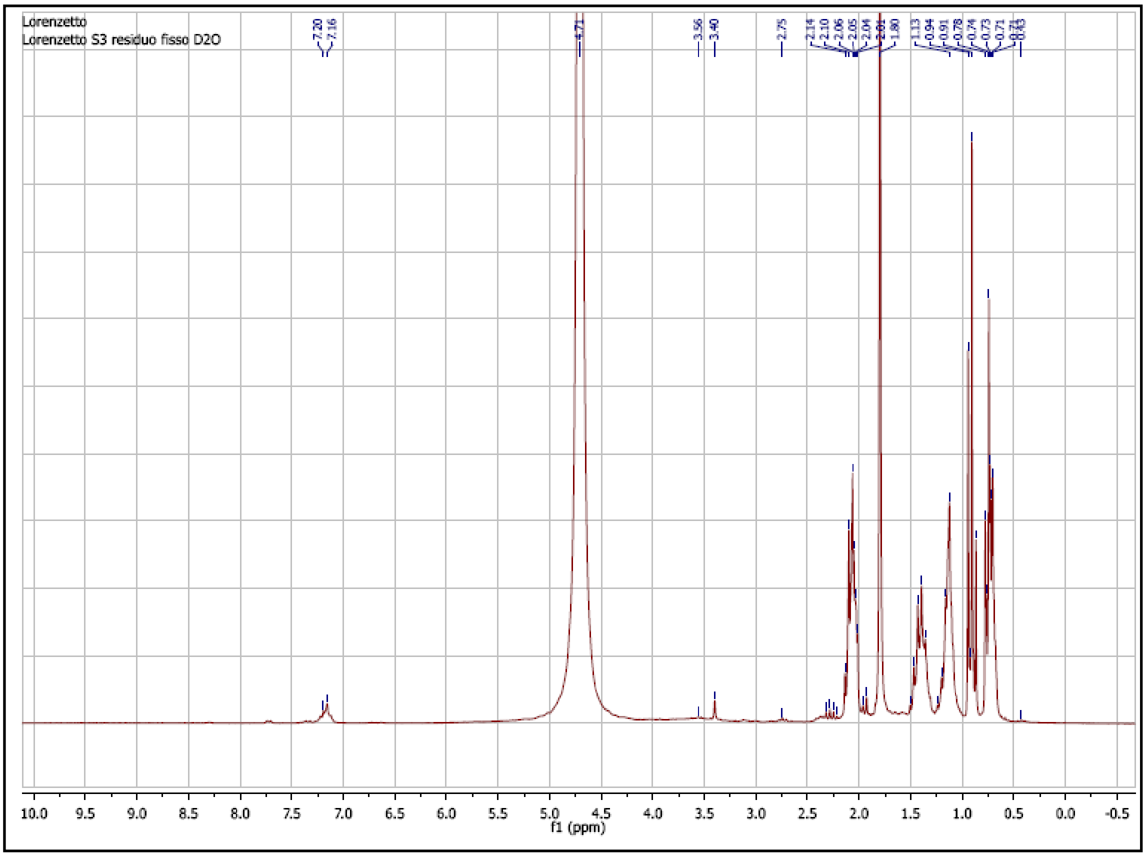


Figure 4.30 ^{1}**H NMR spectrum of S3dry residue recorded on** D_2O **solution.**

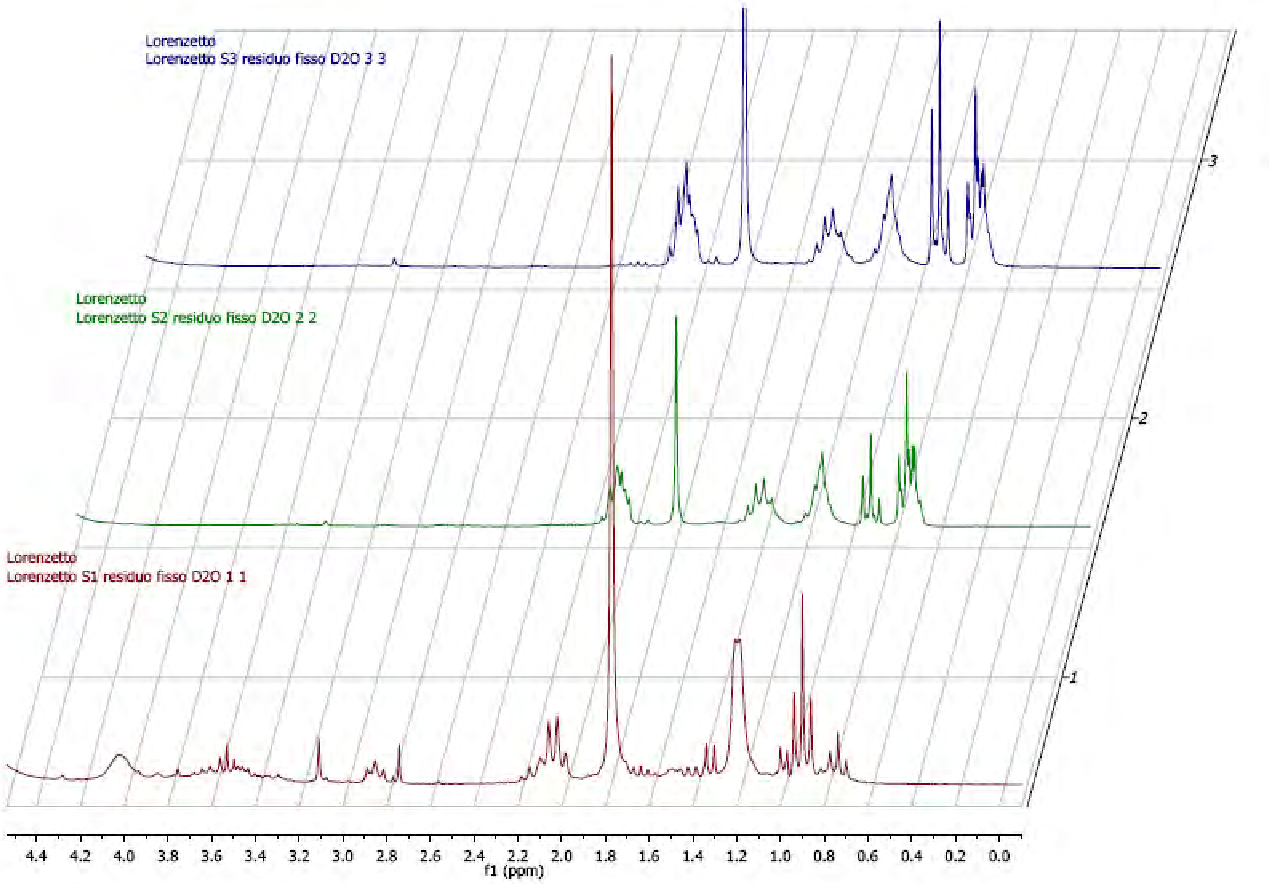


Figure 4.31 Comparison of^{1}H NMR spectra of dry residue of SANA samples recorded on D_2O solution.

Similarly to the series SANA, the Concentrato leachates show very few signals in $CDCl_3$as reported in fig. 5.40 and 5.44 (the singlets at 1.60 and 7.30 ppm are attributable to the residual water and the residual protons of the solvent respectively).

All the spectra in D_2O show a larger amount of organic molecules compared to the chloroform ones but overall the organic content of the Concentrato solutions is very limited if compared to the SANA ones in accordance with the effect of the ageing of the samples described above.

The presence in all the samples of very broad signals in both the 0.5-2.5 ppm and 2.5-4.5 ppm suggest the presence of a very wide range of molecular structures that cannot be easily defined.

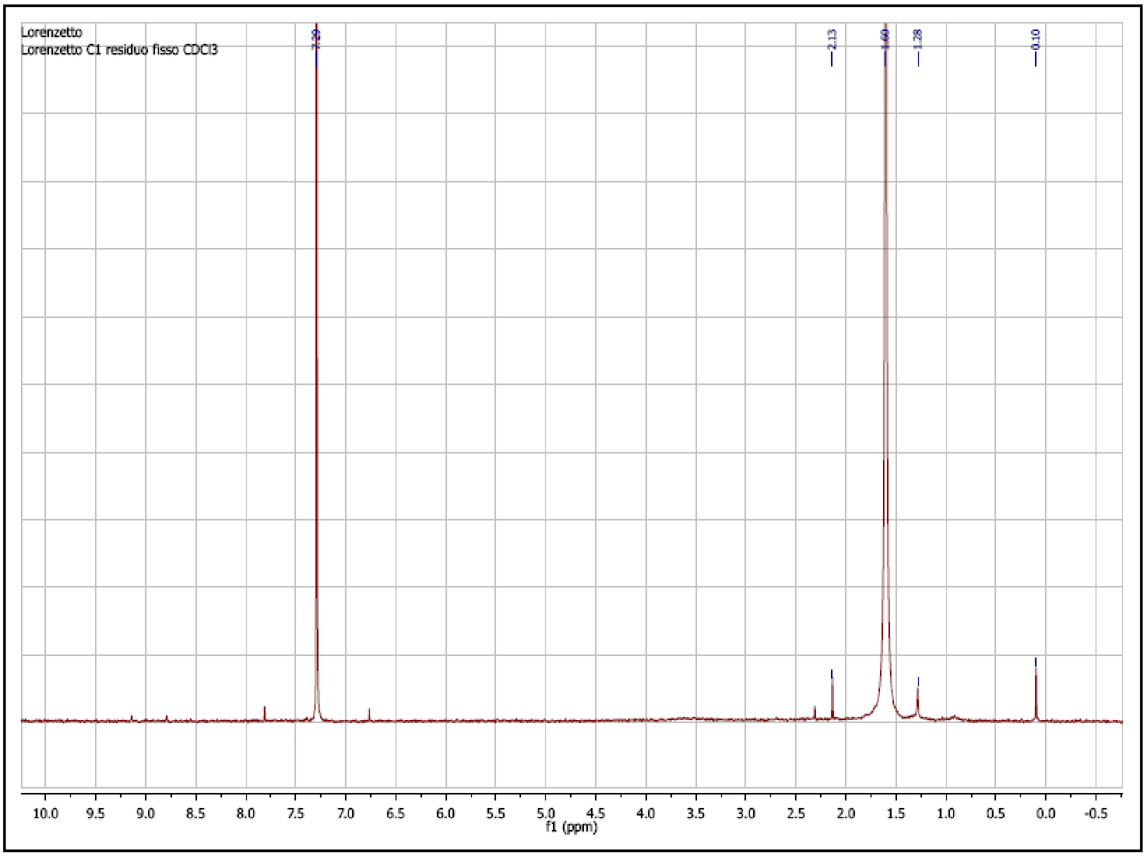


Figure 4.32 ^{1}H NMR spectrum of C1dry residue recorded on $CDCl_3$solution.

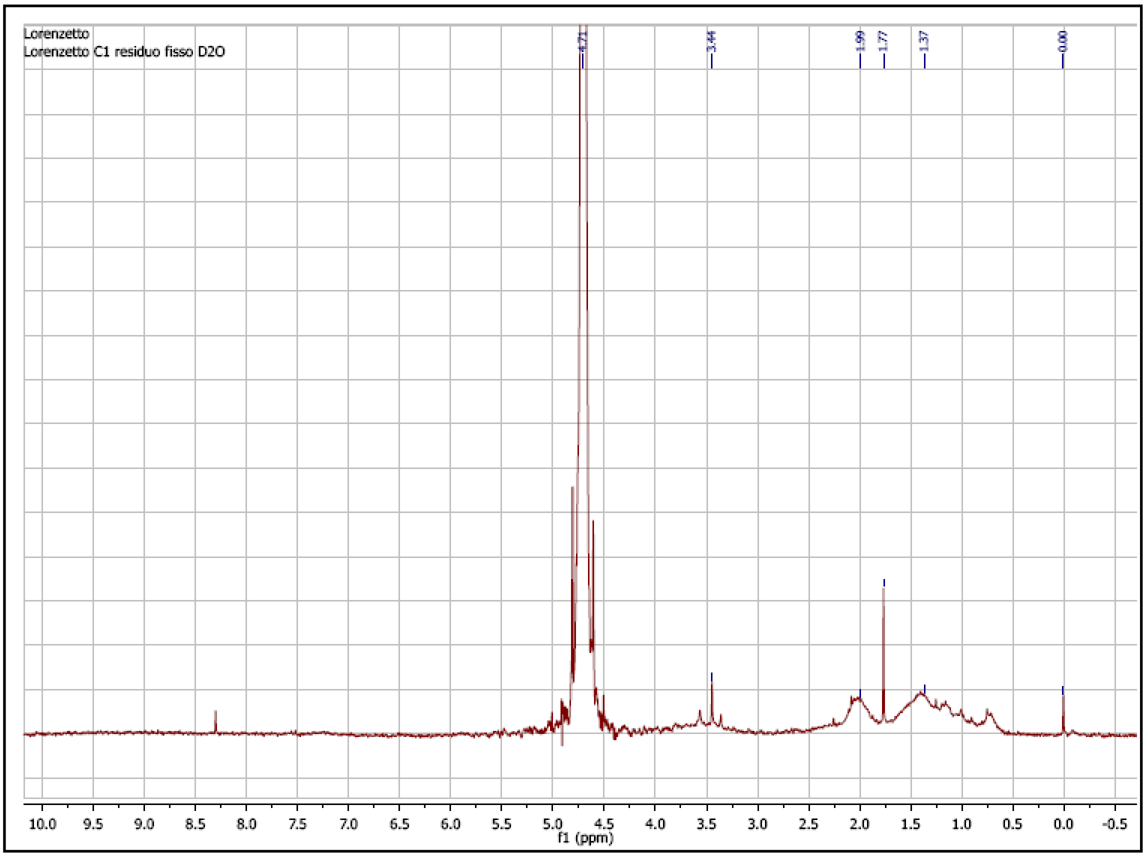


Figure 4.33 ^{1}H NMR spectrum of C1dry residue recorded on D_2O solution.

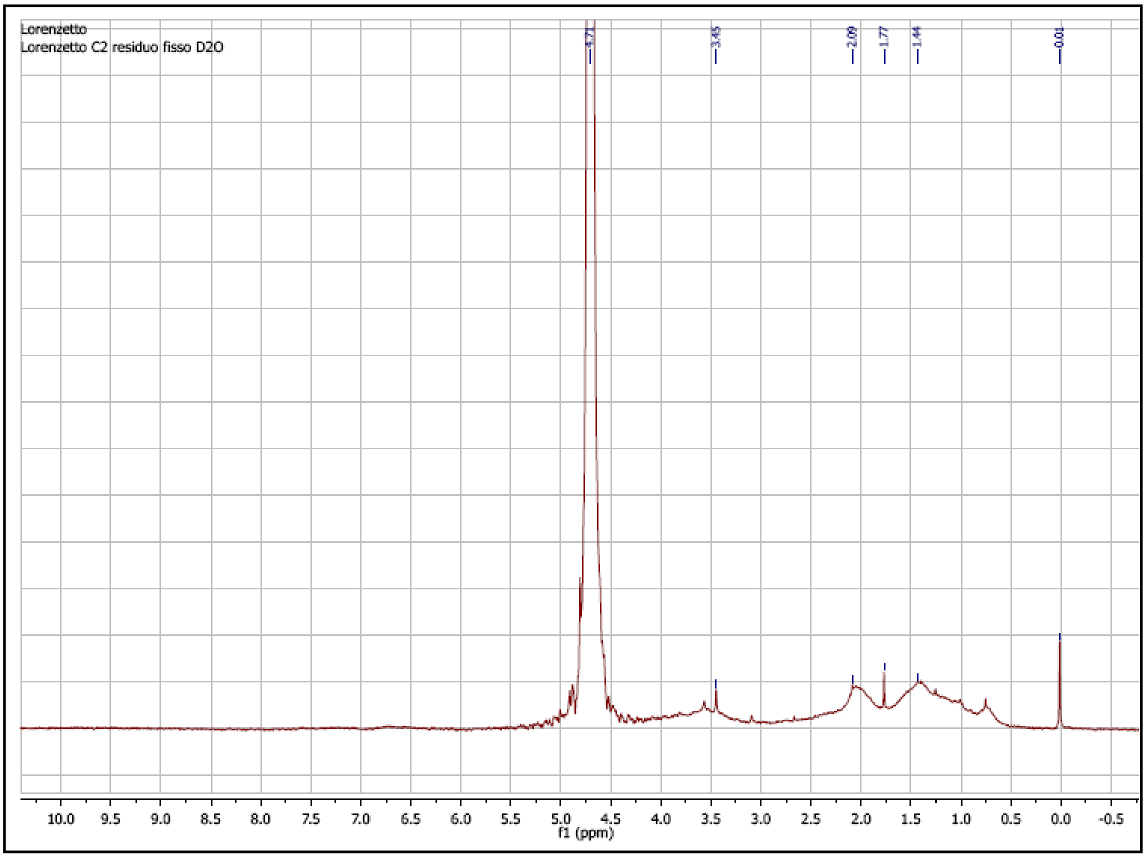


Figure 4.34 ^{1}H NMR spectrum of C2dry residue recorded on D_2O solution.

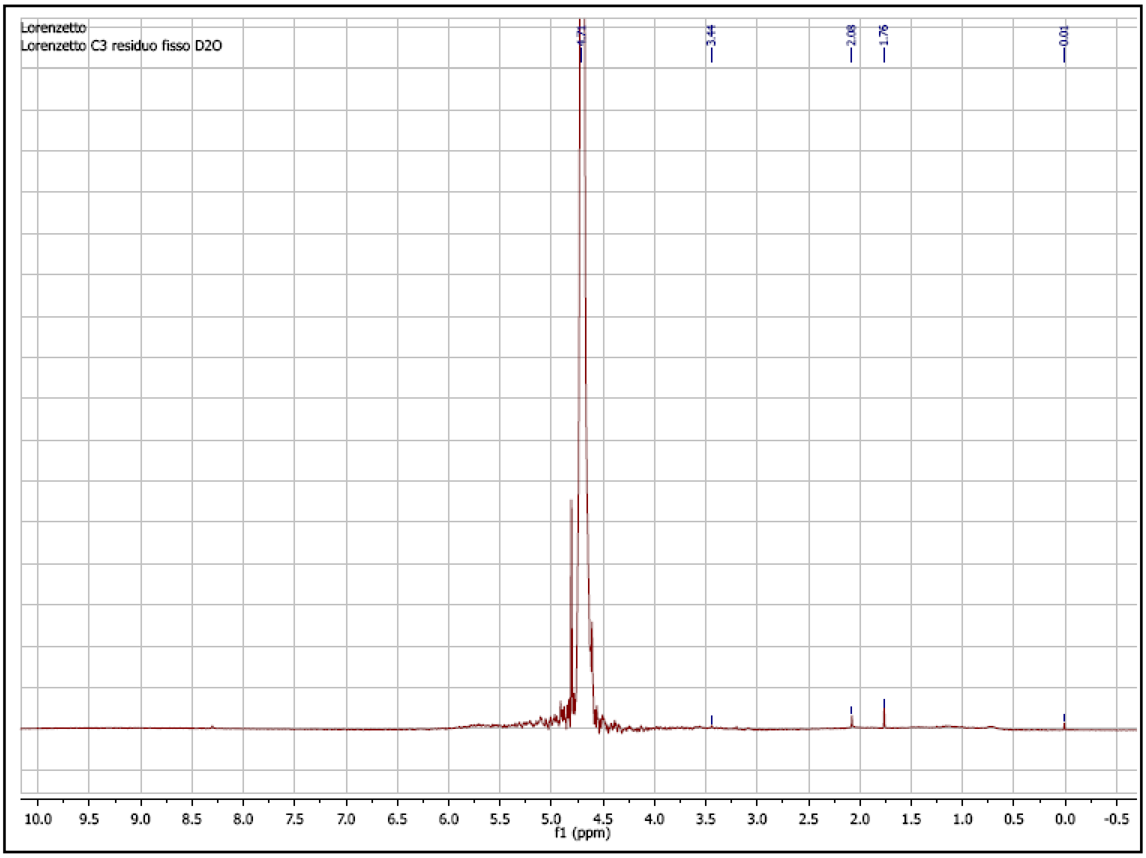


Figure 4.35 ^{1}H NMR spectrum of C3dry residue recorded on D_2O solution.

