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Further steps in the standardization of BOD_5/COD ratio as a biological stability index for MSW

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Summary

In the present work it is first of all presented a general overview about biological stability: how it is defined, when it must be evaluated and why it is so important for describing the quality of solid waste. The attention focuses on the most common methods used for assessing biological stability: aerobic respiration techniques and anaerobic tests. The relevant aspects are analysed, highlighting advantages and disadvantages.

Then the focus shifts on the use of BOD_5/COD ratio as a biological stability indicator. The state of the art is presented. The interest for the BOD_5/COD index comes from the advantages that characterize this parameter: among the others, the possibility to detect dilution effects not always visible with other methodologies.

The next part concerns the description of the research activity. With the aim of standardizing the BOD_5/COD ratio, a series of laboratory tests was conducted on five kinds of solid waste. The work involved a period of research of five months at the Laboratory of Environmental Sanitary Engineering (LISA) of the University of Padua.

The main part of the document is structured as a scientific paper. The discussion about materials and methods adopted is followed by the presentation of results.

In the last part are reported all the data obtained, together with a statistical analysis.

Contents

Introduction

The biodegradable organic fraction of municipal solid waste (MSW) can play a fundamental role in preventing the deterioration of soils and the restoration of their fertility, but also in reducing the emissions of climate-altering gases into the atmosphere. Indeed, once disposed in landfill, the putrescible fraction results the major responsible for the release in the environment of biogas and leachates with a high organic and nitric content. Therefore it is necessary to provide a drastic reduction of its disposal, in order to decrease the emissions of greenhouse gases (especially methane) and, on the other side, to improve the operative conditions in landfill, diminishing the chemical aggressiveness of leachates. For this reason an adequate pre-treatment of waste can guarantee the abatement of the fermentable organic components, also in terms of weight and volume, as well as the elimination of human, animal and vegetal pathogens (APAT, 2008).

The European Landfill Directive (EC/99/31) defines specific targets to reduce the quantity of biodegradable organic matter entering non hazardous waste landfill sites. In order to reach these objectives, some Members States have set up waste management strategies which support the agriculture recovery (MSW or biowaste composting, anaerobic digestion, sewage sludge spreading) (Redon et al., 2005). Some authorities have developed alternative treatment techniques, as the Mechanical Biological Pre-treatment (MBP or MBT) before disposal, aimed at stabilising the putrescible matter contained in MSW. Others have designed systems of sustainable landfilling, in order to reduce the aftercare phase. Many states have also prescribed standards for the acceptance of waste in landfill.

In all these contexts it is evident the need of evaluating the biological stability of the organic matter contained in waste. If the efficiency of biological treatment plants has to be determined, a representative measure of biological stability must then be used. This measure would permit to assess current working plants, to improve biological treatment processes, to design optimized facilities, to determine the potential impact of the final products and of a landfill in all its phases (Barrena et al., 2009).

However, due to the lack of specific indications in the Landfill Directive, an internationally accepted index of biological stability does not exist in the solid waste management field: there is no consensus within the scientific community about the methodology to be used.

To reach this goal, some research groups have been working on this field in last decades (Adani et al., 2004; Cossu and Raga, 2008) and many assays have been developed under aerobic (Barrena et al., 2005) and anaerobic conditions (Hansen et al., 2004). Most of the methodologies studied are based on respirometric techniques (static and dynamic) and methanogenic activity assays. In Chapter 1 is

presented a brief analysis of these test methods, focusing the attention on the main advantages and drawbacks which characterize them.

At present, some standards have been already proposed and some have been also considered in the European legislation drafts and adopted in national regulations by some European countries such as Germany, Italy and England. A brief overview about that is also given.

The need of overcoming the problems related to traditional methodologies and to find a common evaluation basis keeps the interest for biological stability indicators still active. Other research projects have been carried out in recent years and new indices proposed for waste characterization. In this context finds place the development of the BOD_5/COD ratio measured on the eluate of a leaching test. This parameter combines into a single number the comparison of two values obtained through consolidated methods (Biochemical Oxygen Demand after 5 days and Chemical Oxygen Demand). The use of this index was suggested by Cossu et al. (2001).

The attention dedicated to this parameter is mainly due to the reliability of the results provided. It has been demonstrated that it is consistent with traditional biological stability indices (Cossu et al., 2005; Cossu and Raga, 2008). In a recent study, Cossu et al. (2012) concentrated on the effort of standardizing the procedure of assessment of the BOD_5/COD ratio.

The main objective pursued with this research activity is to make further steps in the standardization of the BOD_5/COD parameter, in order to create a fast, economical and simple methodology to evaluate the biological stability of any kind of solid waste.

After a presentation in Chapter 2 of the state of the art about the BOD_5/COD index, the research activity is described in Chapter 3 with details related to the laboratory experience and the test methods adopted.

Chapter 4 represents the main part of the work: it is structured as a scientific paper, containing the presentation and discussion of the results obtained. In the Annex are reported all the analytical data with some further comments and a statistical analysis conducted to better investigate the validity of the conclusions.

Chapter 1

Biological stability of waste

1.1. Importance of biological stability in evaluating waste quality

With the term *biological stability* is generally indicated the status in which, even though optimal physical-chemical conditions are guaranteed for the explication of microbiological activities, the biodegradation processes result rather slowed down (APAT, 2003). Following the degradation of the volatile solids (VS) over time, a kinetic of first order indicates an intense rotting phase, related to a condition of biological instability. The achievement of stability, instead, is individuated by kinetics of second or third order.

According to another definition, biological stability determines the extent to which readily biodegradable organic matter has decomposed (Lasaridi and Stentiford, 1998); it identifies the actual point reached in the decomposition process and represents a gradation on a recognized scale of values, enabling comparison of different biological degradation processes (Barrena et al., 2009).

The more stable is a waste, less environmental impacts it produces. Therefore biological stability is commonly used as a parameter for describing the quality of waste in the MSW management field.

There are several situations in which it is necessary to assess the degree of stabilization of a waste. An example is represented by biological processes, such as composting, bio-drying and bio-stabilization; their objective is the total or partial degradation of the fermentable organic fraction to achieve biological stability (APAT, 2003).

Composting is used to convert putrescible waste into agriculturally useful products. Compost can be defined as a humified, mature and stable material. The biological stability of compost represents a fundamental aspect for product quality assessment, since it influences the response of plants to compost application, its potential for odour generation and pathogen re-growth, biomass re-heating, residual biogas production, phytotoxicity and plant disease suppression ability (Adani et al., 2006).

Several methods have been proposed for measuring compost stability, based on its physical characteristics (pile temperature, aeration demand, odour and colour, optical density of water extracts), chemical features (volatile solids, C/N ratio, COD, polysaccharides, humic substances) and biological features (respiration measured either as O_2 consumption, CO_2 production or heat generation, enzyme activities, ATP content, seed germination and plant growth, etc.). However, none of these has found universal acceptance (Lasaridi and Stentiford, 1998).

Knowing the degree of stability of a compost is useful also to monitor process performances and compare alternative composting solutions, because it affects parameters such as airflow rate and retention time.

Another technique that has established itself in the European context in the last decades is the Mechanical-Biological Treatment (MBT), which has assumed a strategic role in the management of the residual municipal waste. The material exiting MBT plants is still considered a waste, but it can be used in limited amounts in activities of landscaping and environmental recovery or it is placed in landfill (APAT, 2008). Biostabilization and biodrying represent different kinds of MBT; biodrying is usually exploited for the production of RDF (Refuse Derived Fuels).

As reported by many studies, the monitoring of a biological stabilization process may be successfully carried out by measuring the respiration rate or other stability indicators in waste samples taken during the process (Leikam and Stegmann, 1997; Cossu and Raga, 2008).

Similar concepts are fundamental also in the field of wastewater treatment, where the degree of biological stability attained within a certain time is exploited for plant performance monitoring and comparative evaluation of different systems (Lasaridi and Stentiford, 1998). Moreover, sewage sludge is a waste whose stability needs to be evaluated before disposal in landfill or in case of soil application when it is used as fertilizer.

The determination of waste biological stability is a crucial aspect also to fulfil the legal requirements necessary for final waste disposal: the biodegradability must be as low as possible, in order to reduce the landfill emission potential. Indeed modern landfills are based on the concept of sustainability, whereby no environmental problems should be left to future generations. The assessment of biological stability is fundamental also to investigate the behaviour of the different options available for sustainable landfilling.

1.2. Biological stability indices

In literature, the list of parameters considered suitable for estimating the biological stability of solid waste is large. The major classification distinguishes between two types of indices. The first ones are chemical: global analysis of organic content (Solid Volatile Matter, TOC = Total Organic Carbon, leachable TOC) and specific analysis (lignin, cellulose, hemicellulose). The second ones are biological, directly related to the microbial activity and to the putrescible organic matter content: the aerobic respirometric tests (static and dynamic), the anaerobic respirometric tests (biomethane generation potential), the Self heating test commonly used in composting (Decottignies et al., 2005). For each of these indicators, values corresponding to a stabilized matter are described in literature.

The methodologies proposed differ in many key aspects, such as the use of an inoculum, the amount of sample analysed, the water content, the assay temperature (mesophilic or thermophilic)

and the test duration. Moreover, even the expression of the results (oxygen uptake rate or cumulative consumption) and the units (e.g. dry or volatile solids basis) are different among the tests published (Barrena et al., 2009).

Many authors over the years presented partial comparisons and some correlations between indices used for biodegradable organic matter determination (Baffi et al., 2007; Ponsá et al., 2008; Cossu and Raga, 2008). In a study by Barrena et al. (2009) a massive comparison of chemical and biological parameters was carried out in samples from a MBT plant to investigate the suitability and correlation among the methods proposed by different authors or institutions. Two main groups of biological tests were compared, aerobic and anaerobic. As confirmed by other studies, it was concluded that these methodologies (both with advantages and disadvantages) are the most powerful tools to estimate the biodegradability of organic solid wastes. Scientific literature shows that they are the only way to monitor correctly the process performance and the final product stability in modern waste treatment plants (Sánchez, 2009).

Hereafter are discussed two of the most commonly used methodologies for the determination of the biological stability of solid waste; particular attention is given to their possibilities and limits.

1.2.1. Aerobic respiration indices

For determining the biological stability of waste are particularly indicated the so called *respirometric indices*. They are commonly used in the composting field, where the stability of composts is measured via microbial respiration activity tests. These methodologies attempt to quantify the biodegradability of organic matter under near optimal aerobic conditions (Komilis and Kletsas, 2012). According to the conditions adopted in the test, the resulting parameters are classified into static respiration indices (SRI) and dynamic respiration indices (DRI).

The dominant respiration activity indices quantify oxygen consumption and/or carbon dioxide generation due to biomass. The latter are economical, but they do not differentiate between aerobic and anaerobic production of CO_2. Furthermore, they do not take into account that the oxidation degree of the organic matter influences the consumption of O_2 per mole of carbon dioxide produced. As a consequence, the methods based on the determination of the oxygen consumption result preferable, in particular the dynamic ones; this is true mainly in the case of highly putrescible matrices (APAT, 2008).

The static respiration activity may be determined in a respirometer (e.g. Sapromat) or in a batch test using pressure sensors. In both test systems, the CO_2 produced by microorganisms is bonded to soda lime. As a result negative pressure develops. The oxygen consumption is determined stoichiometrically. Compared to the pressure sensor system, the Sapromat has the advantage that the

oxygen consumed by microorganisms is immediately supplied electrochemically and thus, oxygen limitation usually may not occur (Heerenklage and Stegmann, 2005).

For SRI different researchers have used sample weights as low as 20-50 g (dry and wet weight), and variable temperatures, from 20°C (Binner and Zach, 1999; Heerenklage and Stegmann, 2005) up to 37°C (Ponsá et al., 2008). The sample materials need to be adjusted to optimum water content. The latter lies between 50% and 70% of the maximum water holding capacity (WHC) of the sample. The investigation period is at least 4 days long.

The static tests, in absence of continuous aeration, present the disadvantage of limiting the diffusion and dispersion of O_2 within the biomass: as a consequence the degradation processes are slowed down. Moreover, the impossibility of removing the exhausted air from the biomass further reduces the biological activity, both due to the decrease of pH and to the instauration of phenomena of direct toxicity. The latter are caused by the accumulation of CO_2 or other fermentation gases. In addition, it is difficult to estimate the extent of the void spaces, thus the respirometric value obtained is not rigorous (APAT, 2003). Therefore, in general, the results of static respiration methods are underestimated respect to the measurements performed with dynamic tests.

The Dynamic Respiration Index proposed by Adani et al. (2001) was developed at the Department of Vegetal Production (Di.Pro.Ve) of the university of Milan. The method involves a 20 litres adiabatic reactor. The respirometer is composed also of a control cabinet, an air supply system, a PC unit and a biofilter. A temperature compensation electrode and differential-pressure electronic transmitter ensures both oxygen and airflow measurements every 10 s. The instantaneous data are input into the software which calculates the DRI: it represents the O_2 required by microorganisms to degrade the volatile solids unit (VS) in a time unit (h), under optimal conditions. The test-end is decreed when the 12 highest DRI values have been registered (Adani et al., 2004). Therefore, effective test length depends on compost stability degree and lag phase, and ranges from a few hours to a maximum of 4 d (Adani et al., 2006). Ambient temperature for the DRI method is 35°C.

In contrast to the SRI determination, the material is submitted to forced aeration. A sufficient oxygen supply is ensured through high aeration rates, so that even materials with a high biological activity may be examined. Moreover, a larger amount of waste sample is analysed in order to take into account possible inhomogeneities in the material.

The dynamic test simulates as much as possible the real conditions in which the substrates are during the process of biological treatment. Therefore, DRI measurement represents a reproduction of the full-scale process using a laboratory approach (Adani et al., 2004).

This method shows various advantages compared to others (Adani et al., 2006):

- the presence of continuous airflow rate during measurement (dynamic condition) does not limit oxygen transfer through the biomass layer and into the bacterial cells;

- the ability to work on large masses (up to 13 kg) allows the use of full-scale particle size (up to 50 mm), therefore safeguarding the representativeness of the samples and avoiding the very complicated biomass size reduction or sieving. The use of large capabilities is fundamental mainly for analyzing waste categories with a high heterogeneity;
- the dynamic condition adopted, together with an optimal and standardized O_2 concentration in the biomass free air space, allows measurement of the airflow rate required to degrade waste under optimal conditions.

Another strength of the dynamic index is that it does not depend from the size of the reactor, thus the optimal reproducibility of the measure is guaranteed even if containers of different dimensions are used (from 10 to 50 litres). This is possible because the DRI is based on the measurement of the difference in concentration of the oxygen present in the air flux in input and output from the reactor (APAT, 2008).

While anaerobic methods and SRI are to be applied mainly for assessing the biological reactivity of MBT waste, the DRI is also a suitable test to determine the stability of non pretreated sample materials which show a higher biodegradation potential (Heerenklage and Stegmann, 2005).

Many studies demonstrated the good repeatability and reproducibility of the DRI (Adani et al., 2006). The Di.Pro.Ve method demonstrated to well correlate (R^2 = 0.966) with the official standard method ASTM D5975-96, previously proposed by ASTM (1996). It was found that values around 500 and 1000 mgO_2/kgVS/h indicate, respectively, a high and a medium degree of biological stability.

From the many tests that have been proposed in the past, the respirometric ones are recognized as being well tested methods of measuring biological stability (e.g. ASTM, 1996; The U.S. Composting Council, 1997) as they are a direct measure of microbial activity.

However, also these methodologies present some disadvantages. A first limit is related to the high cost of the respirometers, but the main drawback is the low representativeness of the measure under inhibiting conditions: potential toxic substances can alter the consumption of oxygen. Another problem is linked to the presence of biologically inert organic substances in the sample, that cause a dilution effect and decrease the respiration index of the waste (Cossu et al., 2012).

1.2.2. Anaerobic indices

The determination of the residual gas production is one of the most relevant parameters for characterizing mechanically-biologically pretreated residual waste. According to the analytical procedure adopted, it is possible to reproduce in laboratory more or less natural conditions. For estimating the biogas produced by a sample in anaerobic environment are used different techniques, among which the fermentation tests and the incubation tests.

An example of well known fermentation test is the GB_{21} method which has been standardized in Germany and Austria. The gas formation potential of a waste sample may be determined volumetrically using an eudiometer or manometrically using pressure sensors. The material to be analysed (50 gWM = wet matter) is examined with digested sewage sludge and water over a period of at least 21 days at a room temperature of 35°C. In order to ensure an anaerobic process, the free gas volume of the reactor is rinsed using nitrogen. In the eudiometer, the gas production is determined manually per working day; in the manometric test system, the data are stored discontinuously and may be read out via an IR interface for further evaluation purposes (Heerenklage and Stegmann, 2005). The gas production ascertained in the test is given in Nl/kgDM, based on standard conditions. Good correlations between GB_{21} and static respiration index were observed in many studies (Decottignies et al., 2005; Cossu and Raga, 2008).

The determination of the GS_{21} accumulated gas production differs from GB_{21} mainly by the amount of material to be analysed (800-1500 gDM) and by the water balance to be adjusted (100% water holding capacity maximum). No inoculating material is used in this test. The water-saturated sample material is placed onto a screen at the bottom in a 2.5-3 litre reactor. The gas production is measured using an eudiometer. The temperature of the water bath is set to 40°C.

Compared with GB_{21} test, considerably larger sample portions are used for the determination of GS_{21}, therefore inhomogeneities in the sample material may be compensated, where required. In contrast, the test is more complex. As no inoculating agent is added, extended lag phases might occur at the beginning of the test and result in extended investigation periods (Heerenklage and Stegmann, 2005). As regards materials with an increased biological activity, the GS_{21} method is suitable only to a limited extent.

