CHAPTER 1: LITERATURE REVIEW

The chapter briefly reviews solid waste characteristics, methods of solid waste disposal, mechanisms involved in anaerobic bioreactor landfills, Landfill stability parameters and effect of liquid waste addition on degradation of landfill components.

1.1 Solid waste- need for management:

The term solid waste is general and many agencies have defined it in different ways. In the Resource Conservation and Recovery Act (RCRA) the term solid waste is defined as "any solid, semi-solid, liquid, or contained gaseous materials discarded from industrial, commercial, mining, or agricultural operations and from community activities. Solid waste also includes food waste, construction debris, commercial refuse, sludge from water supply or waste treatment plants, or air pollution control facilities, and other discarded materials." (US EPA, 2001) The management of solid waste is a challenge both to industry and researchers because of the material variety and quantity.

The US EPA (2005) estimates that 245 million tons of waste was generated in the year 2005 which is approximately 4.5 pounds waste per capita per day. A critical analysis of constituents of Municipal Solid Waste (MSW) shown in Figure 1 can be used to develop new alternatives for waste management.

The US EPA has proposed the following solid waste management practices to mitigate the waste disposal problem:

Source reduction: manufacture and use of materials which are of lower quantity and less toxic when disposed

Recycling: processing products like plastics which can be recycled and used for making goods.

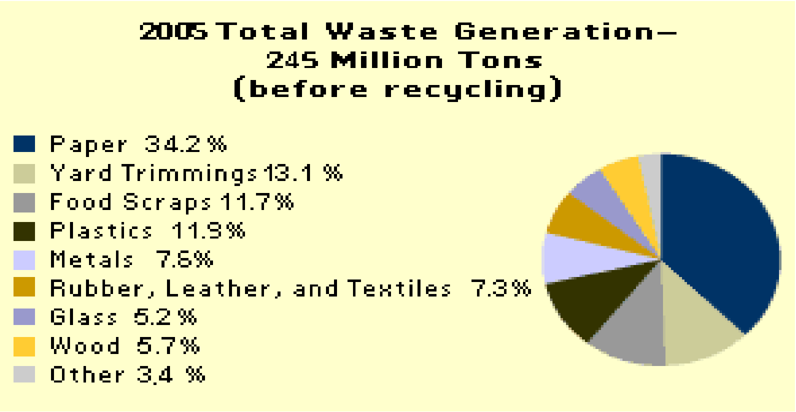


Figure 1.1 Constituents of municipal solid waste (adopted from US EPA 2005)

Composting: preparation of compost from solid waste components such as yard trimmings using microorganisms.

Landfills: MSW is allowed to stabilize in the landfill with an impermeable membrane to avoid ground water contamination and monitoring is conducted to insure that contamination does not occur.

Incineration: This involves combusting MSW to reduce the volume and usually to generate electricity.

Landfill technology has been proven successful for household hazardous wastes which cannot be processed in any other method.

1.2 Landfill technology as an option for solid waste disposal:

There have been some problems associated with the landfills in the past, but the present generation of landfills constructed under US EPA guidelines provides an opportunity for the safe disposal of the MSW. About 54.3 % of the total U.S waste was disposed in landfills in 2005 (US EPA, 2005). The number of landfills has decreased over the years, but the size of landfills has increased which not only gives the advantage of accommodating more waste, but also increases the ease of monitoring. Bioreactor landfills were adopted to decrease the time of degradation by increasing the moisture content of the waste. Shi, et al. (2007) have shown that solid waste obtained from an old landfill had good biodegradability when analyzed under bioreactor conditions. Liquid waste addition to bioreactor landfills is allowed under the RD&D rule in RCRA (Novak, 2006). Commercial liquids and sludges which do not pass the paint filter test are accepted by different landfills to increase the moisture content in the bioreactor landfill for improved performance.

The further classification of bioreactor landfills and their advantages and disadvantages are discussed below.

1.3 Bioreactor landfill:

The Solid Waste Association of North America (SWANA) has defined a bioreactor landfill as "any permitted Subtitle D landfill or landfill cell where liquid or air is injected in a controlled fashion into the waste mass in order to accelerate or enhance biostabilization of the waste"(US EPA, 2003). The major reason for faster degradation of waste in a bioreactor landfill is due to enhanced hydrolysis (Zang, et al. 2007) which makes the substrates available to the microbial consortia. A moisture content above 40 % (Bagchi, 2004) is achieved using lecheate recirculation (Kelly, 2006; Kelly, et al. 2004; Han and Shin, 2002; Nguyen, et al. 2007; Sponza and Agdag, 2004), however recirculation without enough moisture will not result in enhanced degradation (U.S.EPA, 2003). The advantages of the bioreactor landfill also include earlier gas generation, quicker stabilization of leachate, enhanced landfill gas generation and quicker settlement (US EPA, 2003). A comparison of bioreactor and conventional landfills with respect to gas generation is shown in figure 1.2.

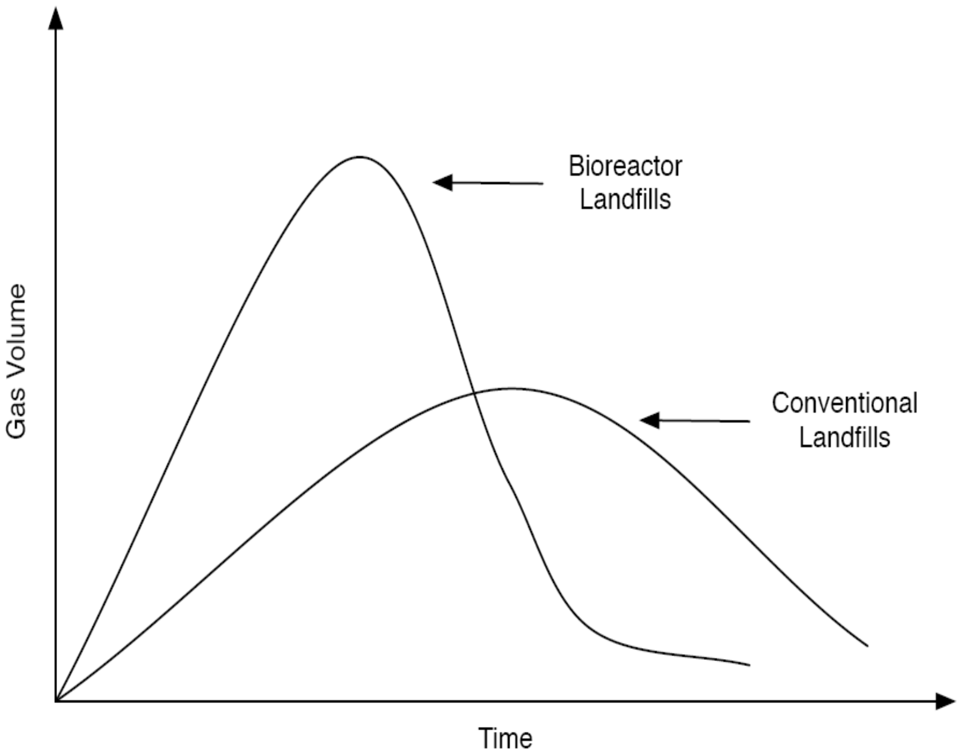


Figure 1.2 Comparison between bioreactor and conventional landfill settlement (adopted from Bagchi 2004)

Bioreactor landfills are classified into Aerobic, Anaerobic, and Mixed.

1.3.1 Aerobic: Aerobic conditions are maintained in the landfill by air injection and lecheate recirculation. The main advantage of these landfills is rapid stabilization of waste based on the fact that aerobic bacteria grow faster. The odors produced by the aerobic reactors are not foul. However, Powell, et al.(2006) have shown that air injection to a landfill results in a decrease in the concentrations of methane and carbon dioxide leading to increased hydrogen sulfide concentration. Proper maintenance of aerobic reactors is required to avoid fire hazards (WM, 2000).

1.3.2 Anaerobic: The degradation of the waste is carried out by anaerobic bacteria. Compared to the aerobic bioreactors, the degradation rate in anaerobic bioreactors is slow. The production of landfill gas from these landfills has drawn considerable attention due the energy conversion ability of methane to generate electricity. However, there is also concern about methane as a greenhouse gas. The initial investment required to set up these landfills is very high.

1.3.3 Hybrid: The hybrid bioreactor consists of lower anaerobic conditions and upper aerobic conditions which can capture the advantages of both aerobic and anaerobic bioreactors.

1.4 Microbiological mechanisms in anaerobic landfills

As mentioned earlier the basic degradation mechanism in anaerobic landfills is anaerobic digestion by a mixed culture of anaerobic and facultative organisms. The primary step of the degradation process in an anaerobic landfill is hydrolysis in which complex insoluble organics are hydrolyzed by extracellular enzymes. The increased moisture content will increase the rate of hydrolysis hence the bioreactor landfills were found to be efficient in performance in terms of rapid degradation and enhanced methane generation (EMCON ASC., 1980). Hydrolysis will reduce the size of the organic molecules which will increase movement of material across bacterial cell membranes (Grady, et al. 1999). The complex organic compounds are degraded to aromatic monomers, carbohydrates, lipids and long chain fatty acids in the primary phase. In the secondary phase these compounds are reduced to volatile fatty acids like acetic, propionic, butyric, iso-butyric, valeric, isovaleric, heptanoic and hexanoic acids (Grady, et al. 1999; Senior, 1990, EMCON ASC., 1980) which can be seen by an increase in volatile fatty acids (VFA) in the leachate. The VFAs are converted to acetic acid by acetogenesis which is carried out by acetogenic bacteria. Methanogens reduce the acetic acid to methane and carbon dioxide (Senior, et al. 1987, EMCON ASC., 1980)

The VFA accumulation results in variation in the pH over time. A pH in the range of 6.8-7.4 is found to be favorable for methanogenic bacteria (Reinhart and Townsend, 1998). Addition of certain wastes has been shown to cause a sudden drop in pH because of rapid accumulation of VFAs and hence buffering and leachate recirculation have been adopted to counter this problem. Initial buffering has shown considerable effect on the overall performance of degradation of waste in anaerobic landfills. The temperature has also been of considerable importance in survival of the methanogenic bacteria (Reinhart and Townsend, 1998).

1.5 Substrates available for degradation:

The primary substrates available in the landfill are readily degradable organic molecules from sources such as food wastes. The secondary substrates are complex organic molecules which are degraded by facultative bacteria upon hydrolytic transformation using extracellular enzymes. Some of the complex organic substances are lignocelluloses, polysaccharides, fat containing organic molecules and proteins. Paper and newsprint have been shown to have considerable lignin content. The effect of liquid waste addition in degradation of lignocelluloses has been studied and is discussed in detail in the following paragraphs.

1.5.1 Major organic carbon sources in refuse:

The major biodegradable polymeric constituents present in solid waste or refuse are classified into four classes, lignocelluloses, polysaccharides, fat-containing organic molecules and proteins.

The lignocelluloses are comprised of lignin, hemicellulose and cellulose. The composition of lignocellulose cannot be described accurately because the composition varies with the specific material under consideration. Dry wood consists of 89-98% of lignocellulose by weight (Colberg, 1988).

1.5.1.1 Lignin

Lignin is considered the most abundant biopolymer after cellulose and hemicellulose. Wood tissues contain 18-30% of dry weight as lignin in the primary, secondary cell walls and middle lamella. The structure of lignin consists of p-hydroxycinnamyl alcohols; coniferyl, p-counmaryl and sinapyl polymerized with each other. The β-aryl ether bond and C-C bonds and binphenyl linkages have been studied in the structure of lignin which might be a reason for its slow degradation in landfill sites (Senior, 1990). A study by Kim (2004) has shown evidence of degradation of lignin and research work by Miroshnikova(2006) has proved that lignin degrades under high temperatures to its monomers.

1.5.1.2 Hemicellulose

The hemicelluloses are present in primary and secondary cell walls and endosperm of certain seeds up to a maximum of 50 % (w/w). Hemicelluloses are a combination of pentoses or hexoses with uronic acids of glucose and galactose. The pentoses identified were L-arabinose, D-xylose while the hexoses identified were D-glucose, D-mannose and D-galactose. Galactans were most resistant hemicelluloses identified among xylans, mannans and galactans, which present in lignified tissue. (Senior 1990)

1.5.1.3 Cellulose

Cellulose is the most abundant polymer on earth and significant portions of solid waste contain cellulose. It constitutes for 35-45% of the woody tissues. Analysis of the cellulose structure shows anhydro-D-glucopyranose units linked by β-D-(1-4) glucosidic bonds.

The fact that lignocelluloses are subject to biodegradation in bioreactor landfills is well documented. The primary focus of the operation of bioreactor anaerobic landfills has been to enhance the methane production and reduction of methane emissions. Methane has been found to be 25 times more harmful than carbon dioxide with respect to green house emissions. The table 1.5 illustrates the biomethane potential of degradable sources in landfill. Biomethane potential is an indicator of landfill gas production and stabilization time.

Degradable Source	**% dry weight**	**Biomethane potential**
Cellulose	51.2	73.4
Hemicelloses	11.9	17.1
Protein	4.2	8.3
Lignin	15.2	0
Starch	0.5	0.7
Pectin	<3.0	-
Soluble sugars	0.35	0.5

Table 1.1 Biochemical Methane potential of different constituents of Municipal Solid Waste (adopted from Bagchi 2004)

1.6 Stages of degradation in anaerobic bioreactor landfill

The stages of degradation in an anaerobic landfill can be classified into 5 phases characterized by changes in the quantity and quality of different gas emissions (Figure 1.6) (WM, 2000; Barlaz, et al. 1989; Tchobanoglous, et al. 1993).

Phase I is characterized by consumption of oxygen and accumulation of moisture as aerobic degradation is faster. Methanogens are very sensitive to oxygen and do not flourish at this stage. Methane is formed at this stage. Ammonia is the major component of gas emitted by degradation of organic nitrogen.

In Phase II, oxygen is consumed. The moisture content increases as a result of aerobic respiration and the aerobic phase transitions to an anaerobic phase. The gas emitted in this phase is primarily composed nitrogen and hydrogen sulfide because of the presence of nitrate and sulfate as terminal electron acceptors.

In phase III, the volatile fatty acids generated by degradation of aromatic monomers, carbohydrates and sugars are decomposed to acetic acid by acetogenesis. The pH drops due to rapid consumption of substrates which results in accumulation of VFAs and the leachate is characterized by highly soluble organic compounds hence increasing the COD levels (Reinhart and Townsend, 1998).

Phase IV is of most interest because of the generation of methane and carbon dioxide which is mainly produced by the methanogenic organisms. Due to the conversion of the acetic acid to methane, the pH is increased to 7 or above in this phases (Young, 1995). If the amount of methanogenesis is less than acetic acid generation, an acidic environment is produced. Under acetic conditions, methanogenic organisms are inhibited. The acetogens are not as robust as other organisms in landfills (Young, 1995). The leachate in this phase is characterized by a carbonate buffer system which restores neutral pH.

Phase V is the final stage of degradation in which residues of organic matter are degraded. The rate of methane and carbon dioxide production decreases due to a decrease in the organic matter in leachate and waste. The degradation of waste reaches a mature stage in this phase.