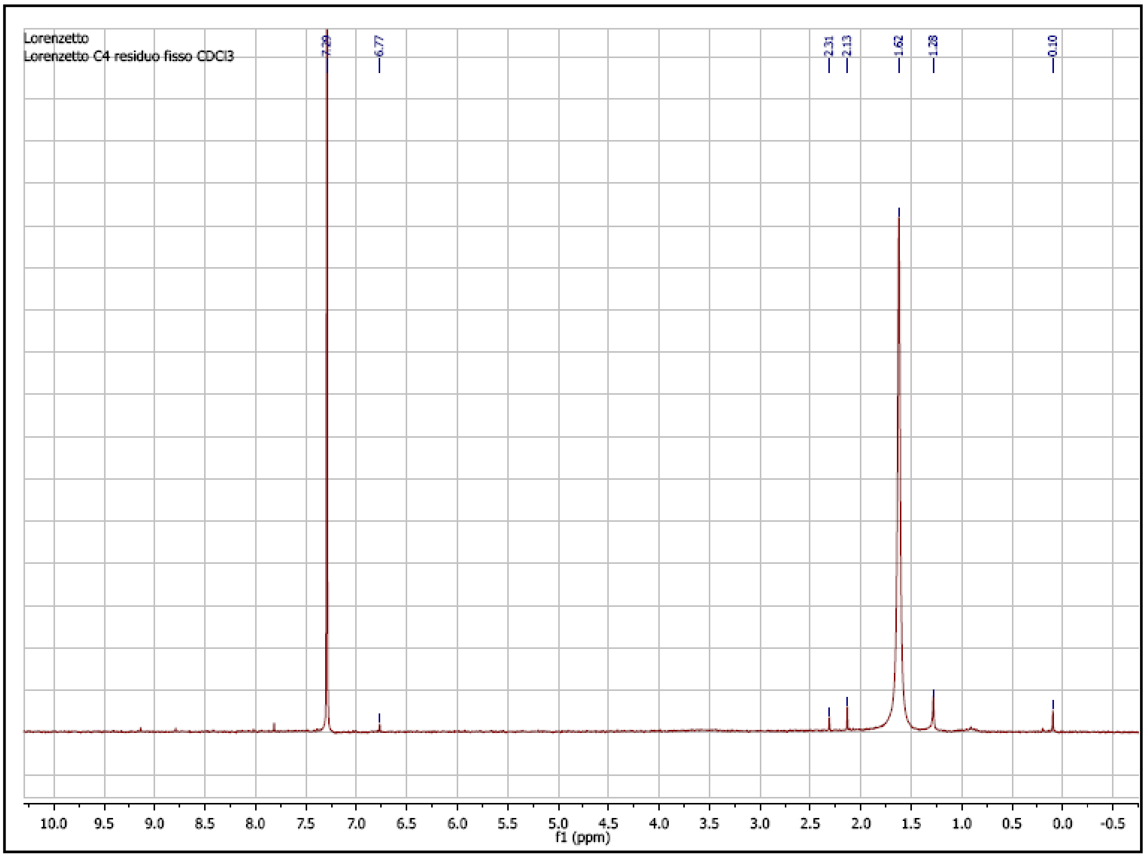


Figure 4.36 ^{1}H NMR spectrum of C4dry residue recorded on $CDCl_3$solution.

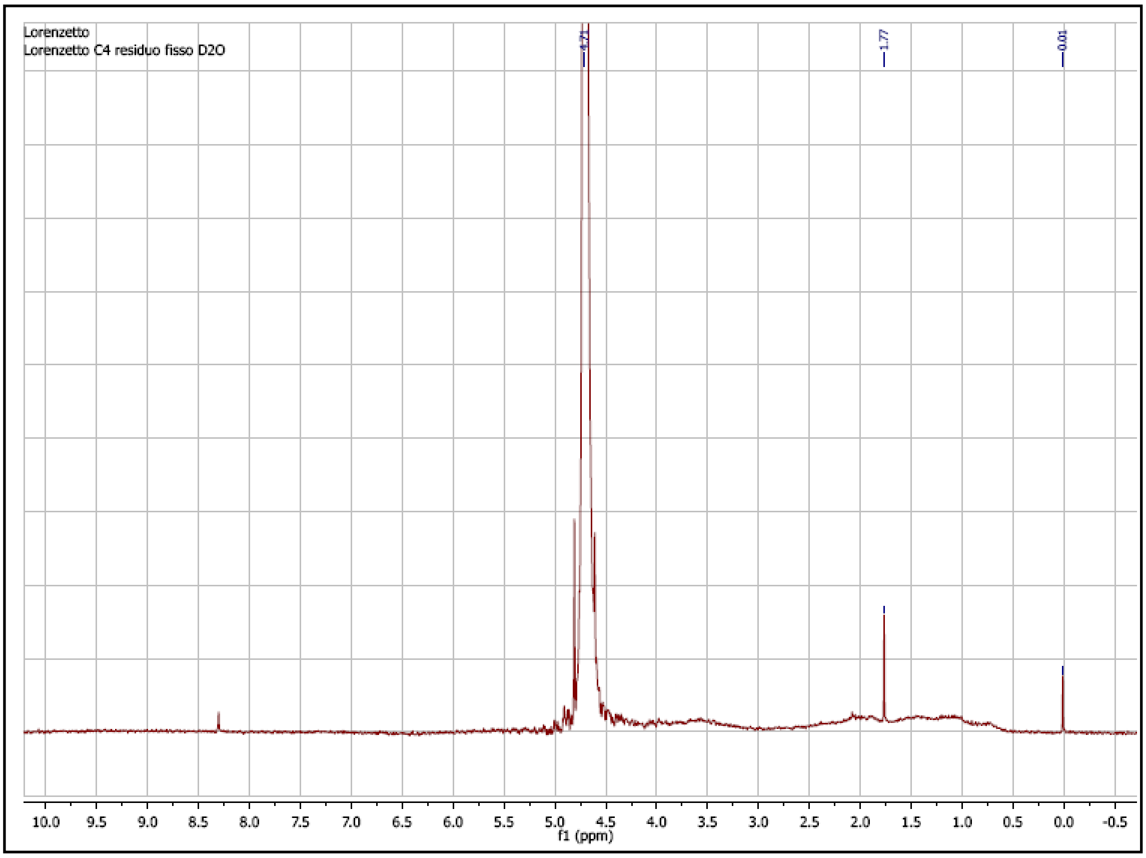


Figure 4.37 ^{1}H NMR spectrum of C4dry residue recorded on D_2O solution.

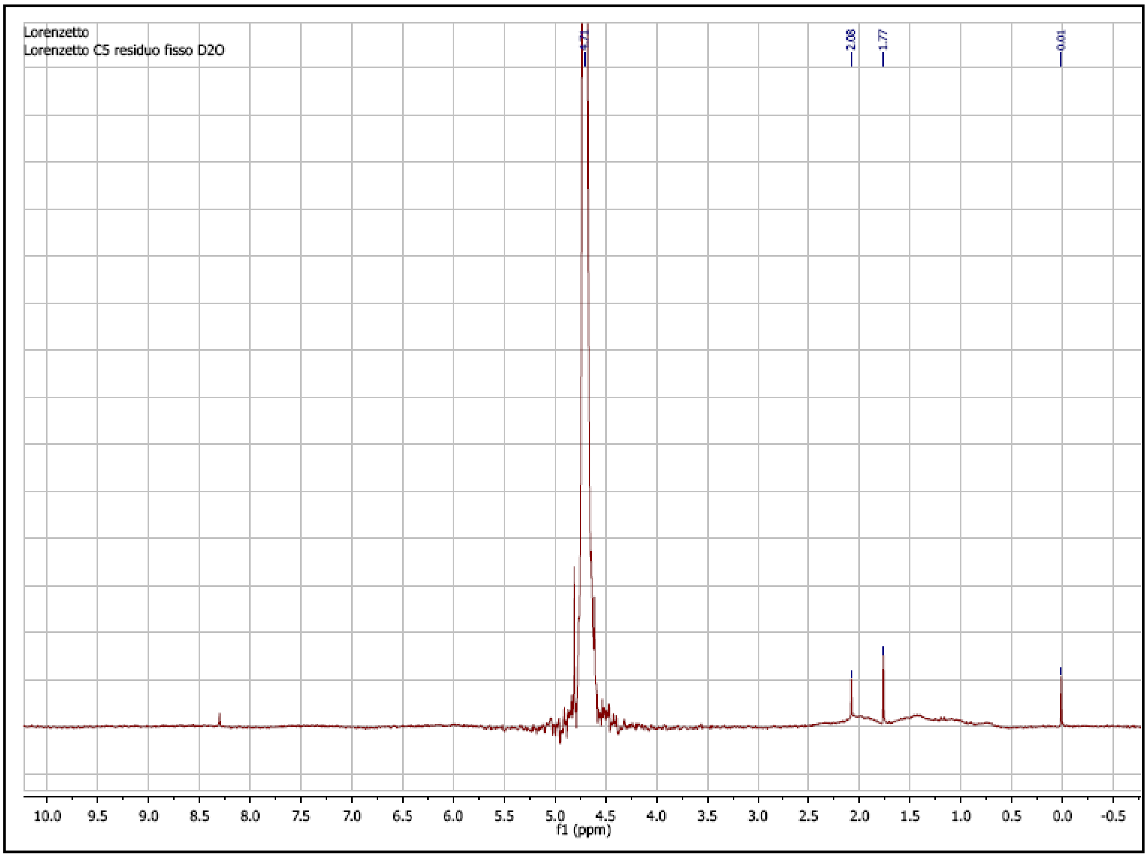


Figure 4.38 ^1H **NMR spectrum of C5dry residue recorded on** D_2O **solution.**

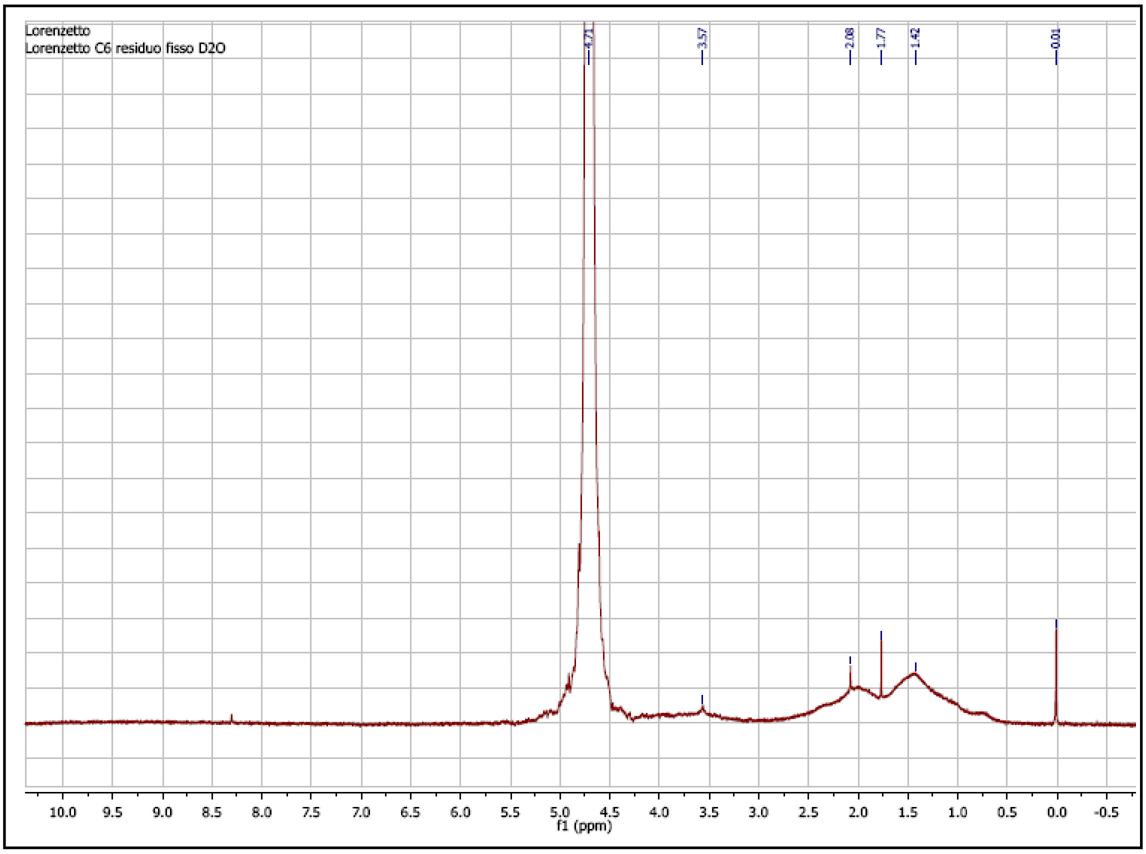


Figure 4.39 ^1H **NMR spectrum of C6dry residue recorded on** D_2O **solution.**

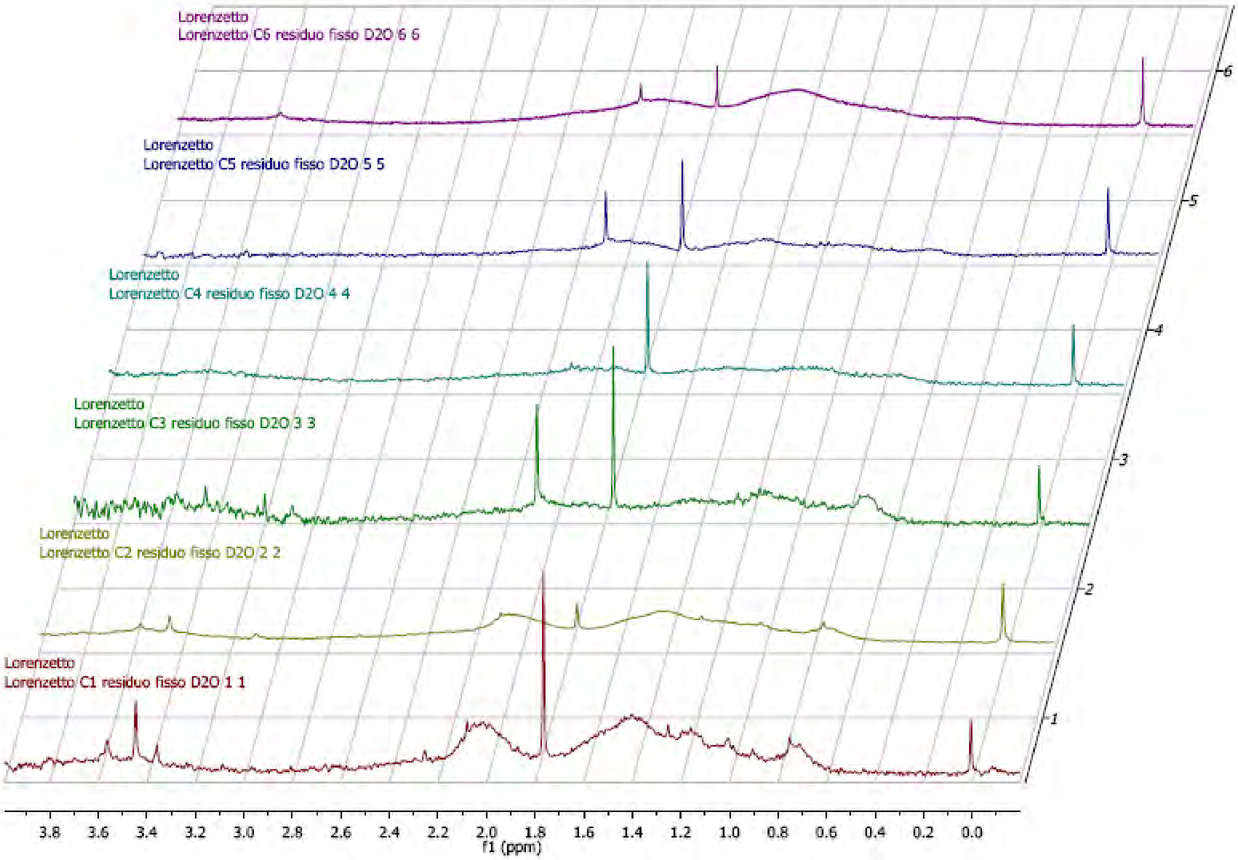


Figure 4.40 Comparison of ^{1}H NMR spectra of dry residue of Concentrato samples recorded on D_2O solution.

The ^{13}C {^1H} NMR analysis have been performed directly on the filtered leachates with the addition of small amounts of D_2O.

The S1 spectrum shows a wide range of signals that can be attributed to organic molecules. In particular, the signals in the range 10-40 ppm refer to aliphatic carbons in alkyl groups, those in the range 50-80 ppm to carbons in multiple bonds and directly attach to oxygen atoms and finally the broad signals at around 180 ppm relative to carboxylic carbons. This is in accordance with the observations of hydroxilated species by proton NMR reported above and infrared spectroscopy for this sample.

All the Concentrato samples show as the only visible signal a singlet at 160.5 ppm that can be attributed to the carbonate ion (CO_3^{2-}) which is present in high concentration as confirmed by ESEM analysis.