A fermentation test lasting for 21 days gives valid indications about the activity of the anaerobic microorganisms present in the sample, but it does not allow to evaluate the potential biogas production, that can be estimated only with tests of longer duration. An example is represented by the tests developed at the University of Vienna (Binner et al., 1999): they last for 90 and 240 days and give indices named GS_{90} and GS_{240}, expressed in Nl/kgDM.

An incubation test presents some relevant advantages compared to fermentation tests: greater portions of sample (>1 kgDM) and optimal conditions ensure a good reproducibility of results in a time interval between 21 and 42 days. Moreover the incubation test can be performed in series and it determines a higher production of biogas, thus it seems more efficient to characterize the behaviour of waste (APAT, 2003).

Several other kinds of anaerobic tests have been proposed by different research groups. However, consistent European standardised methods for the determination of the gas production

potential of waste samples do not exist. The main disadvantage encountered when measuring biological stability through anaerobic techniques is the long time of the test.

1.3. Brief overview on legislation

The EU Landfill Directive dated April 26th 1999 (Council Directive 99/31/EC) defines the requirements on landfill design and operation and sets targets to reduce in a substantial way the amount of biodegradable MSW going to landfill. The reduction rates of putrescible organic matter are defined referring to the quantities generated in 1995: from 2006, 25% reduction; from 2009, 50% reduction; from 2016, 65% reduction.

The targets set in the Landfill Directive must be reached at a national level. Varying measures are implemented in the individual Member States of the European Union to achieve this aim. In Austria, for example, following the publication of the directive, standards were set for the acceptance of waste in landfill based on, among others, the maximum content of organic matter measured as TOC (total organic carbon) and VS (volatile solids).

Later on, in Austria, Binner et al. (1997) proposed to consider a possible update of the national regulation and the utilization of the static respiration activity (AT_4) and the gas formation potential under anaerobic conditions in 21 days (gas generation sum, GS_{21}) as more suitable parameters for describing the biological reactivity of waste. The indications provided by the scientific community were considered by the Austrian government and the successive legislation included the AT_4 and GS_{21} (as well as GB_{21}, anaerobic, measured with a different test) among the parameters for the characterization of the waste before disposal in landfill (BMLFUW, 2002). The limit values for AT_4 and GS_{21} (and GB_{21}) were set respectively to 7 mgO_2/gDM (Dry Matter) and 20 Nl of biogas/kgDM; both tests have to be carried out for assessing the biological stability of waste.

The same parameters were adopted in Germany, where all amounts of waste to be deposited need to be pretreated in order to reduce the emission potential of the biodegradable fraction. The respective criteria are specified in the German Ablagerungsverordnung (Waste Disposal Ordinance) on environmentally compatible storage of waste from human settlements and on biological waste treatment facilities. The main limit values are equal to 5 mgO_2/gDM for the AT_4, 20 Nl/kgDM for the GB_{21}, 18% DM for the TOC index. To check the compliance with these parameters, waste samples are to be taken and analysed at regular intervals. Standard requirements are also defined in the same regulation for the implementation of these analytical methods (Heerenklage and Stegmann, 2005).

In contrast to Germany and Austria, the French Landfill regulation (1997 strengthened in 2001) did not set threshold values for the quality of waste to be deposited. For this reason the MBP were not very developed in France in that period. However, the local authorities showed an increasing interest

in this alternative over the years, because it appeared to be socially better accepted than conventional waste treatment schemes (incineration, sustainable landfilling, bioreactor landfilling, anaerobic digestion, etc.) (Redon et al., 2005).

As concerns Italy, the Dynamic Respiration Index was widely used in all the country to test composts, stabilized wastes, biodried wastes and combustible derived fuel products (Adani et al., 2006). In the light of the provisions of Legislative Decree 31 January 2003 n. 36, transposing Directive 99/31/EC, it became necessary at the national level to take into consideration the possible operational and technical solutions which would allow a more rational management of the putrescible fraction of waste (APAT, 2008). Since 1999 the DRI had become an official test for biological stability determination in the Lombardy Region. Then other Italian Regions also officially adopted this test, until it was recognized at a National level. Threshold values for landfill entrance of waste are also based on TOC on solid and TOC on eluate.

Also other countries have fixed limit values for waste from mechanical and biological pre-treatment of household and related wastes. The project of European Directive on the biological treatment of biowaste entering landfill sites specifies respirometric parameters (SRI and DRI) and threshold values to define the stabilised state. These values are 10 mgO_2/gDM for SRI and 1000 mgO_2/kgVS/h for DRI determined through the Di.Pro.Ve. method.

In the long term, the aim should be to harmonise the methods used for the description of the biological stability of waste, at least throughout Europe. Where required, a modular standardised concept could be developed.

Chapter 2

State of the art of BOD_5/COD ratio

2.1. Early studies

One of the major difficulties found in defining a biological stability index is the heterogeneity of the waste under analysis. In addition to this, there are several drawbacks related to traditional biological indicators. For instance, it could happen that two wastes with a different degree of biological stability, measured through a respiration test, show similar results: this might be due to the instauration of inhibiting conditions in the system. In such a situation the use of a parameter based on the ratio of two indices, one biological and the other chemical, could be able to give more complete information (Salin, 2011). For example the COD test in conjunction with the BOD is helpful in indicating toxic conditions and the presence of biologically resistant organic substances (Sawyer et al., 2002).

Based on these considerations, at the end of the nineties a research group of the University of Padua started to investigate the suitability of the BOD_5/COD ratio to assess the biological stability of waste. COD and BOD are expressed with the same unit of measure (mgO_2/l), thus they can be directly compared.

One of the first studies about the use of BOD_5/COD ratio dates back to 2001. In that period, a joint research project for defining the most suitable parameters for assessing the biological stability of pretreated waste to be disposed in landfill was carried out by Italian National Environmental Protection Agency (ANPA) together with the Universities of Padua and Milan. It was found that respiration indices and BOD_5/COD ratio in leaching tests eluates were the most reliable indicators, as they correlated well between themselves: a very good value for R^2 coefficient, equal to 0.87, was calculated. Lower values (0.60) were available for correlations of BOD_5/COD with BI and with B_{28} (biogas production in wet fermentation test in 28 days). Moreover the measured values seemed to well correspond to the different duration of stabilisation processes for the investigated samples (Cossu et al., 2001).

The following study promoted by APAT in 2003 had a similar goal: defining the most suitable reference criteria, in terms of representativeness, speed of execution, repeatability and cost, for evaluating the biological stability of several kinds of wastes to be disposed in landfill. Among the other test methods, the BOD_5/COD ratio was measured on eluates obtained from leaching tests with a liquid to solid ratio of 20 l/kgTS. For the correlation between BOD_5/COD and RI_4 (mgO_2/gTS) a global R^2 of

0.72 was obtained. A higher coefficient (0.91) was calculated considering only the biostabilized wastes (MBT), while values for residual wastes indicated a worse correlation.

A further study was conducted by Cossu and Raga in 2008 on the characterization of waste excavated from closed landfills and of waste sampled during mechanical-biological pretreatment. Also in that case tests were carried out to investigate the suitability of some methodologies for the assessment of the biological stability of the samples: the results obtained for the respiration index (RI_4) were compared with the biogas production (GB_{21}), the Black Index (BI) and the BOD_5/COD in leaching test eluate. Leaching tests were performed on the waste fraction < 20 mm.

For the excavated waste the values of BOD_5/COD ratio showed no correlation with the other stability tests. According to the authors, this was due to the high degree of heterogeneity in the waste deposited in different parts of the landfill and the consequent different composition of the excavated samples.

Instead good correlations were found for pretreated waste, proving the reliability of the methods used (R^2 = 0.75 for the RI-BOD_5/COD correlation). The biostabilization was simulated in lysimeter: the BOD_5/COD decreased with time following the biological degradation of the material. It was suggested that values lower than 0.1 can be considered typical of well stabilized waste, corresponding to values lower than 5 mgO_2/gDM measured for the respiration index in the same samples.

It was concluded that the effectiveness of biodegradation during waste pretreatment processes can be easily monitored by measuring the respiration index and/or the BOD_5/COD ratio. Even for the characterization of waste from landfills the BOD_5/COD in leaching test eluate may provide further useful information especially in the case of low values of respirometric index. In particular the COD should be used as an additional parameter, as it might occur that the microorganisms are inhibited by the presence of toxic compounds in biodegradable samples. In such cases, high values of COD would be associated with no biological activity and this should suggest the need for further analysis for better characterization of the sample (Cossu and Raga, 2008).

2.2. Recent research

In all the studies mentioned the leaching tests were carried out according to the standard UNI EN 12457-2. A quantity of sample equal to 0.090±0.005 kg of dry weight is put in a HDPE bottle of 1 litre with the necessary distilled water to reach a L/S = 10 l/kgTS. The bottle is agitated for 24 h at a rotation speed of 10 rpm: the dynamic conditions allow to continuously change the contact surface between the solid and the eluent. The eluate obtained is subjected to a 0.45 µm filtration before analysis.

In a recent activity published in 2012, Cossu et al. made a first attempt to standardize the BOD_5/COD parameter by adapting the reference leaching test to the goals of the study. The

methodology was tested under different operating conditions (leaching duration, 6 and 24 h, and static or dynamic test) keeping constant temperature (20°C) and liquid to solid ratio (L/S = 10 l/kgTS). The COD fractioning was introduced.

The static tests were run in HDPE containers of 5 l. The increase of volume was thought to improve the distribution of the liquid on the sample (Salin, 2011). The large container also allowed to work with a more representative sample of waste.

The COD fractioning was based on the differentiation between the soluble fraction (COD_{sol}) and the colloidal fraction (COD_{coll}) using a flocculation method developed by Mamais et al. (1993) after filtering the sample to be analyzed (COD_f = total COD in the sample after 0.45 µm eluate filtration). This method was based on the assumption that a flocculation (by using $Zn(OH)_2$ at pH 10.5) followed by 0.45 µm filtration of the clear supernatant removed the colloidal fraction, producing a filtrate containing only truly soluble organic matter (COD_{sol}) (Mamais et al., 1993). Part of the COD_{sol} is represented by readily biodegradable soluble COD. The relation between the COD and the two mentioned fractions was: $COD_f = COD_{sol} + COD_{coll}$.

The ratio between BOD_5 and the different fractions of COD were compared with the values of the traditional biological stability indices. The study allowed to draw the following conclusions (Cossu et al., 2012):

- the BOD_5/COD ratio is actually comparable with the indices measured directly on the solid sample (RI_7 measured with Sapromat, GB_{21}, Black Index);
- the BOD_5/COD and the BOD_5/COD_{sol} indices are both consistent and significant;
- the parameter is not influenced, for the same test duration, from the type of conditions, static or dynamic;
- it is not influenced by the specific characteristics of the sample (e.g. moisture, size);
- a long test duration of 24 h does not influence significantly the values of BOD_5/COD ratio: a contact time of 6 h is preferable to avoid the beginning of the hydrolysis and oxidation processes.

All these findings allowed to state that the BOD_5/COD ratio could be a useful index for determining the biological stability of waste. As suggested by the authors, further experiments with different kinds of waste are needed in order to confirm the correlations obtained between the stability indices considered.

Chapter 3

Laboratory experience

3.1. Origin of the samples

The research study was developed at the Laboratory of Environmental Sanitary Engineering (LISA) of the University of Padua. The work lasted about five months.

Four typologies of waste were analysed to evaluate the suitability of the BOD_5/COD index to indicate the biological stability of different matrices. The samples were withdrawn in three different plants operating in the Veneto region:

- residual waste after separate collection and mechanically-biologically treated waste (MBT), respectively from the input and output lines of a bio-stabilization plant;
- compost from the combined treatment (anaerobic digestion followed by composting) of the putrescible organic fractions of MSW;
- dried sewage sludge from a municipal wastewater treatment plant.

The residual waste and the MBT waste were collected at a MSW pretreatment plant located in an area where the curbside separate collection is performed for several waste fractions including glass, metals, plastics, paper and biodegradable organic residues from food preparation and gardens. The plant treats a part of the residual waste not separately collected before disposal in landfill, since it has a considerable content of biodegradable matter. The process includes some mechanical steps: bag opening, shredding and two sieving in series (100 mm and 60 mm). The first sample of waste was collected at this point of the treatment. The subsequent biostabilization of the fraction <60 mm is divided in two phases: degradation in biotunnels for 15-20 days and maturation in windrows for a period of 40-60 days. The final product is used as daily top cover for landfill. In Fig. 3.1 are visible some of the windrows of the indoor bio-stabilization plant and the withdrawal of a sample of MBT waste.

The third sample was collected at a plant producing high quality compost from the separately collected putrescible organic fractions of MSW. A selection line pretreats the food residues and the green cuttings by sieving (50 mm) and metals removal. The anaerobic digestion is performed in mesophilic reactors (38°C) where the waste remains for about 35 days. The output digestate is sent to a separation process: the solid parts removed from the liquid are sent to a composting phase lasting for 60-75 days.

The sewage sludge was a mixture of three kinds of residues removed from different points of the wastewater treatment plant: primary settling upstream of the biological processes, secondary settling of the activated sludge and tertiary treatments for nitrogen removal. After thickening and anaerobic digestion in separate lines, the three types of sludge are mixed and centrifuged to reduce the water content.

Fig. 3.1: Biostabilization plant for the pretreatment of residual waste prior to landfilling.

The samples of the various wastes were taken in different moments, in order to work on one matrix at a time and always with fresh waste. Samples received at the laboratory were stored at 4°C and processed within a week from receipt.

3.2. Laboratory activities

The residual waste was tested unaltered and shredded: half of the sample was ground to a size below 4 mm, through the grinding mill RETSCH SM 2000. The shredding procedure was quite hard and long, because it was necessary to reduce the waste dimension in two steps (10 mm and then 4 mm).

Part of each sample was dried at 105°C in order to evaluate the content of moisture and total solids (TS). In Fig. 3.2 is reported a picture of four samples of waste before drying in the oven: big containers were used for non-shredded residual waste and MBT waste in order to perform the measurement on representative portions of sample. The volatile solids content (VS) was then measured.

The respirometric index was determined in triplicate through the Sapromat method which consists in a semi-dynamic test. Knowing the content of dry matter, it was possible to adjust the humidity of the sample to a standard value (50%). The respiration activity was recorded for all the duration of the test (7 days).

COD, BOD_5 and TOC were measured on the eluate obtained by subjecting a given amount of solid sample to a leaching test. The main objective was to run this test under different conditions to understand how they could influence the final results in terms of BOD_5/COD ratio. In total, a series of 120 leaching tests was conducted in static conditions using 9 containers of the volume of 5 litres, made of HDPE. A picture of these vessels is visible in Fig. 3.3.

In Fig. 3.4 are shown some bottles where the eluates were stored before treatment. It is interesting to note that different kinds of waste give to the liquid a different colour. Moreover, eluates of the same waste matrix can display different colours in case of heterogeneous wastes as the residual one, due to differences in composition. This fact highlights the importance of working with samples of waste as much representative and large as possible.

Fig. 3.2: Samples of residual waste ready to be dried in the oven at 105°C for the evaluation of the total solids (TS).

Fig. 3.3: HDPE containers used for the leaching tests.

Fig. 3.4: Some eluates obtained from the leaching of residual waste (foreground) and MBT waste (background).

Fig. 3.5 shows the centrifuge used to pretreat the eluates: they were centrifuged with a given speed and time, in order to standardized the procedure.

Fig. 3.5: Centrifugation of the eluates at 4000 rpm for 15 minutes.

On each eluate, two measurements of COD were done. In Fig. 3.6 are shown the digester in which the chemical oxidation occurs at 150°C and the device performing the automatic titration for the COD measurement.

Fig. 3.6: Samples of eluate ready to be digested (left); automatic titrator for the COD measurement (right).

Also the BOD_5 test was run in duplicate. The dilution method was adopted with bacterial inoculum. A picture of the Winkler bottles used for the tests is given in Fig. 3.7. The concentration of oxygen dissolved in solution at the beginning and after 5 days was measured with an oxygen probe, visible in the same figure. A magnetic stirrer was adopted to homogenize the solution.

The details of the study are presented in the next part or the work, where all the results are reported and discussed.

Fig. 3.7: Measurement of dissolved oxygen (left); Winkler bottles for the BOD_5 test (right).

Chapter 4

Scientific paper

4.1. Abstract

Biological stability is a fundamental parameter for describing the quality of many kinds of waste. Higher stabilization of the organic matter means lower environmental impacts.

In last decades there has been a growing need for defining standard test methodologies suitable for assessing the biological stability of solid waste before, during and after landfilling. Although the most used parameters are the respirometric indices and the biogas production, the BOD_5/COD ratio measured on waste eluate seems equally reliable and it allows to overcome some of their limits.

A first trial of standardizing the parameter BOD_5/COD was done in a project of Cossu et al. (2012). The main goal of this study is to make further steps in the standardization of the parameter, in order to create a reference methodology to measure the biological stability of waste. The procedure should be simple and cheap, repeatable and suitable for any kind of solid waste.

To understand the effect of the main influencing factors, a series of static leaching tests on representative samples of five kinds of waste was carried out under different operative conditions (contact time of 1, 2, 4, 6 h and liquid to solid ratio of 5 and 10).

The BOD_5/COD values do not seem to be particularly influenced from the duration of the leaching test, thus a contact time of 2 h seems sufficient and preferable to speed up the procedure. A liquid to solid ratio of 5 is advisable in order to work with a smaller reactor and to use less water.