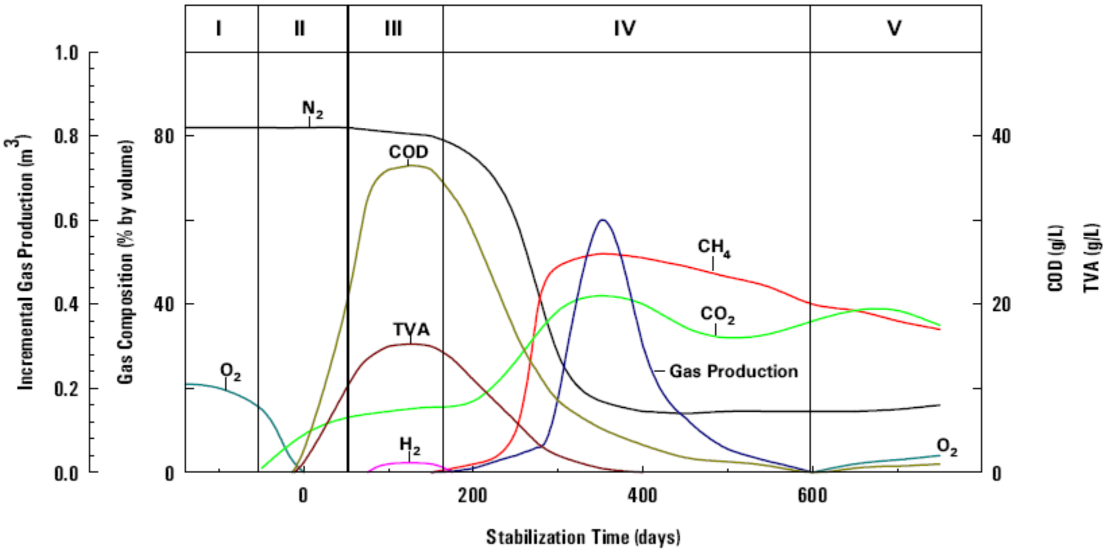


Figure 1.3 Different phases of an anaerobic landfill (adopted from WM, 2000; Pohland, 1986)

1.7 Indicators of landfill stability:

There are no agreed upon indicators of landfill stability. The extent of degradation and stabilization parameters have not been precisely defined (Kelly, et al. 2006), but research has shown that concentrations of lignin, lignin monomers, cellulose and hemicelluloses can indicate the extent of waste degradation. Parameters like the cellulose/lignin (C/L) ratio, cellulose/plastic ratio, volatile solids and biomethane potential (BMP) also give a rough estimate of the stability of waste. The above parameters and their implications on the stability of waste are discussed below.

1.7.1 Lignin

The degradation rate of lignin is very slow (Kelly, 2002) because of its complex structure. However, recent studies have shown that lignin does degrade under anaerobic conditions (Kim, 2004) and elevated temperatures (Miroshnikova, 2006). The measurement of lignin in waste containing plastic is not accurate (Kelly, et al. 2006) because plastic is included in the lignin measurement. The degradation of lignin results in formation of secondary substrates which are eventually converted to VFAs. Komilis and Ham (2003) have shown a reasonable correlation of lignin degradation and volatile solids reduction.

1.7.2 Lignin Monomers

The complex lignin structure when degraded results in compounds such as benzoic acid, syringic acid, catechol, vanillic acid, ferulic acid (Young and Frazer, 1987). The presence of lignin monomers is an indication of the degradation of lignin, and hence the waste.

1.7.3 Cellulose and Hemicelluloses:

Cellulose and hemicelluloses are the most common biopolymers present on earth. These constituents are predominantly present in solid waste so measurement of cellulose and hemicelluloses can give an estimate on extent of degradation of waste. Research by Kelly et al. (2002) has shown that the cellulose content can be reduced to as low as 2-5%. Cellulose degradation up to 91.1% has been identified as complete stabilization by Komilis, et al. (2003). Hemicellulose is an intermediate product obtained in anaerobic degradation of cellulose so determination of hemicellulose concentration indicates the degradation of cellulose (Kim, 2004).

1.7.4 Cellulose /Lignin (C/L) ratio:

Because the degradation of lignin is very slow, a comparison of the C/L ratio serves as a parameter to evaluate the degradation of cellulose in solid waste. The fresh and mature wastes in landfill can be distinguished using the C/L ratio. A decrease in C/L ratio was identified as a sign of increased stability (Komilis and Ham, 2003). A C/L ratio of 4.04 for fresh solid waste was reported to decrease to a value as low as 0.8 upon maturity. Kim (2004) reported that lignin is degradable so a better standard than lignin would serve as a better indicator than C/L ratio. Plastics were found to resist degradation so the C/P ratio would be more appropriate indicator; however measurement of plastics was found to be tedious since it requires hand removal and weighing of plastics (Vellatt, 2007).

1.7.5 Volatile Solids (VS):

Volatile solids represent the volatile fraction of solid waste. The measurement of VS serves as a good indicator of landfill stability (Kelly, 2002). The main advantage of the measurement of VS lies in the ease of measurement. The presence of plastics in the sample might result in some uncertainty of VS measurement (Kelly, 2002; Kelly, et al. 2006). The VS content in stabilized landfill material is measured to be 10-20% (Kelly, 2002).

1.7.6 Biomethane potential:

The biomethane potential (BMP) of different components of the landfill were mentioned earlier, BMP may be considered as anaerobic equivalent to BOD (Kelly, et al. 2006). The methane generation from municipal solid waste can be quantified by the BMP measurement (Kelly, et al. 2006). The BMP measurement can be a supplement to other stability indicators (Kelly, et al. 2006), however the BMP and VS do not correlate well, most likely because the BMP measurement is highly variable (Kelly, et al. 2006). A BMP of 10-20 ml/g was found for stabilized landfills (Kelly, 2002).

1.8 Effect of liquid waste addition in degradation of landfill constituents:

Having defined the constituents and their degradation in anaerobic bioreactor landfills, the effects of addition of certain liquid wastes to an anaerobic landfill are discussed. The effect of addition of distillation waste, surfactant waste and paint waste are discussed in detail.

1.8.1 Distillation waste:

The distillation of ethyl alcohol from sugarcane, beet and flower extracts has been extensively used to produce ethane. Wine production also generates waste similar in composition. The sugar beet waste is comprised of lignocellulosic material after extraction of sugar (Almudena, et al. 2006). An increase in the quantity of distillation wastes has created a problem with its treatment since only 40% of the organic material is converted to the desired product and the remaining material ends up in the waste (Leon, et al. 2006). The disposal of these liquid wastes into landfills will reduce the burden of additional treatment and provide additional moisture content for bioreactor landfills. Research on the effect of the addition of distillation waste to an anaerobic bioreactor landfill is lacking.

As mentioned earlier, sugars are the secondary substrates formed upon degradation of the complex molecules so the next immediate step in the degradation of the sugars is the formation of the fatty acids. Hence addition of distillation waste to an anaerobic bioreactor landfill might result in rapid acidification due to rapid accumulation of fatty acids. This may result in unbalanced digestion (Huntan, et al. 2000; Veeken, et al. 2000; Boualgui, et al. 2005, Vellatt, 2007). If favorable conditions exist then the fatty acids can be further degraded and as a result, the addition of distillation waste will enhance the performance of the anaerobic bioreactor landfill and increase in the methane gas produced (Knol, et al. 1978; Huntan, et al. 2000) and the volatile solids concentration in the waste can be reduced drastically (Knol, et al 1978).

The degradation of sugars to fatty acids and further degradation to acetic acid might be very rapid, but if the next step of methanogenesis is not as rapid as acetogenesis then the resulting conditions would be unfavorable for the formation of methane and inhibit the hydrolysis of the organic matter (Hutnan, et al. 2000; Veeken, et al. 2000; Bouallagui, et al. 2005).

1.8.2 Surfactant waste:

Surfactants are used widely in various applications such as in the clean up of petroleum product spills. Surfactants have been reported to be in use in the textile industry, metal processing industry etc. The global market for surfactants is reported to be 1.2 billion dollar (Porter, 1994). Slaxk, et al. (2005) report surfactants could have considerable effect on landfills if accepted as a waste. The effect would be specific to type of surfactant used (Kjeldsen, et al. 2002). If the concentration of surfactant exceeds a particular level, this might result in inhibition of biological activity (Pennel, et al. 2002). The inhibition might be attributed to prevention of transport of nutrients into the cells (Gavala and Ahring 2002). Vellatt (2007) has shown high concentrations of surfactants result in inhibition of degradation, hence influencing methanogenesis (Riediker, et al. 2000). Surfactants that are anionic in nature have been shown to enhance biological activity rather than cationic ones (Scherbakova, et al. 1999). Anionic surfactants of this kind include sodium lauryl sulfate and salts of alkyl benzene sulfonates. The straight alkyl chains have been shown to be used by bacterial group as source for growth (Anderson, 1964).

1.8.3 Paint waste:

Paint contains numerous chemical compounds which are mixed with thinners or solvents, mainly petroleum products such as kerosene, xylene, acetone, ketones. Paint waste may contain hazardous compounds like chlorinated solvents (Kaelin, 1999). The manufacturers of paint are recommended to determine if the waste generated is hazardous (USEPA, 2002). One reason for generation of paint waste might be the excessive preparation of paint beyond that required (Kaelin, 1999).

The effect of a paint waste on a landfill will be dependent on the concentration of the constituents of the paint (Lambolez, et al. 1994). The exposure to paint waste by humans has resulted in health hazards such as Wilms' tumor (Tsai, et al. 2006). The leachate generated from landfills accepting the paint waste is sometimes found to be toxic (Lambolez, et al. 1994; Vaajasaari, et al. 2004). The presence of formaldehyde in the landfill samples might result in inhibition of biological activity (Vaajasaari, et al. 2004) and degradation could be retarded due to the inhibition in the biological activity. Organisms which were reported to be affected by leachate from landfills receiving paint waste were algae and photobacterium etc (Lambolez, et al. 1994). The research findings regarding the effect of paint wastes and the reason for inhibition of biological activity and toxicity are yet to be consolidated.

In summary, three types of liquid wastes, distillation waste, surfactant waste and paint waste are added to landfill. All may impact landfill bioreactors, but the concerntrations at which they are detrimental are not known. This research has been conducted to evaluate the impact these waste.

CHAPTER 2: EFFECT OF LIQUID WASTE ADDITION TO AN ANAEROBIC

BIOREACTOR LANDFILL

2.1 Introduction:

Waste minimization has been the primary focus of EPA and the bioreactor landfill has emerged as a prospective option to stabilize solid waste. Increased moisture content has been the key to successful operation of bioreactor landfills (WM, 2000). The acceptance of liquid wastes by bioreactor landfills has become a tool for landfill operators to use to maintain the moisture content and it also serves as a means of waste disposal for liquid waste generators. The Outerloop bioreactor landfill, Kentucky is reported to accept different liquid wastes (Novak, 2006). However, the effect of waste such as distillation waste, paint waste and surfactant wastes on overall landfill performance in particular is not well known.

Previous research by Vellatt (2007) has shown that the performance of reactors containing distillation, paint and surfactant wastes was not appreciable compared to the control reactors. Sugar waste or distillation waste addition in substantial amounts to an anaerobic landfill resulted in an increase in the volatile fatty acid production due to unbalanced digestion (Huntan, et al. 2000), which can accumulate and drop the pH, resulting in a decrease in anaerobic activity. Paint waste addition has shown some inhibition to methanogenesis in the reactors and this was thought to be due to the presence of toxic compounds in the waste (Vaajasaari, et al. 2004). The surfactant waste at a 250 mg/L concentration was shown to have an inhibitory effect. (Vellatt, 2007)

This research was designed to further investigate the problems encountered by the sudden pH drop in the distillation waste reactors, the strong inhibition in paint waste reactors and decreased performance of the surfactant waste reactors. An attempt was made to increase the initial buffer capacity by adding sodium bicarbonate at a concentration of 3000 mg/L and ammonium chloride at a concentration of 2000 mg/L. A significant amount of ferrous sulfate, up to 50 mg/L, was also added to enhance the growth conditions of the initial microorganism culture.

The pH, volatile solids, total solids, methane, carbon dioxide and total gas generation were measured. The lignin, cellulose and hemicellulose content were measured on a percentage basis. The leachate was analyzed for volatile fatty acids.

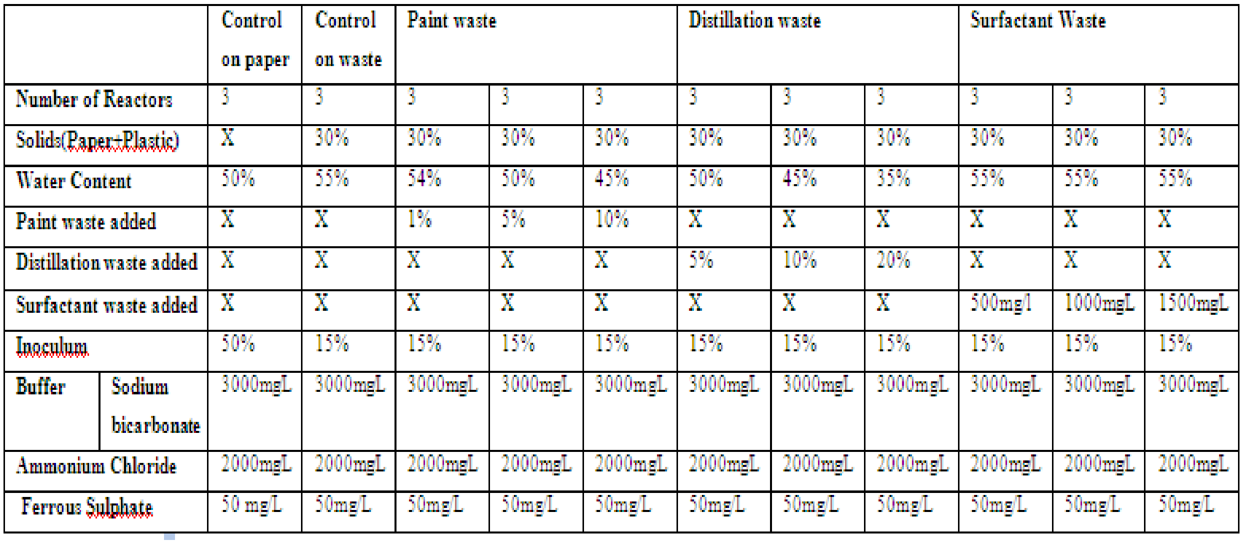
2.2 Materials and Methods:

2.2.1 Experimental Design:

The experimental study was performed on 3 types of liquid wastes, paint, surfactant and distillation wastes. The reactors were set up in triplicate by mixing the synthetic landfill with the liquid wastes in 3 different concentrations. The moisture content in the reactors was kept at 70% which includes the liquid wastes that were added. Two triplicate sets of reactors were set up as controls on paper and liquid waste. The control for the liquid waste had no liquid waste added while the control on the synthetic landfill material had no paper added.

The synthetic landfill material was a mixture of newspaper, cardboard and office paper. The selection was based on the fact that paper constitutes 30% of the landfill materials (US EPA 2005). The solids constituted for 30% by weight of the reactor while the liquids constituted 70% by weight. The 30% solids includes 10% plastic and the proportions in which the papers were added were 50% newspaper, 25% office paper and 25% cardboard. Fifteen percent of the total weight contained sludge as a source of inoculum which was included in 70% liquid fraction.

The different concentrations adopted for the distillation waste were 5, 10 and 20% by weight from a waste source provided by Waste Management, Inc. For paint waste, these were 1, 5 and 10% while surfactant waste was added at 500, 1000, 1500mg/L of the liquid added to the reactor. The wastes were added to distilled water and the moisture content was maintained at 70% of the total weight of the reactor. The liquid fraction was buffered with sodium bicarbonate; ammonium chloride and ferrous sulfate were added to the microorganism consortia at concentrations of 3000, 2000, 50 mg/L, respectively. The wastes and the inoculum added were considered as liquids and the solids present in them were not taken into consideration. The experimental matrix designed is shown in the Table 2.1.