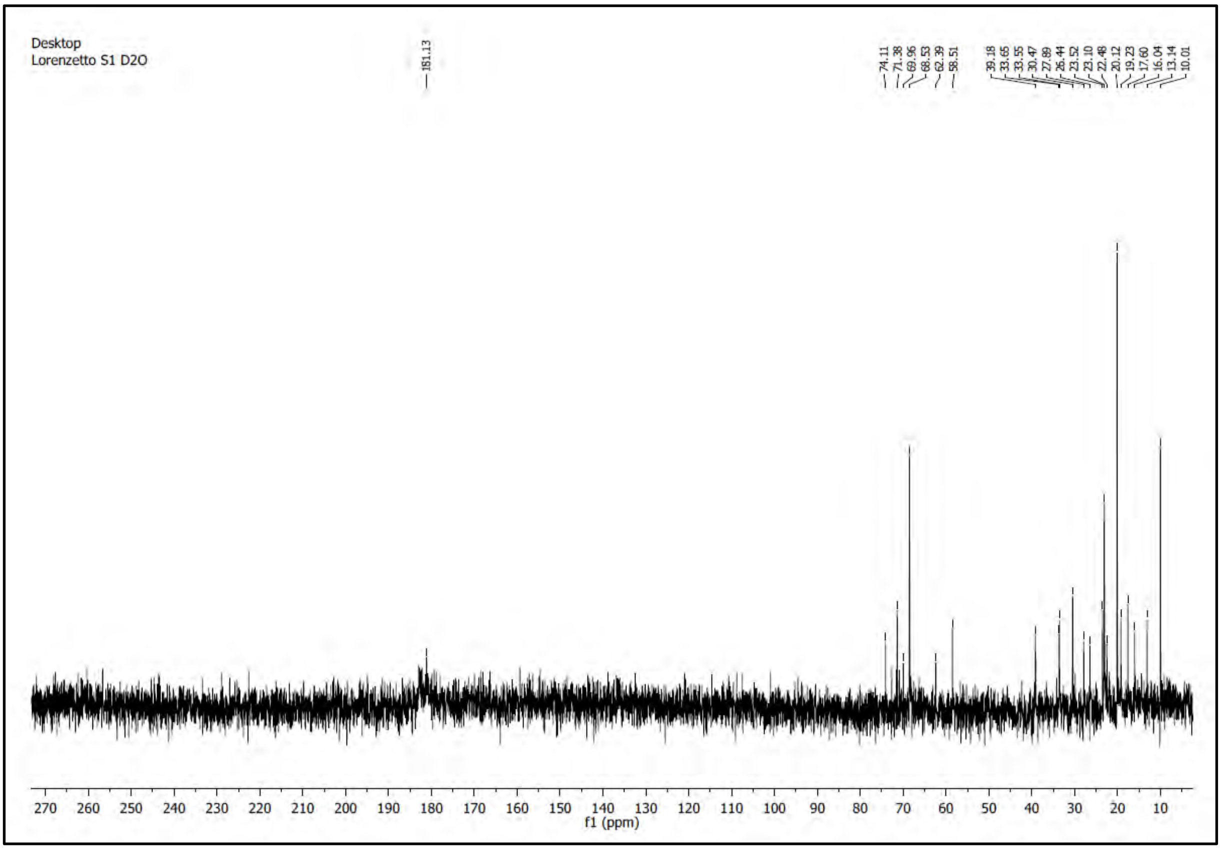


Figure 4.41 ^{13}C NMR spectrum of S1 recorded on D_2O solution.

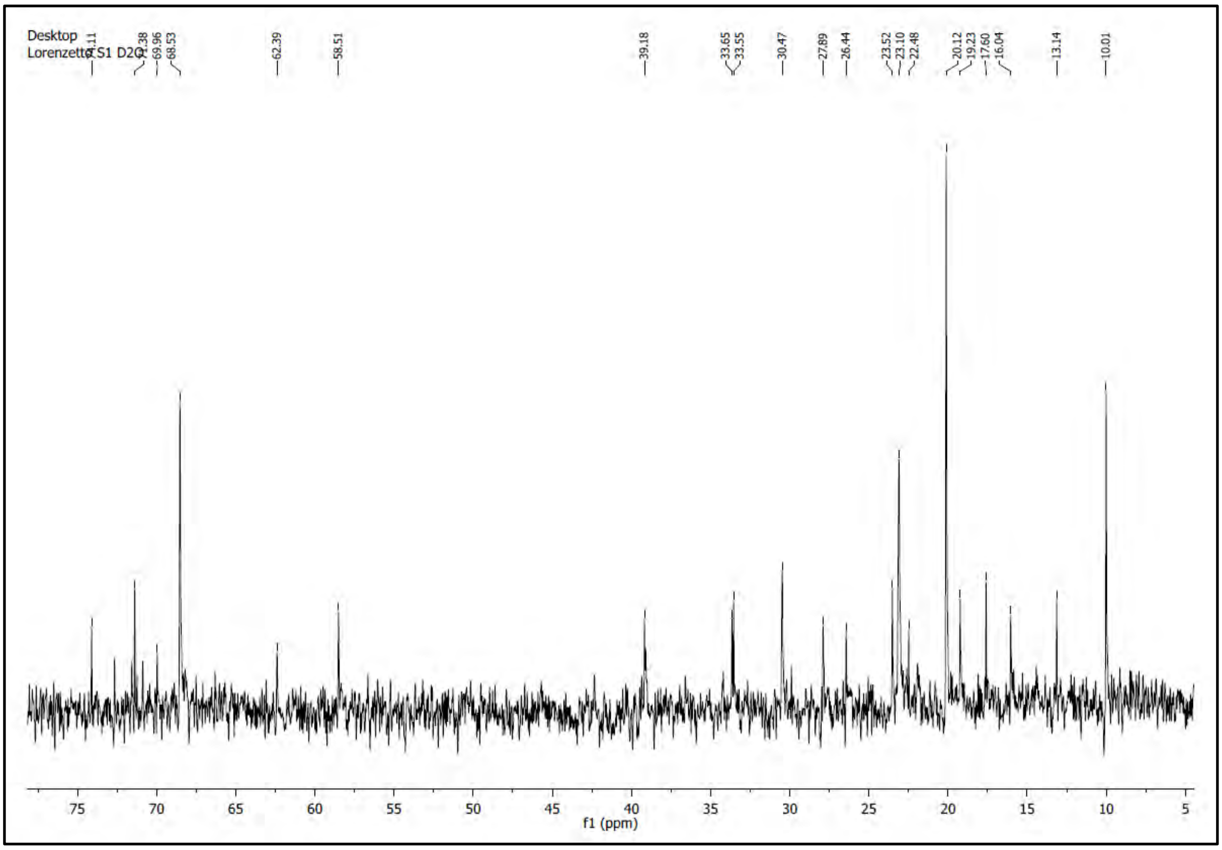


Figure 4.42 05.0-80 ppm section of S1 ^{13}C NMR spectrum in D_2O solution.

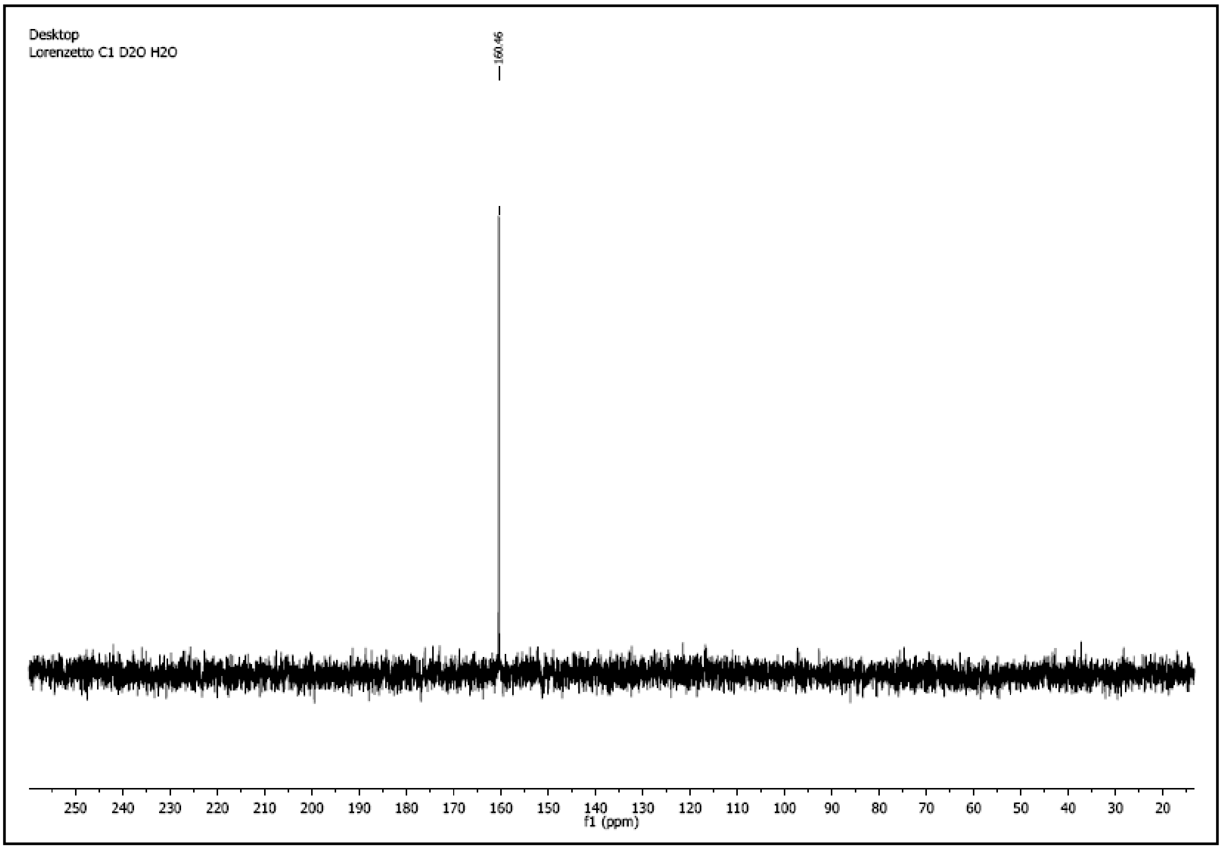


Figure 4.43 ^{13}C NMR spectrum of C1 recorded on D_2O solution.

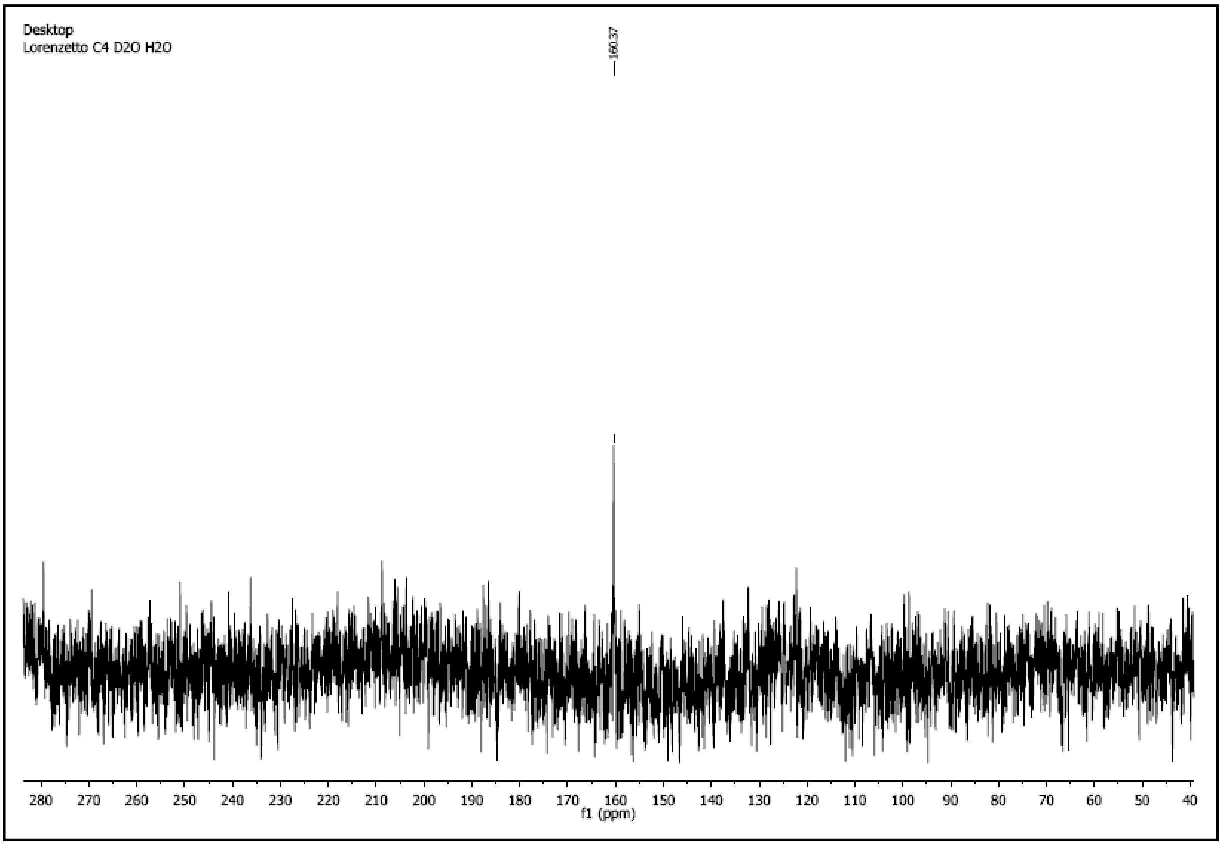


Figure 4.44 ^{13}C NMR spectrum of C4 recorded on D_2O solution.

4.1.6 ICP-OES

The ICP-OES analysis was performed by Dr.Annalisa Sandon at LISA laboratory at Voltabarozzo. The results of SANA samples are reported in the following tables and figures. For S1 and S2 samples belonging to the same column the metal concentration trend in leachate over time is also reported (figure 4.49, 4.50) in order to better understand the behaviour of the metal content during the degradation process that occurs in the landfill.

Sample	**Cr (µg Cr/l)**	**Cu (µg Cu/l)**	**Fe (µg Fe/l)**	**Ni (µg Ni/l)**	**Pb (µg Pb/l)**	**Zn (µg Zn/l)**
S1	289.00	779.00	63869.00	583.00	64.00	11522.00
S2	25.5	225	17333	460	24.4	700

Table 4.5 ICP-OES analysis results.

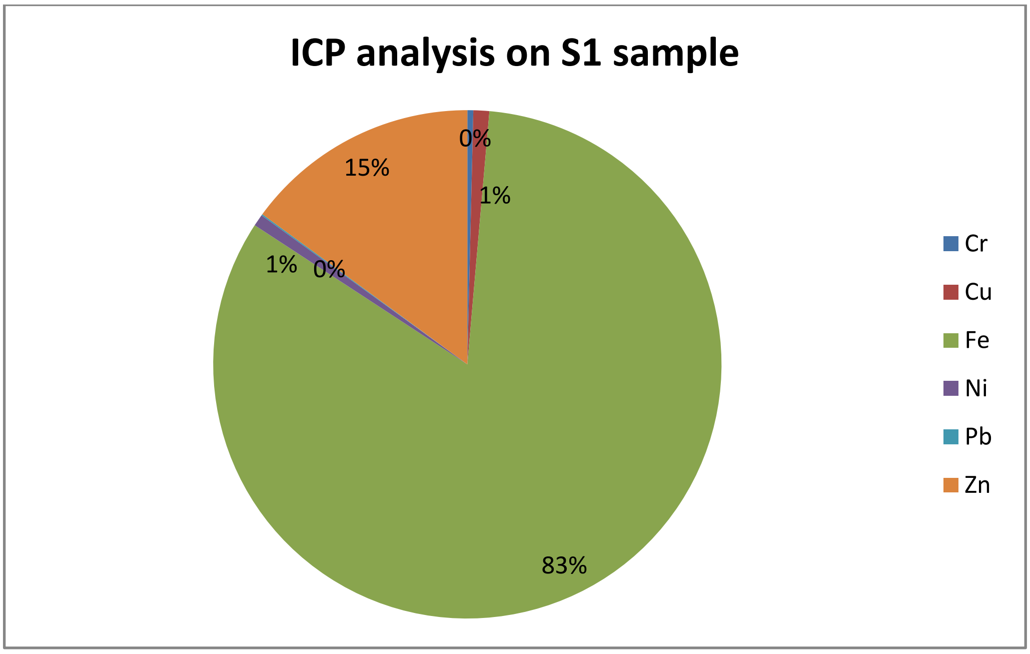


Figure 4.45 Percentage of heavy metals detected on S1 sample.

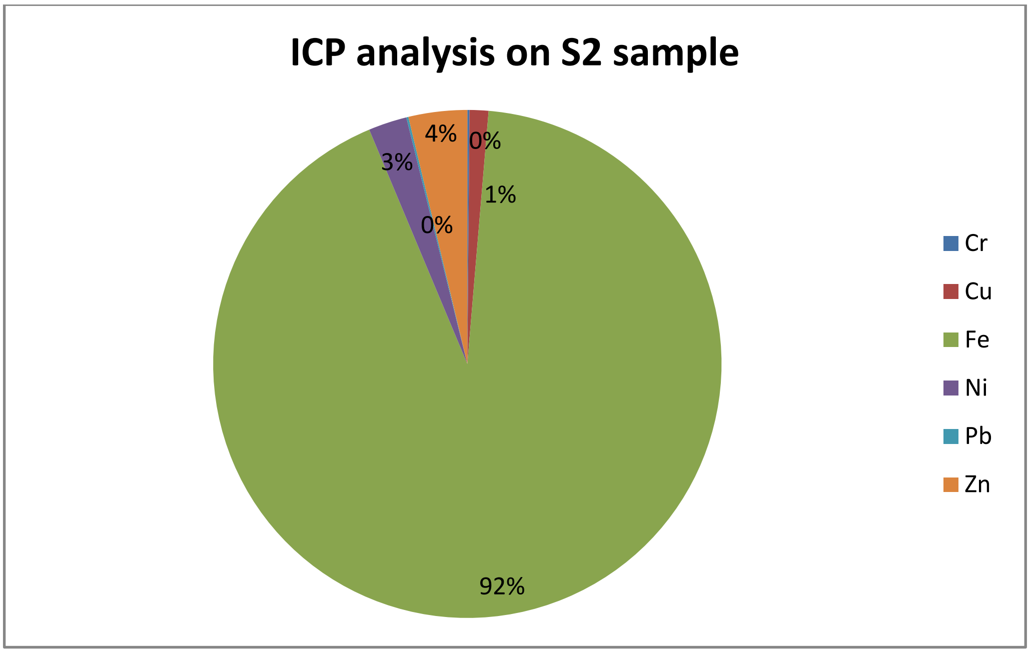


Figure 4.46 Percentage of heavy metals detected on S2 sample.

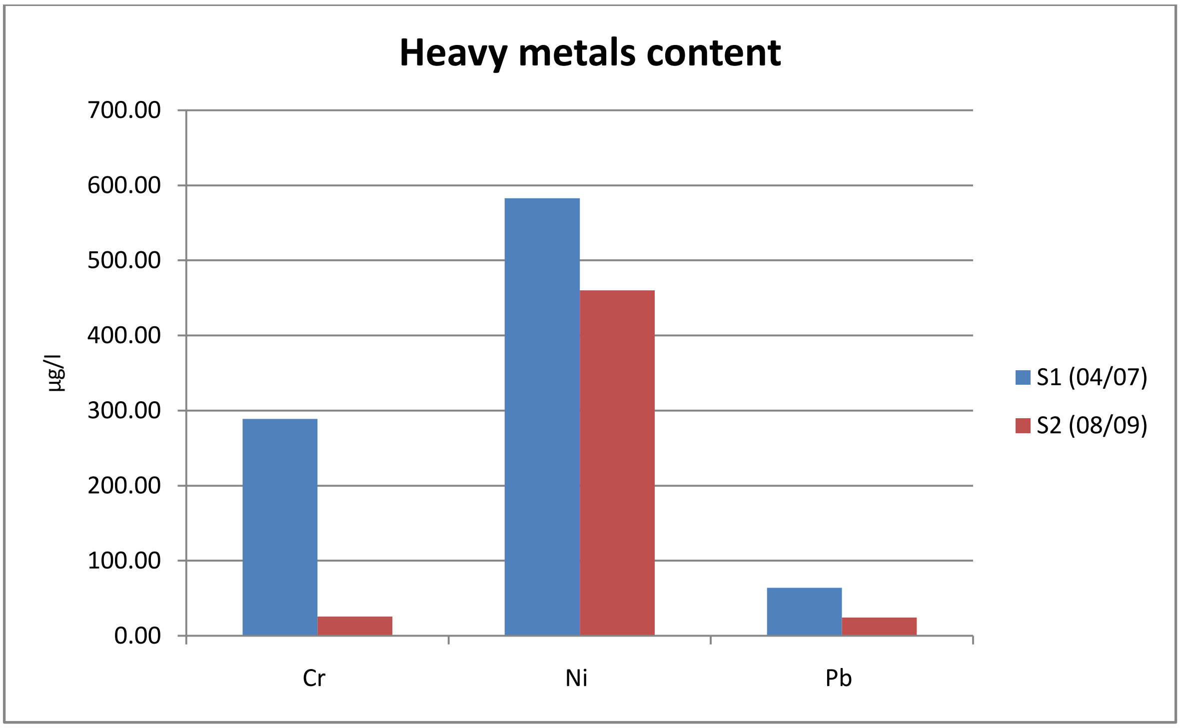


Figure 4.47 Heavy metals content on S1 and S2 samples.