The grinding phase results unnecessary for the preparation of the sample, because the values of BOD_5/COD obtained for shredded and non shredded residual waste are not different on average. The filtration of the eluate before analysis can be substituted by centrifugation, since the two separation methods give consistent results. The centrifugation has been standardized by setting a given speed and time of rotation.

The entire procedure results simplified and shortened; the total time necessary to evaluate the BOD_5/COD ratio is about one week. The methodology gives good results for all the kinds of waste tested and it is representative of their different degree of biological stabilization. The parameter is significant and consistent with the respirometric indices measured directly on solid sample. Compared to other stability parameters, the BOD_5/COD ratio gives a better indication of the actual biodegradability of a waste, because its value cannot be affected by dilution effects related to the presence of impurities in the sample.

4.2. Introduction

Biological stability is a fundamental parameter for describing the quality of many kinds of waste. Higher stabilization of the organic matter means lower environmental impacts.

The European Landfill Directive EC/99/31 introduced the concept of the need for a reduction of the quantities of biodegradable organics to be disposed in landfill. To achieve this goal, an increasing number of industrial plants have been designed in the past decades. The bulk municipal solid waste (MSW) stream and the source-selected putrescible fraction of MSW, characterized by a high organic content, are being treated in a large number of different facilities such as mechanical-biological treatment (MBT), anaerobic digestion and composting plants. Their main objective is to reduce the content of putrescible matter in order to decrease the environmental impacts of the waste when landfilled (e.g. odour production, self-heating and self-combustion, biogas production, leachate and pathogens re-growth) (Barrena et al., 2009).

The biological stability of waste can be achieved also during and after landfilling by the use of in situ techniques, according to different concepts and technologies such as semi-aerobic landfill (Matsufuji et al., 2000), forced aeration and flushing (Cossu et al., 2003).

Although the Directive has set targets to avoid, or reduce, landfilling of non-stable organic materials, no official parameters and limit values were indicated for the description of the quality of waste in terms of residual biodegradability (Cossu and Raga, 2008). Thus, parallel to the development of waste treatment techniques, there has been a growing need for finding standard test methodologies suitable for determining the biological stability of waste. This evaluation is useful before landfilling to define waste acceptance criteria, but also during disposal and at the end of the aftercare phase. Indeed the control of biodegradable substances has direct consequences on the short and long-term emission potential and environmental impact of MSW landfill sites. Besides that, test methods and parameters for assessing the biological stability of waste are needed for several other aims (Cossu and Raga, 2008):

- evaluating the effectiveness of the degradation process during high quality compost production from the separately collected putrescible organic fraction of municipal solid waste or from other biodegradable waste;
- estimating the reduction of biological activity of solid waste as a result of aerobic or anaerobic stabilization processes before disposal in landfill;
- assessing the effects of the aerobic conditions in innovative aerobic or semi-aerobic landfills;
- characterizing existing landfills in terms of emission potential in view of possible remediation;
- monitoring in situ aeration processes on the deposited waste for old landfills remediation.

After the implementation of the European legislation, some member states have set their own parameters and limit values for the characterization of the biological stability of waste. Despite the efforts made for years to find a common accepted basis, consistent European standardised methods for the determination of the emission potential of waste samples do not exist yet.

The research projects undertaken by many authors in last decades considered a large number of possible solutions for the evaluation of waste biological stability. Among these the most used are the respirometric indices and the anaerobic tests based on biogas production. The former can be carried out under static or dynamic conditions for many kinds of organic waste (Adani et al., 2004; Barrena et al., 2009). To the second group belongs the biomethane potential production (GB_{21}) measured in 21 days (Heerenklage and Stegmann, 2005). These methodologies are well known and several studies demonstrated the good correlation among them (Decottignies et al., 2005; Cossu and Raga, 2005; Ponsá et al., 2008; Wagland et al., 2009). However, such indices present various limits, linked to some of the following disadvantages:

- high cost of the respirometers;
- long time of the anaerobic tests;
- low representativity in inhibiting conditions that can alter the consumption of oxygen, or in presence of biologically inert organic substances decreasing the respiration indices of the waste due to a dilution effect.

To overcome these drawbacks other parameters, among which the BOD_5/COD ratio, have been proposed (Cossu et al., 2001; Cossu and Raga, 2008). This index is measured on the eluate obtained from a waste leaching test. It presents some relevant advantages (Cossu et al., 2012):

- requires standard equipments that are present in any laboratory;
- is a quite simple and cost effective procedure;
- is representative of the presence of toxic or inhibiting substances;
- is not influenced by dilution effects due to the presence of impurities in the sample;
- is suited both for coarse and finely shredded materials;
- the testing time is short.

The BOD_5/COD index is among the tests considered by the international research community for possible utilization as a biological stability indicator; in fact there is currently the need to establish strategic parameters, methods and limit values at a European level (Cossu and Raga, 2008). A first trial of standardizing the test was done in a project of Cossu et al. (2012).

The main objective of this study is to make further steps in the standardization of the parameter BOD_5/COD to create a reference methodology for measuring the biological stability of waste. The procedure should be simple, cheap, repeatable and suitable for any kind of waste.

Many factors are involved in a leaching test, such as contact time between eluent and waste, temperature, liquid to solid ratio, static or dynamic conditions, type of liquid, kind of waste, etc. In general, leachability depends also on other physical parameters (homogeneity, particle size, porosity, permeability of the solid phase), as well as on pH and redox conditions (Parodi et al., 2011). The influence of the main ones has been studied by testing the methodology under different operating conditions (leaching duration and liquid to solid ratio). With the aim of simplifying the procedure, only the static test was taken into consideration, since Cossu et al. (2012) highlighted no difference between the results of static and dynamic leaching.

With the method developed by Cossu et al. (2012) it was also demonstrated that a long leaching test duration (24 h) does not influence significantly the values of BOD_5/COD ratio: a contact time of 6 h seems preferable to avoid the beginning of the hydrolysis and oxidation processes. To further reduce the testing time, the COD fractionating method has not been considered in this case.

In view of establishing which are the best conditions to measure the BOD_5/COD ratio, the aims of this work are:

- understand if contact times shorter than 6 hours are sufficient for the leaching test;
- analyse the effects of using different L/S ratios;
- work with a large reactor volume in order to deal with a greater and more representative sample of waste;
- evaluate the possibility of working directly on waste as it is, without shredding;
- compare the BOD_5/COD ratio with the respirometric index, to confirm the good correlation with traditional stability parameters;
- test the methodology on different types of waste.

4.3. Materials and methods

4.3.1. Waste samples

The waste materials used for this study were related to different waste management situations. Representative samples were collected from full-scale plants situated in Northern Italy:

- waste A and B: residual solid waste, after separate collection of different materials (plastics, glass, paper, cans and putrescible fraction), mechanically pretreated in view of bio-stabilization (shredded and sieved at 60 mm);

- waste C: residual waste aerobically biostabilized for about 15-20 days in biotunnels and 40-60 days in windrows for maturation (mechanical-biological pre-treatment - MBT) (<60 mm);
- waste D: compost of anaerobic digestate from the undersieve of municipal solid waste putrescible fraction (<50 mm);
- waste E: dried sewage sludge from a municipal wastewater treatment plant (mixture of primary, secondary and tertiary sludge).

Compared to the study of Cossu et al. (2012), an additional matrix was analysed to better understand the behaviour of the BOD_5/COD parameter with different typologies of municipal waste. The samples of waste A, B and C were collected according to the Italian reference method UNI 10802 (2004). A random sampling was carried out to obtain a big primary sample. By successive reductions, a secondary sample of half weight was formed. After homogenization, representative samples were taken and transferred immediately to the laboratory where they were maintained at a temperature of 4 °C to hinder the biological activity until the tests.

In Fig. 4.1 is reported the composition of the waste samples expressed as percentage of the total weight.

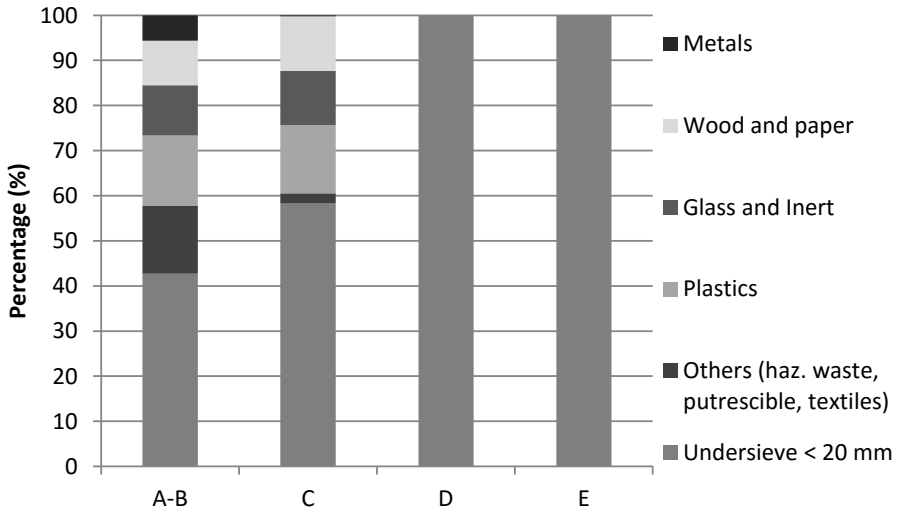

Fig. 4.1: Composition of the different waste samples (A and B = residual solid waste after separate collection, mechanically pretreated (<60 mm); C = aerobically stabilized MBT waste (<60 mm); D = compost of anaerobic digestate of MSW putrescible fraction undersieve (<50 mm); E = dried sludge from municipal wastewater treatment).

4.3.2. Leaching test

Cossu et al. (2012) demonstrated that the BOD_5/COD ratio does not seem to be influenced, for a given duration of the leaching test, from the type of conditions, static or dynamic. This represents an

advantage in the simplification of the methodology. For this reason, all the leaching tests were performed under static conditions, in HDPE containers of 5 l, on about 700 g of sample. De-ionized water was used as the eluent; the required liquid to solid ratio was reached taking into consideration the initial moisture of the sample, as indicated in the standard UNI EN 12457-2. This standard was taken as starting point, but the leaching test was adapted to the objectives of this research study (for example working with a bigger sample of waste).

The tests were carried out with four different contact times (1, 2, 4 and 6 h) and two liquid to solid ratios (L/S = 5 or 10 l/kgTS). The temperature of the laboratory was kept constant, at 20±2 °C. The size of the samples was unaltered, with exception of the residual solid waste which was analyzed both shredded, with a size <4 mm (matrix A), and not shredded (matrix B). All the tests were performed in triplicate, for a total of 24 leaching tests for each waste matrix.

The wastes were tested unaltered because Cossu et al. (2012) showed that the BOD_5/COD ratio is not much influenced by the size of the sample. Furthermore the shredding procedure requires a long time and proper equipment; this treatment may need more subsequent steps to reduce progressively the size of the waste to the desired dimension (e.g. 4 mm). The reduction of biomass size is particularly complicated in the case of wet samples (Adani et al., 2006), as it is for residual solid waste. Without shredding the preparation of the leaching test results simplified and speeded up. The possibility of working directly on a waste without pre-treatment makes the BOD_5/COD ratio more competitive respect to other stability parameters, as the dynamic respiration index. Such a test is also more realistic because it works on waste as it is. However, the residual waste was analyzed both ground and unaltered.

It is important to underline that, for a given waste matrix and L/S, four distinct triplets of leaching tests were conducted to study the influence of the duration (1, 2, 4, 6 h). This means that the eluate was not extracted at different times from the same container: in that case the removal of a part of the liquid would have altered the conditions of the test.

In order to limit any biological activity before analysis, all the eluates were stored in HDPE bottles at 4°C and the analysis were carried out promptly.

4.3.3. Stability indices on the eluate

The eluates obtained from the leaching tests were analyzed promptly to determine the following parameters:

- Biochemical Oxygen Demand (BOD_5), determined according to the Italian standard method IRSA-CNR 29/2003 vol. 2 n. 5120 B2. A volume of the eluate to be tested is placed in a Winkler bottle (volume around 280 ml). The bottle is then filled with dilution water saturated in

oxygen and containing bacterial inoculum and the nutrients required for the biological growth. The bottle is stored in the dark at a temperature of 20±0.5 °C for 5 days. The oxygen concentration in the bottle, before and after 5 days of incubation, is measured with a dissolved oxygen probe.

- Chemical Oxygen Demand (COD), measured according to the Italian standard method IRSA-CNR 29/2003 vol. 2 n. 5130. The organic material in the eluate to be tested is chemically oxidized (digested) using potassium dichromate in acid solution. After 2 h of digestion the residual dichromate is measured by automatic titration with iron (II) ammonium sulphate.
- Total Organic Carbon (TOC), measured according to the Italian standard method IRSA-CNR 29/2003 vol. 2 n. 5040. A volume of the eluate is diluted and injected in a reactor where the carbon is thermally oxidized to CO_2. The latter is determined by an infrared detector that gives the concentration of the total or inorganic carbon through comparison with reference calibration curves.

The TOC test was chosen as a means of comparison to help in the interpretation of the results. It is a reliable method which gives a good indication of the organic carbon present in the liquid.

All these methods were applied to the eluate from leaching test after a physical separation method, which consisted on a centrifugation of the solution at 4000 rpm for 15 minutes. The clear supernatant was separated from the bottom residue to be ready for the analysis. The BOD_5 and COD tests were performed in duplicate.

4.3.4. Eluate pretreatment

The standard UNI EN 12457-2, taken as initial reference for the leaching test, indicates to filtrate the eluate with a 0.45 µm filter before analysis. This step takes a quite long time to treat even a small amount of liquid, thus it lengthens considerably the duration of the entire procedure. For this reason it was preferred to adopt a centrifugation process. The point was to understand if also this separation method could be standardized. A comparison between filtration and centrifugation was made using matrix D, chosen because it is constituted by a homogeneous waste, giving results easy to interpret.

Some eluates were filtered through a 0.45 µm filter membrane with a vacuum pump. A comparison was then made between the COD measured on the filtered samples (COD_f) and the centrifuged ones (COD_c), in order to understand how big was the difference in the results.

In Fig. 4.2 is shown the relationship between the two types of COD for eight samples of waste D. The COD_f corresponds on average to 85% of the COD_c, for both liquid to solid ratios. It is possible to see that the trend is very similar.

The centrifugation process was adopted instead of filtration because the latter takes a quite long time, especially with samples with a high content of suspended matter. This problem was more evident for the leaching tests with L/S ratio equal to 5, since the eluate was more concentrated and filtration required a longer time.

In view of speeding up the measurement of the BOD_5/COD index the preparation of the eluate through centrifugation appears more adequate.

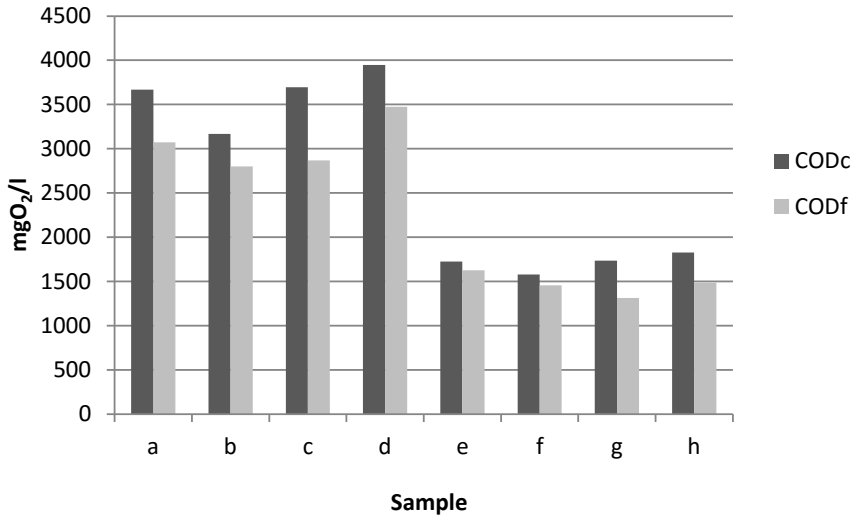

Fig. 4.2: Comparison between the COD after centrifugation (COD_c) and filtration (COD_f) of the eluate obtained from leaching tests on waste matrix D (compost). Samples a-d: L/S=5; samples e-h: L/S=10.

4.3.5. Respirometric index on solid phase

The following parameters were measured directly on the solid samples, without any pre-treatment:

- Total Solids (TS) and Volatile Solids (VS), determined on about 30 g of material according to the Italian standard gravimetric method IRSA-CNR Q 64/84 vol. 2 n. 2.
- Respirometric Index after 4 and 7 days (RI_4 and RI_7), expressed both in terms of mgO_2/gTS and mgO_2/gVS, determined on about 30 g of sample by means of the Sapromat equipment, Model E (APAT, 2003). All the samples were tested in wet conditions, obtained by adding a quantity of water to reach 75% of the maximum field capacity, equivalent to a moisture content of 50% on dry matter (UNI/TS 11184, 2006). The measurement was done in triplicate.

The respirometric index was not analyzed in unaltered conditions, since the previous study showed that a small quantity of humidity seems too low to support the biological activity; the values

obtained under wet conditions appear more representative of the real biodegradability of the waste and less influenced by the characteristics of the sample (Cossu et al., 2012).

It was chosen to adopt the respirometric index as a basis for the comparison of the results, because it is an aerobic method as the BOD_5 test. Previous studies already highlighted the good correlation of BOD_5/COD ratio and static RI with other biological stability indicators, such as dynamic respiration index (Cossu et al., 2001; APAT, 2003), GB_{21} and Black Index (Cossu and Raga, 2008; Cossu et al., 2012).

4.4. Results and discussion

4.4.1. Leaching test

COD and BOD_5 values from the leaching tests under different operative conditions are represented in Fig. 4.3 for the various samples.