	Control on paper	Control on waste	Paint waste			Distillation waste			Surfactant Waste		
Number of Reactors	3	3	3	3	3	3	3	3	3	3	3
Solids(Paper+Plastic)	X	30%	30%	30%	30%	30%	30%	30%	30%	30%	30%
Water Content	50%	55%	54%	50%	45%	50%	45%	35%	55%	55%	55%
Paint waste added	X	X	1%	5%	10%	X	X	X	X	X	X
Distillation waste added	X	X	X	X	X	5%	10%	20%	X	X	X
Surfactant waste added	X	X	X	X	X	X	X	X	500mg/l	1000mgL	1500mgL
Inoculum	50%	15%	15%	15%	15%	15%	15%	15%	15%	15%	15%
Buffer Sodium bicarbonate	3000mgL	3000mgL	3000mgL	3000mgL	3000mgL	3000mgL	3000mgL	3000mgL	3000mgL	3000mgL	3000mgL
Ammonium Chloride	2000mgL	2000mgL	2000mgL	2000mgL	2000mgL	2000mgL	2000mgL	2000mgL	2000mgL	2000mgL	2000mgL
Ferrous Sulphate	50 mg/L	50mg/L	50mg/L	50mg/L	50mg/L	50mg/L	50mg/L	50mg/L	50mg/L	50mg/L	50mg/L

Table 2.1 Experimental matrix

The setup of reactors was carried out in the glove box in which anaerobic conditions were maintained by ultra pure nitrogen gas. After the reactors were filled with the mixture of synthetic landfill and wastes the lids were sealed using a pipe joint compound and insulation tape to make sure no air intrusion took place. The reactors were connected to a 5 L Tedlar bag for collection of gas emitted from the reactor. Each reactor was checked to make sure no leaks were present and these were then incubated at 37^0 C. Samplings were done once every 20 days and the analyzed.

2.3 Materials:

2.3.1 Reactor:

To account for the corrosive environment during the anaerobic digestion of the solid waste 1L PTFE Nalgene bottles from Fisher scientific were selected as reactors. The gas bags of 5L capacity attached to the reactors for collection of the gas emissions were from Fisher Scientific.

2.3.2 Synthetic Landfill:

The synthetic landfill material used in the study was a mixture of 50% newspaper, 25% office paper and 25% cardboard. The newspaper was the Collegiate Times. Office paper and cardboard were generated by the Environmental Engineering department at Virginia Tech. The paper was shredded to 0.5”X1” size. The plastic that was added was obtained by cutting zip ties into chips of 0.5”X1” size to maintain consistency.

2.3.3 Inoculum or seed:

The sludge from secondary treatment was obtained form the Pepper’s Ferry Wastewater treatment facility as a source of methanogenic bacteria.

2.3.4 Wastes:

All the wastes were provided by Mr. Gary Hater of Waste Management, Inc. except for the surfactant waste. Because anionic surfactants are used in metal processing, textile, detergents manufacturing industries, an equal mixture of dodecyl benzene sulfonate and sodium lauryl sulfate obtained from Sigma Aldrich Ltd was used as the surfactant waste. The surfactant waste mixture was added to the liquid fraction on w/v basis.

2.3.5 Sample collection:

Sampling was done once in every 20 days. The paint waste and control reactors were started first followed by the distillation waste and surfactant waste reactors. Hence the number of readings obtained for the later were less. Sample collection was carried out in a glove box at room temperature by purging with ultra pure nitrogen gas. The material in the reactors was subjected to manual mixing followed by collection of 10-15 gm of the sample into an aluminum pan. The leachate was extracted from the sample using a garlic extractor and transferred to a 15ml centrifuge tube for further analysis of VFA. The sealed reactors were put back for digestion at 37^0C. The sample was collected and dried at 105^0C for a period of 24 hours and milled to fine powder of 10mm size using Thomas scientific Wiley mill. The powder was further analyzed for VS, lignin, cellulose and hemicelluloses.

2.3.6 Analytical Methods:

2.3.6.1 pH:

The pH of the samples were measured after the mixture of sample and distilled water in 1:1 ratio was allowed to equilibrate for 5 hours using a pH meter.

2.3.6.2 Total Solids and Water content:

Standard method 2540G (APHA 1998) was adopted for measuring the total solids. The samples were weighed before and after being dried for 24 hours at 105^0C. The loss in weight with respect to original weight expressed as the percent total solids.

2.3.6.3 Volatile Solids (VS):

Standard method 2540G (APHA 1998) was adopted for the VS measurement. About 200 mg of the powdered sample was weighed and dried at 550^0C for 20 minutes. The initial and final weights were recorded and the relative difference with respect to original weight gives the measure of the VS.

2.3.6.4 Gas emissions, methane and carbon dioxide generation:

The gas collected in tedlar bags was measured using a gas measurement device and expressed in mL. The percentage of Carbon dioxide and methane was analyzed using a Shimadzu GC 14A with thermal conductivity detector. A 100µL of gas was injected into the machine for measurement and the value obtained was used in calculating the total amount generated from the total gas generation. The calibration was done using different concentrations of 99.9% pure methane and carbon dioxide.

2.3.6.5 Lignin, Cellulose and Hemicelluloses:

ASTM E 1758-95 ^{e1} was adopted for measurement of lignin, cellulose and hemicelluloses. About 300 mg of the powdered sample was placed in a 16 mL vial and 3 mL of 72% H_2SO_4 was added for hydrolysis. The mixture was vortexed every 15 minutes over a 2 hour period and the temperature was maintained at 30^0C in a water bath. The contents were transferred to a 250 mL bottle by adding 84 mL of nanopure water by thorough washing of the contents of the 16 mL vials. The 250 ml bottles were autoclaved at a temperature of 121^0C for 1 hour. The solids from the solution from these bottles were filtered using a TSS glass stand filter. The filters were weighed after baking at 105^0C and then weighed after baking at 550^0C for 20 minutes. The difference in weights gave the amount of lignin in the sample. The same procedure was adopted for standards of lignin and cellulose from Sigma Aldrich and the percentage recovery was determined and the value was incorporated in all the calculations. The filtrates were added with calcium carbonate to maintain a pH in between 4 and 6. The suspension of the filtrates was filtered using 0.25µm filter and the solution was analyzed using a high performance liquid chromatograph with a HPX-87C carbohydrate column (*Biorad*) and refractive index detector.

2.3.6.6 Volatile fatty acids:

The leachate obtained from the samples was analyzed for acetic, butyric, iso butyric, heptanoic, proponoic, valeric, isovaleric and caprionic acids. The extracted leachates were thawed and filtered through a 0.45 µm filter after centrifuging for 10 minutes. The filtrate (0.99 mL of filtrate and 0.01 mL of phosphoric acid) was analyzed using a Shimadzu GC 14A with a flame ionization detector. The sample was acidified to maintain the Vast in the acid phase. Five standards were prepared using standard volatile fatty acids obtained from Supelco. The dilution water using for preparation of standards was nanopure water, blank samples were also analyzed to avoid any interference of seed.

2.4 Results and Discussions:

The measured parameters are graphically shown in figures 2.1to 2.69 and trend lines were drawn to assess the overall performance of the reactors under the influence of additions of different liquid wastes. The significant affects of each waste liquid are discussed in the following paragraphs, corresponding to the type and amount each waste added to the reactors.

2.4.1 Paint waste:

The paint waste reactors were characterized by a greater decrease in volatile solids compared to the control reactors. The volatile solids concentration shown in figure 2.1

indicates the extent of degradation in the reactor and shows that as the amount of paint waste increased, degradation also increased. The buffering and the nutrients added to the reactors could be one of the reasons for the enhanced performance of the reactors. The 10% paint waste reactors had a higher rate of decrease in volatile solids compared to the 1% and 5% paint waste reactors. However, the magnitude of the difference was not large (figure 2.2).

The analysis of the cumulative total gas generated (figure 2.3) from the paint waste reactors shows a high emission rate from the paint waste reactors. The total gas emitted from the 10% paint waste reactors was 2.5 times more than that of the control (figure 2.3). The gas generation trend in the paint waste reactors was similar to the control (figure 2.3) which indicates that the addition of paint waste does not result in negative performance of the reactors. The reason for high amount of gas emission in the paint waste reactors might be the presence of a high COD. The COD value of paint waste was observed to be 237,500 mg/l. The rate of gas generation increased with the increase in the amount of paint waste added. The methane generated was also greater than the control (figure 2.6). Overall, the rate of gas generation data is comparable to the rate of VS reduction data (figures 2.2 and 2.4). Both indicate that paint waste up to 10% is beneficial as long a sufficient nutrients and buffering are present (figures 2.5, 2.6, 2.7 and 2.8).

In the initial 50 day period of degradation, paint waste reactors generated a high amount of methane. In the later stages, from day 80 to day 120, the gas production rate was similar to the control (figure 2.5). This suggests that the paint waste contained readily degradable organics. The percentage VS of the paint waste were observed to be

86. The carbon dioxide trend was similar to the methane generation. The 10% paint waste reactors had a high emission rate of carbon dioxide compared to 1% and 5% paint waste reactors and the control (figure 2.8).

The pH of the paint waste reactors followed a similar trend to the control reactors, indicating no inhibition. The pH over the 60-80 day period was relatively constant in the range of 7-7.5 (figure 2.9).

The trend of the volatile fatty acids (figure 2.10) shows that the generation and consumption of volatile fatty acids was consistent with the amount of gas generated and the extent of degradation observed. The control reactors and paint reactors had the same trend in fatty acid production. However, the concentration of the fatty acids in control reactors was higher than in the paint waste reactors. The 1% paint waste reactors contained more volatile fatty acids compared to the other paint waste reactors. The 60-80 day period shows a large drop in fatty acids. The individual volatile fatty acids, acetic, propionic, butyric and valeric acids were analyzed, and the data shown in figures (2.11, 2.12, 2.13, 2.14) follows the same trend as the sum of fatty acids and the one important finding was that the generation of the acetic acid in 1% paint waste reactors was very high compared to other reactors. The concentration of other fatty acids generated in the 1% paint waste reactors was also high compared to other paint waste reactors.

The moisture content in the paint waste reactors and the control was very similar. The moisture content (figure 2.15) was in the range of 72-82% which is a favorable amount for efficient degradation. The cellulose in the paint waste and control had a decreasing trend which shows that cellulose is being degraded (figure 2.16). However the lignin percentage (figure 2.17) in the control and paint waste reactors had a slightly increasing trend and the hemicellulose (figure 2.18) was relatively constant over the entire period of observation. The cellulose to lignin ratio (figure 2.19) was analyzed and shows a decreasing trend in the control and paint waste reactors, which indirectly supports the decrease in cellulose and increase in lignin on a percentage basis. However, the data cannot be used to determine if lignin is being degraded. The ratio of cellulose to plastic was evaluated which shows a decreasing trend (figure 2.20) which is a good indication of the cellulose degradation rate in the reactors. The ratio of cellulose of plastic dropped from 3 to 0.5 over 150 days of observation. The dry weights of the solids in the reactor were measured and the ratio of dry weight to plastic was calculated (figure 2.21). The lignin to plastic ratio was plotted (figure 6.64) which showed a decreased trend which suggests that lignin content is degrading compared to the plastics. The hemicellulose to plastic ratio (figure 6.67) has also shown a decrease in hemicellulose with respect to plastic. The plots have shown some scatter but the trends fairly give a rough idea about the degradation mechanism in the system.

2.4.2 Distillation Waste:

A plot of the change in volatile solids over the time shown in (figure 2.22). For the distillation waste, this shows that the rate of volatile solids reduction in all the distillation waste reactors is much less than that of the control reactors (figure 2.23). It appears that there is some inhibition of degradation due to the high amount of volatile fatty acids generated (figure 2.24) and the resulting acidic condition of the reactors. The buffering added to the reactors at the beginning of the test was insufficient for maintaining the pH around neutral. The pH in the distillation waste reactors was in the range of 5-6 (figure 2.25).

The cumulative gas emitted (figure 2.26) in the distillation waste reactors was very low compared to that of the control reactors which indicates a strong inhibition to the biological activity. However, the rate of gas generation from the 5% distillation waste reactors was significantly more than the other distillation reactors (figure 2.27). Huntan, et al.(2000) have proved that the increased methane generation is observed when the conditions are favorable in spite of accumulation of fatty acids. The cumulative methane gas generation (figure 2.28) in the distillation waste reactors shows strong inhibition at the 10% to 20% addition levels, probably due to high amount of volatile fatty acids generation. The rate of Methane gas generation was low (figure 2.29), however the 5% distillation waste reactors began to generate some methane after 120 days of incubation (figure 2.28). The pH in the 5% reactor was somewhat higher than the 10% and 20% reactors so the generation of methane could indicate that recovery in the 5% reactor was taking place. The carbon dioxide emission (figures 2.30, 2.31) was similar to that of the methane.

The distillation waste reactors were characterized by high concentrations of volatile fatty acids (figures 2.32, 2.33, 2.34, 2.35 and 2.36) compared to the control. The rapid accumulation of volatile fatty acids might be attributed to the presence of readily degradable COD content in the distillation waste solution, the COD of the distillation waste was 812,500 mg/l which is approximately 3.5 times that of the paint waste solution. The total volatile fatty acids concentration (figure 2.32) was characterized by a sudden drop during the 60-80 day period of observation which might indicate some amount of acclimation occurred in the reactors. The concentration of propionic acid increased after 100 days and no strong conclusion can be made from this observation.

The moisture content in the distillation waste reactors was lower than that of the control reactors (figure 2.36) which is in between the 60-80% limit for good methane generation (EMCON ASC., 1980).

The percentage of cellulose (figure 2.37) in the distillation waste reactors showed a slight increasing trend while the lignin measurements (figure 2.38) show a slight decrease and the percentage hemicellulose (figure 2.39) concentrations were fairly constant. The possible conclusion which can be drawn from this observation is that the rate of degradation of lignin is faster than cellulose and hemicellulose and the rate of degradation of hemicellulose is faster than cellulose. The plots of cellulose/lignin, cellulose/plastic, lignin/plastic and hemicellulose/plastic have shown some scatter but the trends fairly give a rough idea about the degradation mechanism in the system. The cellulose to lignin ratio (figure 2.40) was observed to increase with time, while the cellulose to plastic (figure 2.41) and dry weight to plastic ratios (figure 2.42) showed a slight decrease. Plastic does not degrade in the reactors so the reason for decrease in the ratio indicates degradation of the waste. The lignin to plastic ratio (figure 6.65) has shown a slight decreasing trend which restates the fact that plastic does not degrade in the bioreactor landfill (Kim, 2004). The hemicellulose to plastic ratio (figure 6.68) also had a slight decreasing trend, but no direct correlation based on these ratios can be made with respect to the degradation limits because of variability in plastic collection during the sampling process.

2.4.3 Surfactant waste:

The volatile solids concentration (figure 2.43) in surfactant waste reactors have shows a trend similar to that of the control reactors, emphasizing the fact that the degradation in the surfactant waste reactors was similar to the control reactors. The rate of degradation of volatile solids had a constant trend in all the surfactant waste reactors (figure 2.44). The cumulative gas generation curve (figure 2.45) for the surfactant waste reactors showed some inhibition during the 30-50 day period however the rate of gas generation was comparable to control after that period. The methane and carbon dioxide generation curves followed the similar trend to that of the cumulative gas (figures 2.46, 2.47, 2.48, 2.49 and 2.50).

The pH (figure 2.51) in the surfactant waste reactors was fairly constant at 8 without much variance compared to the control reactors. The volatile fatty acid generation (figures 2.52, 2.53, 2.54, 2.55 and 2.56) was comparable to that of the control reactors. The trend of volatile fatty acid generation showed an even chain with peaks at 10 days and 80 days. The trend in fatty acid generation might suggest degradation of long chain surfactants, producing VFAs. The highest concentration of the fatty acids was observed in 1500mg/L surfactant waste.

The moisture content (figure 2.57) in the surfactant waste reactors was observed to be 65-75%, similar to that of control. The lignin, cellulose and hemicellulose measurements were made on percentage basis. The trend observed for the cellulose (figure 2.58) and hemicellulose (figure 2.59) was that these were fairly constant, while the lignin (figure 2.60) measurements had a decreasing trend. The reason could be the rate of degradation of the cellulose and hemicellulose was low compared to that of the lignin. The ratio of cellulose to lignin (figure 2.61) was analyzed and the ratio increased over time, suggesting that the lignin is degrading at a faster rate compared to cellulose. The cellulose to plastic (figure 2.62) and dry weight to plastic (figure 2.63) ratios show a decrease over time which indicates that the cellulose is degrading with respect to plastic. The lignin to plastic (figure 2.66) and hemicellulose to plastic (figure 2.69) ratios were plotted the trends observed were decreasing which gives an indication that the lignin is degrading compared to plastic, but the ratio calculation is dependent on the amount of plastic hand picked from the reactor which resulted in some scatter.