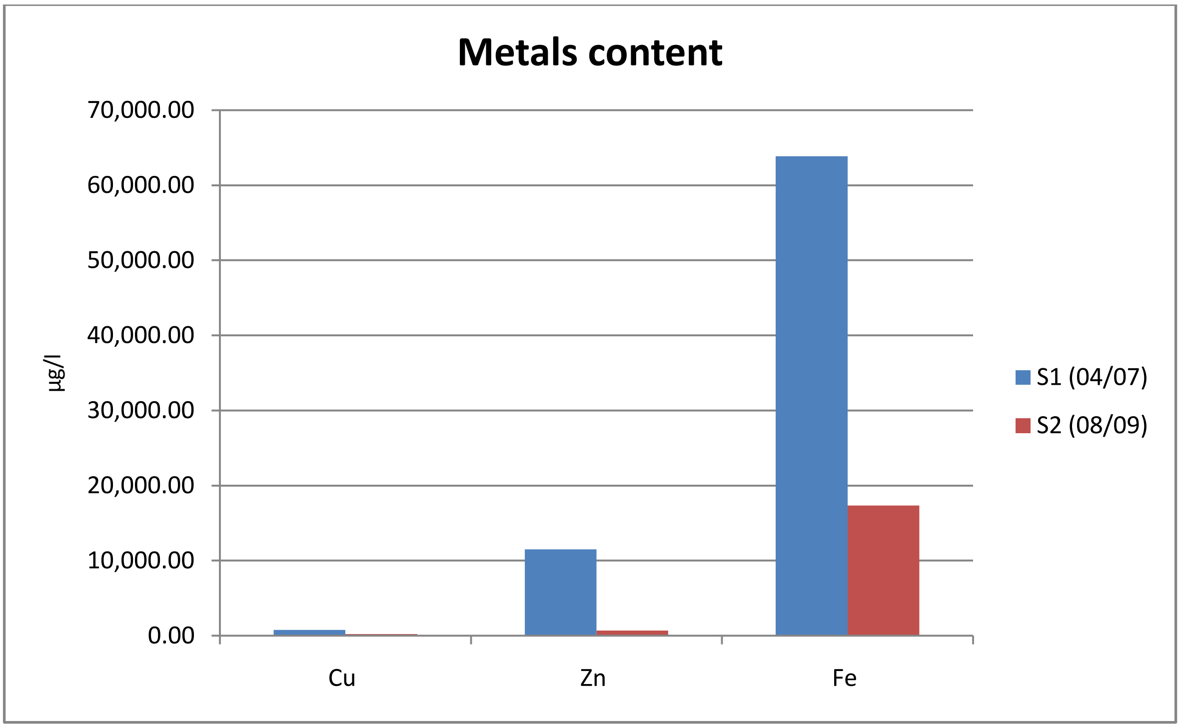


Figure 4.48 Metals content on S1 and S2 samples.

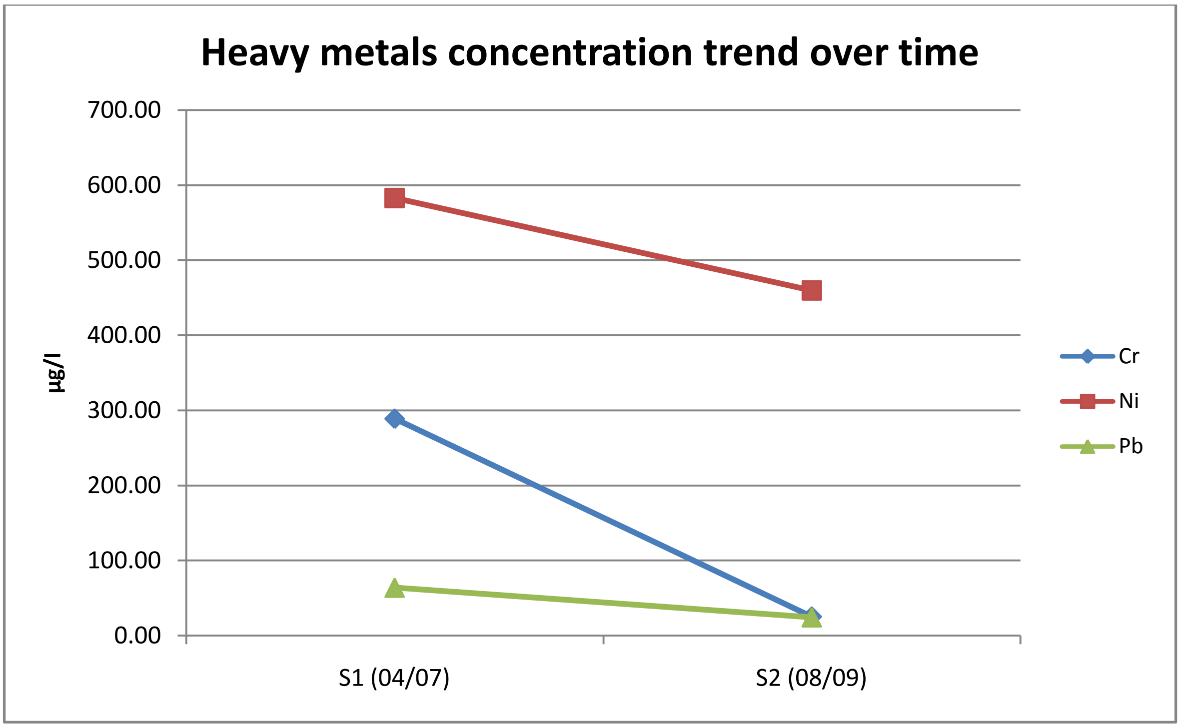


Figure 4.49 Heavy metals concentration trend over time on SANA samples.

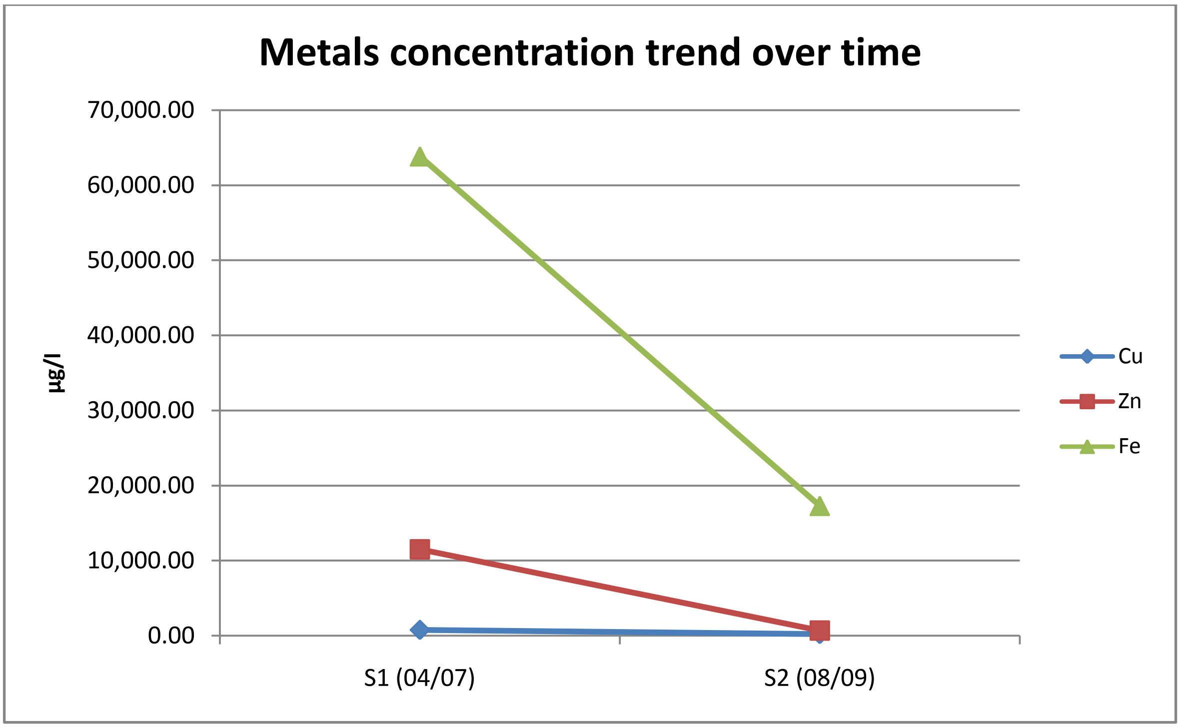


Figure 4.50 Metals concentration trend over time on SANA samples.

The ICP results show the presence of certain types of metals in leachate samples. As it is possible to notice from the figures 4.45 and 4.46, the most concentratedmetal is iron (92% and 83%) with values higher than those of any other metal. The high concentration of iron is associated to the fact that the leachate derives from a municipal solid waste landfill where iron is usually the metal more present. Results reveals also the presence, albeit in a much less concentration, of some environmental hazardous heavy metals such as chromium, lead and nickel below the Italian law limits apart for the Chromium in the S1 sample. Attention must be taken on these metals because they are highly toxic to human health and the environment. In particular, chromium can cause lung cancer, lead creates dysfunction to nervous system and nickel arouses allergic skin reactions.

In Figure 4.48 is possible to analyze the trend over time of metals concentration in the leachate samples derived from SANA management. It can be noticed how certain types of metals such as iron and zinc are reduced drastically in the first months due to the degradation that occurs in the landfill. In fact, the increase in pH of the leachate with subsequent increase in hydroxyde ion concentration can cause the precipitation of slightly soluble metals hydroxyde $Fe(OH)_3$and $Zn(OH)_2$. Therefore, these metals can represent a disposal problem in the early period of the landfill management since it will have large quantities in output in the initial phase of the landfill life. Thus preventive measures should be taken for ther management. Other metals such as nickel and lead degrade within the landfill very slowly and therefore represent a disposal problem in the advanced stages of management of the landfill. These metals that are more persistent in the leachate should be monitored carefully as they are heavy metals that are toxic and can pollute the surrounding environment, especially groundwater and soil.

Concerning the results of ICP-OES analysis on Concentrato samples, it is important to underline that every sample comes from a specific aerobic or anaerobic treatment as it is illustrated in the table 4.6.

		INPUT (1 l/week)	AERATION (l/d)
ANAEROBIC	**C1**	100% RO concentrate	-
	C2	50% RO concentrate +50% water	-
	C3	100% water	-
AEROBIC	**C4**	100% RO concentrate	50
	C5	50% RO concentrate +50% water	50
	C6	100% water	50

Table 4.6 Management of the columns. The table shows the proportion of water and concentrate injected in every columns, and reports the daily air flowrate.

The results of the analysis on the C1-6 samples are reported in the following table.

Sample	**Cr (μg Cr/l)**	**Cu (μg Cu/l)**	**Fe (μg Fe/l)**	**Ni (μg Ni/l)**	**Pb (μg Pb/l)**	**Zn (μg Zn/l)**
C1	1113.33	1280	6033.33	850	153	3766.67
C2	1090.0	1383.3	4133.3	830.0	112.7	1713.3
C3	136.7	7133.3	4600.0	553.3	70.3	5066.7
C4	234.0	1310.0	8466.7	373.3	52.0	1523.3
C5	307.3	1613.3	27666.7	430.0	95.0	3666.7
C6	356.7	1393.3	36666.7	416.7	118.7	2523.3

Table 4.7 Metals concentration in Concentrato samples.

Observing all the results, it can be noticed that the metal content vary according to the leachate treatment changing both in value and in percentage. In particular, the metals concentrations are generally higher in anaerobic leachate than in aerobic one. As it is possible to notice in the figure 4.49, also the metals distribution is more heterogeneous in the anaerobic leachate. As for the SANA samples, the most concentrated metal is iron, especially in the aerobic leachate with a value up to 36666 μg/l and a content that ranges from 26 to 92%, probably due its low reduction potential. Copper is present in a concentration which ranges from 1280 μg/l to 7133.3 μg/l constituting the 3-

41% of the samples while zinc constitutes the 6-29% of the total metal content with concentrations in the range from 1523.3 µg/l to 5066.7 µg/l.

The heavy metals content instead represent a very low fraction: lead is less than 1%, nickel is the 1-9% and the chromium is the 1-12%. These heterogeneous results are mainly due to the different treatments that undergo the columns from which come the leachates.

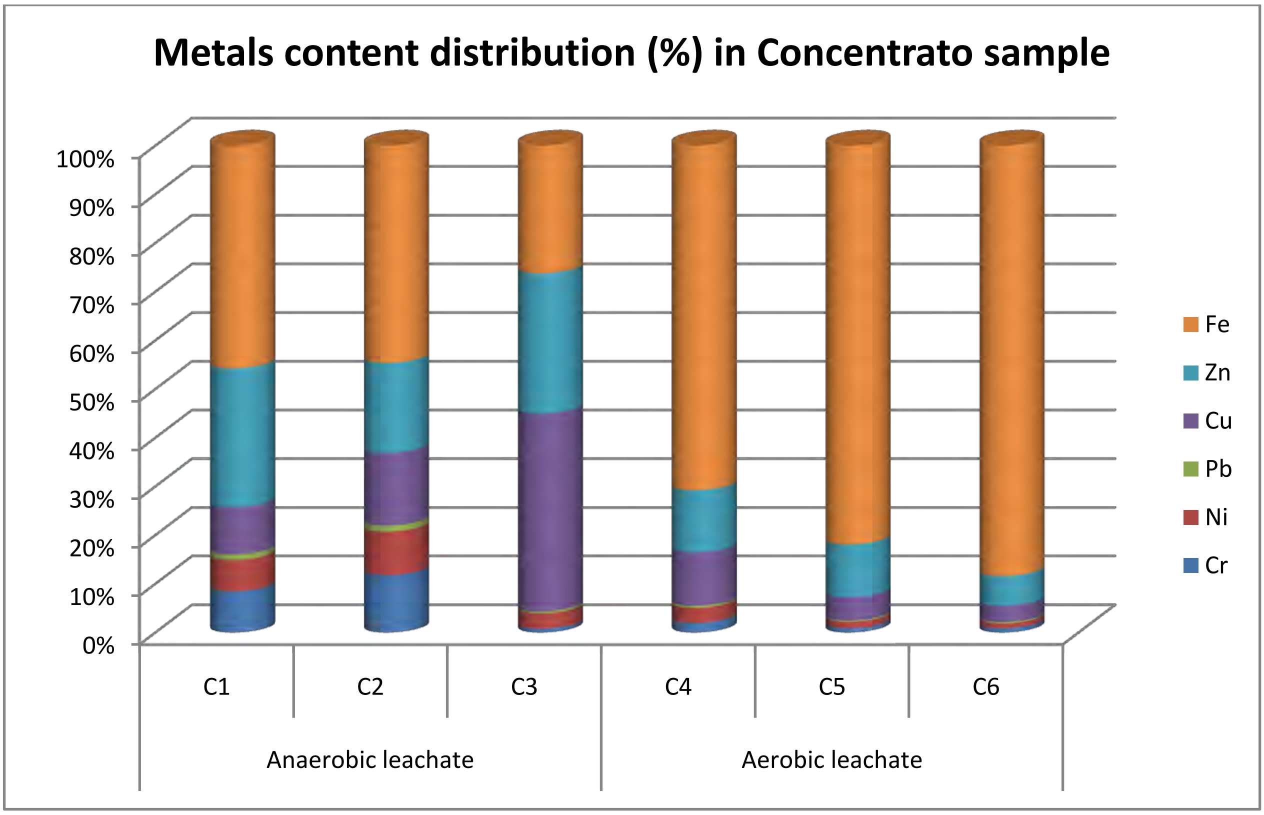


Figure 4.51 Metals distribution on Concentrato samples.

Focusing on the heavy metals content (figure 4.52), it is possible to notice that, as observed in general, anaerobic leachates contain clearly higher concentrations compared to the aerobic leachate (both in absolute and in percentage). In particular, in the anaerobic leachates the maximum concentrations of chromium, nickel and lead are respectively 1113.33 µg/l, 850 µg/l and 153 µg/l while in the aerobic leachate their maximum concentrations are respectively 356.7 µg/l, 430 µg/l and 118.7 µg/l.

Therefore, the ICP-OES results suggest that the aeration has a relevant effect on the heavy metals mobilization and content in the leachate. In fact, their lower concentration in the aerobic leachate confirms that aerobic landfills have a more efficient reduction of heavy metals content. H. Kim et al. explained that metal concentrations in leachate of an aerobic landfill dramatically reduced as waste stabilized, while no significant change were observed in the anaerobic landfill. Therefore, if it is assumed that an anaerobic landfill at the final stage of waste degradation will change to aerobic conditions thanks to air intrusion, the metal concentration in landfill leachate is expected to become substantially lower with time.

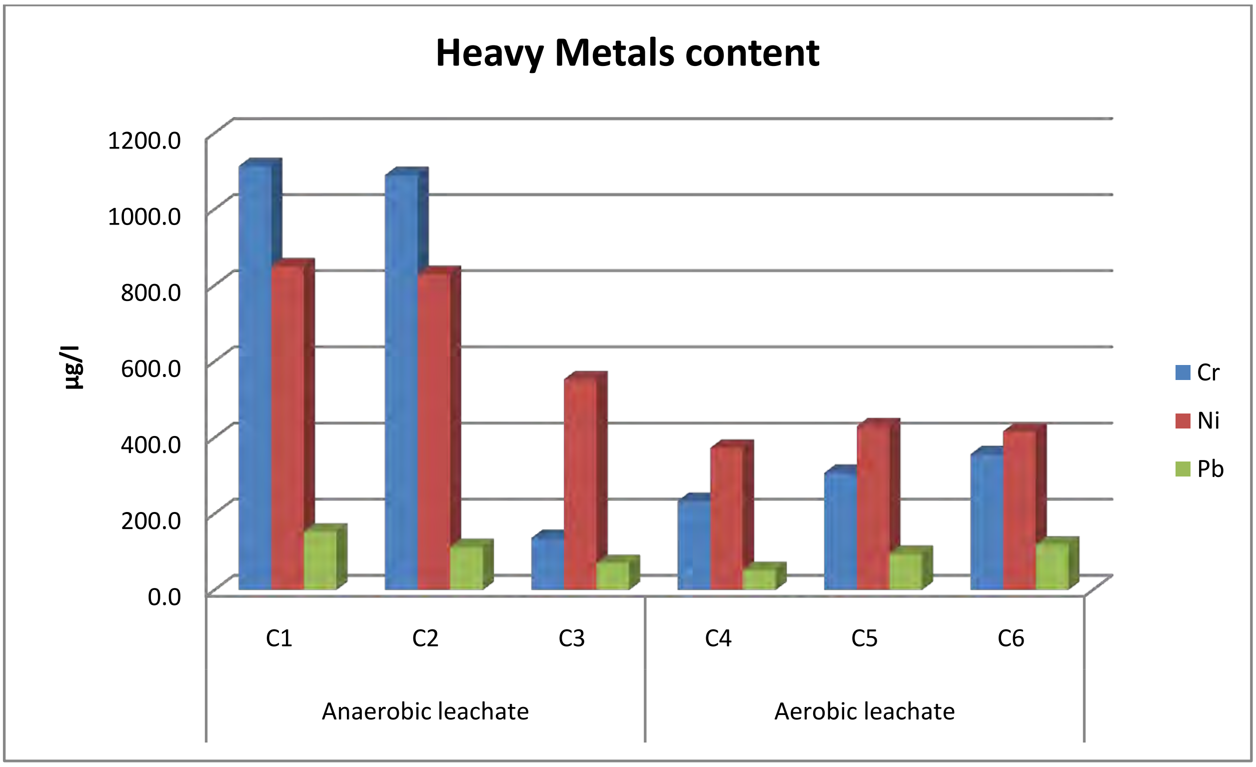


Figure 4.52 Heavy metals content on Concentrato samples.