As expected, the concentrations obtained for L/S=10 are in all cases half, as order of magnitude, of those related to L/S=5 due to the dilution effect. This is a first indication of the fact that the release of organic substances in the water phase during leaching is probably not so different for the two liquid to solid ratios.

The values are highly variable for the diverse kinds of waste. Ground waste A (size < 4 mm) is characterized by values that are double of those of B; this is due to the larger exchange surface caused by shredding. Matrices C, D and E present regular results, while A and B are subjected to a higher variability of values.

In general it can be observed that the test duration does not seem to influence significantly the release of COD and BOD_5 under both L/S conditions. As order of magnitude, the values are similar for shorter and longer contact times. It must not be excluded that a duration of 1 or 2 hours could be sufficient for the leaching process, because there is no particular evidence of the contrary. A test of 2 hours would allow to start the analysis of the sample in the same day, without needing to refrigerate it during night before the measurement of COD.

Data of COD, BOD_5 and TOC were averaged over time. The results of the calculations are visible in Table 4.1.

In Fig. 4.4 are shown the values of BOD_5/COD (dimensionless) compared to BOD_5/TOC (mgO_2/mgC). The two indices display the same trend for all the waste matrices; this is a prove of the reliability of the data obtained, because both COD and TOC are a measure of the total content of organic matter present in the sample.

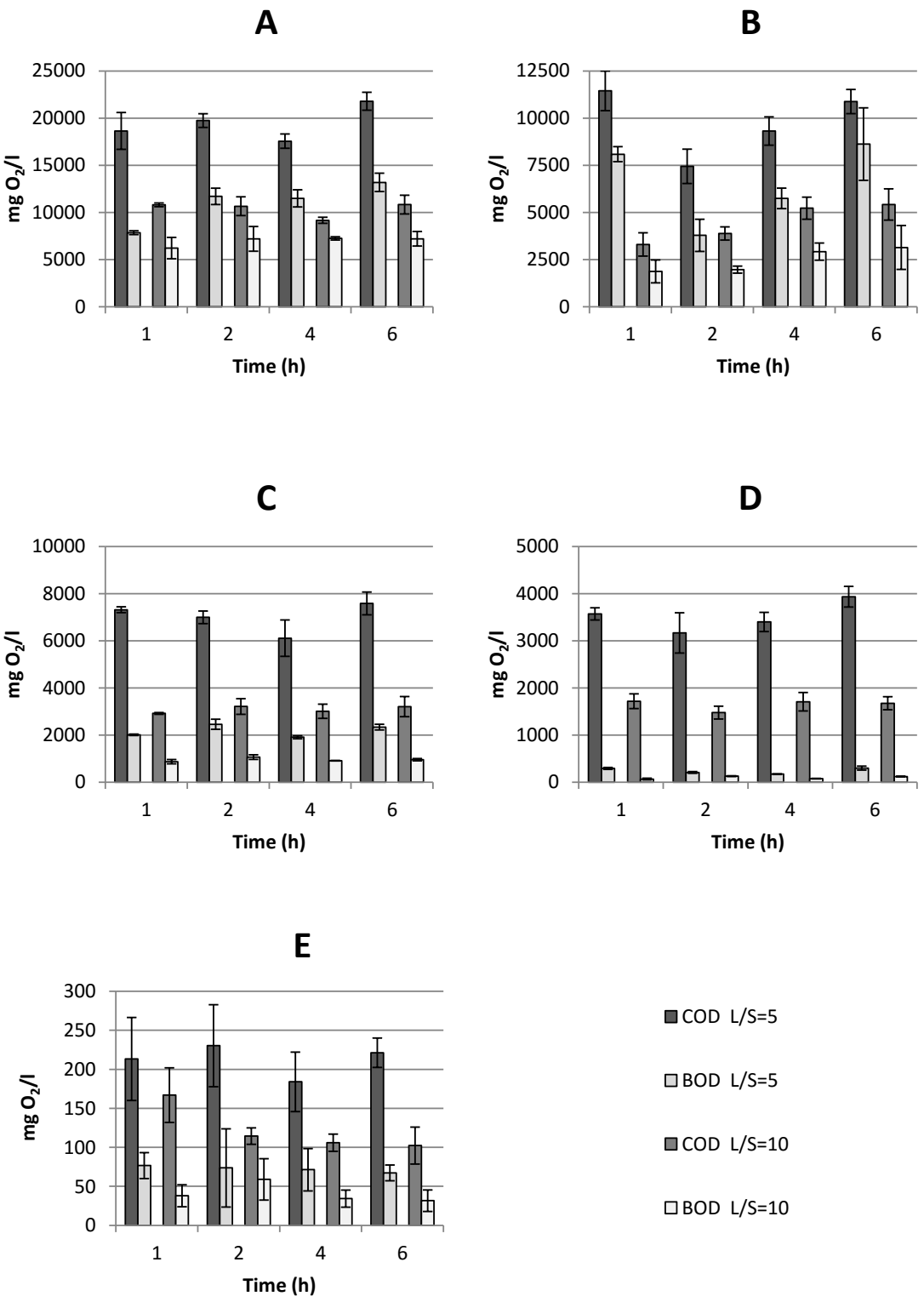

Fig. 4.3: COD and BOD_5 values from the leaching test under diverse operative conditions (contact time and L/S ratio) for the different waste samples. Standard deviations are calculated based on triplets of values.

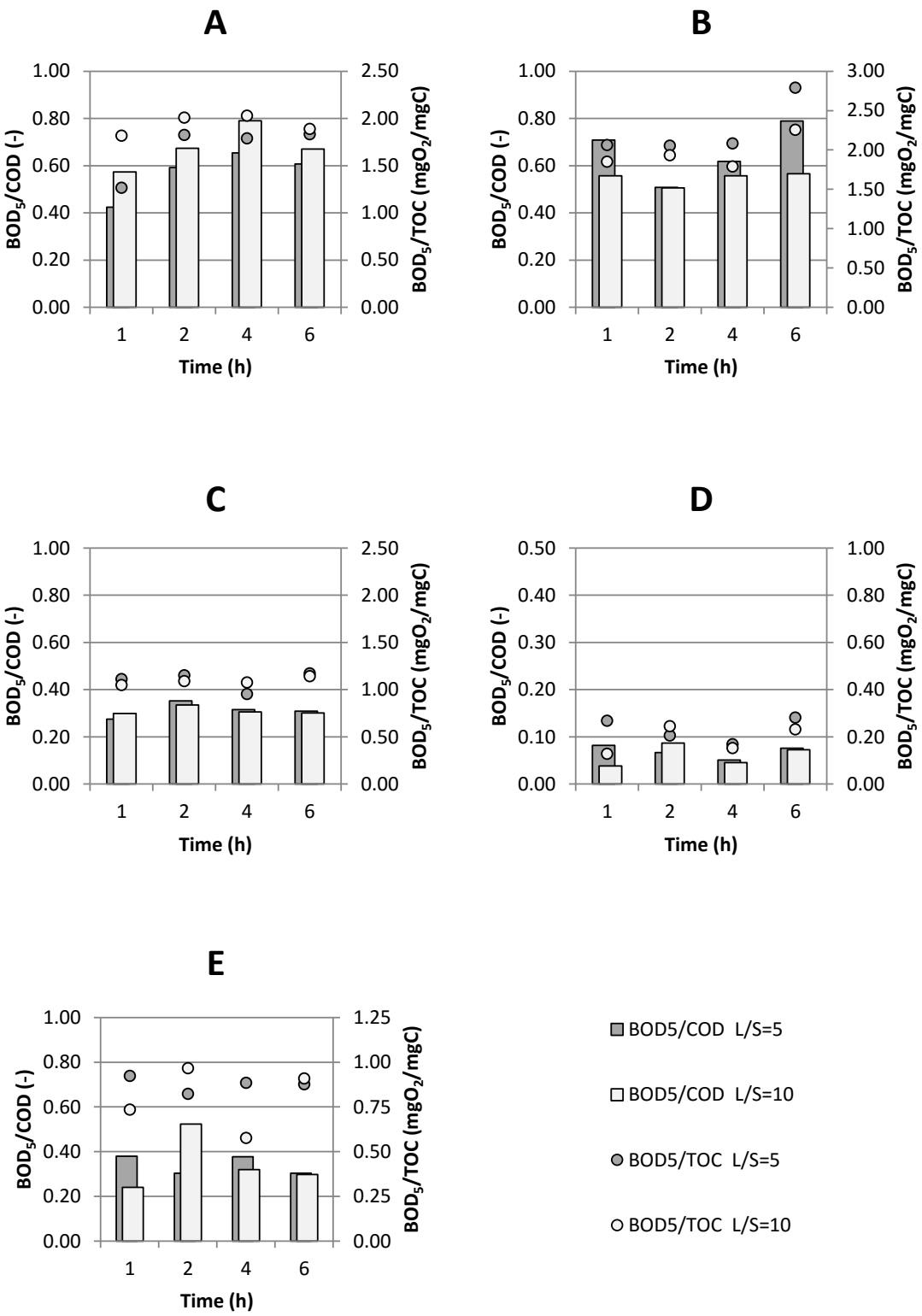

Fig. 4.4: BOD_5/COD and BOD_5/TOC values from the leaching test under diverse operative conditions (contact time and L/S ratio) for the different waste samples.

Table 4.1: Values of COD, BOD_5 and TOC averaged over time.

	Units	L/S	A	B	C	D	E
COD	mgO_2/l	5	19428	9769	7001	3517	212
		10	10360	4454	3086	1644	122
BOD_5	mgO_2/l	5	11053	6557	2178	243	72
		10	6958	2472	951	98	41
TOC	mgC/l	5	6566	2900	1985	1045	81
		10	3588	1264	873	514	53

The BOD_5/COD ratio does not seem to be much influenced by the liquid to solid ratio, especially for waste C and D. In a study by Parodi et al. (2011) about the optimization of the leaching test procedure, a L/S of 10 was chosen as it was expected to promote appropriate contact between the waste and the eluent. In the present case it was possible to achieve the same effect even with a lower ratio. In this regard, a L/S equal to 5 is advisable because it would allow to waste a lower quantity of water and to handle less eluate. Also the container used for the leaching test could be reduced in size.

In some cases the BOD_5/COD ratio is slightly higher for the tests of longer duration, but the difference does not seem particularly significant to justify the use of 4 h or 6 h test duration, as suggested earlier. To speed up the measurement a lower contact time should be preferred.

Despite the difference in absolute values of COD and BOD_5 between waste A and B already mentioned, these matrices present on average the same result in terms of BOD_5/COD. This is possible just because this parameter is expressed as a ratio, thus it is evenly able to indicate which is the percentage of really biodegradable substance over the total organic content. This fact evidences that the shredding procedure is not necessary. The possibility to work with waste as it is without pre-treatments gives to the parameter BOD_5/COD a great advantage respect to other biological stability indices.

The results obtained for waste A and B are in accordance with those reported by Cossu et al. (2012); the values are a bit lower maybe due to the higher COD, because of the adoption of the centrifugation process instead of filtration.

In Table 4.2 are summarized the final BOD_5/COD ratios characterizing the five wastes, calculated as mean of the values related to the different contact times, for a given L/S. By averaging the results also respect to L/S, it is possible to see that matrices A and B display a very similar BOD_5/COD index.

The same calculations were done for the BOD_5/TOC ratio.

Table 4.2: Final values of BOD_5/COD and BOD_5/TOC averaged over time.

	Units	L/S	A	B	C	D	E
BOD_5/COD	-	5	0.57	0.66	0.31	0.07	0.34
		10	0.68	0.55	0.31	0.06	0.35
		Average	**0.63**	**0.61**	**0.31**	**0.07**	**0.35**
BOD_5/TOC	mgO_2/mgC	5	1.68	2.25	1.10	0.23	0.88
		10	1.94	1.96	1.09	0.19	0.80
		Average	**1.81**	**2.11**	**1.10**	**0.21**	**0.84**

4.4.2. Respirometric index on solid phase

In Table 4.3 are shown the respirometric indices determined on solid phase, which have to be compared with those measured on the eluate of leaching test (BOD_5/COD and BOD_5/TOC) reported in Table 4.2. The RI values are in accordance with those indicated by Cossu et al. (2012) for matrices A, B and C. Sample B presents the highest respirometric index, typical of municipal waste with a residual content of biodegradable substances.

Table 4.3: Characterization of the samples and values of respirometric indices for the different wastes. TS = total solids; VS = volatile solids; M = moisture content; RI_4 = respirometric index after 4 days; RI_7 = respirometric index after 7 days.

	Units	A	B	C	D	E
Characterization						
TS	%	67	60	69	72	37
VS	%TS	48	68	47	52	44
M	%	33	40	31	28	63
Respirometric indices						
RI_4	mgO_2/gTS	27.1	59.2	19.5	7.9	26.6
	mgO_2/gVS	56.5	87.7	42.0	15.2	60.6
RI_7	mgO_2/gTS	61.1	81.1	35.9	12.9	37.1
	mgO_2/gVS	127.4	120.1	77.3	24.8	84.4

An anomalous behaviour was found for shredded waste A: its respirometric index is lower respect to that observed for matrix B. This might appear in contrast with the results of previous studies. As demonstrated by Redon et al. (2005), sample preparation (sampling, shredding or sieving) significantly affects the respiration activity. The authors obtained values of RI_4 expressed per unit of total solids

(TS) higher for shredded waste samples in comparison to what was measured in the sieved samples; that was probably due to the increased availability of organic compounds to biological degradation caused by grinding, which augments the specific surface (Redon et al., 2005).

Similar considerations were reported by Binner et al. (1997). On the contrary, in this study, the values of RI_4 and RI_7 of the ground waste in terms of total solids are lower than those of the waste as it is (Table 4.3). The explanation of this fact is probably related to a different phenomenon: the device used for shredding the waste overheated during the process, and the high temperature reached caused the death of a part of the microorganisms naturally present in the waste. Since the measurement of RI does not require any inoculum, the analysis resulted impaired.

The correlation between BOD_5/COD and RI_7 is reported in Fig. 4.5. The correlation coefficient R^2 is equal to 0.97 for L/S=5 and 0.78 for L/S=10. These values are in line with those obtained in previous studies about MBT wastes (Cossu et al., 2001; Cossu and Raga, 2008), or even higher.

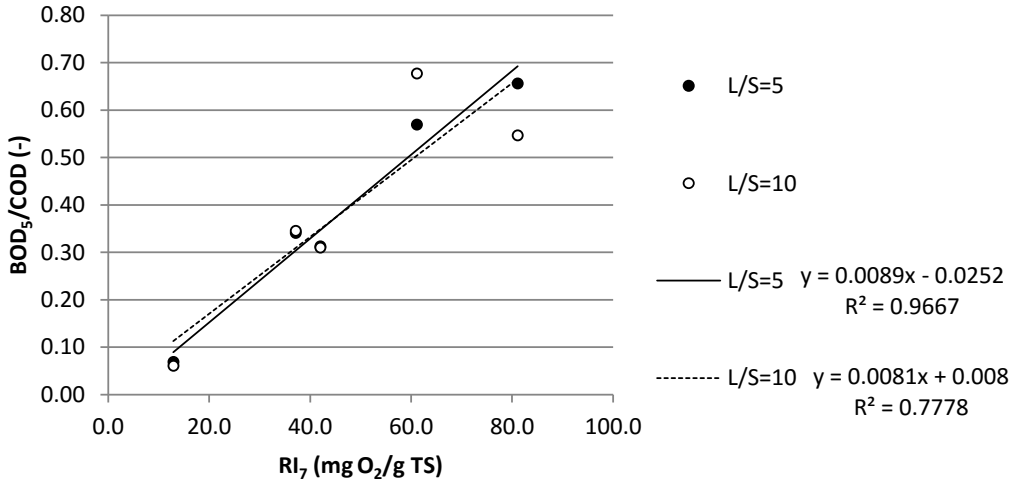

Fig. 4.5: Correlation between BOD_5/COD ratio and respiration index (RI_7) based on the values obtained for all the kinds of waste tested.

It can be concluded that the BOD_5/COD ratio is in line with the respirometric index on solid phase, except in the case of results from leaching test with L/S=10 for waste A and B. This is not in contrast with a project supported by APAT (2003) where the correlation obtained for residual waste was worse than that related to pre-treated waste. APAT reported also that it was possible to obtain higher values of R^2 when the calculation was done considering separately the wastes related to different origins. In this case that was not necessary because the R^2 values are very high even by considering all the matrices in a single calculation. Nevertheless, the results obtained should be verified with wastes of different characteristics compared to MSW, such as those with a high content in fats that have low solubility as suggested by Cossu et al. (2012).

4.4.3. Comparison among the various indices

In Fig. 4.6 is visible a further comparison among the respirometric indices and the stability parameters measured on the eluate of the leaching test under different conditions. The values are normalized considering as a unit value the indices obtained for sample D, calculated as follows:

N_i = stability index value for the i-waste/stability index value for waste D .

As demonstrated above, the BOD_5/COD ratios are in line with the respirometric indices. The good correlation was already proved in previous studies (APAT, 2003; Cossu et al., 2010). This is a further confirmation of the fact that the BOD_5/COD is consistent and can be used as stability parameter. Its greatest advantage respect to other indices is that it can be used against cheating.