2.4.4 Statistical Analysis:

Due to very less number of data points the t-test to differentiate the effect of the addition of waste to the reactors gave ambiguous P-values; however the data points were fit using regression analysis the R- squared values were calculated (Table 2.2).

	%Cellulose	%Lignin	%Hemicellulose	Cellulose/lignin	Cellulose/plastic	Dry wt/ plastic
Control	0.0264	0.3379	0.0371	0.2268	0.7628	0.4264
Paint waste 1%	0.0564	0.8221	0.2028	0.4673	0.4314	0.555
Paint waste 5%	0.4772	0.7874	0.0303	0.7338	0.7781	0.7399
Paint waste 10%	0.1602	0.7109	0.0079	0.6422	0.7385	0.7569
Distillation waste 5%	0.0061	0.0719	0.5098	0.0415	0.5031	0.4475
Distillation waste 10%	0.8675	0.3137	0.378	0.5605	0.7543	0.6463
Distillation waste 20%	0.2325	0.7251	0.0536	0.5936	0.8322	0.3615
Surfactant waste 500mg/L	0.0031	0.2286	0.0739	0.1929	0.1068	0.1719
Surfactant waste 1000mg/L	0.3614	0.0476	0.0963	0.156	0.8407	0.7162
Surfactant waste 1500mg/L	0.0822	0.2044	0.7119	0.3054	0.8697	0.6487

Table 2.2 R-squared values for different plots

2.5 Conclusions:

2.5.1 Paint waste:

It can be observed that all the paint waste reactors had good degradation. However, the 1% and 5% paint waste reactors had high concentrations of volatile fatty acids compared to 10% paint waste reactors and the gas emissions from 10% paint waste reactors was significantly higher, so it could be concluded that the 10% paint waste had better degradation compared to other paint waste reactors. Research by Vellatt (2007) has shown that paint waste added above 7.5% can be highly inhibitive. The reason for the better performance of the paint waste reactors in this study could be the addition of buffer and nutrients during the initial setup of the reactors. The paint waste reactors have performed very much similar to the control reactors. Vaajasaari et al., (2006) have shown that landfill leachate is sometimes found to be toxic due to the paint waste addition, the present study shows that the paint waste used for addition was not characterized by hazardous compounds since there has been no heavy inhibition on the microbial activity. A study on liquid waste addition based on the COD of the liquids might be beneficial to compare all the waste on a common parameter and there by find the variation in the performance.

2.5.2 Distillation waste:

The distillation waste reactors have shown inhibition but the degradation in the 5% distillation waste reactors was high compared to the 10% and 20% distillation waste reactors. The buffer capacity added in the initial setup was useful in controlling the pH by avoiding the sudden drop of pH observed by Vellatt (2007). However, the pH range in all the reactors was around 5-6, based on this observation it can be suggested that an increase in the buffer capacity and nutrients and decreasing the distillation waste concentration below 5% can improve the overall performance of the reactors. As stated above the performance of distillation waste reactors at 0.3 % and 2.3% and 3.3% with same buffer capacity might be a good estimate which is equivalent to the paint waste reactors on COD basis. The accumulation of volatile fatty acids in the reactors due to unbalanced digestion was thought to be a major cause for inhibition by decreasing the microbiological activity as shown by Boualgui, et al.(2005).

2.5.3 Surfactant waste:

Anionic surfactants sodium lauryl sulfate and dodecyl benzene sulfonate were used in the present study. The overall performance of the surfactant waste reactors was good. Scherbakova, et al.(1999) have shown that anionic surfactants have enhanced biological activity compared to the cationic surfactants, however study by Vellatt (2007) indicated that the surfactant waste (anionic) added above 500mg/L could be inhibitory. The different concentrations of surfactants used in this study were 500 mg/L, 1000 mg/L and 1500 mg/L. The initial stages of the reactors were characterized by inhibition but the degradation began to increase in the later stages this is evident in the trend of the gas generation and trend in the volatile fatty acid generation. The 1500 mg/L surfactant waste generated high volatile fatty acid concentrations; however, the gas generation was similar for all the concentrations of the surfactant waste reactors. The buffering and nutrient addition could be one possible reason for some improvement in the reactor performance even at high concentrations compared to that of Vellatt (2007). Kjeldsen, et al.(2002) have shown that the effect of surfactant waste addition to the landfill is specific to the type of surfactant being added, further study on different types of surfactants added to the bioreactor landfills might give a good understanding on variation of the overall performance of the bioreactor landfill under surfactant addition.

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http://www.epa.gov/nrmrl/pubs/600r07060/600R07060.pdf

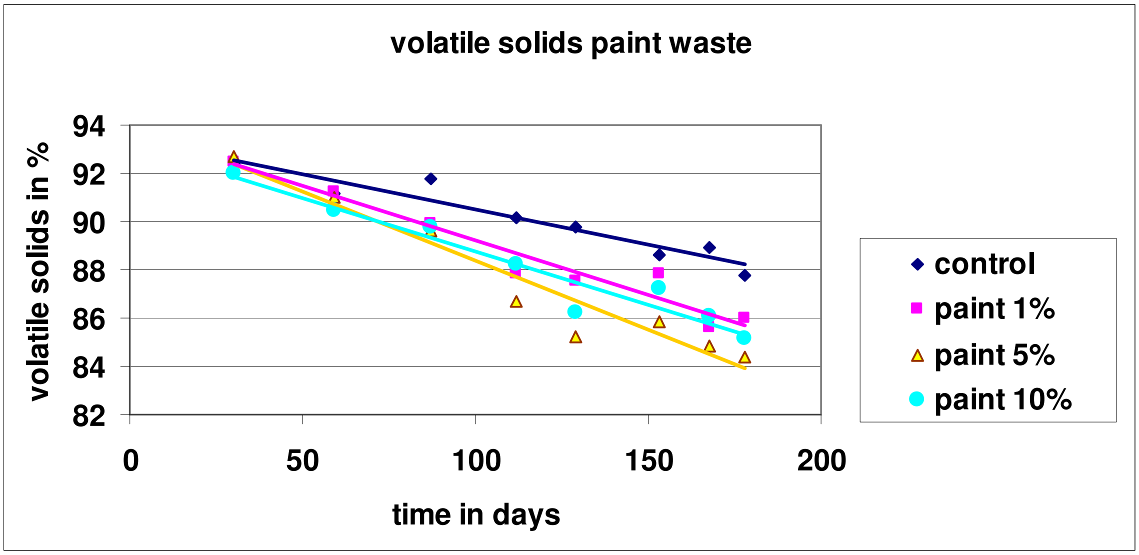

Figure 2.1: Volatile solids in control and paint waste reactors.

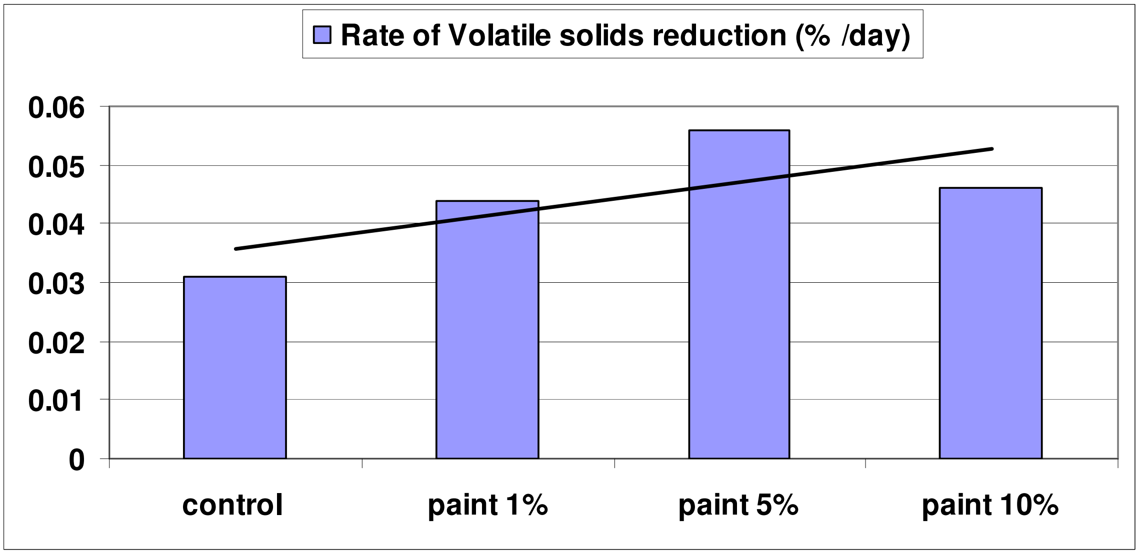

Figure 2.2: Rate of volatile solids reduction in control and paint waste reactors.

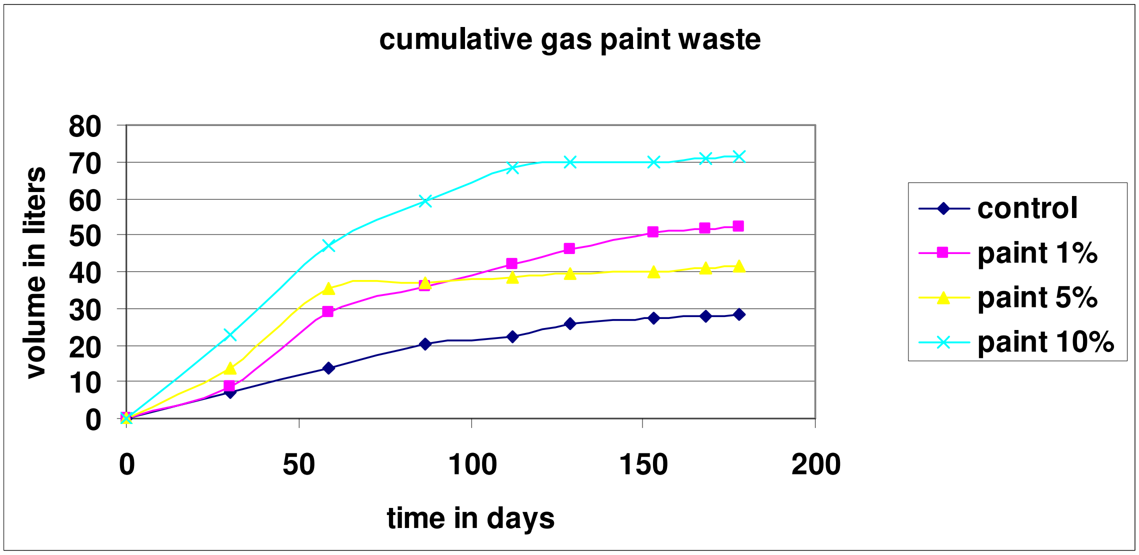

Figure 2.3: Cumulative total gas in control and paint waste

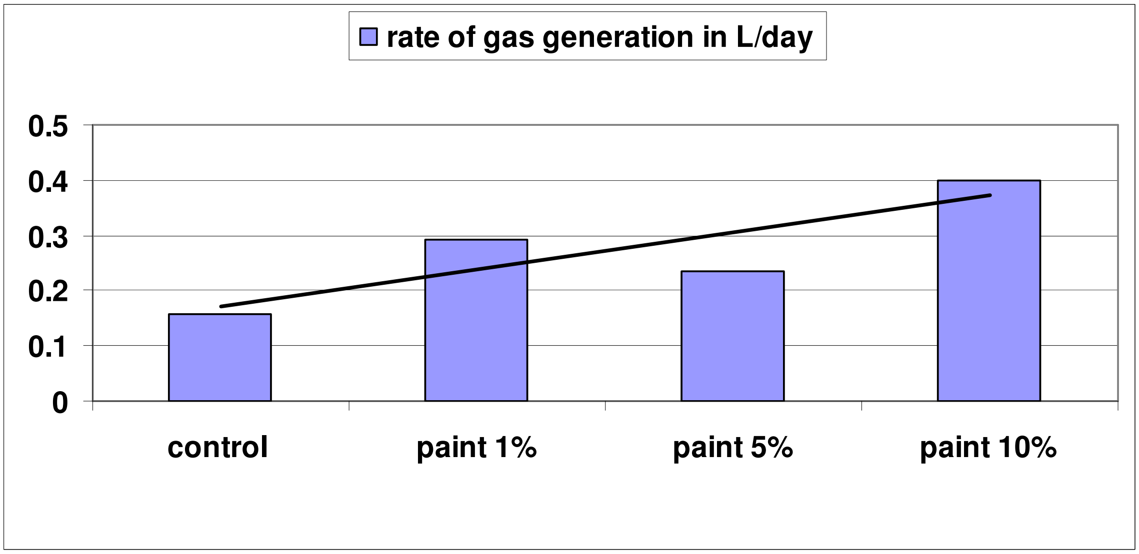

Figure 2.4: Rate of total gas generation in control and paint waste

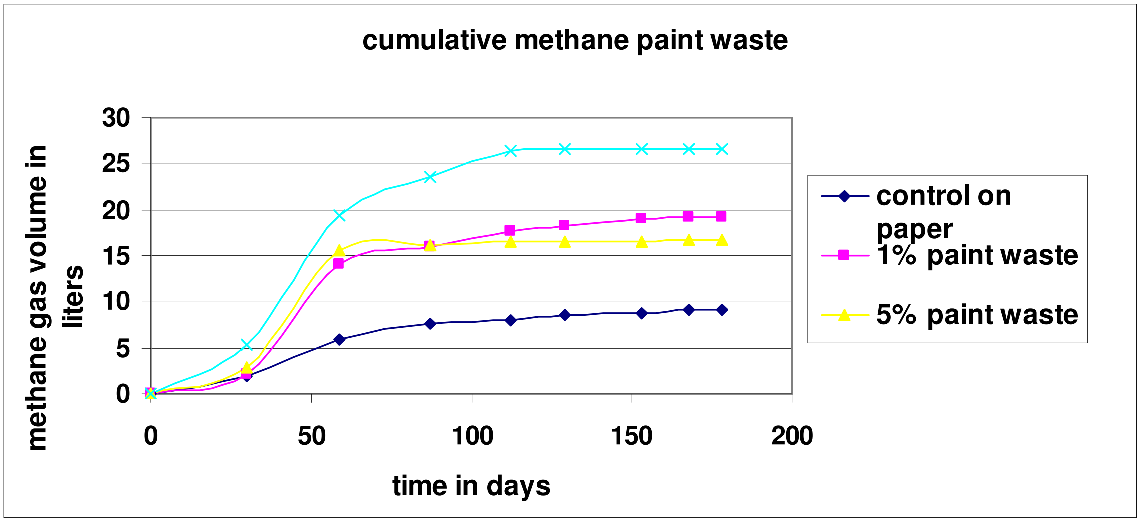

Figure 2.5: Cumulative methane in control and paint waste reactors.