These results confirm the importance of the aeration because it clearly increases the metals removal efficiency compared to the anaerobic treatment, producing a leachate more stabilized and sanitized.

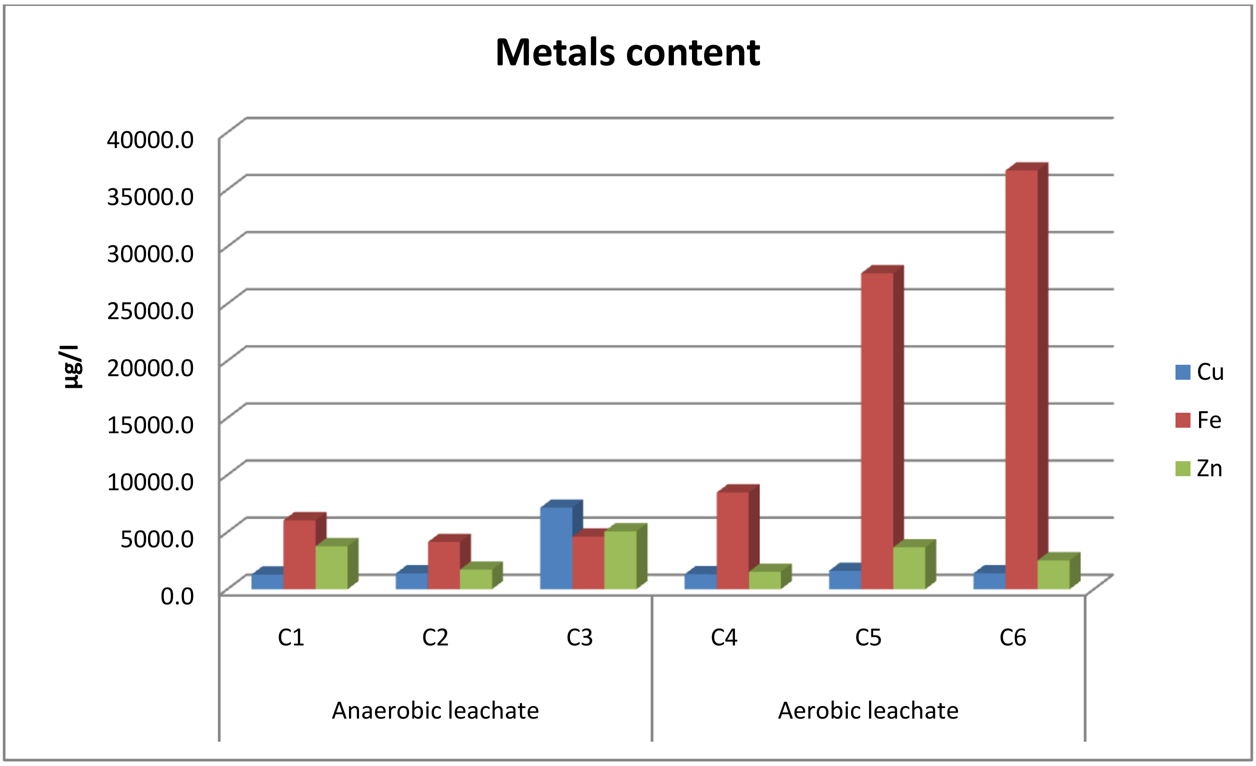


Figure 4.53 Metals content on Concentrato samples.

4.1.7 Evaluation of the physical fractionation

Among the most diffused physical speciation analysis is the separation of suspended solids or colloidal fractions and their mass determination. Through centrifugation, it is possible to separate the suspended colloidal phase from the dissolved one. This process is important because the colloidal fraction, mainly composed of macromolecular organic and/or inorganic agglomerates, has a fundamental role in metals speciation. In fact, it is well known that a considerable but highly varying part of heavy metals are associated with the colloidal fraction (Jensen et al., 1999).

The amount of the colloidal fractions of the SANA and Concentrato samples are reported in the table 4.18 both in concentration and percentage.

Sample	**Colloidal fraction (> 0.001μm)**	
	[g/l]	% on the total
S1	3.140	0.319
S2	1.840	0.185
S3	0.780	0.078
C1	0.470	0.047
C2	1.380	0.139
C3	0.440	0.044
C4	0.130	0.013
C5	0.090	0.009
C6	0.170	0.017

Table 4.8 Colloidal fraction of the Concentrato samples.

The amount of colloidal material indicates that in all the six Concentrato samples the content correspond to a very low fraction of the total with percentages lower than 0.2%.

Considering the SANA samples, the results indicate that colloidal fraction decreases over time (S1 > S2 > S3). As a general trend, is possible to notice that the samples characterized by greater colloidal fractions, contain larger amounts of heavy metals.

Concentrato samples results show clearly that the anaerobic leachate sample (C1, C2, C3) have always a higher amount of colloidal fraction than the aerobic leachate sample (C4, C5, C6). In fact, the amount of colloidal fraction in the anaerobic leachate sample ranges from 0.440 to 1.380 g/l while in the aerobic one it ranges only from 0.0090 to 0.170 g/l. Since anaerobic leachate samples have a higher heavy metals content, as illustrated in the previous paragraphs, also in this case the colloidal fraction is proportional to the heavy metals content.

To assess the amount of metals in the colloidal phase we decided to perform the ICP-OES analysis of one of the sample (C1) by treating it with a base (KOH) to increase the pH and favour the agglomeration of the colloidal phase and by centrifugation to isolate the soluble fraction. In Table 4.9 the ICP-OES on untreated C1 and treated one are reported.

Sample	**Cr (μg Cr/l)**	**Cu (μg Cu/l)**	**Fe (μg Fe/l)**	**Ni (μg Ni/l)**	**Pb (μg Pb/l)**	**Zn (μg Zn/l)**
C1 untreated	334	384	1810	255	45.9	1130
C1 treated with base	212	214	587	194	< 10	248

Table 4.9 ICP results on C1 treated with base on C1 untreated.

The results show a general reduction of all metals content with the most evident decrease for iron, lead and zinc. Therefore is possible to deduce that colloidal fraction actually contains a large amount of metals with some elements present in higher amount (Fe, Pb, Zn) compared to others (Cr, Cu, Ni).

This confirms the association of transition metals centres in the colloidal fraction in the leachate in accordance with the investigation by Jensen et al. (1999) and by Klein and Niesser (1996).

This information is of a fundamental importance because colloids, since they have a macromolecular structure characterized by an higher hydrodynamic volume, are easier to remove from the leachate by physical filtration on a solid liner.

Some other information on the samples can be deduced from the total solid fraction left after vacuum drying since it contains all the species suspended or dissolved, both organic and inorganic present in the leachate. The total solid fraction of all the SANA and Concentrato series samples have been weighed and the results are reported in the following table.

Sample	Total solid fraction [g/l]
S1	16.982
S2	16.028
S3	14.128
C1	12.780
C2	9.700
C3	5.450
C4	8.700
C5	8.050
C6	10.560

Table 4.10 Total solid fraction of the leachates.

The results indicate a large amount of solid fraction much higher than the metal content revealed by ICP-OES and mainly formed by organic species or inorganic salts as observed through NMR and ESEM analysis.

4.1.8 Evaluation of the analytical detection methods

The analytical techniques applied in our study although limited in number, succeeded in giving information on various aspects of the chemical content of the leachates. In the following table, we summarized the analytical goal of every method and the relative revelation limit.

Analysis name	Working principle	Analysis goal	Detection limit
ESEM	Scanning electron microscope	Analyze the morphology of the sample surface	ppm
ESI-MS	Electrospray mass spectrometry	Analyze organic compounds	ppm
FT-IR	Infrared adsorption spectroscopy	Identify the type of bonds	ppb
GC-MS	Gas chromatography and mass spectrometry	Analyze volatile organic compounds	ppm
ICP-OES	Atomic emission spectroscopy	Measure total metal content	ppb
NMR	Magnetic resonance spectrometry	Analyze organic compounds	ppm

Table 4.11 Summary scheme of the analyses performed, their working principle, their goal and their detection limits.

Therefore, in general, we can state that the only technique that allows the identification of metals in trace amount in such small volumes of samples is the ICP-OES analysis. All the other techniques can clarify the nature of the chemical environment in which those metals are presents and the molecules or ions with which they can interact.

4.2 Effect of the interaction of metals in leachate with different stationary phases

Further insight in the nature of the metal content of leachates can be found in the way they interact with different stationary phases. For this reason, we decided to perform a series of filtration experiments using solid liners of different chemical compositions: the vermiculite and active carbon, exploiting the efficiency of the ICP-OES technique in determining traces of metals for their quantification after the treatment. This can be considered an indirect method to evaluate the speciation of heavy metals in the leachates produced in different conditions (aerobic and anaerobic). The ICP-OES analysis of the six Concentrato samples before and after the filtration by solid liners have been compared. Furthermore, the metals removal efficiency by the different stationary phases have been assessed.

The filtration procedure is reported in detail in the materials and methods chapter, section 3.4.2.

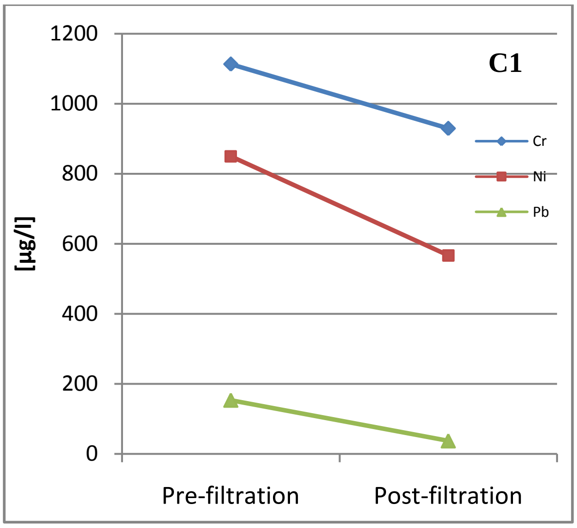
4.2.1 Evaluation of filtration through activated carbon

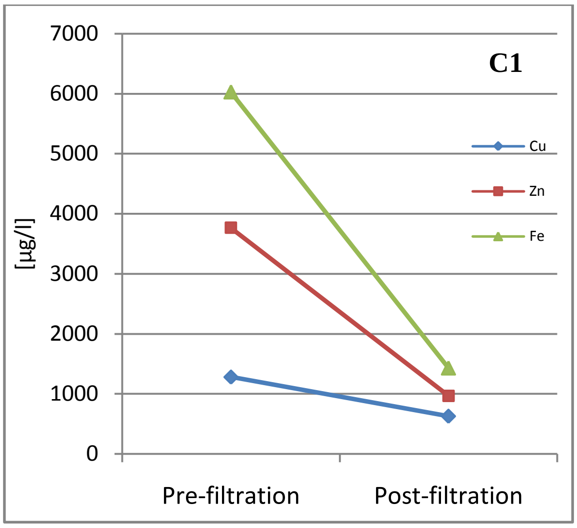
The table 4.12 reports the ICP-OES analysis results on Concentrato samples after filtration by active carbon. These data show a clear reduction of metals content thanks to the absorption property of the active carbon. In particular, the absorption is attributed to acidic sites on the surface of the carbon (Sato et al., 2007) in which the mechanism of absorption occurs through the exchange of ions H^+ or by the formation of complexes with negatively charged sites.

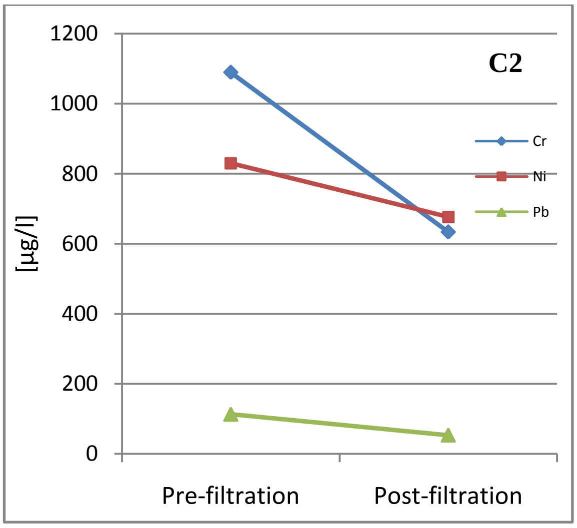
Sample	**Cr (µg Cr/l)**	**Ni (µg Ni/l)**	**Pb (µg Pb/l)**	**Cu (µg Cu/l)**	**Zn (µg Zn/l)**	**Fe (µg Fe/l)**
C1	930.0	626.7	1430.0	566.7	37.3	966.7
C2	633.3	1130.0	1520.0	676.7	53.0	930.0
C3	94.7	5066.7	1970.0	443.3	52.7	3316.7
C4	194.3	1160.0	7933.3	308.3	52.3	1110.0
C5	204.0	1420.0	25600.0	309.3	90.3	1676.7
C6	363.3	1446.7	29400.0	806.7	184.3	2136.7

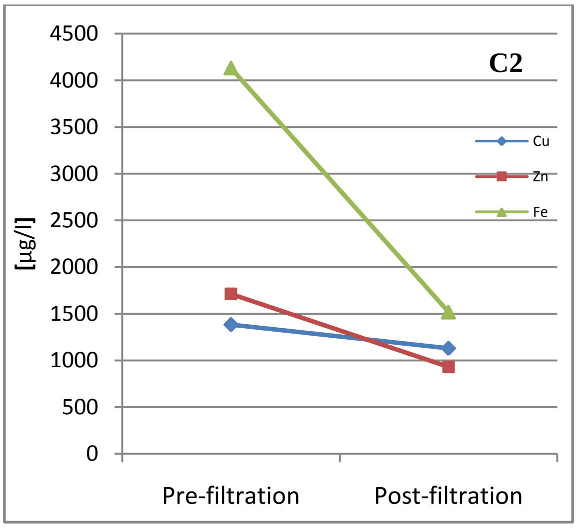
Table 4.12 Metals concentration after filtration by active carbon.

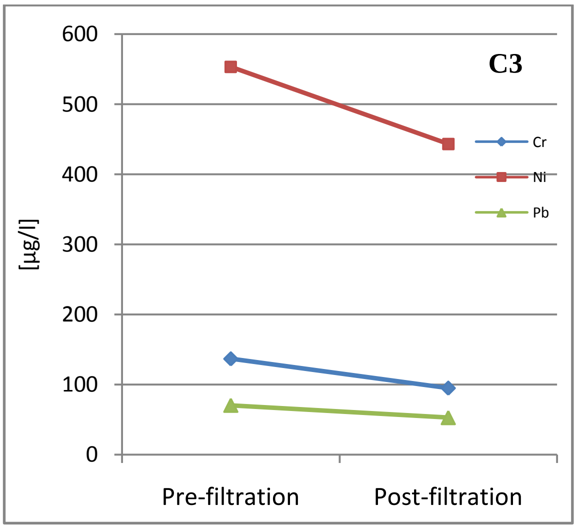
The data after filtration can be compared to the data of the original samples in order to emphasize the concentration trend in the Concentrato samples as illustrated in the following figures.

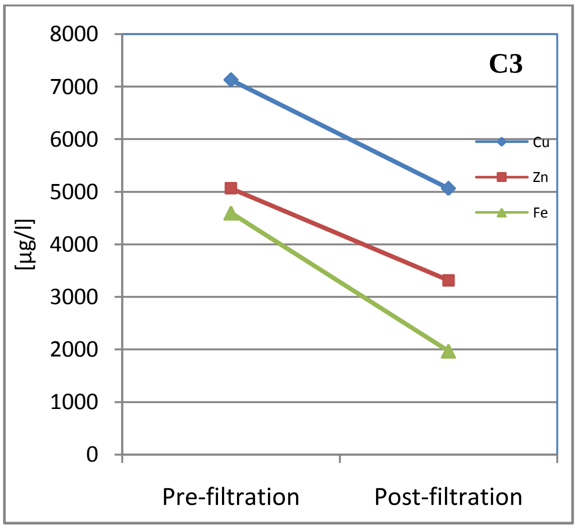

C1
[µg/l]
1200
1000
800
600
400
200
0
Cr
Ni
Pb
Pre-filtration
Post-filtration


C1
[µg/l]
7000
6000
5000
4000
3000
2000
1000
0
Cu
Zn
Fe
Pre-filtration
Post-filtration


C2
[µg/l]
1200
1000
800
600
400
200
0
Cr
Ni
Pb
Pre-filtration
Post-filtration


C2
[µg/l]
4500
4000
3500
3000
2500
2000
1500
1000
500
0
Cu
Zn
Fe
Pre-filtration
Post-filtration


C3
[µg/l]
600
500
400
300
200
100
0
Cr
Ni
Pb
Pre-filtration
Post-filtration


C3
[µg/l]
8000
7000
6000
5000
4000
3000
2000
1000
0
Cu
Zn
Fe
Pre-filtration
Post-filtration

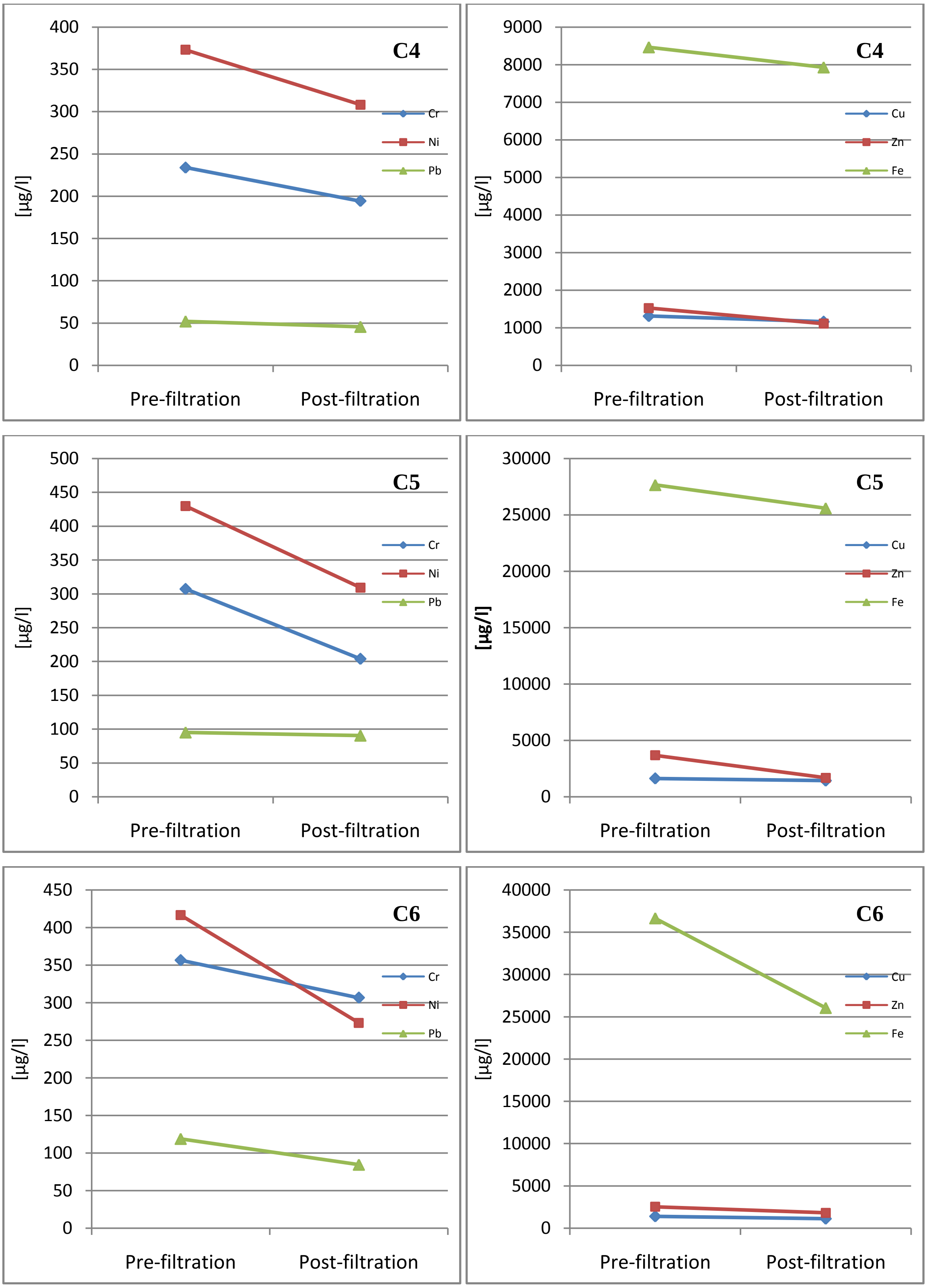


Figure 4.54 Heavy metals (on the left) and metals (on the right) concentration trend after filtration on the six Concentrato samples.