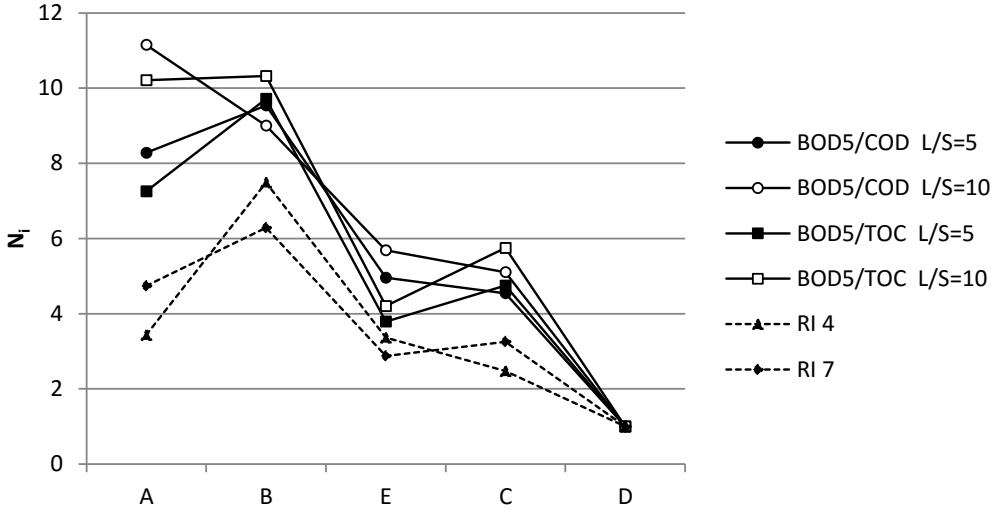

Fig. 4.6: Normalized values (Ni) of different stability indices (RI_4 = respirometric index after 4 days (mgO_2/gTS); RI_7 = respirometric index after 7 days (mgO_2/gTS); BOD_5/COD (-) and BOD_5/TOC (mgO_2/mgC) at diverse leaching conditions) for the various waste samples.

In order to respect landfill acceptance criteria, it may occur that a sample of waste to be subjected to analysis is mixed with biologically stable materials to decrease its mean emission potential. While a respirometric index is not able to detect this dilution effect, the parameter BOD_5/COD is expressed as a ratio that encloses in a single number a comparison between the amount of organic substance present in the waste (COD) and the fraction of it which is actually biodegradable (BOD). In this way the final result is not affected by impurities. Instead the respirometric index is not always reliable and may give results sometimes difficult to interpret; the values are referred to the whole waste mass (dry matter content) or to the volatile solids, resulting in both cases affected by the presence of non putrescible materials.

4.5. Conclusions

With the aim of standardizing the measurement procedure, a series of leaching tests was conducted by varying the most relevant parameters to understand how they affect the BOD_5/COD ratio and which are the best working conditions.

The BOD_5/COD values do not seem to be particularly influenced, for the same liquid to solid ratio, from the duration of the leaching test. As a consequence a contact time of 2 h seems sufficient and preferable to speed up the procedure.

A statistical analysis was not useful in this study because the amount of data was not so large to represent a meaningful statistical sample. Further research could be advisable to confirm the findings.

Even for the liquid to solid ratios no significant difference was found when calculating the value of BOD_5/COD. Thus a L/S of 5 results preferable in order to work with a smaller reactor, to waste less water and to manage a lower quantity of eluate.

The findings obtained demonstrate that the BOD_5/COD ratio behaves well with different kinds of waste because it gives indications of the diverse degree of stabilization which characterizes them. It is not influenced by the specific features of the sample (e.g. moisture and size). As expected, the most homogeneous results were achieved for compost, sludge and especially for the MBT waste.

The grinding phase did not result necessary for wastes with a great size. The values of BOD_5/COD obtained for shredded and non shredded residual waste are not different on average. The process requires a quite long time and proper equipment, and may need more subsequent steps to reduce progressively the size of the waste. Without this pre-treatment the preparation of the leaching test results simplified and speeded up.

In was demonstrated that the filtration of the eluate before analysis is not indispensable and can be substituted by centrifugation, since the two separation methods give consistent results. The process was standardized by setting a given speed and time of rotation. Also this modification is fundamental to shorten the time of analysis of the parameter BOD_5/COD.

With all these considerations the entire procedure results simplified, shortened and repeatable; the total time necessary to evaluate the BOD_5/COD ratio is about one week, affected mainly by the duration of the BOD_5 test, which is the rate determining step of the procedure.

The results obtained also confirmed that the BOD_5/COD ratio is a useful parameter for determining the biological stability of waste. It is significant, consistent and comparable with the respirometric indices measured directly on the solid samples for all the wastes tested.

This index presents several advantages: it is quite simple, cheap and requires standard equipment usually present in a chemical laboratory.

Compared to other stability indices, the BOD_5/COD ratio gives a better indication of the actual biodegradability of a waste, because its value cannot be affected by dilution effects related to the presence of impurities in the sample.

Further experiments on new types of waste may help to confirm the correlations observed between the stability indices considered. Future research should be aimed at:

- testing the methodology on other waste matrices under the set of conditions and steps defined with this study (for example, working on a completely unaltered residual waste);
- making further comparisons between the BOD_5/COD ratio thus standardized and the dynamic respiration index;
- increasing further the volume of the reactor, in order to work with larger and more representative samples of refuse, especially for wastes characterized by a very variable composition;
- defining specific BOD_5/COD threshold levels for various kinds of waste that allow to classify them as biologically stable or unstable.

Chapter 5

Annex

5.1. Results of the analysis on the eluate

From Table 5.1 to Table 5.5 are shown the results of COD, BOD_5 and TOC obtained for the five waste matrices tested. Since the analysis of the eluate from leaching test for COD and BOD_5 was done in duplicate, the values of these parameters were calculated as the average between each couple of measurements (not reported here). Then the BOD_5/COD and BOD_5/TOC ratios were computed.

For each contact time (1, 2, 4, 6 h) at a given liquid to solid ratio the leaching test was done in triplicate, thus also the mean among the three values have been reported for all the parameters.

The final results were obtained from averaging the values over time, under the hypothesis that the parameters are not influenced by the duration of the leaching test.

From Fig. 5.1 to Fig. 5.20 are graphically reported the values indicated in Table 5.1 - Table 5.5. The plots of the parameters should help in understanding how the release of organic substances develops over time and if it is affected by the L/S ratio.

An anomalous behaviour is detected for waste B, in the case of leaching test of 2 hours and L/S=5. The COD is low, probably due to the composition of that specific sample. Indeed the result is consistent with the TOC value. Since also the BOD_5 is small, the final value of BOD_5/COD is similar to those related to the other contact times and it is also consistent with that measured for L/S=10. This is an example of the advantage of expressing the biological stability index through a comparison (ratio) between two quantities.

In the graphs are also reported the regression lines of the data and their equations. Many lines display an angular coefficient near zero. In some cases the slope is even negative; this helps in affirming that there is no evidence of a higher release of organic substances in the eluent for increasing duration of the leaching test.

As concerns the BOD_5/COD index, the two interpolating lines should ideally interpose if it were true that the parameter is not influenced by the liquid to solid ratio. This occurs for waste C, D and E. As already discussed, wastes A and B are characterized by a higher variability of results, due to differences in the samples. Looking at matrix A, the BOD_5/COD is on average higher for L/S=10, while for matrix B it seems higher for L/S=5. Thus it is not possible to conclude that one of the two liquid to solid ratios is surely better than the other.

Table 5.1: Values of COD (mgO_2/l), BOD_5 (mgO_2/l), TOC (mgC/l), BOD_5/COD (-) and BOD_5/TOC (mgO_2/mgC) measured for waste A on the eluates obtained from the leaching test under different operative conditions.

	Time (h)	Sample	COD	BOD_5	BOD_5/COD	TOC	BOD_5/TOC
L/S 5	1	$A_{1\text{-}5}$ a	16542	7744	0.47	6210	1.25
		$A_{1\text{-}5}$ b	20409	7716	0.38	6090	1.27
		$A_{1\text{-}5}$ c	18962	8078	0.43	6290	1.28
		Average	**18637**	**7846**	**0.42**	**6197**	**1.27**
	2	$A_{2\text{-}5}$ a	19009	11192	0.59	6510	1.72
		$A_{2\text{-}5}$ b	20461	12699	0.62	6230	2.04
		$A_{2\text{-}5}$ c	19735	11203	0.57	6520	1.72
		Average	**19735**	**11698**	**0.59**	**6420**	**1.83**
	4	$A_{4\text{-}5}$ a	16704	10601	0.63	5560	1.91
		$A_{4\text{-}5}$ b	17801	11431	0.64	7090	1.61
		$A_{4\text{-}5}$ c	18160	12421	0.68	6720	1.85
		Average	**17555**	**11485**	**0.65**	**6457**	**1.79**
	6	$A_{6\text{-}5}$ a	20814	14029	0.67	7260	1.93
		$A_{6\text{-}5}$ b	22715	12119	0.53	7140	1.70
		$A_{6\text{-}5}$ c	21826	13397	0.61	7170	1.87
		Average	**21785**	**13182**	**0.61**	**7190**	**1.83**
	Mean over time		***19428***	***11053***	***0.57***	***6566***	***1.68***
L/S 10	1	$A_{1\text{-}10}$ a	10706	6011	0.56	3385	1.78
		$A_{1\text{-}10}$ b	10667	5186	0.49	3230	1.61
		$A_{1\text{-}10}$ c	11026	7426	0.67	3585	2.07
		Average	**10799**	**6207**	**0.57**	**3400**	**1.82**
	2	$A_{2\text{-}10}$ a	9748	5735	0.59	3530	1.62
		$A_{2\text{-}10}$ b	10498	8278	0.79	3495	2.37
		$A_{2\text{-}10}$ c	11721	7555	0.64	3715	2.03
		Average	**10655**	**7189**	**0.67**	**3580**	**2.01**
	4	$A_{4\text{-}10}$ a	9348	7158	0.77	3580	2.00
		$A_{4\text{-}10}$ b	9343	7437	0.80	3620	2.05
		$A_{4\text{-}10}$ c	8788	7119	0.81	3500	2.03
		Average	**9160**	**7238**	**0.79**	**3567**	**2.03**
	6	$A_{6\text{-}10}$ a	9761	7717	0.79	3850	2.00
		$A_{6\text{-}10}$ b	11730	7565	0.64	3830	1.98
		$A_{6\text{-}10}$ c	10981	6314	0.57	3740	1.69
		Average	**10824**	**7198**	**0.67**	**3807**	**1.89**
	Mean over time		***10360***	***6958***	***0.68***	***3588***	***1.94***

Table 5.2: Values of COD (mgO_2/l), BOD_5 (mgO_2/l), TOC (mgC/l), BOD_5/COD (-) and BOD_5/TOC (mgO_2/mgC) measured for waste B on the eluates obtained from the leaching test under different operative conditions.

	Time (h)	Sample	COD	BOD_5	BOD_5/COD	TOC	BOD_5/TOC
L/S 5	1	$B_{1\text{-}5}$ a	10419	7857	0.75	3815	2.06
		$B_{1\text{-}5}$ b	12522	8546	0.68	4170	2.05
		$B_{1\text{-}5}$ c	11400	7858	0.69	3780	2.08
		Average	**11447**	**8087**	**0.71**	**3922**	**2.06**
	2	$B_{2\text{-}5}$ a	8492	4336	0.51	2220	1.95
		$B_{2\text{-}5}$ b	6961	4209	0.60	1675	2.51
		$B_{2\text{-}5}$ c	6870	2799	0.41	1650	1.70
		Average	**7441**	**3781**	**0.51**	**1848**	**2.05**
	4	$B_{4\text{-}5}$ a	9727	5312	0.55	2875	1.85
		$B_{4\text{-}5}$ b	8447	5561	0.66	2495	2.23
		$B_{4\text{-}5}$ c	9768	6354	0.65	2925	2.17
		Average	**9314**	**5742**	**0.62**	**2765**	**2.08**
	6	$B_{6\text{-}5}$ a	11400	10838	0.95	3430	3.16
		$B_{6\text{-}5}$ b	11068	7435	0.67	2770	2.68
		$B_{6\text{-}5}$ c	10160	7587	0.75	3000	2.53
		Average	**10876**	**8620**	**0.79**	**3067**	**2.79**
	Mean over time		***9769***	***6557***	***0.66***	***2900***	***2.25***
L/S 10	1	$B_{1\text{-}10}$ a	3194	1749	0.55	1020	1.71
		$B_{1\text{-}10}$ b	3964	2526	0.64	1286	1.96
		$B_{1\text{-}10}$ c	2741	1330	0.49	710	1.87
		Average	**3299**	**1868**	**0.56**	**1005**	**1.85**
	2	$B_{2\text{-}10}$ a	4251	2175	0.51	1192	1.82
		$B_{2\text{-}10}$ b	3555	1821	0.51	894	2.04
		$B_{2\text{-}10}$ c	3835	1894	0.49	978	1.94
		Average	**3880**	**1963**	**0.51**	**1021**	**1.93**
	4	$B_{4\text{-}10}$ a	4559	2457	0.54	1456	1.69
		$B_{4\text{-}10}$ b	5673	3367	0.59	1854	1.82
		$B_{4\text{-}10}$ c	5431	2933	0.54	1572	1.87
		Average	**5221**	**2919**	**0.56**	**1627**	**1.79**
	6	$B_{6\text{-}10}$ a	6271	4294	0.68	1998	2.15
		$B_{6\text{-}10}$ b	5368	3156	0.59	1330	2.37
		$B_{6\text{-}10}$ c	4614	1967	0.43	876	2.24
		Average	**5418**	**3139**	**0.57**	**1401**	**2.26**
	Mean over time		***4454***	***2472***	***0.55***	***1264***	***1.96***

Table 5.3: Values of COD (mgO_2/l), BOD_5 (mgO_2/l), TOC (mgC/l), BOD_5/COD (-) and BOD_5/TOC (mgO_2/mgC) measured for waste C on the eluates obtained from the leaching test under different operative conditions.

	Time (h)	Sample	COD	BOD_5	BOD_5/COD	TOC	BOD_5/TOC
L/S 5	1	$C_{1\text{-}5}$ a	7194	2046	0.28	1880	1.09
		$C_{1\text{-}5}$ b	7315	1997	0.27	1780	1.12
		$C_{1\text{-}5}$ c	7442	1991	0.27	1765	1.13
		Average	**7317**	**2011**	**0.27**	**1808**	**1.11**
	2	$C_{2\text{-}5}$ a	6693	2522	0.38	2280	1.11
		$C_{2\text{-}5}$ b	7085	2634	0.37	2250	1.17
		$C_{2\text{-}5}$ c	7205	2220	0.31	1880	1.18
		Average	**6994**	**2459**	**0.35**	**2137**	**1.15**
	4	$C_{4\text{-}5}$ a	5791	1838	0.32	2075	0.89
		$C_{4\text{-}5}$ b	6991	1962	0.28	1990	0.99
		$C_{4\text{-}5}$ c	5549	1919	0.35	1935	0.99
		Average	**6110**	**1906**	**0.31**	**2000**	**0.95**
	6	$C_{6\text{-}5}$ a	7735	2450	0.32	2020	1.21
		$C_{6\text{-}5}$ b	7043	2210	0.31	1855	1.19
		$C_{6\text{-}5}$ c	7974	2352	0.29	2110	1.11
		Average	**7584**	**2337**	**0.31**	**1995**	**1.17**
	Mean over time		***7001***	***2178***	***0.31***	***1985***	***1.10***
L/S 10	1	$C_{1\text{-}10}$ a	2952	976	0.33	924	1.06
		$C_{1\text{-}10}$ b	2923	825	0.28	786	1.05
		$C_{1\text{-}10}$ c	2877	812	0.28	778	1.04
		Average	**2917**	**871**	**0.30**	**829**	**1.05**
	2	$C_{2\text{-}10}$ a	2858	1159	0.41	1070	1.08
		$C_{2\text{-}10}$ b	3257	964	0.30	876	1.10
		$C_{2\text{-}10}$ c	3518	1071	0.30	982	1.09
		Average	**3211**	**1064**	**0.34**	**976**	**1.09**
	4	$C_{4\text{-}10}$ a	2692	923	0.34	818	1.13
		$C_{4\text{-}10}$ b	3291	915	0.28	916	1.00
		$C_{4\text{-}10}$ c	3044	900	0.30	816	1.10
		Average	**3009**	**913**	**0.31**	**850**	**1.08**
	6	$C_{6\text{-}10}$ a	2738	937	0.34	792	1.18
		$C_{6\text{-}10}$ b	3575	1010	0.28	922	1.10
		$C_{6\text{-}10}$ c	3307	918	0.28	798	1.15
		Average	**3206**	**955**	**0.30**	**837**	**1.14**
	Mean over time		***3086***	***951***	***0.31***	***873***	***1.09***

Table 5.4: Values of COD (mgO_2/l), BOD_5 (mgO_2/l), TOC (mgC/l), BOD_5/COD (-) and BOD_5/TOC (mgO_2/mgC) measured for waste D on the eluates obtained from the leaching test under different operative conditions.