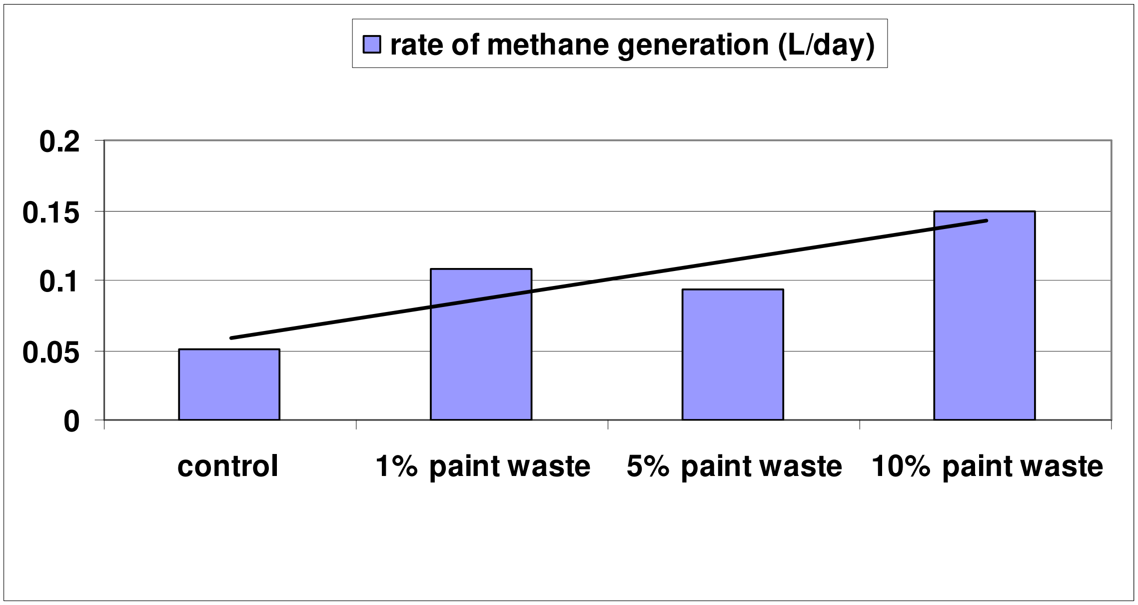

Figure 2.6: Rate of methane generation in control and paint waste

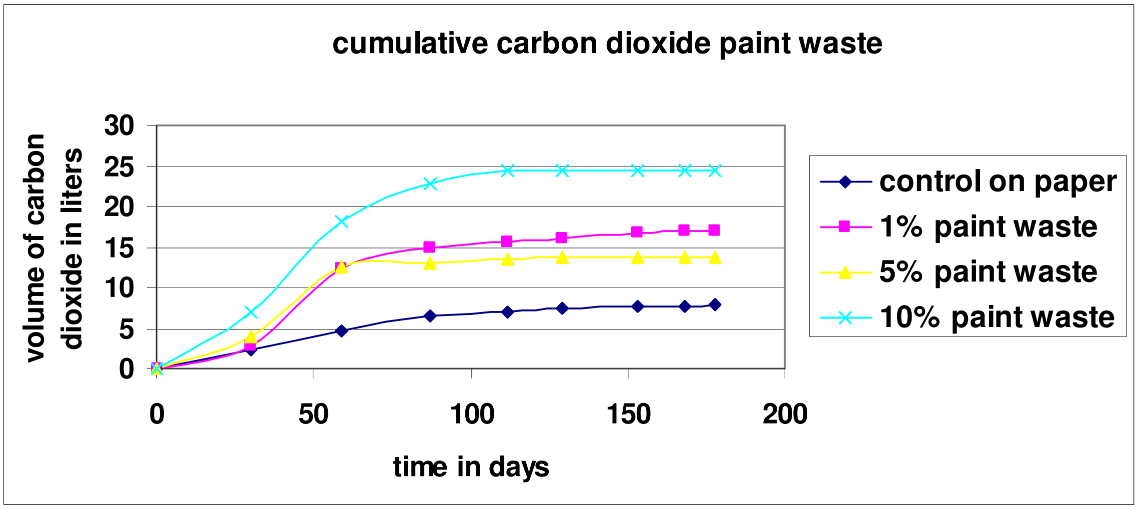

Figure 2.7: Cumulative carbon dioxide in control and paint waste reactors.

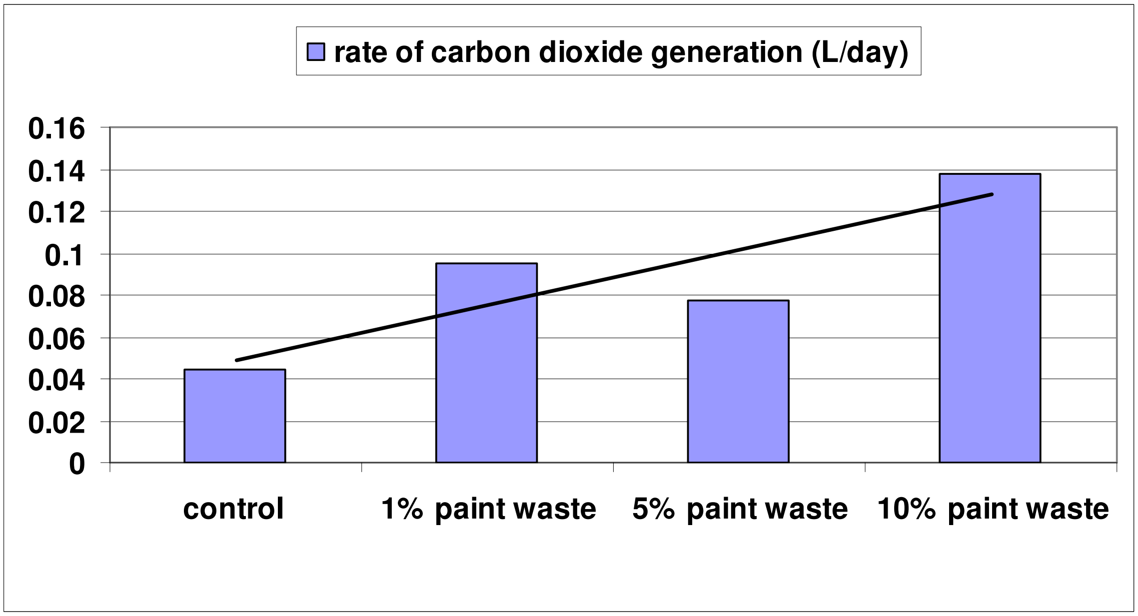

Figure 2.8: Rate of carbon dioxide generation in control and paint waste

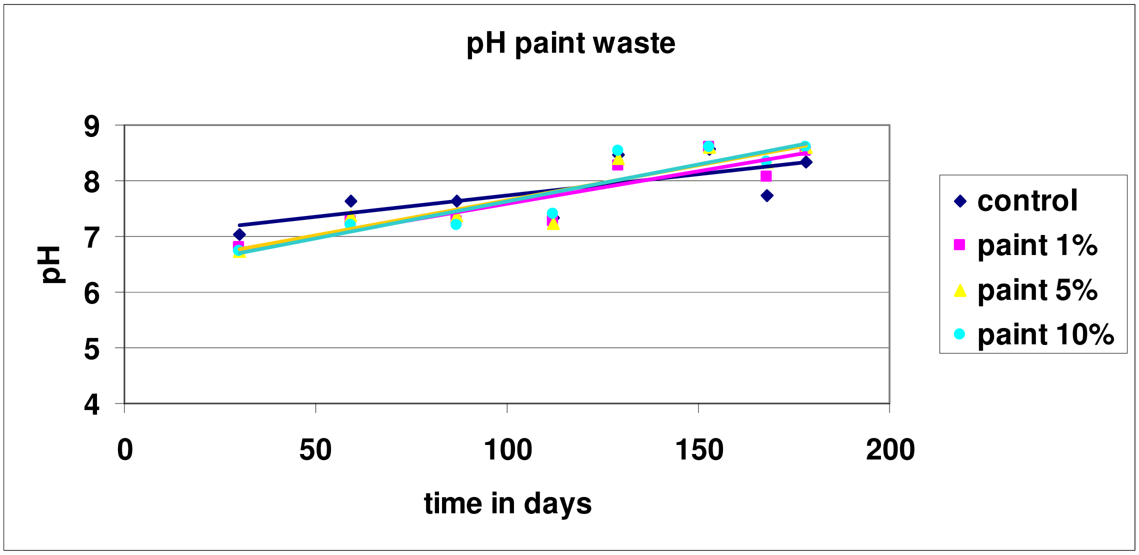

Figure 2.9: pH in control and paint waste reactors.

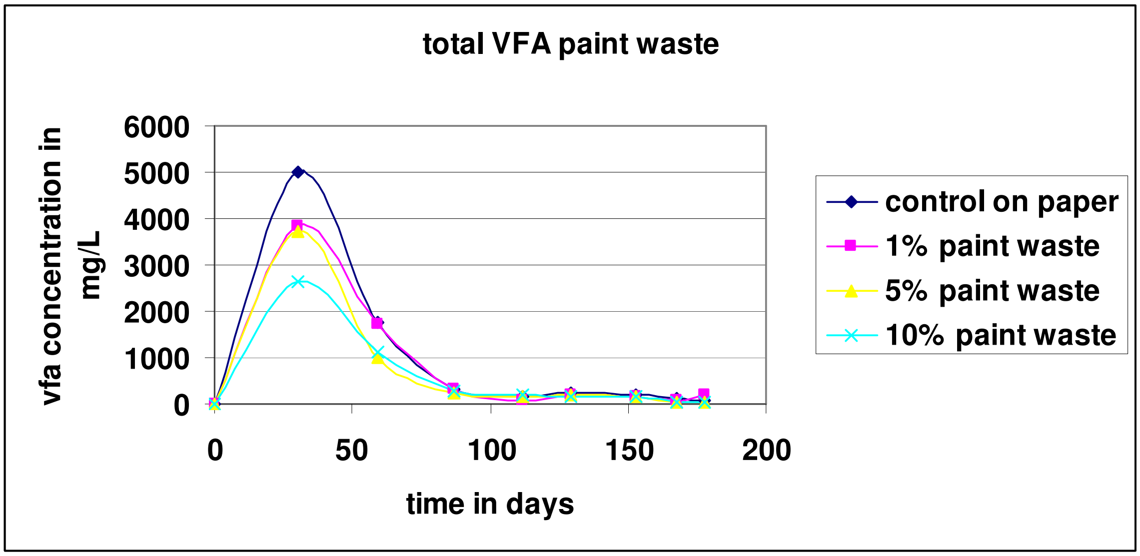

Figure 2.10: Total volatile fatty acids in control and paint waste reactors.

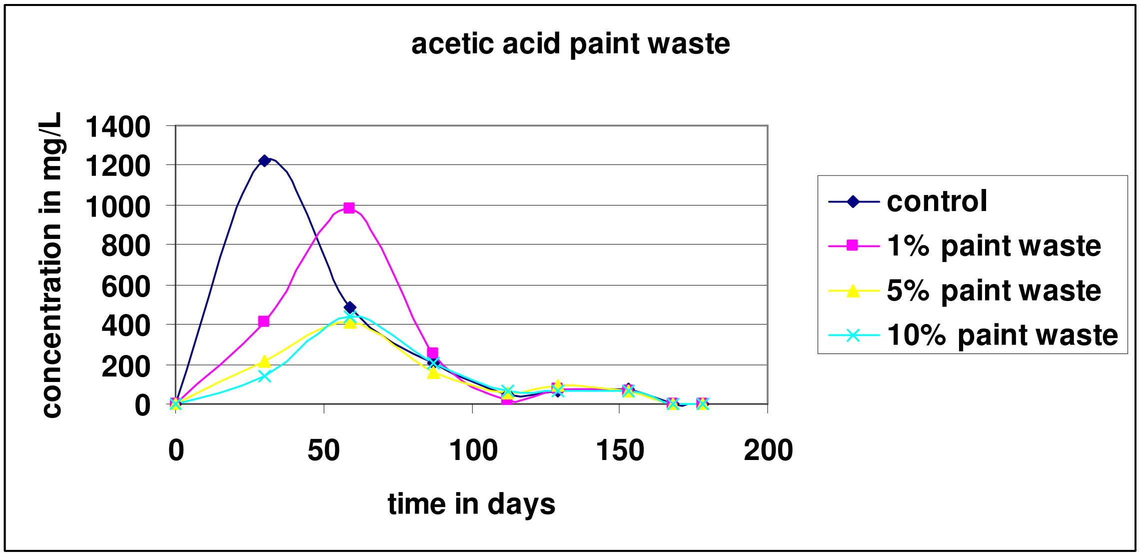

Figure 2.11: Acetic acid in control and paint waste reactors.

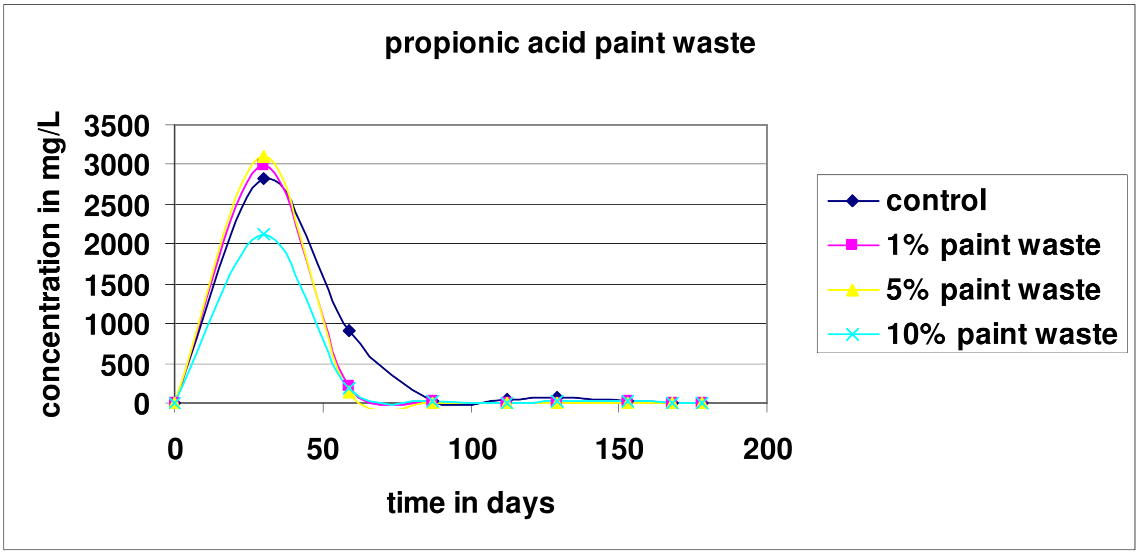

Figure 2.12: Propionic acid in control and paint waste reactors.

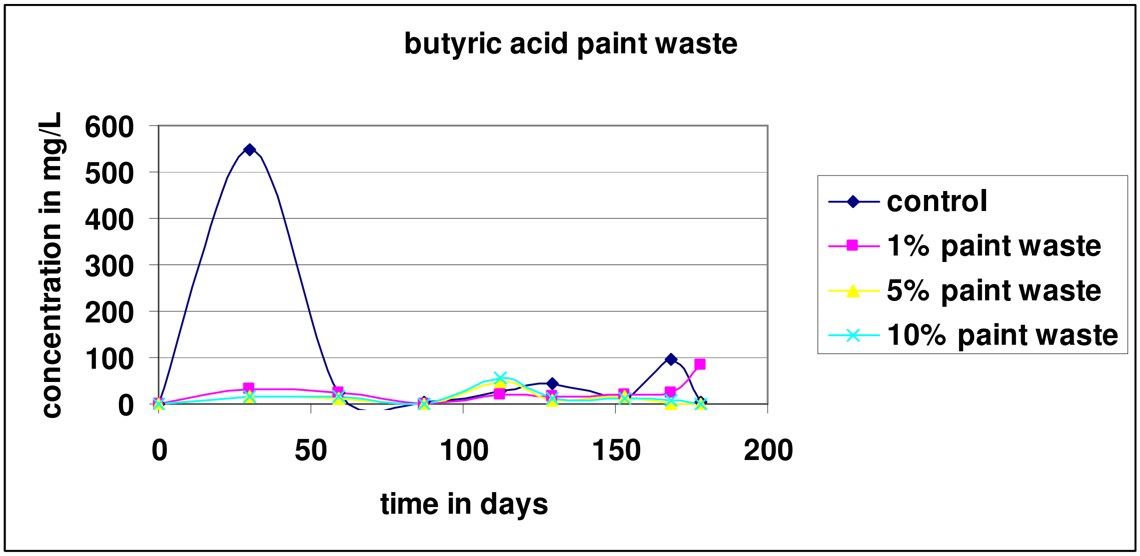

Figure 2.13: Butyric acid in control and paint waste reactors.