As can be seen from the figure 4.54, all metals undergo a reduction after filtration through activated carbon confirming the great retention property of the material. It can be noticed that the attenuation is more enhanced in the case of leachate coming from the anaerobic reactor. Taking into account the total adsorption, the total metal attenuation of the anaerobic leachate (C1: 65%; C2: 47%; C3: 38%) is higher than the total metal attenuation of the aerobic leachate (C4: 10%; C5: 13%; C6: 29%).

Active carbon	**Adsorption efficiency %**	**Cr**	**Cu**	**Fe**	**Ni**	**Pb**	**Zn**	**Total adsorption**
Anaerobic leachate	**C1**	16%	51%	76%	33%	76%	74%	65%
	C2	42%	18%	63%	18%	53%	46%	47%
	C3	31%	29%	57%	20%	25%	35%	38%
Aerobic leachate	**C4**	17%	11%	6%	17%	12%	27%	10%
	C5	34%	12%	7%	28%	5%	54%	13%
	C6	14%	20%	29%	34%	29%	29%	29%

Table 4.13 Efficiency of heavy metals adsorption by active carbon on Concentrato samples.

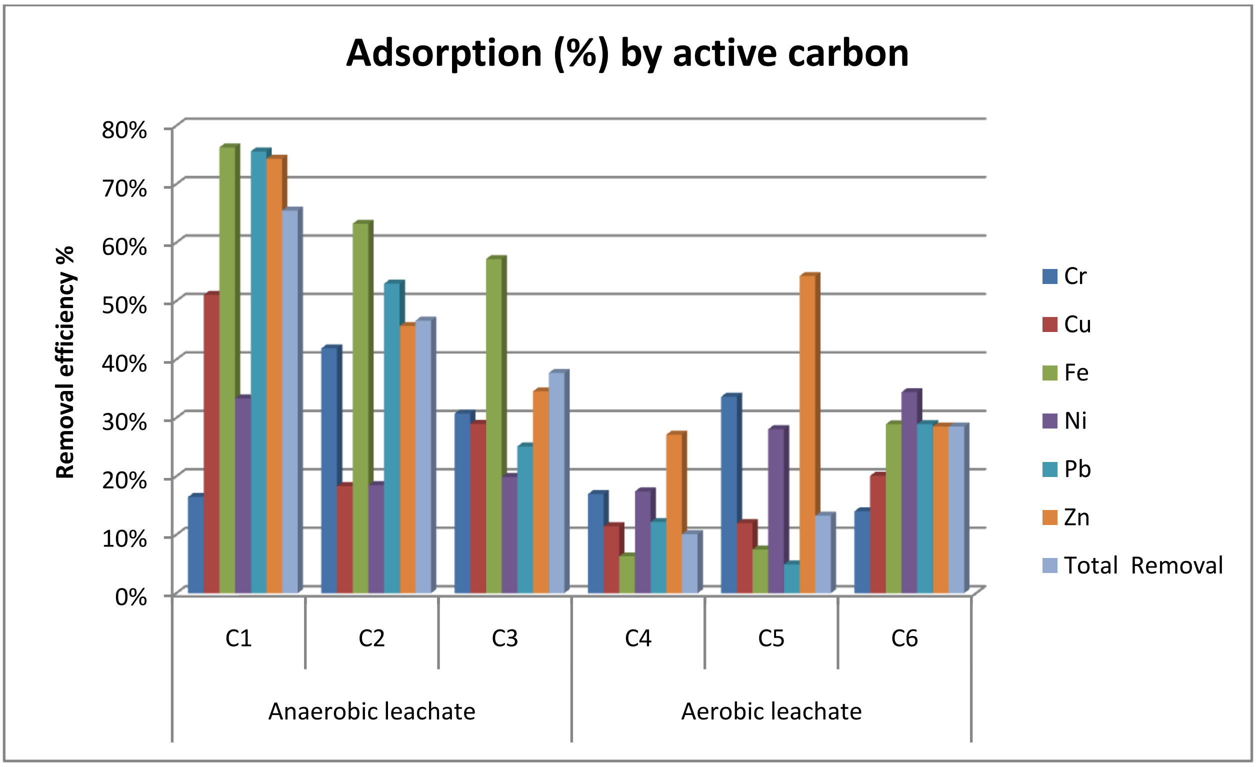


Figure 4.55 Adsorption efficiency (%) by active carbon on Concentrato samples.

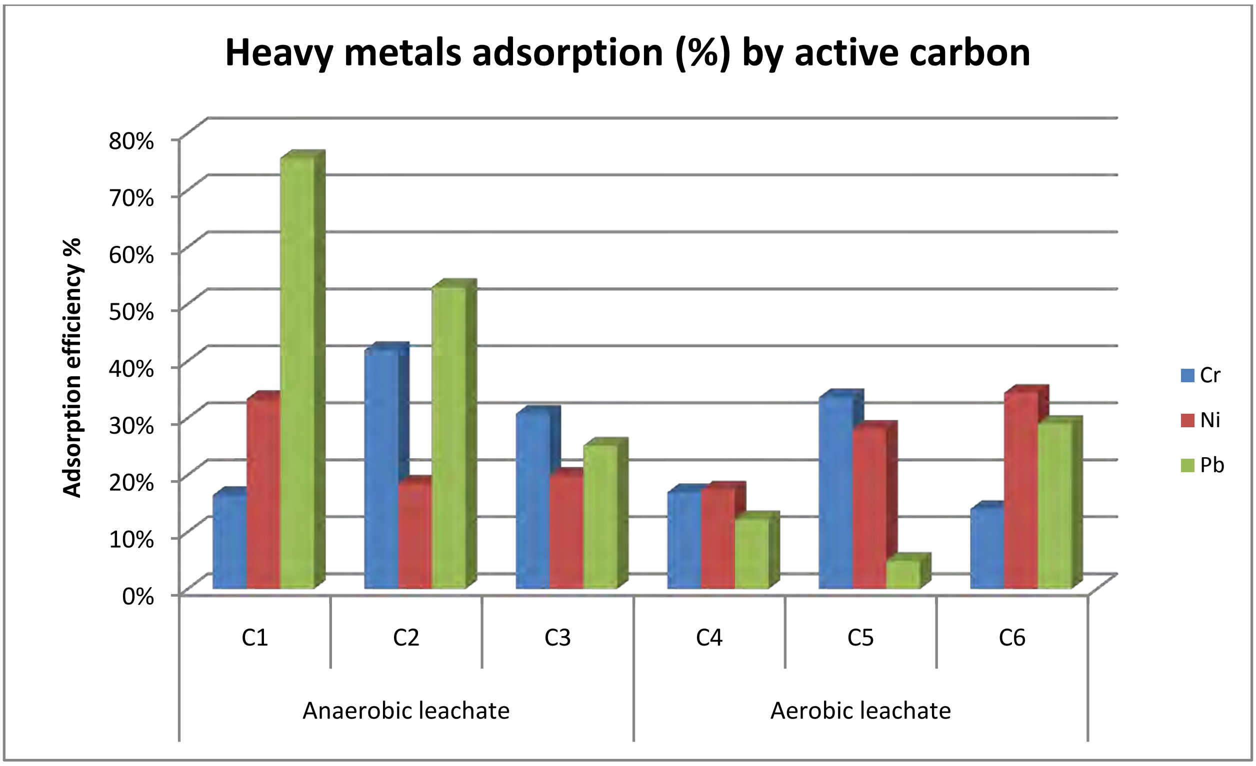


Figure 4.56 Heavy metals adsorption efficiency (%) by active carbon on Concentrato samples.

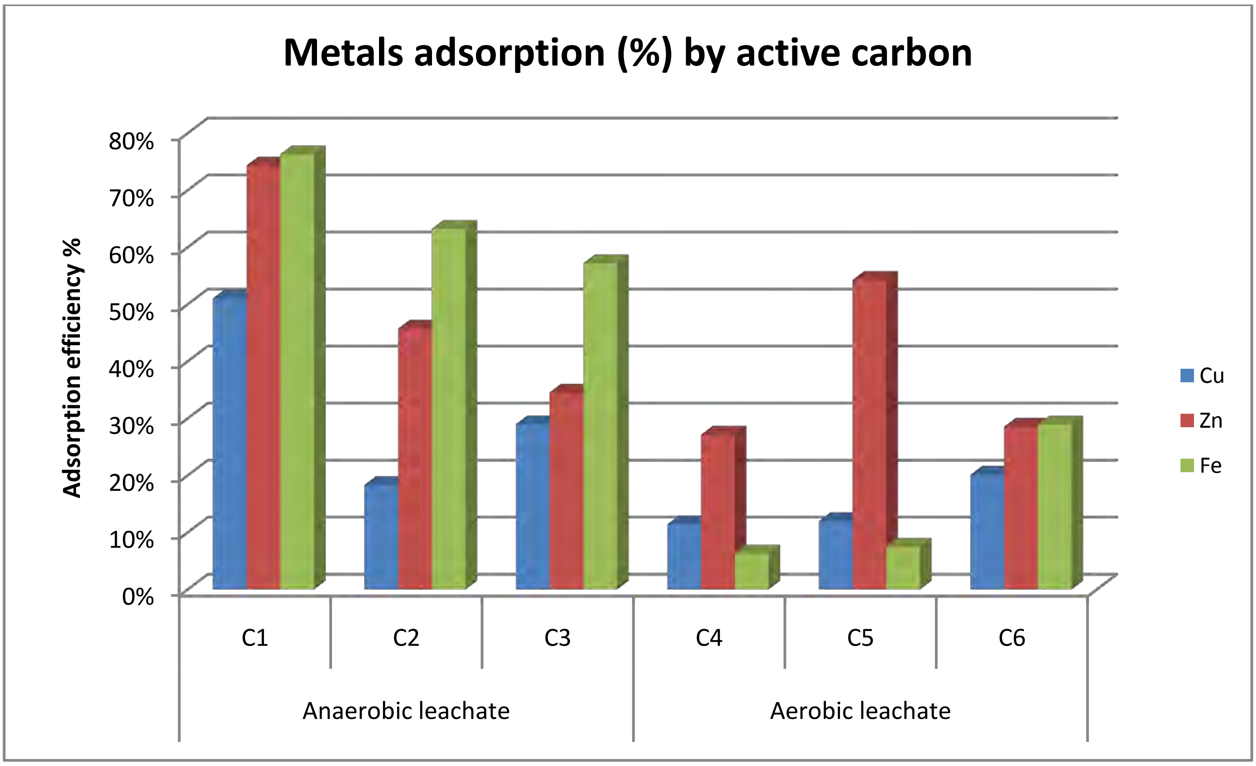


Figure 4.57 Metals adsorption efficiency (%) by active carbon on Concentrato samples.

In particular, as illustrated in the table 4.13 and in the figures 4.55, 4.56, 4.57, the greater reduction difference between anaerobic and aerobic leachate regards iron, lead and zinc. The percentages of adsorbed iron, lead and copper are equal respectively to 57-76%, 25-76% and 29-51% in the anaerobic leachate and to 6-29%, 5-29% and 11-20% in the aerobic leachate. Chromium and zinc present a small difference of attenuation between anaerobic (Cr: 16-42%, Zn: 35-74%) and aerobic (Cr: 17-34%, Zn: 27-54%) samples. Nickel is the only element that has an average higher reduction in the aerobic leachate (27%) compared to the anaerobic one (22%). Zinc is the metal for which active carbon has the highest removal efficiency with an average adsorption equal to 44% probably due with its affinity with oxygen based ligands such as the groups present on the surface of the solid liner material. Also iron and lead present a great reduction equal respectively to 40% and 33% while chromium (26%), nickel (25%), and copper (24%) are adsorbed in smaller quantity.

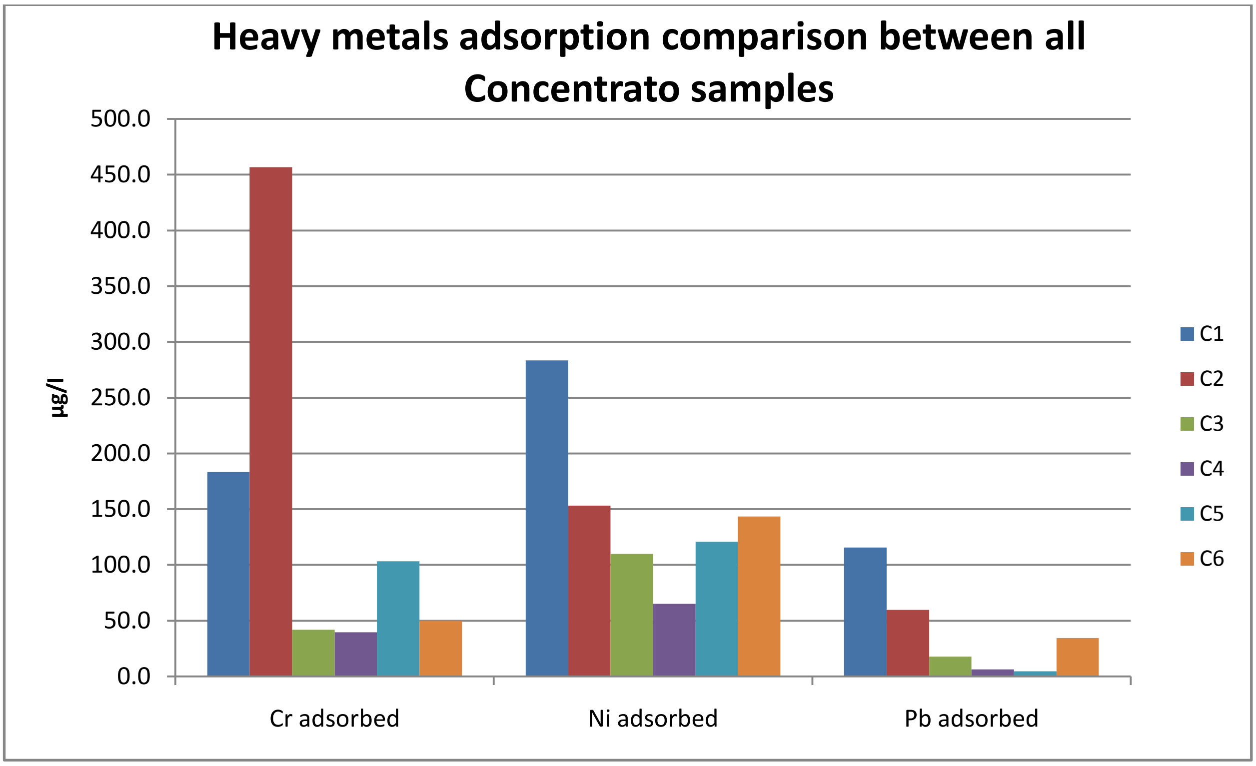


Figure 4.58 Heavy metals adsorption by active carbon.

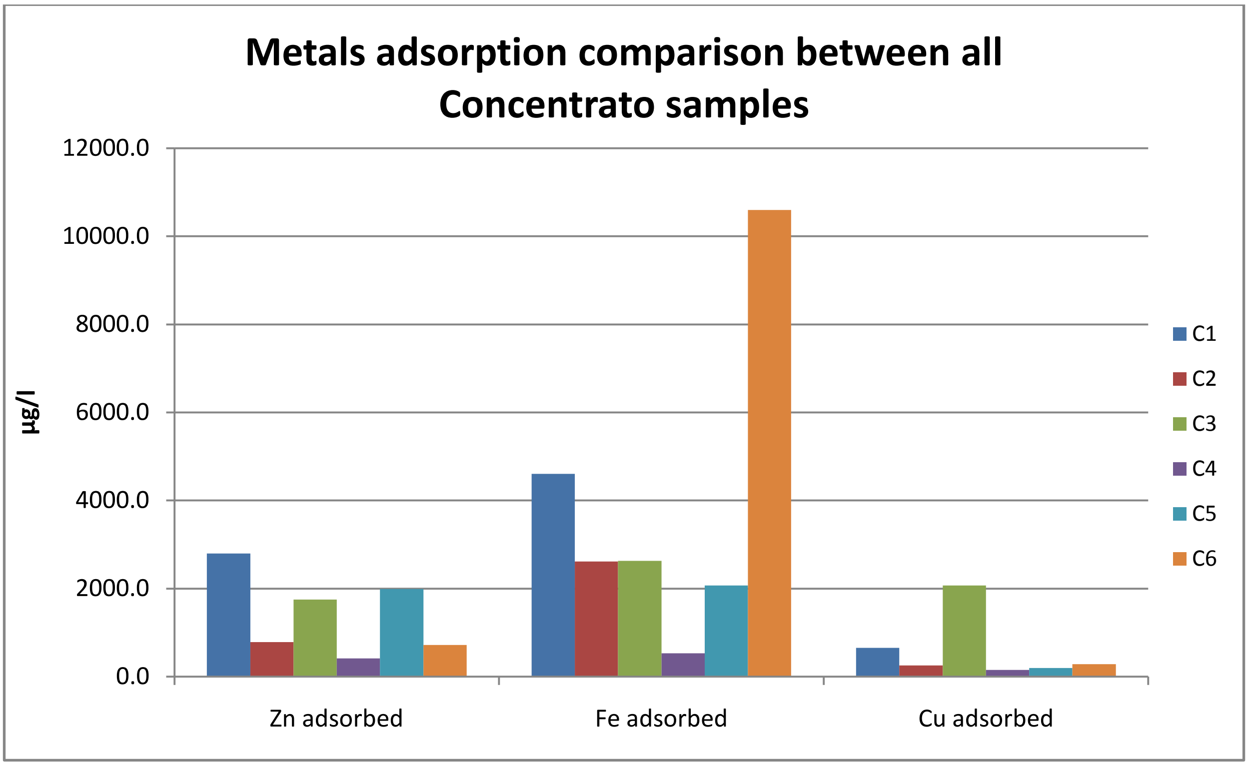


Figure 4.59 Metals adsorption by active carbon.