	Time (h)	Sample	COD	BOD_5	BOD_5/COD	TOC	BOD_5/TOC
L/S 5	1	$D_{1\text{-}5}$ a	3423	280	0.08	1160	0.24
		$D_{1\text{-}5}$ b	3619	316	0.09	1060	0.30
		$D_{1\text{-}5}$ c	3668	281	0.08	1055	0.27
		Average	**3570**	**292**	**0.08**	**1092**	**0.27**
	2	$D_{2\text{-}5}$ a	3556	186	0.05	945	0.20
		$D_{2\text{-}5}$ b	2710	218	0.08	1020	0.21
		$D_{2\text{-}5}$ c	3234	218	0.07	1045	0.21
		Average	**3167**	**207**	**0.07**	**1003**	**0.21**
	4	$D_{4\text{-}5}$ a	3486	172	0.05	1065	0.16
		$D_{4\text{-}5}$ b	3545	172	0.05	985	0.17
		$D_{4\text{-}5}$ c	3166	173	0.05	1005	0.17
		Average	**3399**	**172**	**0.05**	**1018**	**0.17**
	6	$D_{6\text{-}5}$ a	4126	294	0.07	1160	0.25
		$D_{6\text{-}5}$ b	3983	344	0.09	1005	0.34
		$D_{6\text{-}5}$ c	3695	260	0.07	1035	0.25
		Average	**3934**	**299**	**0.08**	**1067**	**0.28**
	Mean over time		***3517***	***243***	***0.07***	***1045***	***0.23***
L/S 10	1	$D_{1\text{-}10}$ a	1871	77	0.04	570	0.14
		$D_{1\text{-}10}$ b	1559	46	0.03	470	0.10
		$D_{1\text{-}10}$ c	1724	77	0.04	504	0.15
		Average	**1718**	**67**	**0.04**	**515**	**0.13**
	2	$D_{2\text{-}10}$ a	1322	119	0.09	512	0.23
		$D_{2\text{-}10}$ b	1528	129	0.08	512	0.25
		$D_{2\text{-}10}$ c	1579	136	0.09	538	0.25
		Average	**1476**	**128**	**0.09**	**521**	**0.25**
	4	$D_{4\text{-}10}$ a	1499	82	0.05	502	0.16
		$D_{4\text{-}10}$ b	1888	73	0.04	530	0.14
		$D_{4\text{-}10}$ c	1734	73	0.04	462	0.16
		Average	**1707**	**76**	**0.05**	**498**	**0.15**
	6	$D_{6\text{-}10}$ a	1554	122	0.08	528	0.23
		$D_{6\text{-}10}$ b	1646	129	0.08	522	0.25
		$D_{6\text{-}10}$ c	1826	113	0.06	512	0.22
		Average	**1675**	**121**	**0.07**	**521**	**0.23**
	Mean over time		***1644***	***98***	***0.06***	***514***	***0.19***

Table 5.5: Values of COD (mgO_2/l), BOD_5 (mgO_2/l), TOC (mgC/l), BOD_5/COD (-) and BOD_5/TOC (mgO_2/mgC) measured for waste E on the eluates obtained from the leaching test under different operative conditions.

	Time (h)	Sample	COD	BOD_5	BOD_5/COD	TOC	BOD_5/TOC
L/S 5	1	$E_{1\text{-}5}$ a	152	79	0.52	78.2	1.01
		$E_{1\text{-}5}$ b	241	59	0.24	74.0	0.80
		$E_{1\text{-}5}$ c	247	92	0.37	95.5	0.96
		Average	**213**	**77**	**0.38**	**82.6**	**0.92**
	2	$E_{2\text{-}5}$ a	274	131	0.48	98.0	1.34
		$E_{2\text{-}5}$ b	172	38	0.22	77.5	0.49
		$E_{2\text{-}5}$ c	245	52	0.21	80.9	0.64
		Average	**230**	**74**	**0.30**	**85.5**	**0.82**
	4	$E_{4\text{-}5}$ a	205	87	0.42	84.8	1.03
		$E_{4\text{-}5}$ b	207	87	0.42	81.2	1.07
		$E_{4\text{-}5}$ c	140	40	0.29	71.8	0.56
		Average	**184**	**71**	**0.38**	**79.3**	**0.88**
	6	$E_{6\text{-}5}$ a	202	62	0.31	83.9	0.74
		$E_{6\text{-}5}$ b	224	61	0.27	72.1	0.85
		$E_{6\text{-}5}$ c	239	79	0.33	75.6	1.04
		Average	**221**	**67**	**0.30**	**77.2**	**0.88**
	Mean over time		***212***	***72***	***0.34***	***81.1***	***0.88***
L/S 10	1	$E_{1\text{-}10}$ a	166	23	0.14	52	0.44
		$E_{1\text{-}10}$ b	203	40	0.20	53	0.75
		$E_{1\text{-}10}$ c	133	51	0.38	51	1.01
		Average	**167**	**38**	**0.24**	**52**	**0.73**
	2	$E_{2\text{-}10}$ a	105	53	0.51	97	0.55
		$E_{2\text{-}10}$ b	126	36	0.29	44	0.81
		$E_{2\text{-}10}$ c	114	88	0.78	57	1.54
		Average	**115**	**59**	**0.52**	**66**	**0.97**
	4	$E_{4\text{-}10}$ a	119	47	0.40	63	0.75
		$E_{4\text{-}10}$ b	100	28	0.28	57	0.49
		$E_{4\text{-}10}$ c	100	28	0.28	57	0.49
		Average	**106**	**34**	**0.32**	**59**	**0.58**
	6	$E_{6\text{-}10}$ a	115	42	0.37	35	1.21
		$E_{6\text{-}10}$ b	117	37	0.32	40	0.93
		$E_{6\text{-}10}$ c	75	16	0.21	27	0.58
		Average	**102**	**32**	**0.30**	**34**	**0.91**
	Mean over time		***122***	***41***	***0.35***	***53***	***0.80***

Waste matrix A

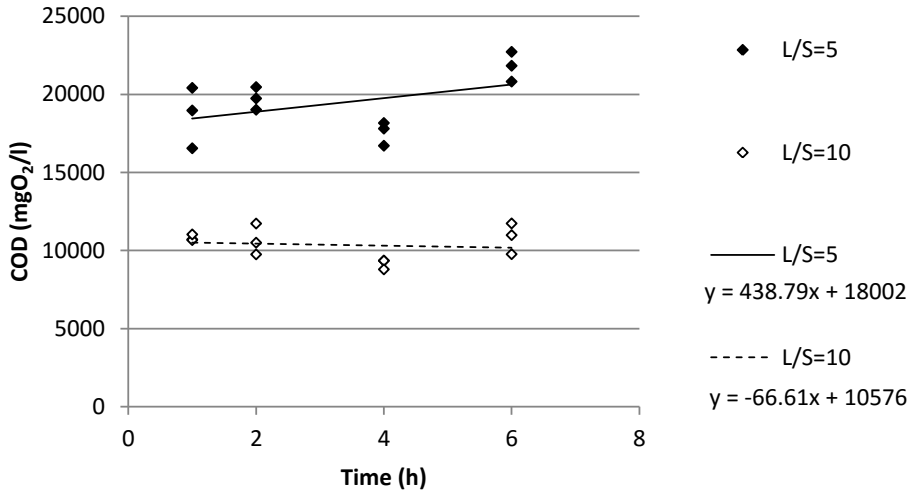

Fig. 5.1: COD values of waste matrix A from leaching tests under different operative conditions.

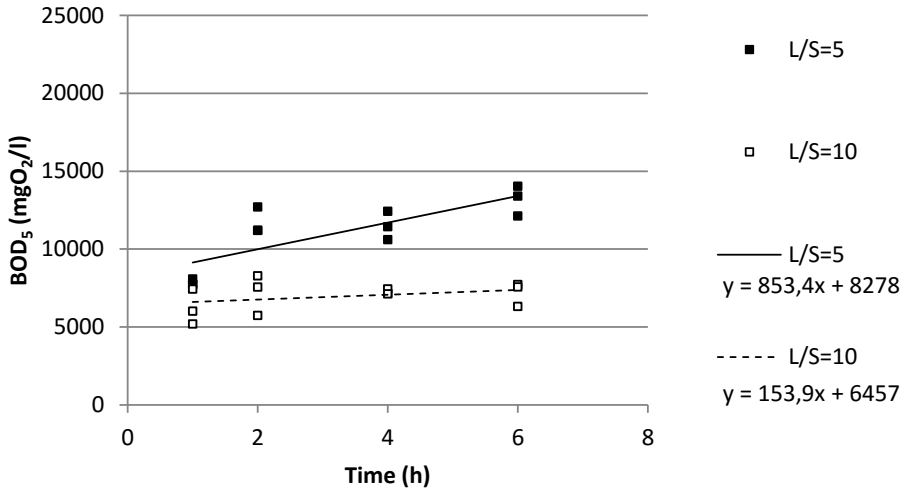

Fig. 5.2: BOD_5 values of waste matrix A from leaching tests under different operative conditions.

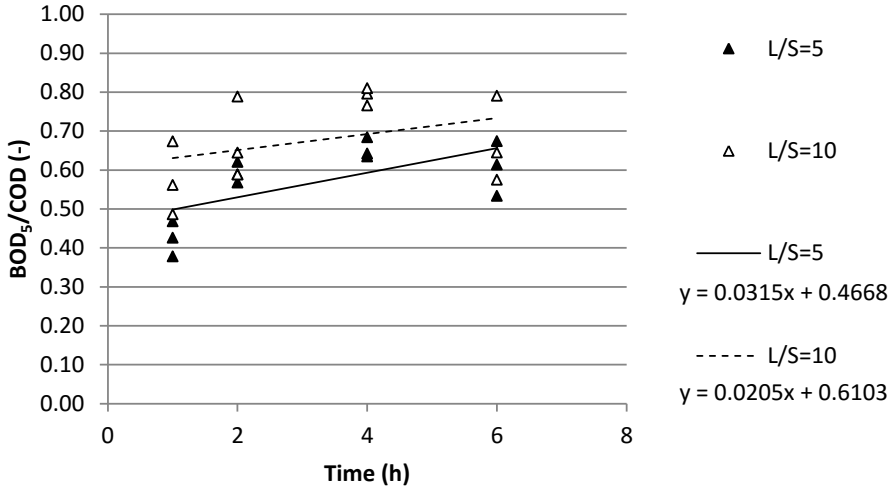

Fig. 5.3: BOD_5/COD values of waste matrix A from leaching tests under different operative conditions.

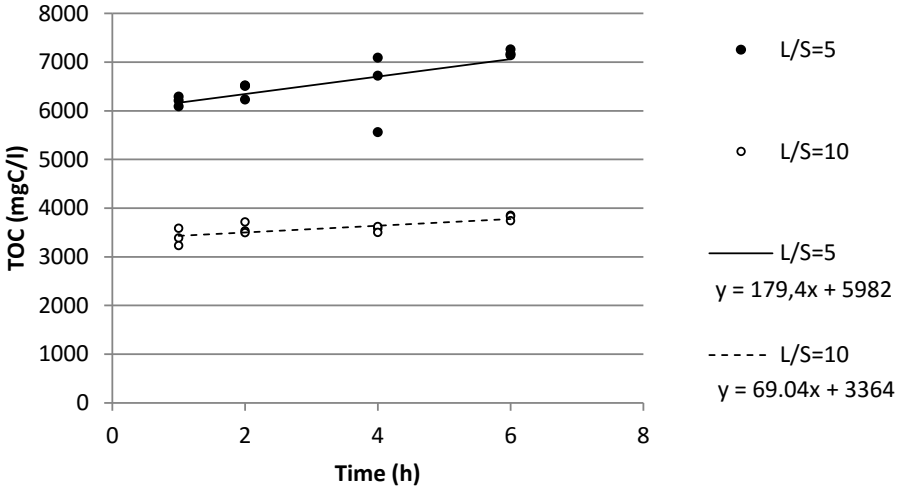

Fig. 5.4: TOC values of waste matrix A from leaching tests under different operative conditions.

Waste matrix B

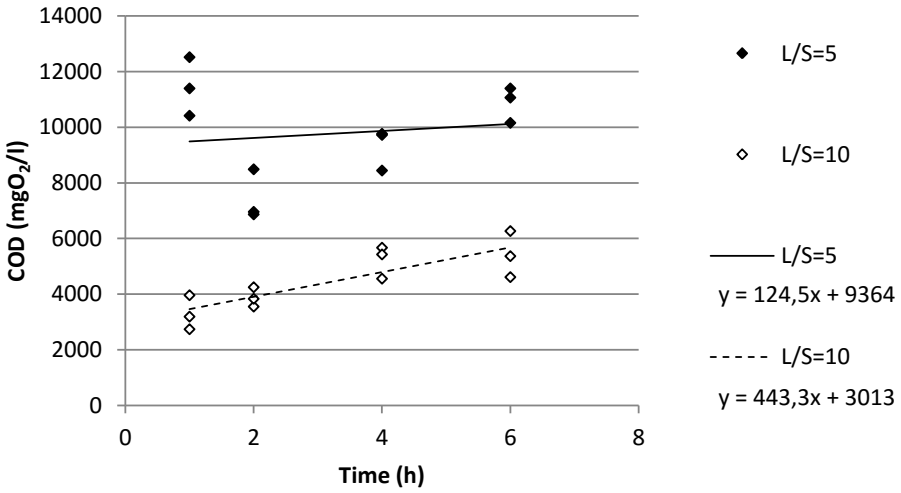

Fig. 5.5: COD values of waste matrix B from leaching tests under different operative conditions.

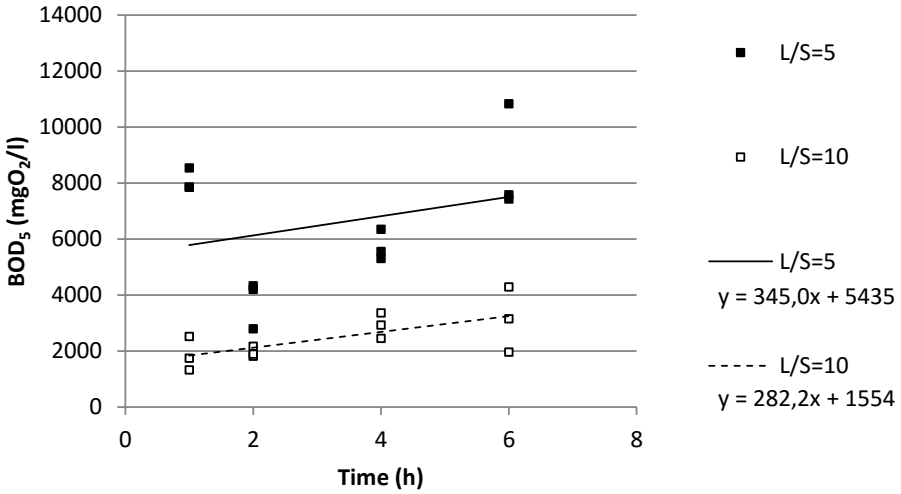

Fig. 5.6: BOD_5 values of waste matrix B from leaching tests under different operative conditions.

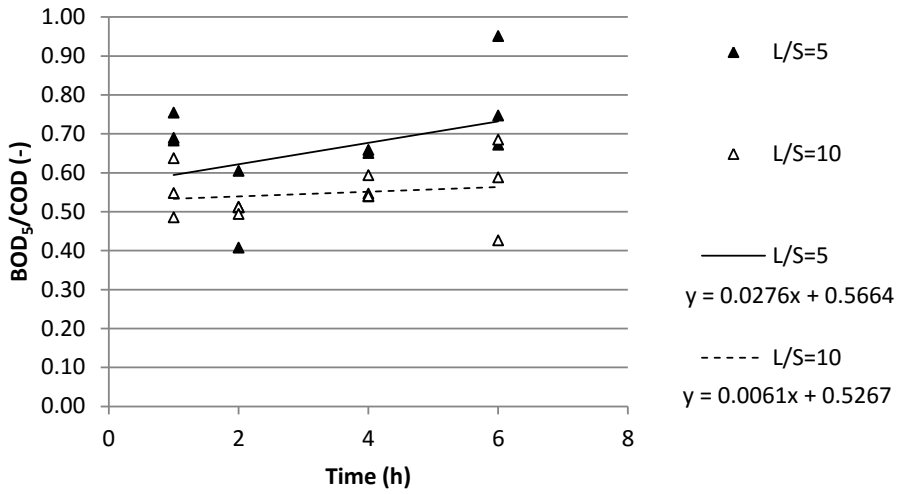

Fig. 5.7: BOD_5/COD values of waste matrix B from leaching tests under different operative conditions.

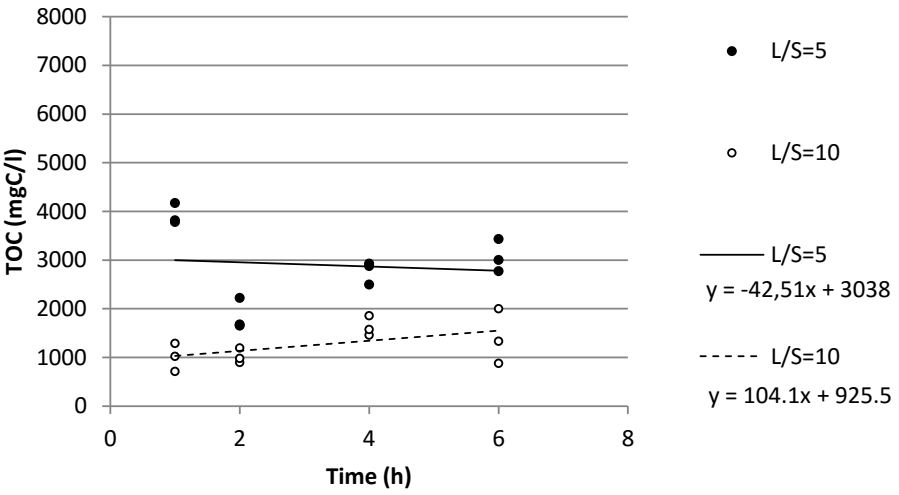

Fig. 5.8: TOC values of waste matrix B from leaching tests under different operative conditions.