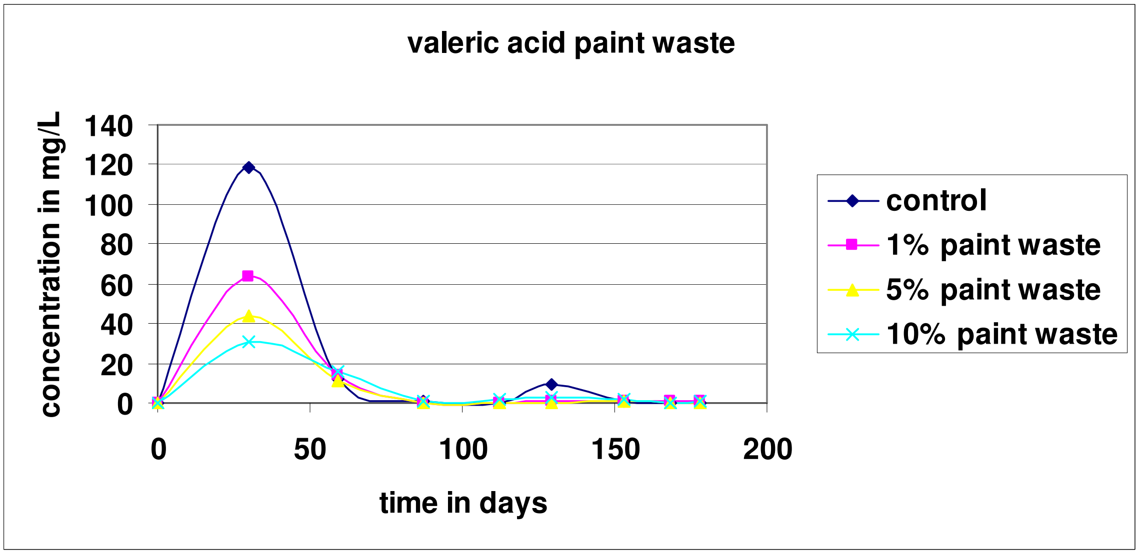

Figure 2.14: Valeric acid in control and paint waste reactors.

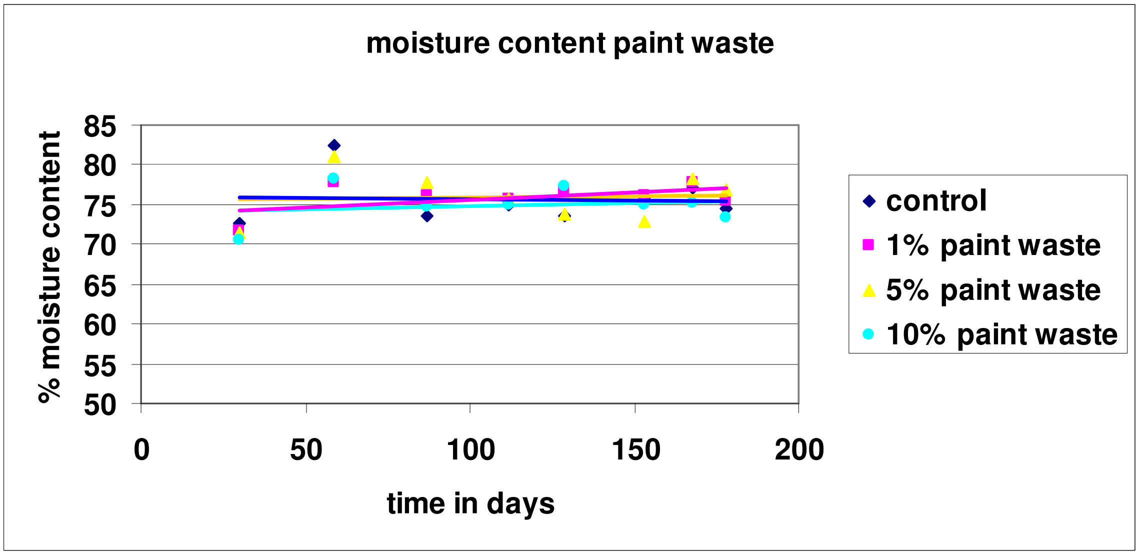

Figure 2.15: Percentage moisture content in control and paint waste reactors.

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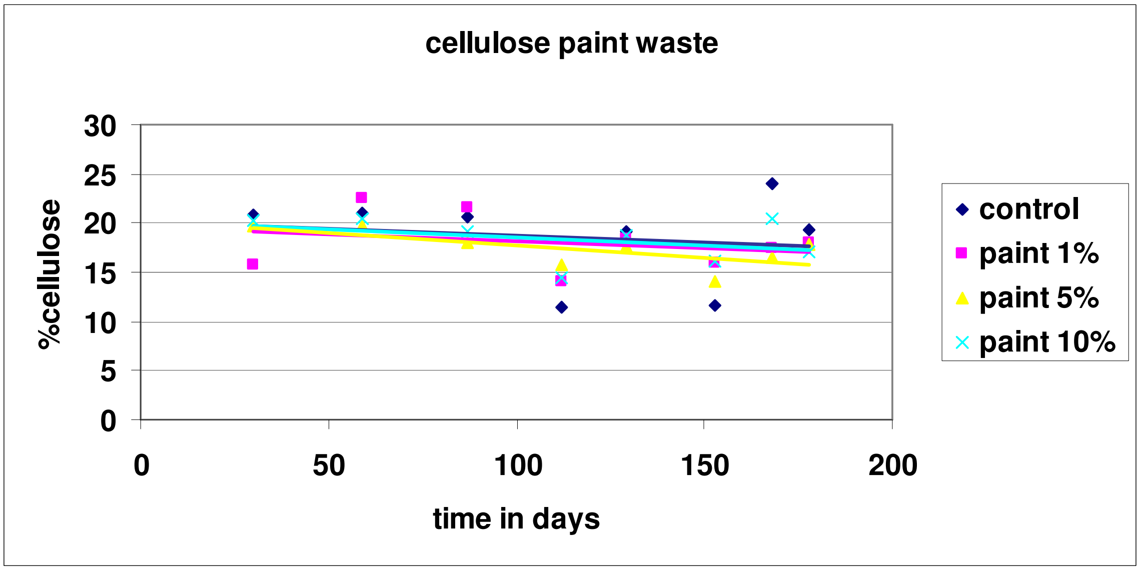

Figure 2.16: Percentage cellulose in control and paint waste reactors.

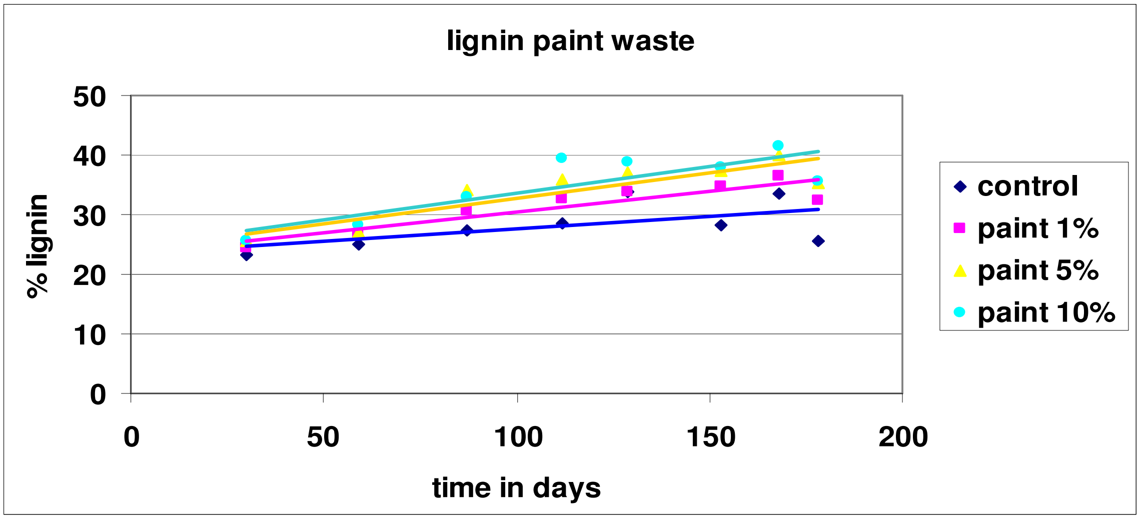

Figure 2.17: Percentage lignin in control and paint waste reactors.

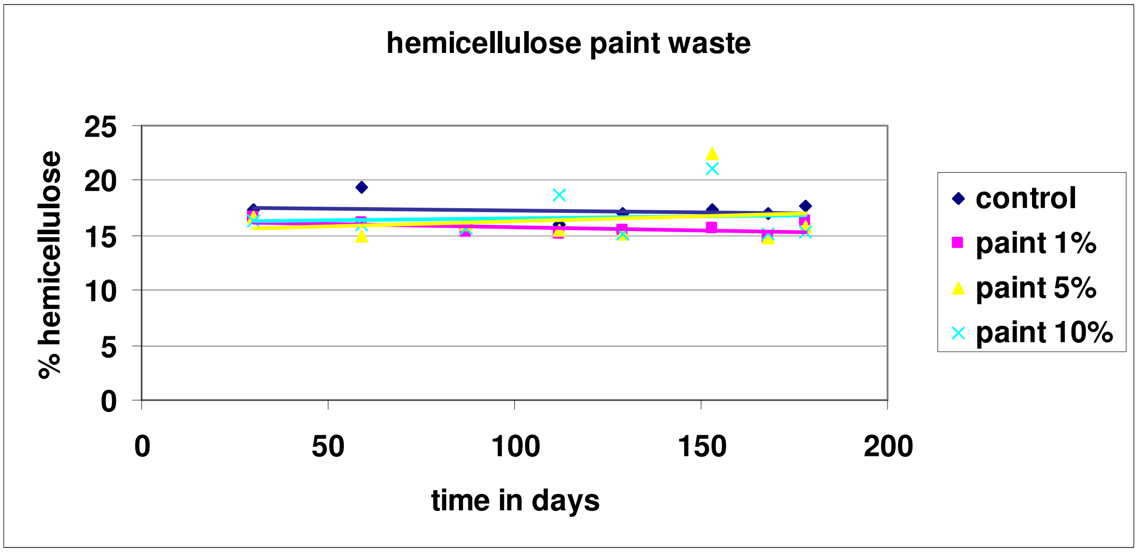

Figure 2.18: Percentage hemicellulose in control and paint waste reactors.

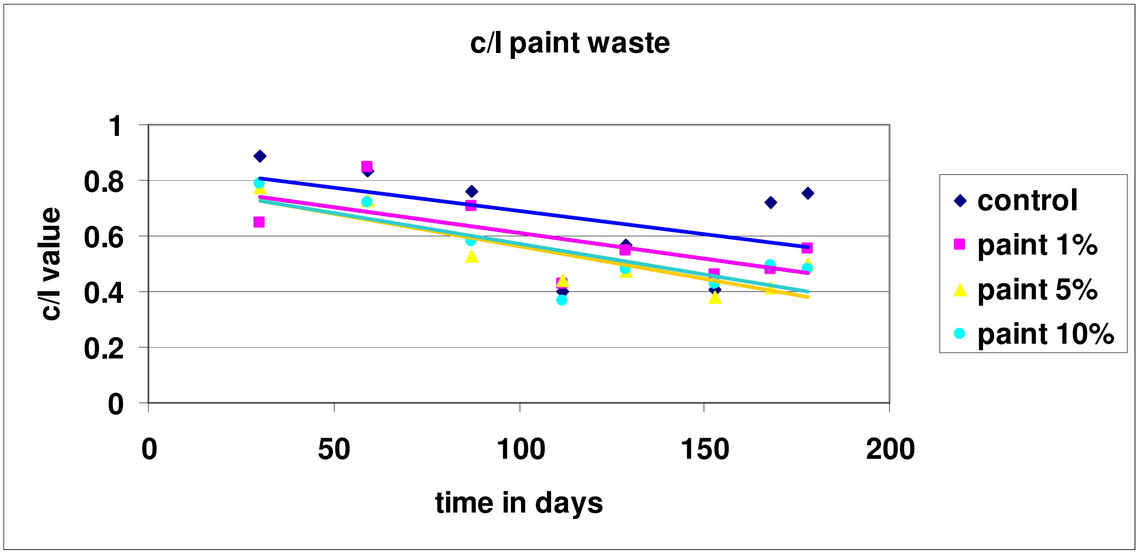

Figure 2.19: Cellulose to Lignin ratio in control and paint waste reactors.

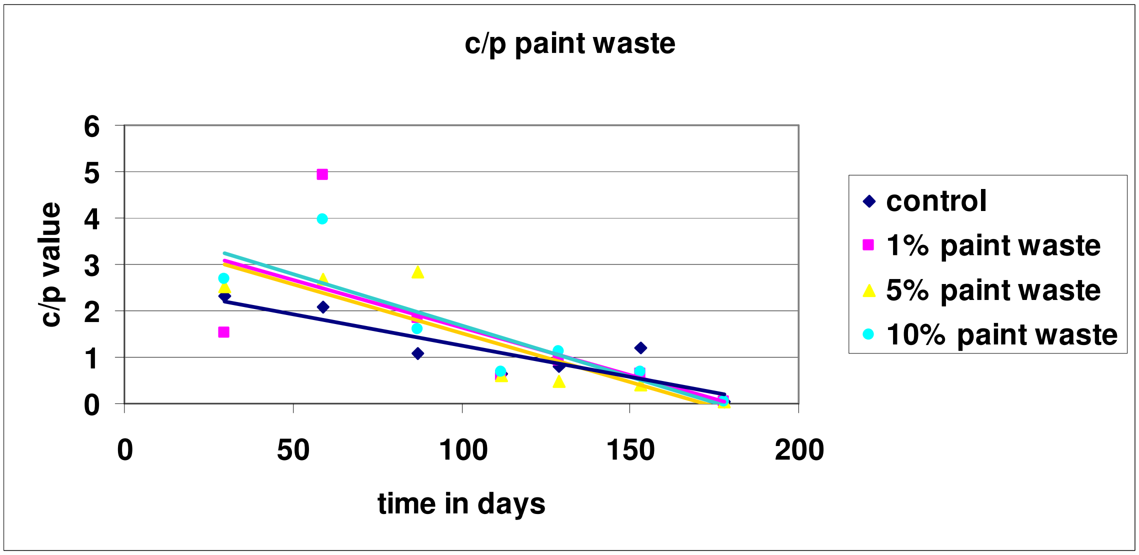

Figure 2.20: Cellulose to Plastic ratio in control and paint waste reactors.

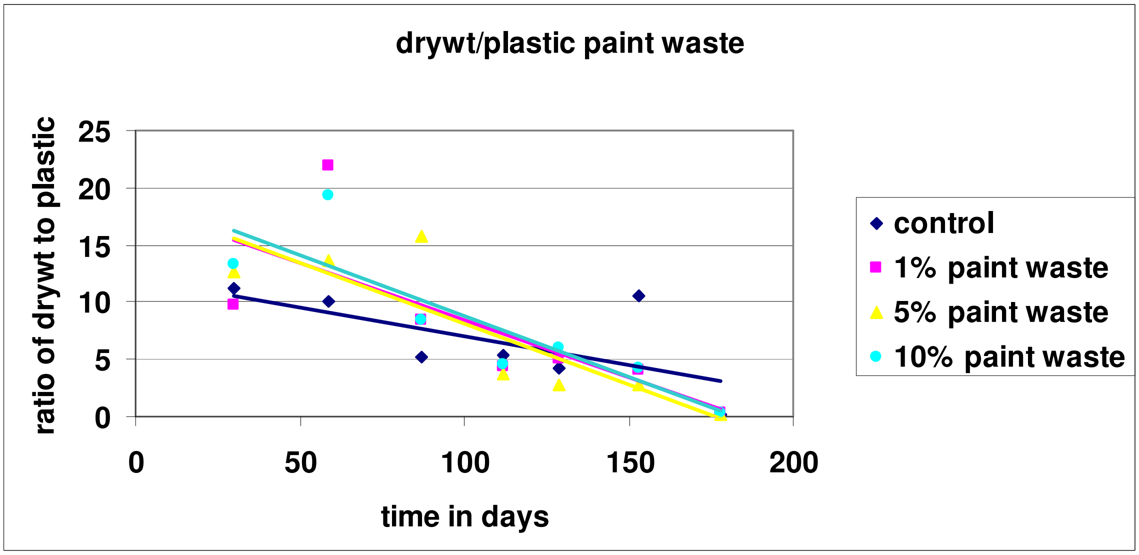

Figure 2.21: Dry weight to Plastic ratio in control and paint waste reactors.