In terms of absolute metal concentration variation (figures 4.58, 4.59), iron is characterized by the greatest reduction, especially in the anaerobic sample, with an average total adsorption equal to 3841 µg/l. This is probably due to the fact that this metal has the highest concentration in all the original samples and can act as a scavenger towards other metals that can bind to the solid sorbent. Copper and zinc present an average reduction equal respectively to 599 µg/l and 1409 µg/l. Among the heavy metals, nickel and chromium are the most adsorbed element, with an average value equal respectively to 145.95 µg/l and 145.84 µg/l, while lead has an average attenuation of 40 µg/l. Overall, the absolute adsorption capacity of active carbon, increases in the following order: Pb < Cr < Ni < Cu < Zn < Fe.

The obtained results show that the selected active carbon is characterized by great heavy metals retention in leachate. Therefore, thanks to its property, it could be used as solid liner to treat leachate containing heavy metals in a process that can be in situ or off site.

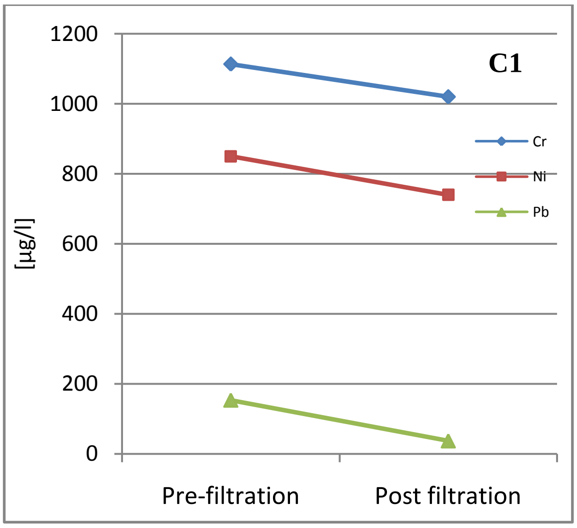
4.2.2 Evaluation of filtration through vermiculite

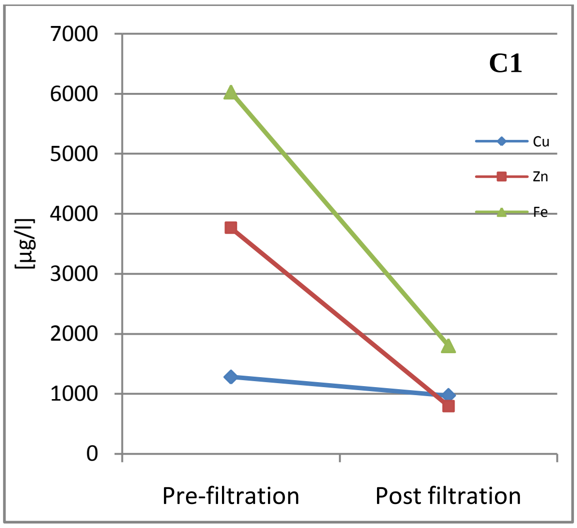
The ICP-OES analysis results of the Concentrato samples after filtration by vermiculite are illustrated in table 4.14. Also in this case, the leachate exiting the solid liner presents an evident reduction of the metals content. Vermiculite absorbs the metals on the negative charged sites that are predominantly present on the surface of its layered particles. The absorption can take place through two different mechanisms: cation exchange in the interlayers through interactions between ions and permanently negative charges or through the formation of complexes at the clay particle edges (Abollino et al., 2003).

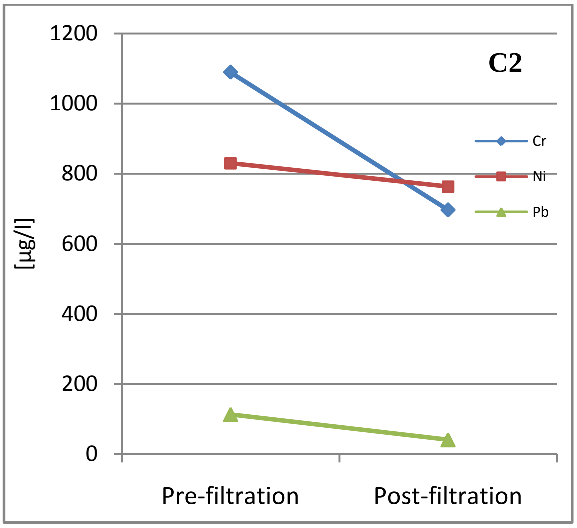
Sample	**Cr**	**Cu**	**Fe**	**Ni**	**Pb**	**Zn**
	(µg Cr/l)	**(µg Cu/l)**	**(µg Fe/l)**	**(µg Ni/l)**	**(µg Pb/l)**	**(µg Zn/l)**
C1	1020.0	970.0	1803.3	740.0	36.7	796.7
C2	696.7	1300.0	1843.3	763.3	40.3	853.3
C3	101.0	6000.0	2143.3	510.0	53.7	2516.7
C4	210.0	1326.7	7133.3	386.7	42.3	933.3
C5	203.7	1326.7	25133.3	390.0	42.3	1136.7
C6	346.7	1146.7	23733.3	436.7	353.3	1833.3

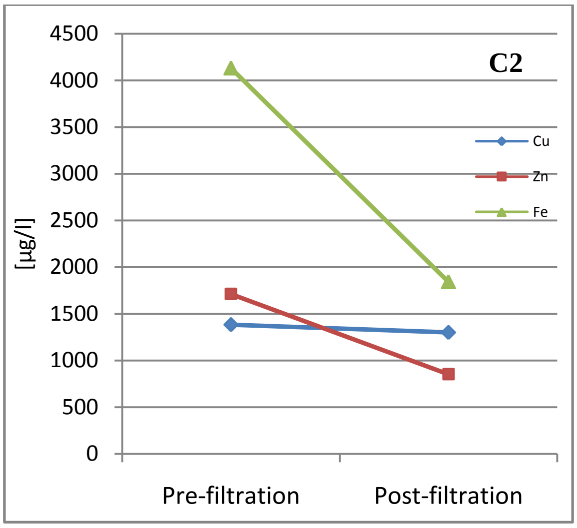
Table 4.14 Metals concentration after filtration by vermiculite.

The data of the metal content after filtration are compared to the data before the filtration in order to assess the vermiculite adsorption efficiency. The following figure reports the metal content trend before and after filtration by vermiculite.






C2
[µg/l]
1200
1000
800
600
400
200
0
Cr
Ni
Pb
Pre-filtration
Post-filtration


C2
[µg/l]
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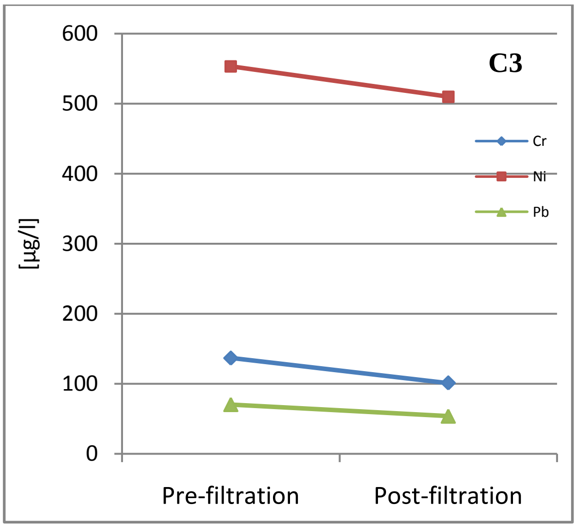
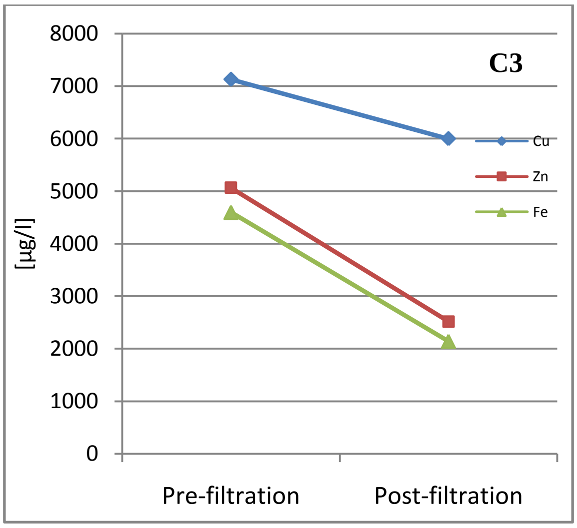
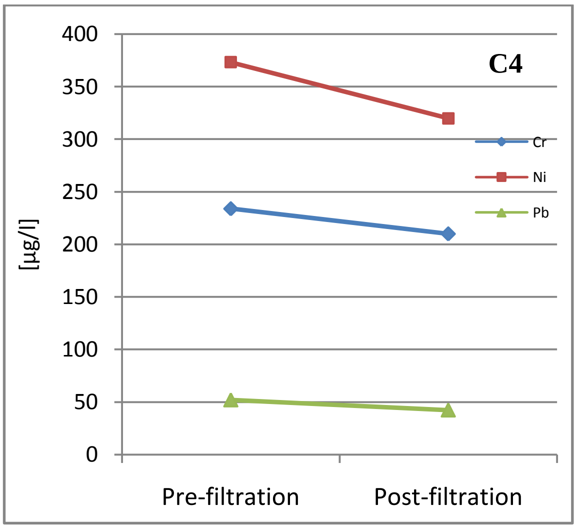
4000
3500
3000
2500
2000
1500
1000
500
0
Cu
Zn
Fe
Pre-filtration
Post-filtration


C3
[µg/l]
600
500
400
300
200
100
0
Cr
Ni
Pb
Pre-filtration
Post-filtration


C3
[µg/l]
8000
7000
6000
5000
4000
3000
2000
1000
0
Cu
Zn
Fe
Pre-filtration
Post-filtration


C4
[µg/l]
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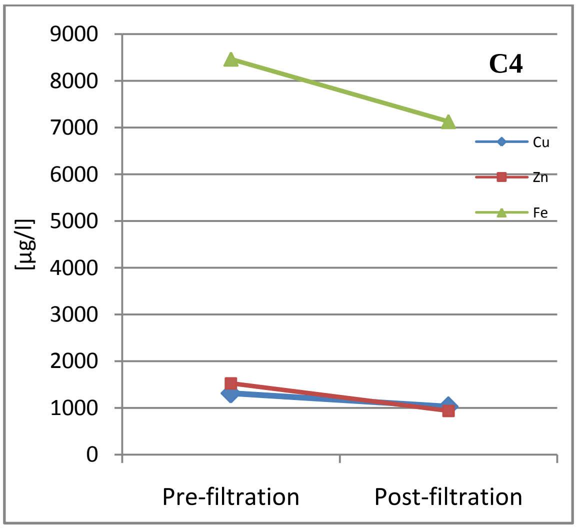
350
300
250
200
150
100
50
0
Cr
Ni
Pb
Pre-filtration
Post-filtration


C4
[µg/l]
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
Cu
Zn
Fe
Pre-filtration
Post-filtration

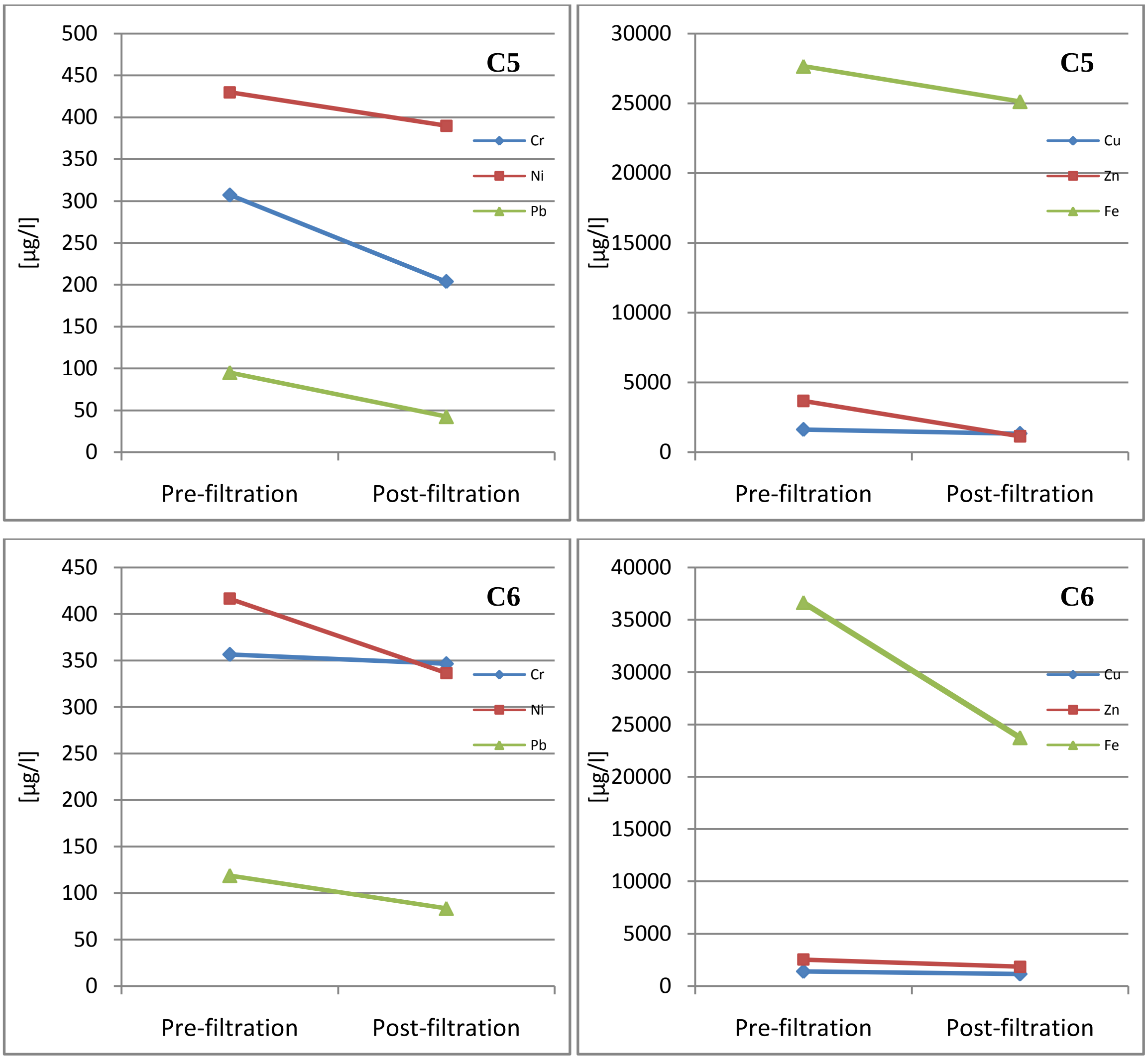


Figure 4.60 Heavy metals (on the left) and metals (on the right) concentration trend after filtration on the six Concentrato samples.

The figure 4.60 confirms that all the metals are in lower concentration after the filtration by vermiculite confirming the great retention properties of the material even though they comparable to results obtained with active carbon. This can indicate that the main adsorption mechanism is probably the binding to anionic oxygen sites on the material.

Vermiculite	Adsorption efficiency %	Cr	Cu	Fe	Ni	Pb	Zn	Total adsorption
Anaerobic Leachate	C1	8%	24%	70%	13%	76%	79%	59%
	C2	36%	6%	55%	8%	64%	50%	41%
	C3	26%	16%	53%	8%	24%	50%	36%
Aerobic leachate	C4	10%	22%	16%	14%	19%	39%	19%
	C5	34%	18%	9%	9%	55%	69%	16%
	C6	3%	18%	35%	19%	30%	27%	34%

Table 4.15 Heavy metals adsorption efficiency by vermiculite on Concentrato samples.

It can be notice that, also in this case, the anaerobic leachate sample shows a greater metal attenuation.

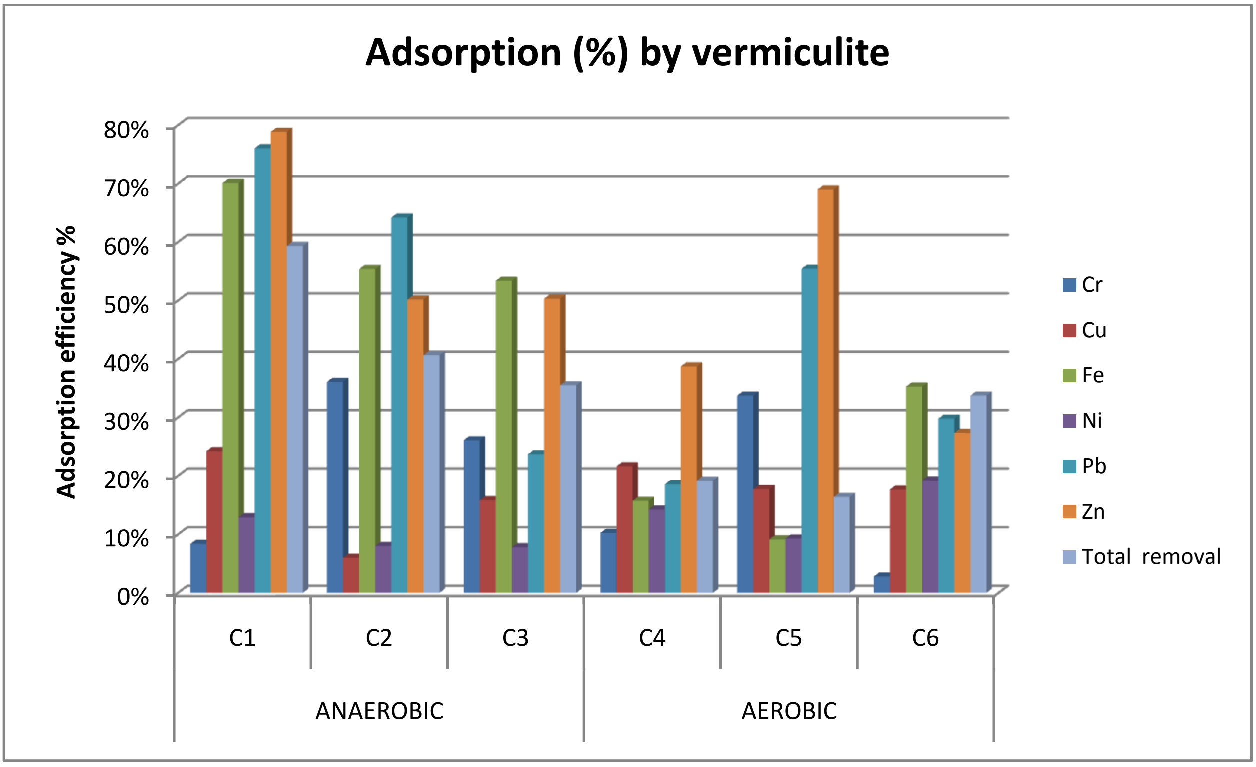


Figure 4.61 Adsorption efficiency (%) by vermiculite on Concentrato samples.