Waste matrix C

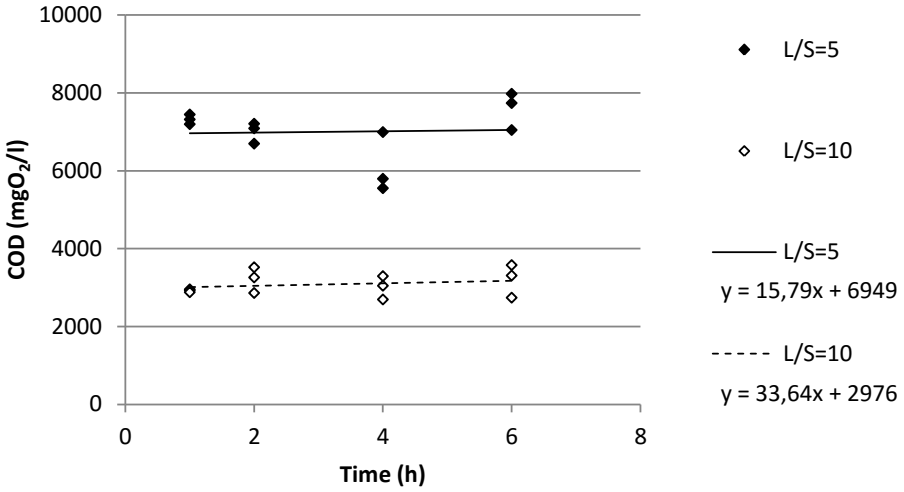

Fig. 5.9: COD values of waste matrix C from leaching tests under different operative conditions.

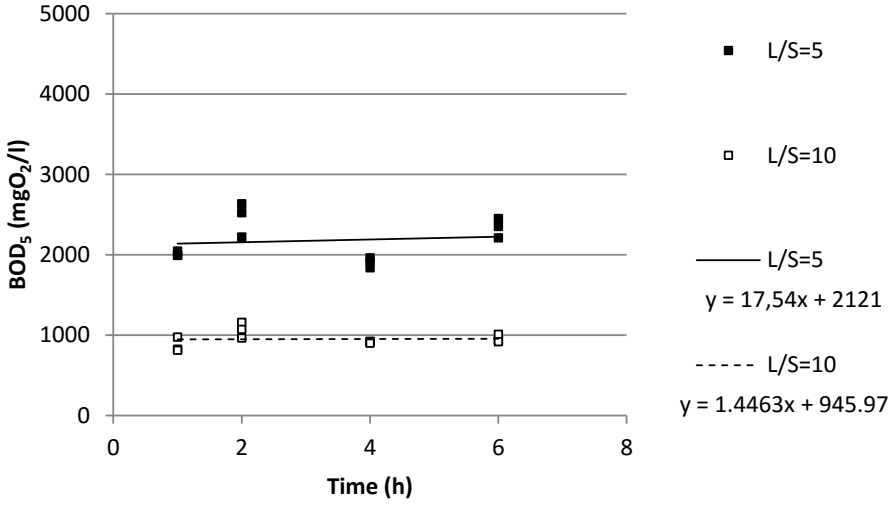

Fig. 5.10: BOD_5 values of waste matrix C from leaching tests under different operative conditions.

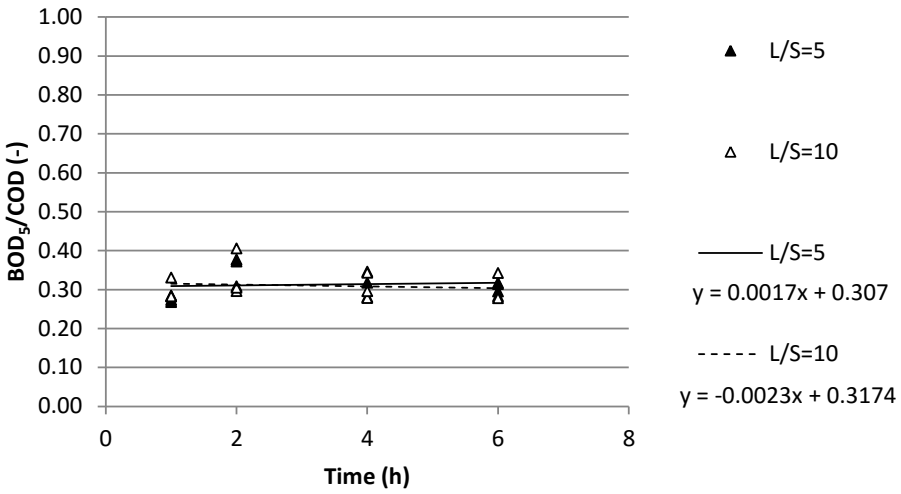

Fig. 5.11: BOD_5/COD values of waste matrix C from leaching tests under different operative conditions.

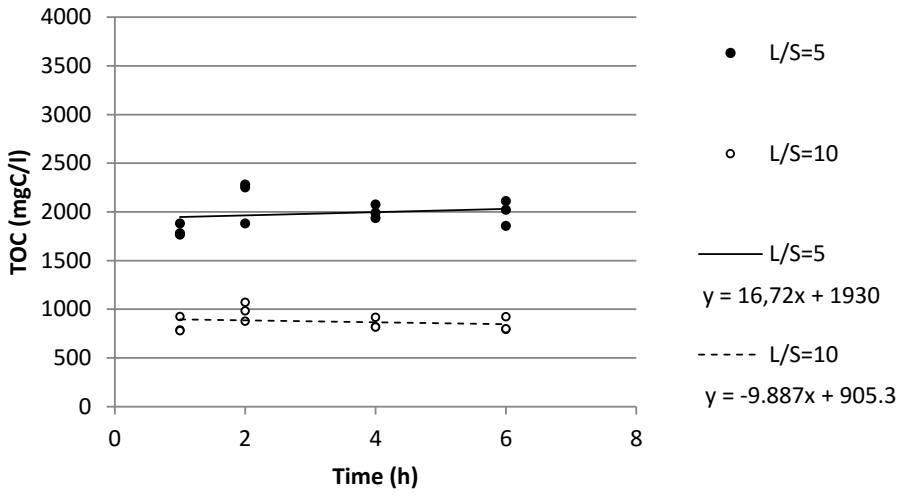

Fig. 5.12: TOC values of waste matrix C from leaching tests under different operative conditions.

Waste matrix D

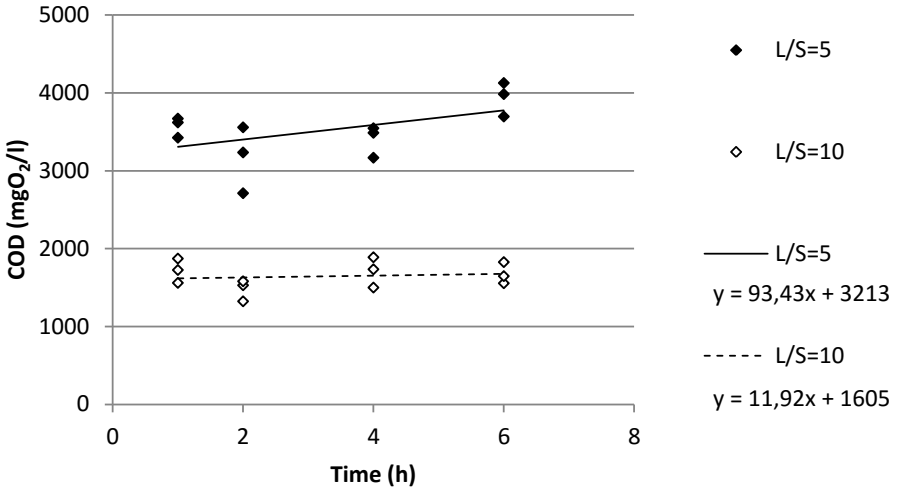

Fig. 5.13: COD values of waste matrix D from leaching tests under different operative conditions.

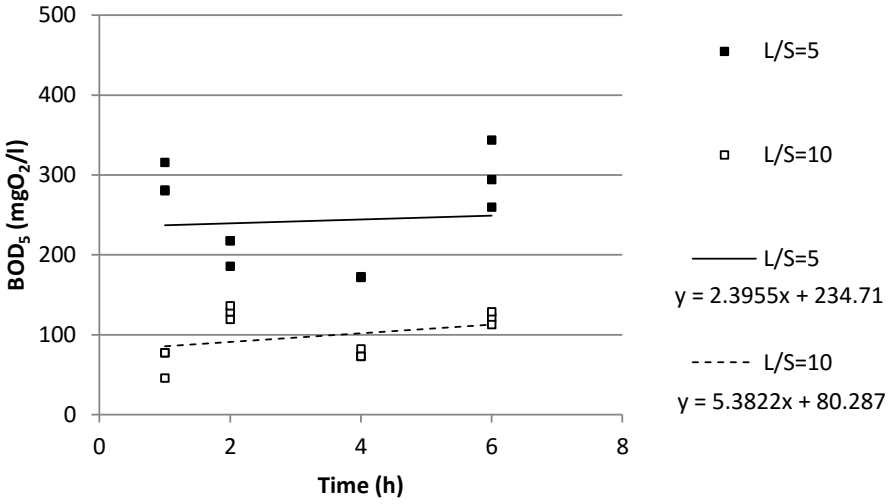

Fig. 5.14: BOD_5 values of waste matrix D from leaching tests under different operative conditions.

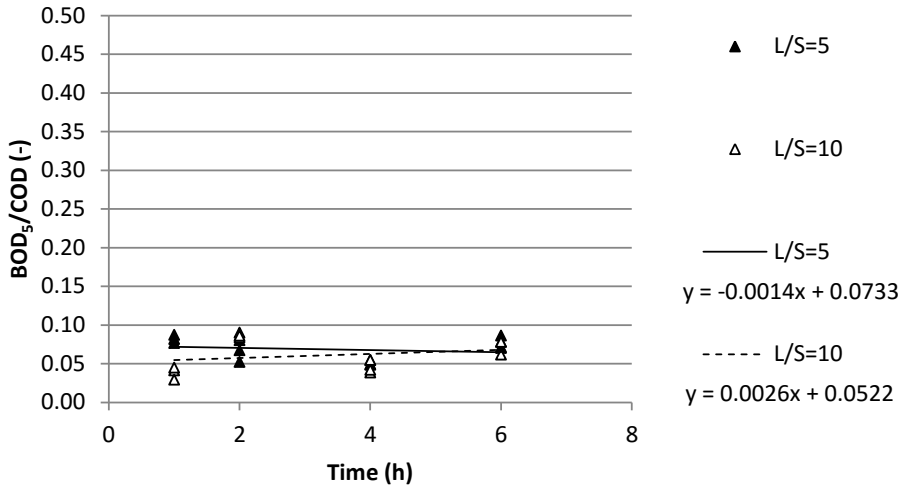

Fig. 5.15: BOD_5/COD values of waste matrix D from leaching tests under different operative conditions.

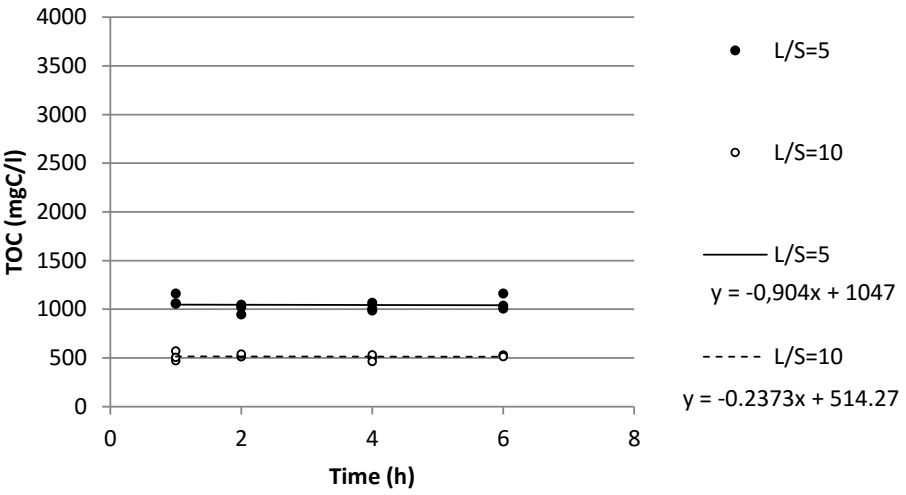

Fig. 5.16: TOC values of waste matrix D from leaching tests under different operative conditions.

Waste matrix E

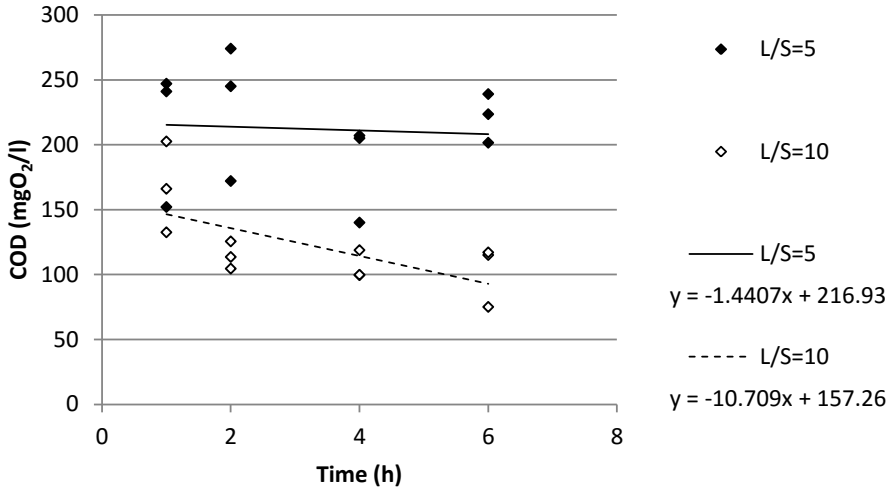

Fig. 5.17: COD values of waste matrix E from leaching tests under different operative conditions.

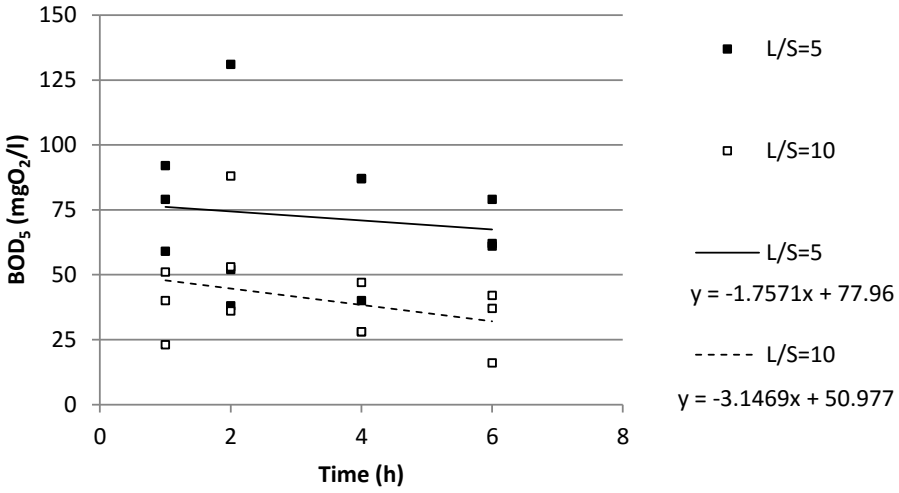

Fig. 5.18: BOD_5 values of waste matrix E from leaching tests under different operative conditions.

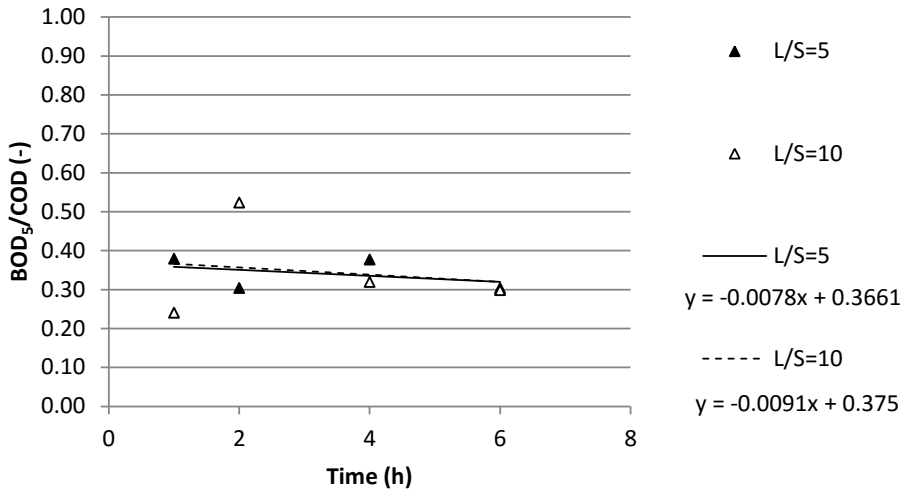

Fig. 5.19: BOD_5/COD values of waste matrix E from leaching tests under different operative conditions.

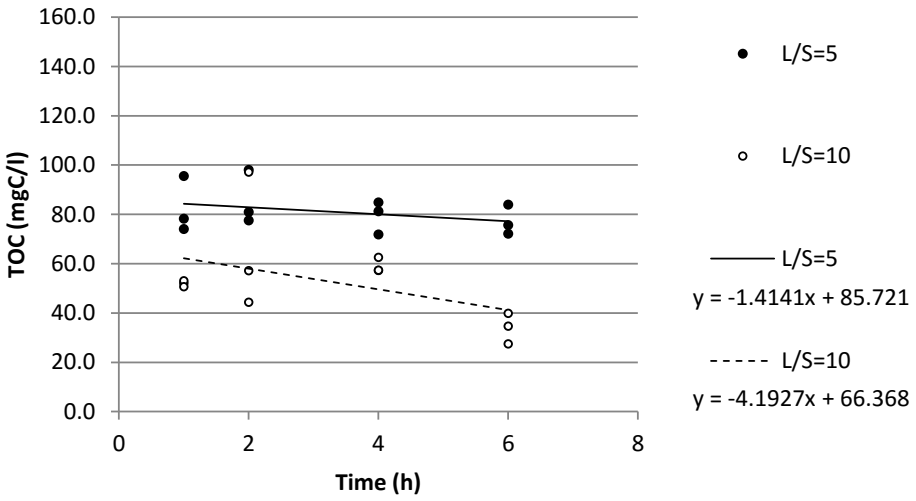

Fig. 5.20: TOC values of waste matrix E from leaching tests under different operative conditions.