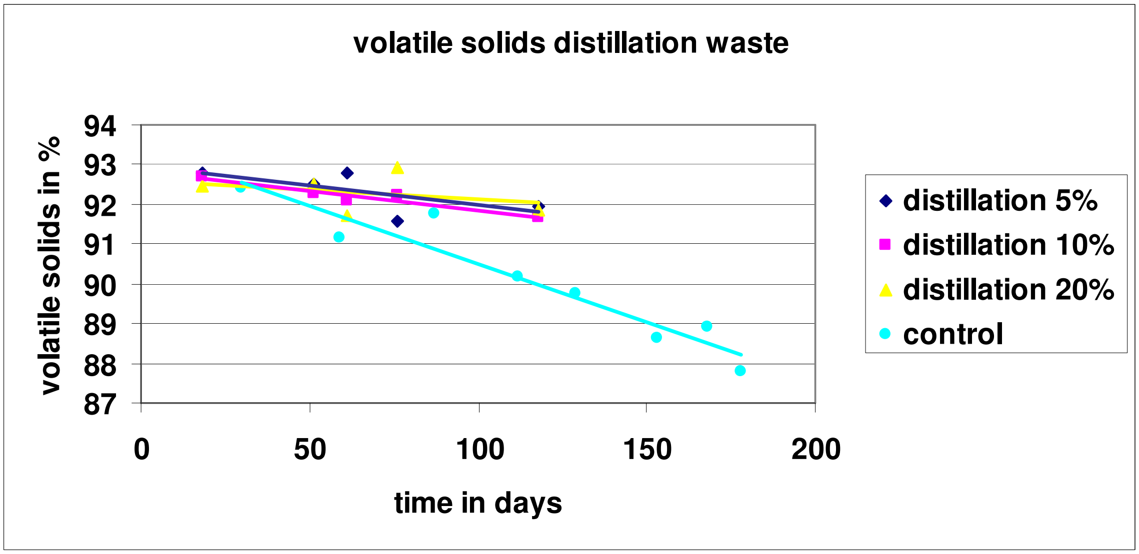

Figure 2.22: Volatile solids distillation waste reactors.

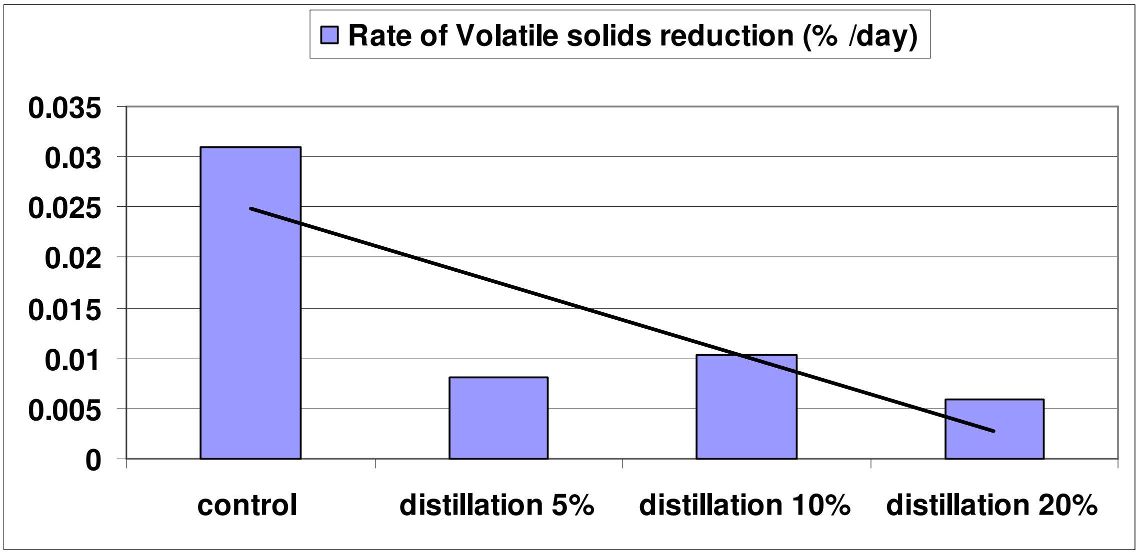

Figure 2.23: Rate of volatile solids reduction in control and distillation waste reactors.

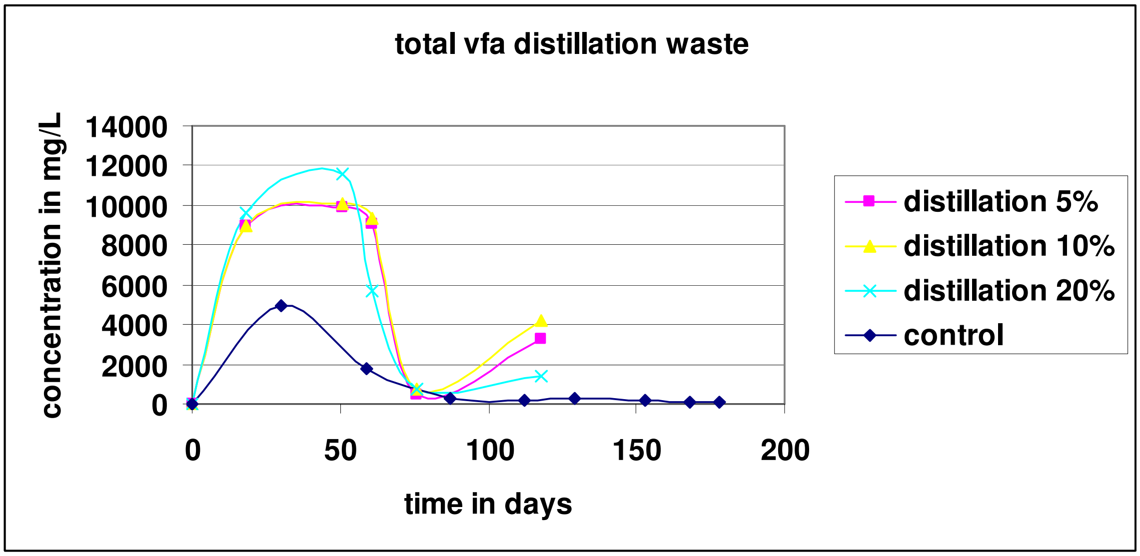

Figure 2.24: Total volatile fatty acids in control and distillation waste reactors.

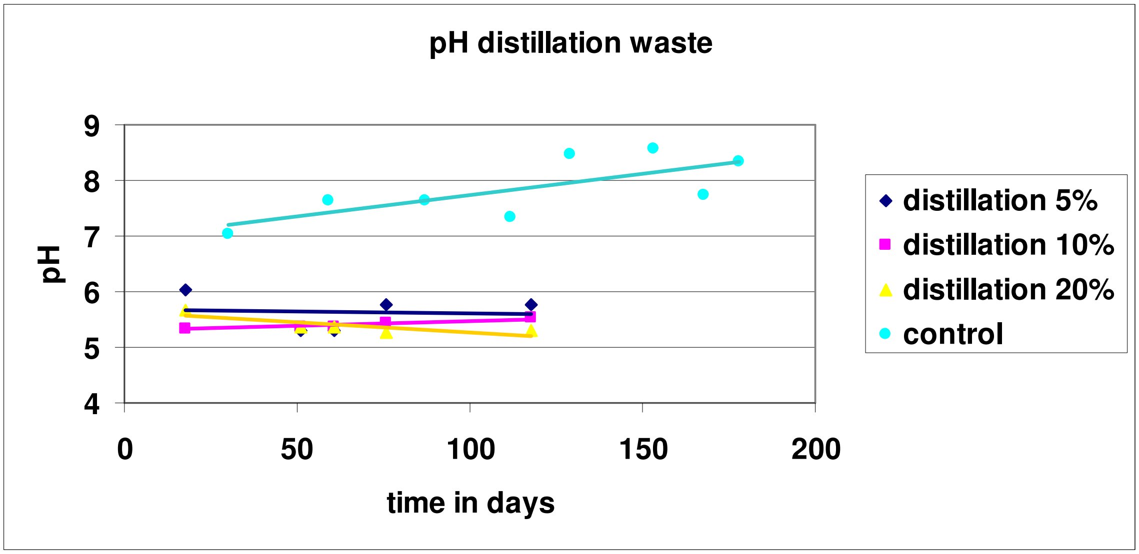

Figure 2.25: pH in control and distillation waste reactors.

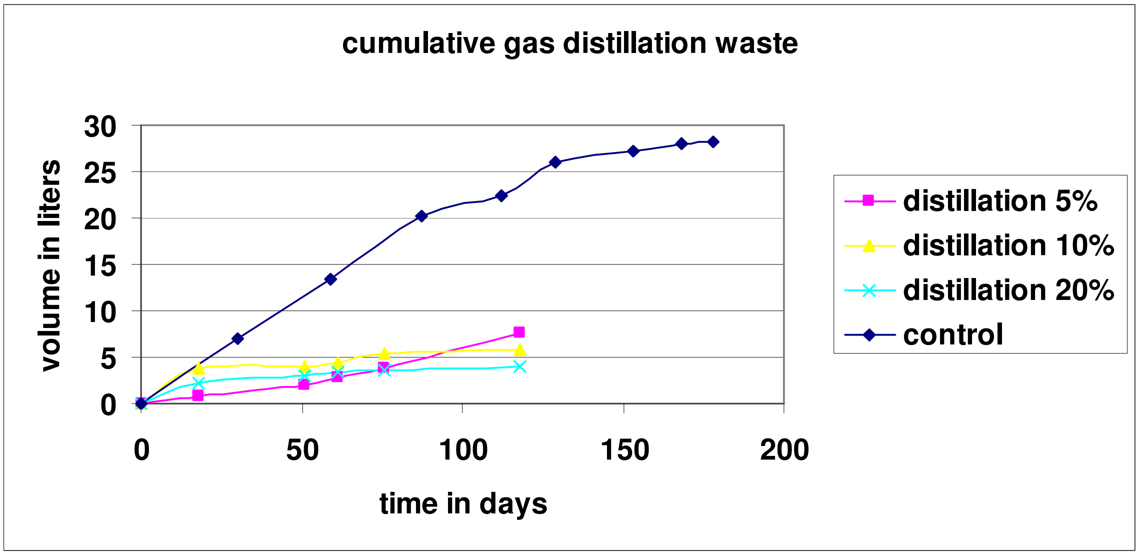

Figure 2.26: Cumulative total gas in control and distillation waste reactors

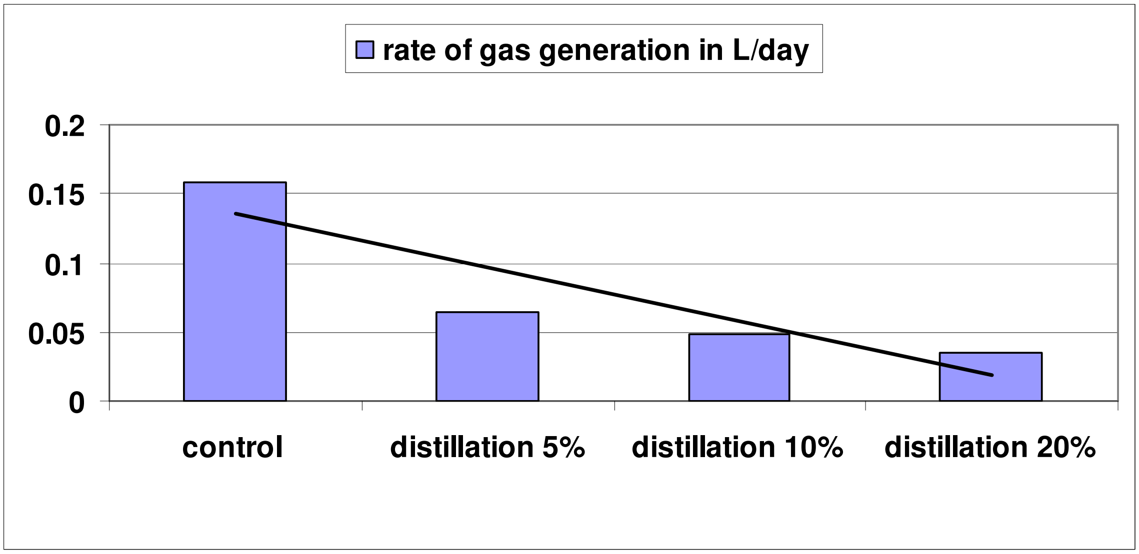

Figure 2.27: Rate of total gas generation in control and distillation waste reactors

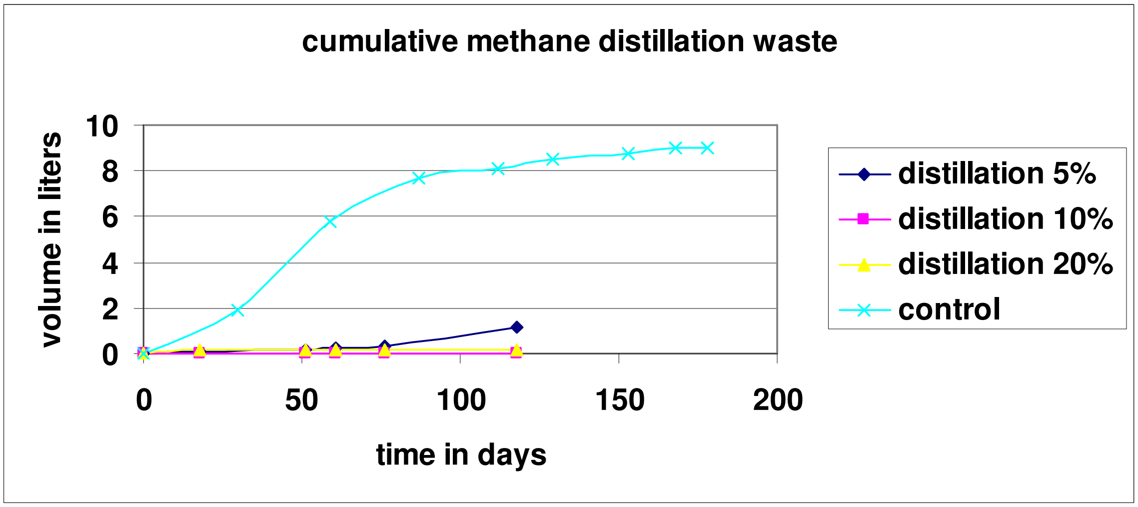

Figure 2.28: Cumulative methane in control and distillation waste reactors

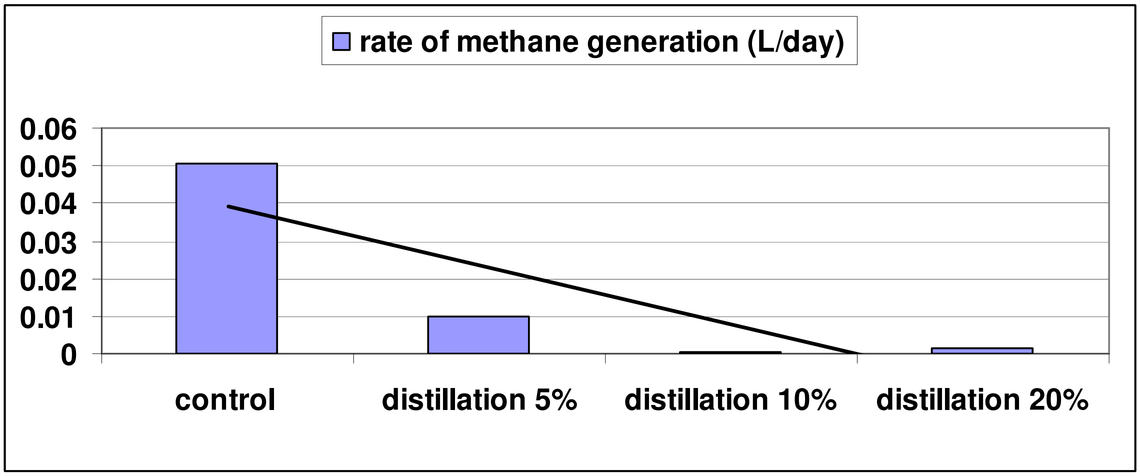

Figure 2.29: Rate of methane generation in control and distillation waste reactors