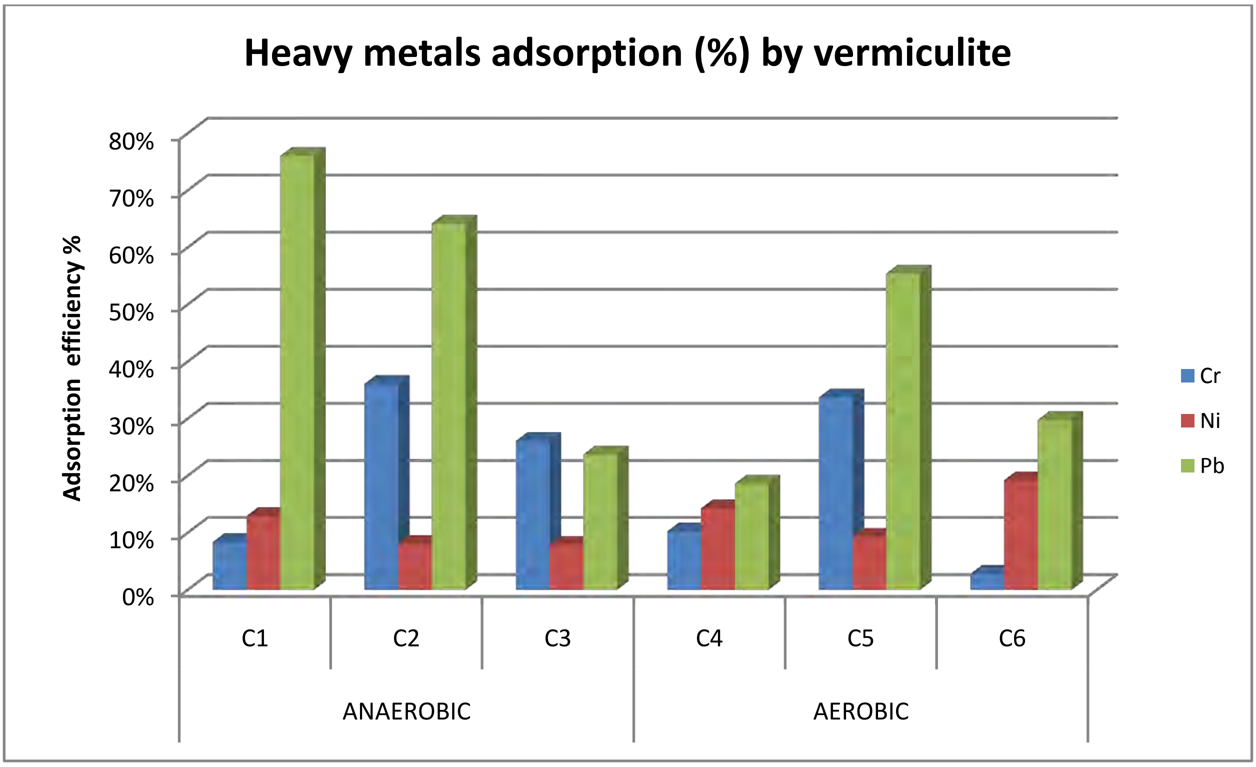


Figure 4.62 Heavy metals adsorption efficiency (%) by vermiculite on Concentrato samples.

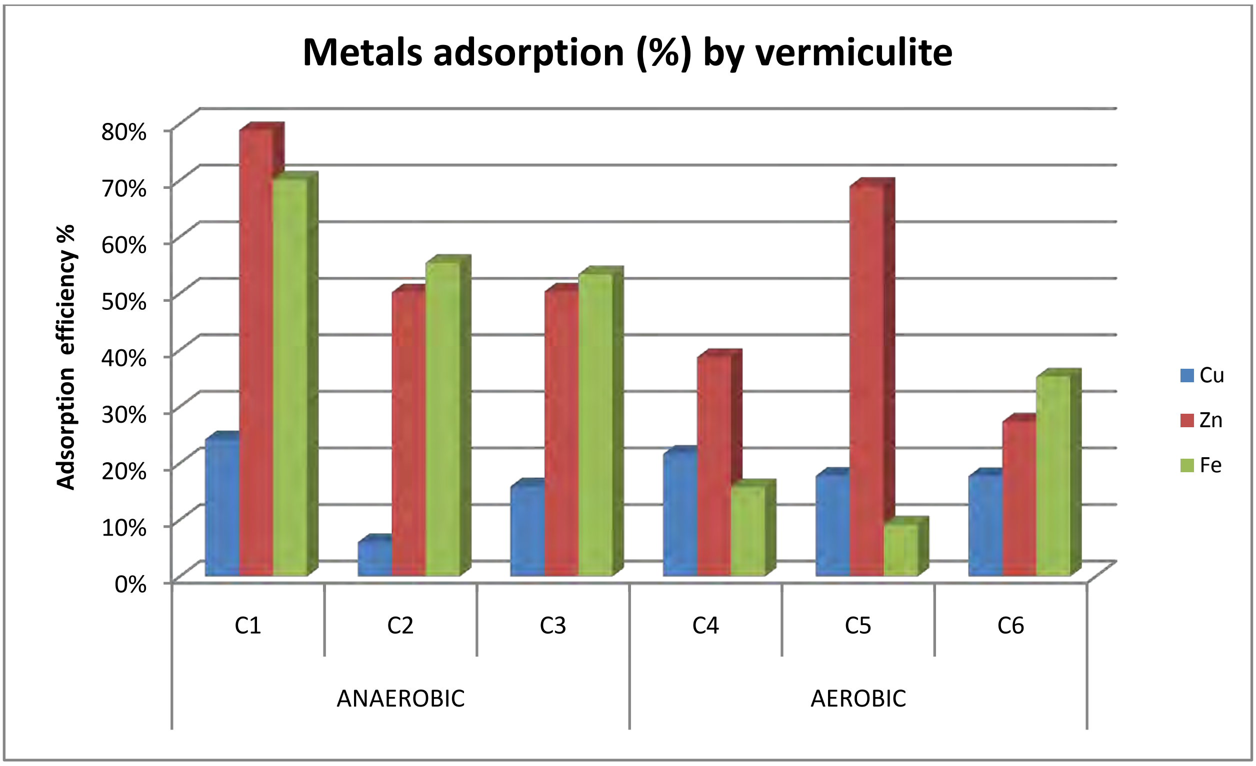


Figure 4.63 Metals adsorption efficiency (%) by vermiculite on Concentrato samples.

As can be seen from the table 4.15 and the figures 4.60, 4.62, 4.61 all the anaerobic leachate samples (C1: 59%; C2: 41%; C3: 36%) present a total adsorption greater than the aerobic leachate samples (C4: 19%; C5: 16%; C6: 34%). The larger attenuation difference between anaerobic and aerobic leachates regards iron, lead and zinc. The percentages of adsorbed iron, lead and zinc in the anaerobic leachates are respectively equal to 53-70%, 24-76%, 50-79% while they are equal to 9-35%, 19-55% and 27-69% in the aerobic ones. Chromium presents a low difference in attenuation between anaerobic (8-36%) and aerobic leachates (3-34%) while copper and nickel have a higher reduction in the aerobic leachates (Cu: 18-22%, Ni: 9-19%) than in the anaerobic ones (Cu: 6-24%, Ni: 8-13%). Zinc is the most adsorbed metal also by vermiculite with an attenuation equal to 52%. Lead an iron present a great attenuation equal respectively to 45% and 40% while chromium copper and nickel has a low reduction equal to 20%, 17% and 12%.

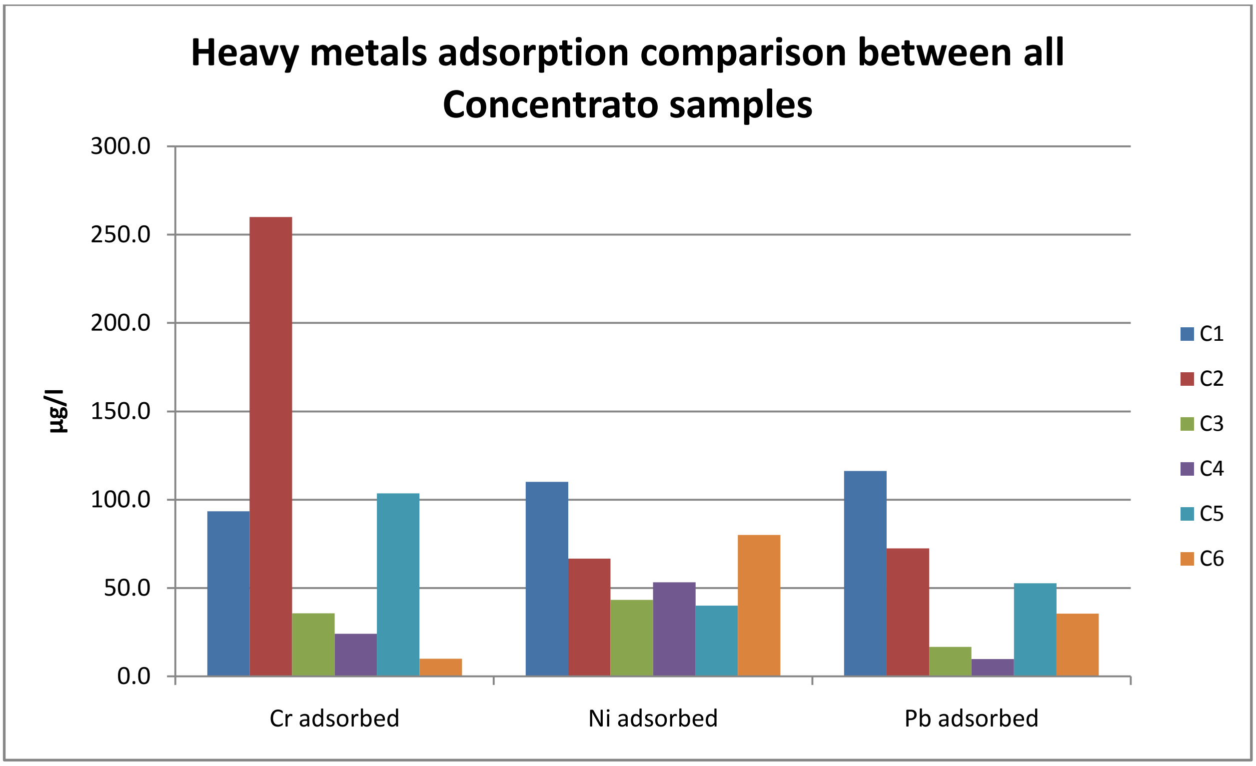


Figure 4.64 Heavy metals adsorption by vermiculite on Concentrato samples.

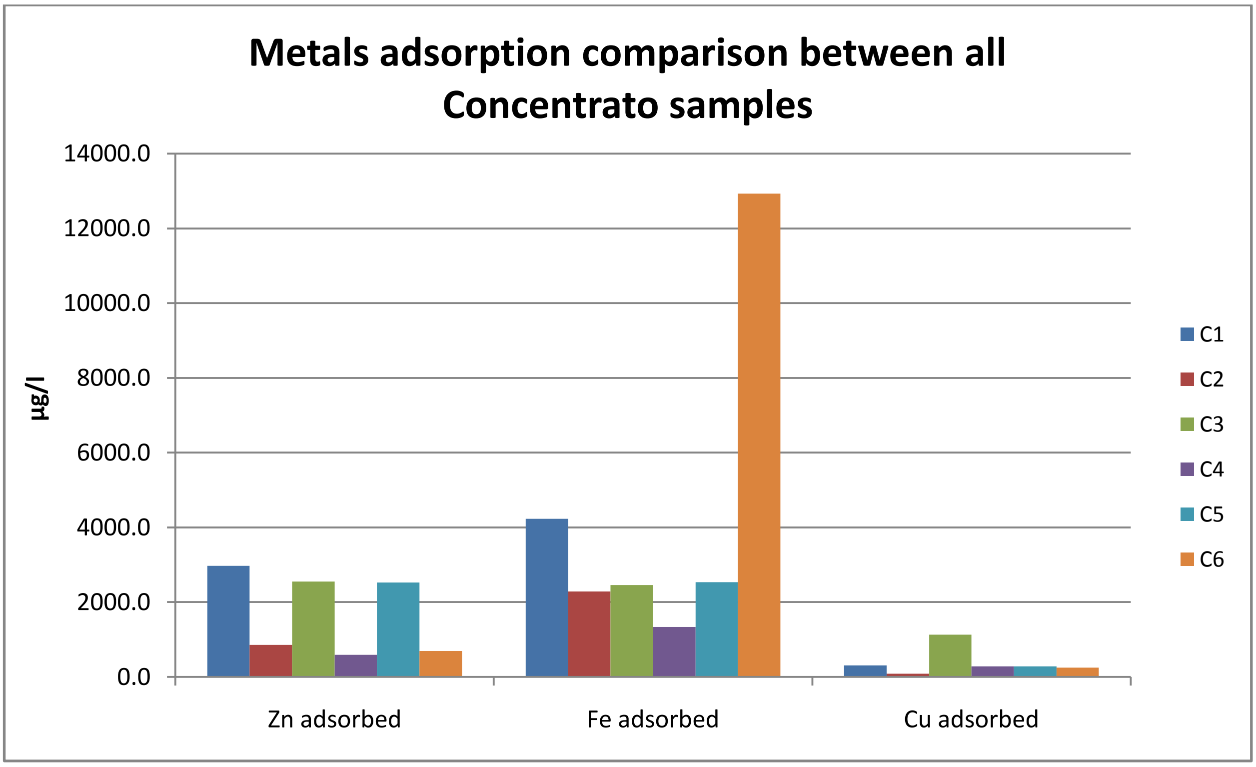


Figure 4.65 Metals adsorption by vermiculite on Concentrato samples.

In terms of absolute metal concentration variation, as illustrated in figures 4.64, 4.65, iron is the metal characterized by the highest attenuation with an average reduction by filtration equal to 4296 μg/l. As said before, this result is due to its high concentration in the original leachates. In fact, it is more likely to occupy the active sites of vermiculite limiting the removal of other metals present in lower amounts. Copper and zinc have an average reduction equal respectively to 390 μg/l and 1698 μg/l while chromium, nickel and lead have respectively: 88 μg/l, 65 μg/l, 50 μg/l. Therefore, the absolute adsorption capacity of vermiculite increases in the following order: Pb < Ni < Cr < Cu < Zn < Fe. It can be noted that the reduction order is the same as for active carbon.

The assessment of the sorption capacity of vermiculite demonstrates that this clay is a good sorbent towards the examined metals contained in the landfill leachates and therefore this material could be used as geological landfill barrier.

5. CONCLUSIONS AND FUTURE DEVELOPMENTS

In this thesis, the speciation of heavy metals in landfill leachate derived from different treatments and their attenuation in the filtration through different stationary phases have been studied. The leachate samples analysed derived from LISA laboratory and are of two series: SANA (landfill management divided into three steps: semi-aerobic, anaerobic and aerobic) and Concentrato (landfill management with Ro concentrate recirculation) in the reported experiment proved to contain low metals concentration. Therefore, the only technique suitable and effective to detect those levels of heavy metals in the leachate is the ICP-OES technique. However, this technique is destructive and therefore it doesn't allow to gather information about the chemical speciation of individual metallic elements. Nevertheless, the application of several other analytical techniques such as ESEM, GC-MS, ESI-MS, FT-IR and NMR, with higher detection limits compared to ICP but capable of revealing the chemical composition of the leachates matrix, proved to be important in defining the possible forms in which the heavy metals are present and in which they interact with solid liners.

In particular, the following observation can be made:

- GC-MS suggests the presence of organic molecules that are either too small to be separated from the eluent or too complex and polar such as polyalcohols or carboxylic acids.

- ESEM analysis detects the presence as main ionic species alkaline and alkaline earth cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) and environmentally diffused anions such as chloride and carbonate that can coordinate transition metals centres or form insoluble salts (*e.g.* $PbCl_2$ and $PbCO_3$).

- FT-IR and NMR analysis show the presence of complex organic species in higher concentration in SANA leachates compared to Concentrato ones with a time dependence on their composition as can be seen comparing samples S1 and S2 or S3. All the samples proved to contain aliphatic derivatives with higher concentration of acidic and hydroxilated species in solution in the youngest leachate. These species can be responsible for the coordination of multiple metallic centres forming macromolecular systems and colloidal particulate. Ageing seems to have limited effect on the aliphatic species, which being persistent could represent a risk to be considered for further treatment on the leachate.

- Heavy metals speciation in terms of elemental analysis was produced only by ICP-OES technique revealing that anaerobic leachates was characterized by higher heavy metals concentrations (Cr: 136.7-1113.3µg/l; Ni: 553.3-850.0 µg/l; Pb: 70.3-153.0 µg/l) while aerobic leachates has a low heavy metals amounts (Cr: 234.0-356.7 µg/l; Ni: 373.3-416.7 µg/l; Pb: 52.0-118.7 µg/l).

- The colloidal and the total solid fractions are present in greater amount in anaerobic leachates (0.47-1.38 g/l and 12.78 g/l) than in the aerobic ones (0.09-0.17 g/l and 8.7 g/l).

Studying the interaction of the metals in the leachate with different stationary phases (active carbon or vermiculite), it is possible to obtain information about the relationship between their form in the leachate and the landfill treatment (aerobic or anaerobic). The results show some interesting differences between aerobic and anaerobic leachate. In particular:

- Anaerobic leachates are characterized by a more marked attenuation of metals content (36-65%) after contact with stationary phases compared to aerobic leachates (10-34%).

- Filtration process through active carbon and vermiculite, although they have different elemental composition, show similar removal efficiencies of metals (34% and 35% respectively) suggesting that the mechanism of adsorption for the heavy metals present in the leachate could be similar and involved the interactions with oxygen based anionic groups on the surface of the solid liners particles.

The results obtained suggest that the metals concentration in aerobic leachates could depend on the greater oxidation of organic and organometallic species, consequently inducing the liberation of uncoordinated metal ions in solution and favouring their further oxidation and/or their inertisation by forming insoluble inorganic compounds that therefore separate from the leachate. They also suggest that metals can strongly associate with colloidal species or form complexes with organic compounds. This is of particular importance during the filtration process by the stationary phases since colloids and organic compounds are characterized by high hydrodynamic volumes and therefore can be removed more easily. In fact, the higher is the colloidal fraction the more efficient is the reduction of metals content considering the synergic effect of chemical adsorption of ion in solution and physical filtration of particulate.

On the basis of the observations made in this work, some future developments can be proposed:

- Due to the relative low concentration of heavy metals in municipal solid waste landfill leachate, the use of larger sample volumes could permit the application of preconcentration techniques allowing the use of a wider range of analytical techniques in their speciation study. In fact, analytical detection limits represent a significant problem (Baun and Christensen, 2004). In order to overcome this drawback, it is suggests performing a preconcentration process by dialysis. This process allows to eliminate interfering ions and small organic molecules and to concentrate the transition metal species. This may need a scale up of the landfill reactor simulator.

- Since leachates represent very complex matrices to study in terms of composition both organic and inorganic, the use of liquid separation techniques could be useful. In particular, we suggest the application of HPLC-MS (high performance liquid chromatography-mass spectrometry) technique that is characterized by high sensitivity and selectivity. This technique separates different ionic forms by liquid chromatography and, through mass spectrometry, detects information on their nature more precise and accurate than other methods.

- Finally, thanks to the numerous different solid liners that are applied or have been proposed for application, the study could involve a wider range of stationary phases materials to draw a more complete picture of the heavy metals adsorption in the filtration process. In this respect, the filtration system prototype proposed could be suitably modified to contain larger amounts of leachate and temperature or pressure control systems.

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