5.2. Statistical analysis

To know if the indices measured on the eluate were really affected by the leaching test conditions, a statistical analysis of the data was performed, although triplets of data were a poor basis to represent significant statistical samples. The aim was to understand if the values of COD, BOD_5 and TOC statistically change as increasing the contact time and how this factor and the liquid to solid ratio influences the BOD_5/COD parameter. Three kinds of statistical tests were used, whose results are discussed hereafter.

5.2.1. One-way analysis of variance

To check the effects of using different contact times, the ANOVA (ANalysis Of VAriance) was exploited. The test was carried out by fixing the liquid to solid ratio to 5 or 10, assuming each time a new variable among COD, BOD_5, TOC and BOD_5/COD. In all the cases four independent samples of three data were available, characterized by diverse contact times (1, 2, 4 or 6 h) and by the same L/S. The populations from which the samples were ideally extracted were supposed to be normally distributed with equal variances.

The problem was to understand if the difference among the means of the samples was significant, i.e. if it indicated an actual diversity of the four populations from which the samples were extracted or it fell within the normal variability of the sample means of a same population; in the latter case the differences may be attributed to casual fluctuations. The aim was to prove, through the sample means, the zero hypothesis:

H_0: $\mu_1 = \mu_2 = \mu_3 = \mu_4$

against the alternative hypothesis that some μ_i were different:

H_1: $\mu_i \neq \mu_j$ for some i and j.

It was fixed a significance level α=0.05. In Table 5.6 are shown the results of the one-way ANOVA; when the p-value is <0.05, the zero hypothesis cannot be accepted, meaning that the four means are statistically different.

It is possible to see that the best results were obtained for TOC. It can be noticed also that the zero hypothesis results verified in more cases for L/S=10. In nearly half of the cases the zero hypothesis should be rejected.

If the averages had resulted statistically equal, this would have meant that the release of substances into the liquid would be the same for any contact time between 1 hour and 6 hours. However, although in many cases the mean values seem statistically different, this is not sufficient to conclude that a longer test duration necessarily causes a higher release.

Table 5.6: p-values obtained from the one-way analysis of variance to test the influence of the leaching test duration on the BOD_5/COD index, for a fixed L/S ratio. The underlined values are those for which the zero hypothesis can be accepted.

	L/S	COD	BOD_5	TOC	BOD_5/COD
A	5	0.014	2.4E-04	0.079	0.001
	10	0.063	0.513	0.017	0.099
B	5	0.002	0.002	1.4E-04	0.032
	10	0.008	0.126	0.147	0.772
C	5	0.025	0.002	0.102	0.042
	10	0.594	0.049	0.153	0.688
D	5	0.043	0.001	0.316	0.013
	10	0.280	2.7E-04	0.797	1.8E-04
E	5	0.603	0.984	0.706	0.724
	10	0.025	0.280	0.106	0.179

5.2.2. t - test

To evaluate the effects of the liquid to solid ratio on BOD_5/COD index, a t-test was carried out. In fact in this case the factor had only two levels (L/S = 5 or 10), therefore only two groups of data had to be compared, fixing each time a different duration of the leaching test. The aim was to establish if the means of the two populations were statistically equal (zero hypothesis). A significance level α of 0.05 was fixed. In Table 5.7 are visible the p-values obtained.

Table 5.7: p-values obtained with the t-Test to analyse the influence of the liquid to solid ratio (L/S) on the BOD_5/COD index, for a fixed leaching test duration. The underlined values are those for which the zero hypothesis can be accepted.

Duration (h)	A	B	C	D	E
1	0.089	0.055	0.301	0.004	0.271
2	0.317	0.980	0.710	0.136	0.278
4	0.002	0.230	0.756	0.362	0.388
6	0.465	0.118	0.760	0.687	0.916

It is possible to see that nearly all the p-values are greater than 0.05, thus the hypothesis of equality between the averages can be accepted. It could be concluded that the liquid to solid ratio

does not affect the results of the leaching tests; nevertheless, also this conclusion is based on small statistical samples and further data are advisable to confirm the finding.

5.2.3. Two-way analysis of variance

The statistical significance of the BOD_5/COD values was also checked by means of a two-way ANOVA at 5% level of probability. The test was done on the usual two experimental factors:

- a: contact time at 4 levels (1, 2, 4, 6 h);
- b: liquid to solid ratio at 2 levels (5, 10 l/kgTS).

For each combination of levels, three observations were available. The objective of the two-way analysis was to calculate the probability with which the variable BOD_5/COD was affected by the factors. The following zero hypothesis were subjected to verification at a significance level $\alpha=0.05$:

- H_0^a: all the means of the groups of data characterized by the same liquid to solid ratio are equal, meaning that the response does not depend on the contact time factor;
- H_0^b: all the means of the groups of data characterized by the same leaching test duration are equal, meaning that the response does not depend on the L/S factor;
- H_0^*: there are no interactions between the two factors (a and b).

The three hypothesis could be accepted if the relative p-values were >0.05. In Table 5.8 are visible the p-values calculated with the two-way ANOVA. The analysis revealed that both contact time and L/S ratio seem to affect the BOD_5/COD index (at $p < 0.05$), excepted for waste C and E. The two-way ANOVA also showed that the BOD_5/COD is influenced to a much greater extent by the duration factor than by the L/S factor; this occurs for waste A and D, but not for matrix B, whose BOD_5/COD ratio is more affected by the L/S factor.

For nearly all the wastes, at a significance level of 5%, it was judged non significant the interaction between the two factors; this means that contact time and L/S play independent roles.

Table 5.8: p-values resulting from the two-way analysis of variance. The underlined values are those for which the zero hypothesis can be accepted.

	A	B	C	D	E
Influence of time	0.001	0.022	<u>0.072</u>	5.5E-05	<u>0.450</u>
Influence of L/S	0.002	0.007	<u>0.858</u>	0.031	<u>0.935</u>
Interaction	<u>0.673</u>	<u>0.167</u>	<u>0.760</u>	6.7E-05	<u>0.143</u>

5.2.4. Conclusions

The statistical tests were implemented with the objective of helping in the interpretation of the results. However, this analysis was limited by the amounts of data, that were small to represent significant statistical samples. Thus, it was judged not very useful for drawing substantial conclusions. For this reason, the considerations reported in Chapter 4 did not take into account the findings obtained with the statistical analysis.

Further investigations on the waste samples are necessary; they would allow to increase the number of data for a better statistical analysis, in order to confirm or refute the findings.

5.3. Respirometric index

From Fig. 5.21 to Fig. 5.24 are shown the respiration activities of the samples over time in terms of mgO_2/gTS, measured with the Sapromat device. Each material has been examined three times. From Table 5.9 to Table 5.12 are reported the values of the respirometric index after 4 and 7 days. The final result characterizing each waste matrix is the average of the three values obtained.

As already discussed, waste A presents a lower RI than waste B, due the decrease of the content of microorganisms in the sample caused by the shredding procedure. It is possible to see that the difference between the two respiration activities is larger at the beginning and diminishes at the end of the test. As noticed by Binner et al. (1997), the effects of different sample processing get less significant with rising test duration. In this case, a reason for that might be the different lag period, longer for samples A for the regrowth of the microbiological flora.

In Fig. 5.25 are reported the average curves of all the waste matrices to have an idea of the different respiration activities.

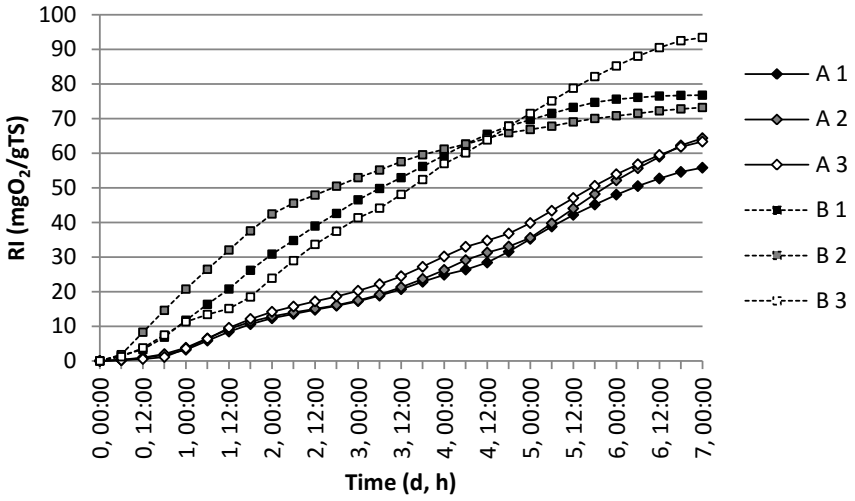

Fig. 5.21: Respiration activity measured in triplicate for waste A (shredded) and B (unaltered) on solid samples.

Table 5.9: Respirometric Index (RI) after 4 and 7 days of the three samples analysed for waste A and B, respectively shredded and unaltered (residual solid waste after separate collection, mechanically pretreated < 60 mm).

	RI_4		**RI_7**	
Sample	mgO_2/gTS	mgO_2/gVS	mgO_2/gTS	mgO_2/gVS
A1	24.9	51.9	55.8	116.3
A2	26.3	54.8	64.3	134.0
A3	30.2	62.9	63.3	131.9
Average	**27.1**	**56.5**	**61.1**	**127.4**
B1	59.4	88.0	76.7	113.6
B2	61.1	90.5	73.2	108.4
B3	57.0	84.4	93.4	138.4
Average	**59.2**	**87.7**	**81.1**	**120.1**

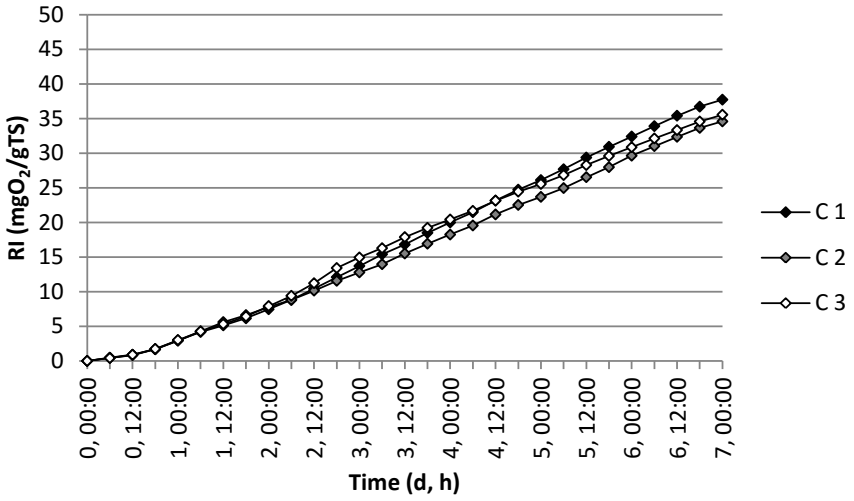

Fig. 5.22: Respiration activity measured in triplicate for waste C on solid samples.

Table 5.10: Respirometric Index (RI) after 4 and 7 days of the three samples analysed for waste C (aerobically stabilized MBT undersieve < 50 mm).

	RI_4		**RI_7**	
Sample	mgO_2/gTS	mgO_2/gVS	mgO_2/gTS	mgO_2/gVS
C1	20.0	43.0	37.7	81.1
C2	18.2	39.1	34.6	74.4
C3	20.4	43.9	35.5	76.3
Average	**19.5**	**42.0**	**35.9**	**77.3**

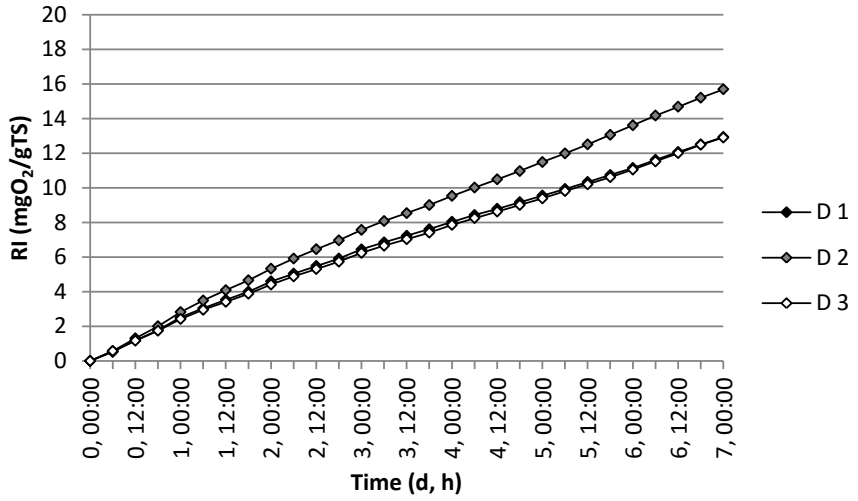

Fig. 5.23: Respiration activity measured in triplicate for waste D on solid samples.

Table 5.11: Respirometric Index (RI) after 4 and 7 days of the three samples analysed for waste D (compost of anaerobic digestate of MSW putrescible fraction undersieve < 50 mm).

	RI_4		**RI_7**	
Sample	mgO_2/gTS	mgO_2/gVS	mgO_2/gTS	mgO_2/gVS
D1	8.0	15.4	12.9	24.8
D2	9.5	18.3	15.7	30.2
D3	7.8	15.0	12.9	24.8
Average	**7.9**	**15.2**	**12.9**	**24.8**

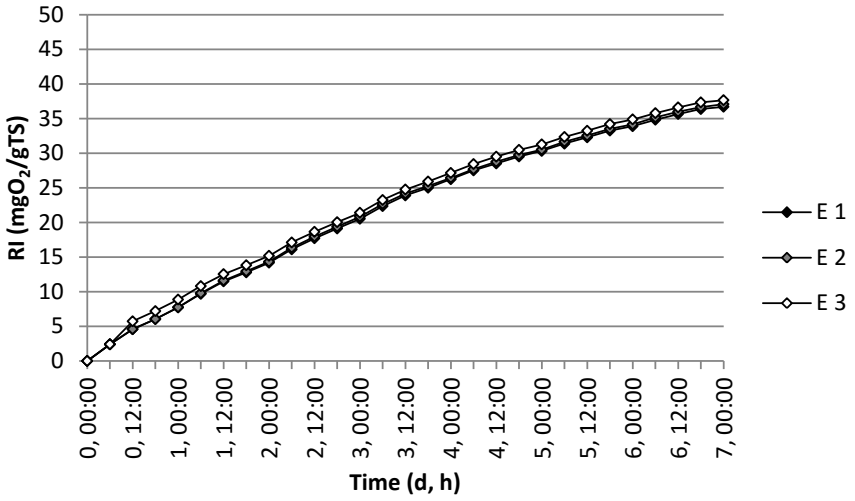

Fig. 5.24: Respiration activity measured in triplicate for waste E on solid samples.

Table 5.12: Respirometric Index (RI) after 4 and 7 days of the three samples analysed for waste E (dried sludge from municipal wastewater treatment).

	RI_4		**RI_7**	
Sample	mgO_2/gTS	mgO_2/gVS	mgO_2/gTS	mgO_2/gVS
E1	26.2	59.5	36.7	83.4
E2	26.4	60.0	37.1	84.3
E3	27.1	61.6	37.6	85.5
Average	**26.6**	**60.6**	**37.1**	**84.4**

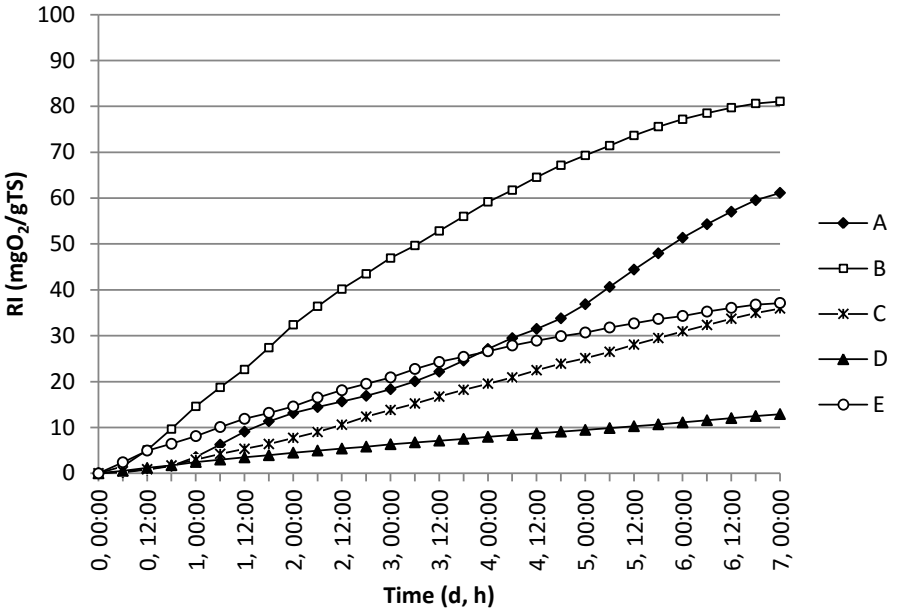

Fig. 5.25: Average respiration activity of the five waste matrices.

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