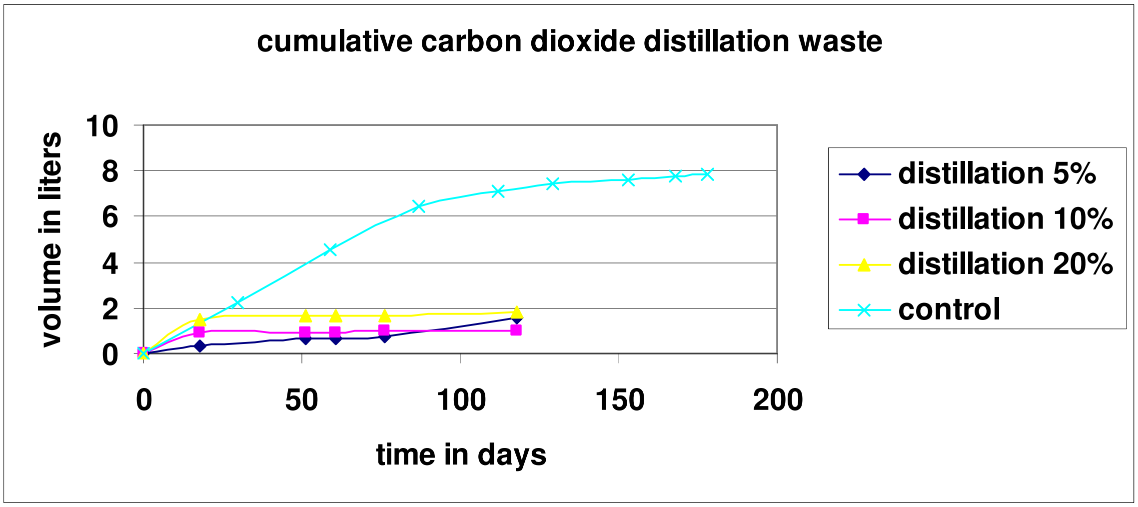

Figure 2.30: Cumulative carbon dioxide in control and distillation waste reactors

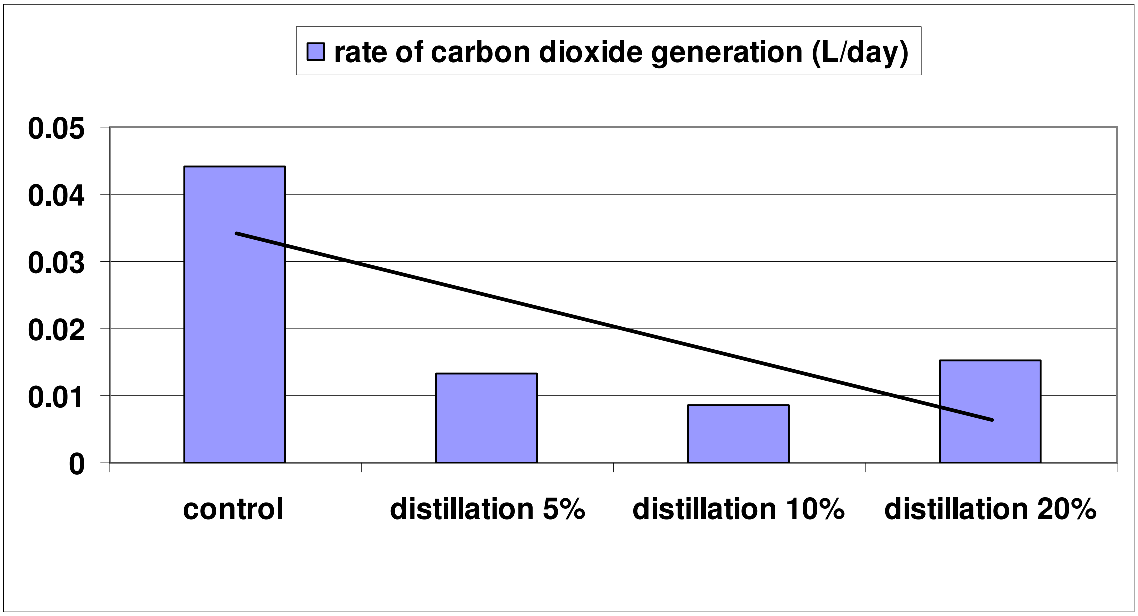

Figure 2.31: Rate of carbon dioxide generation in control and distillation waste reactors

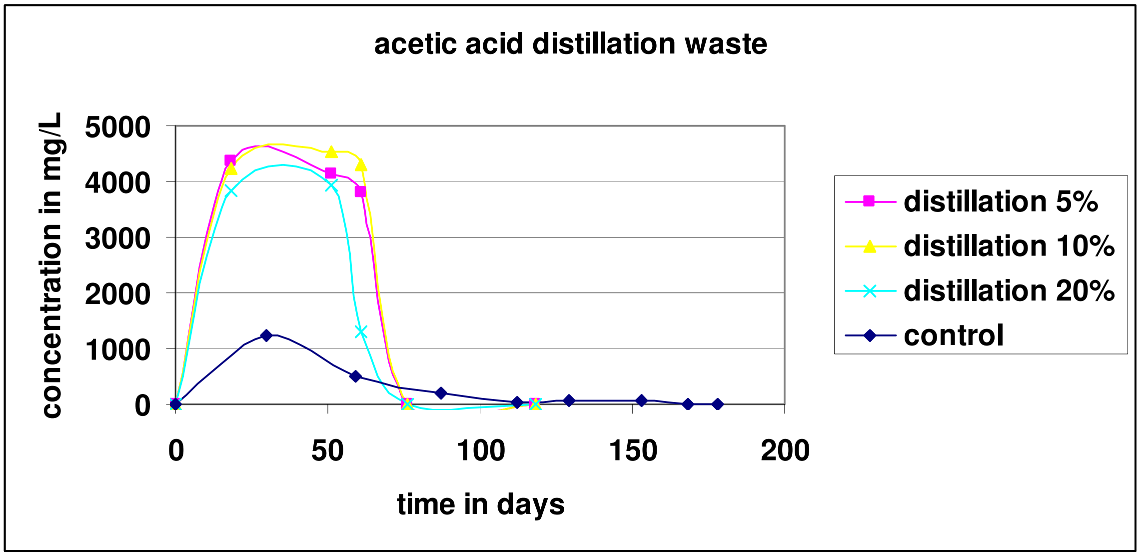

Figure 2.32: Acetic acid concentration in control and distillation waste reactors

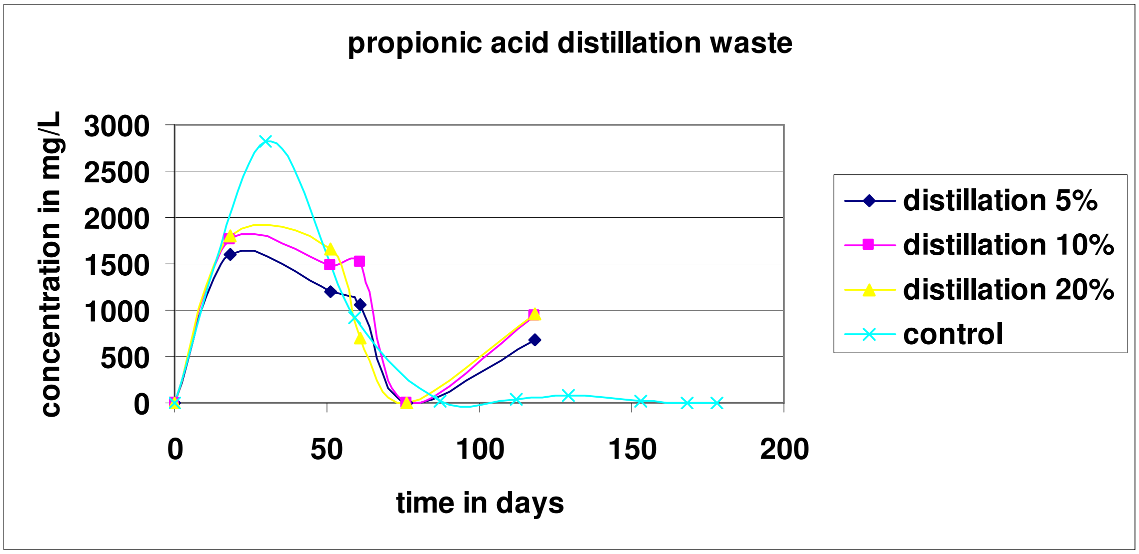

Figure 2.33: Propionic acid concentration in control and distillation waste reactors

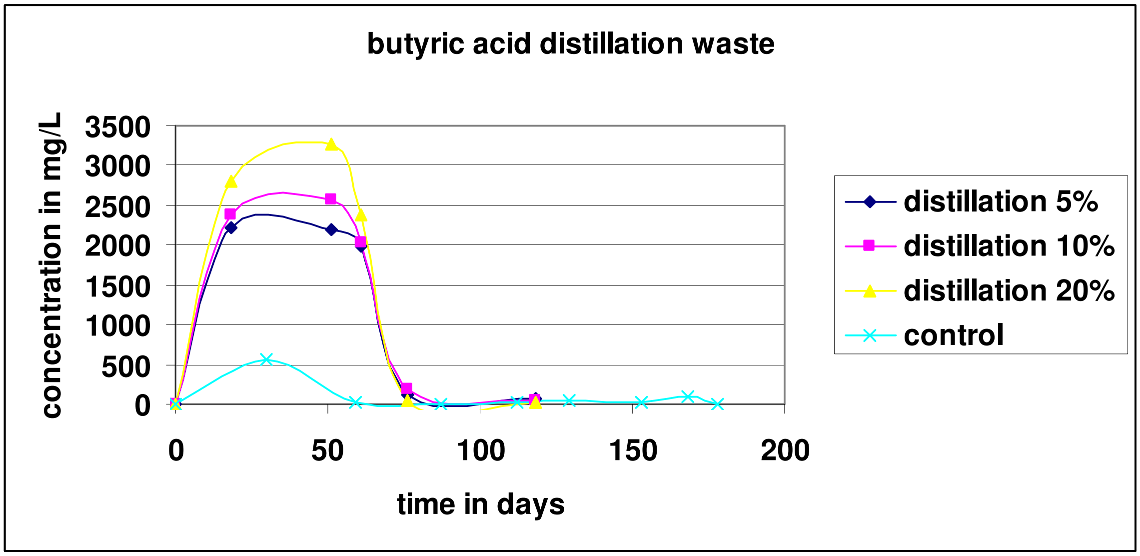

Figure 2.34: Butyric acid concentration in control and distillation waste reactors

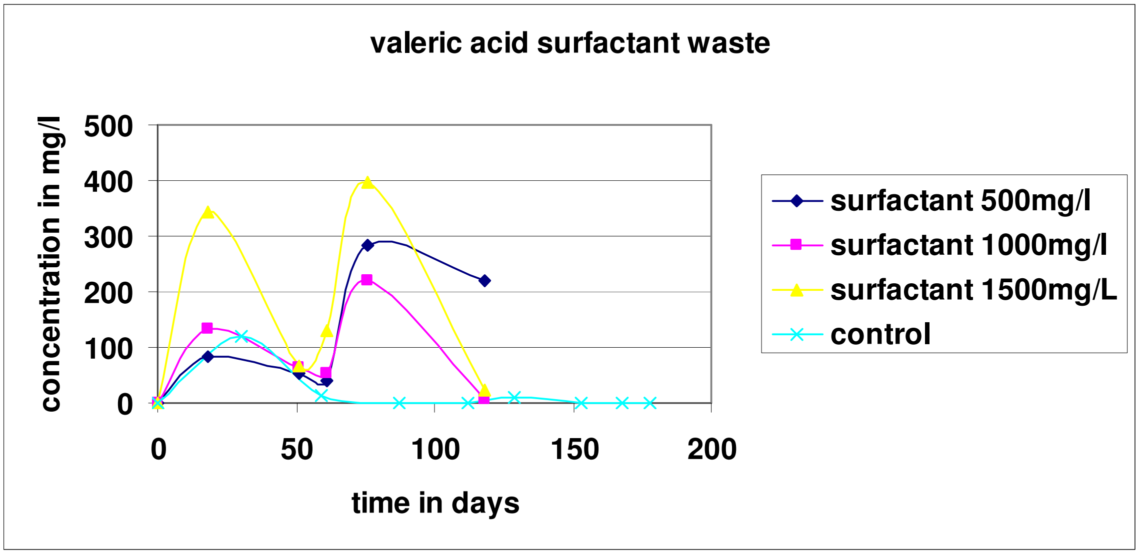

Figure 2.35: Valeric acid concentration in control and distillation waste reactors

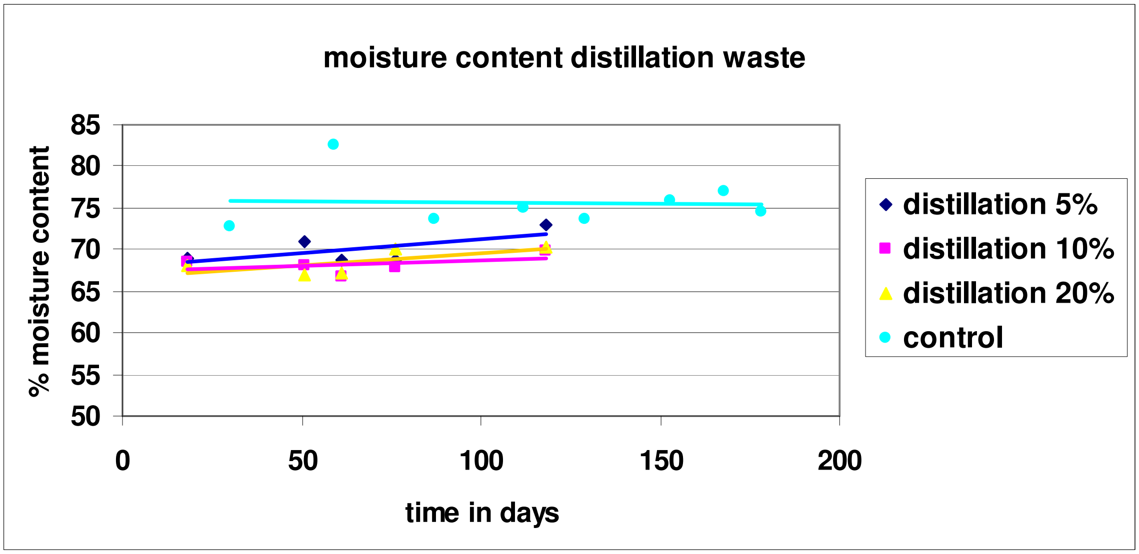

Figure 2.36: Percentage moisture content in control and distillation waste reactors

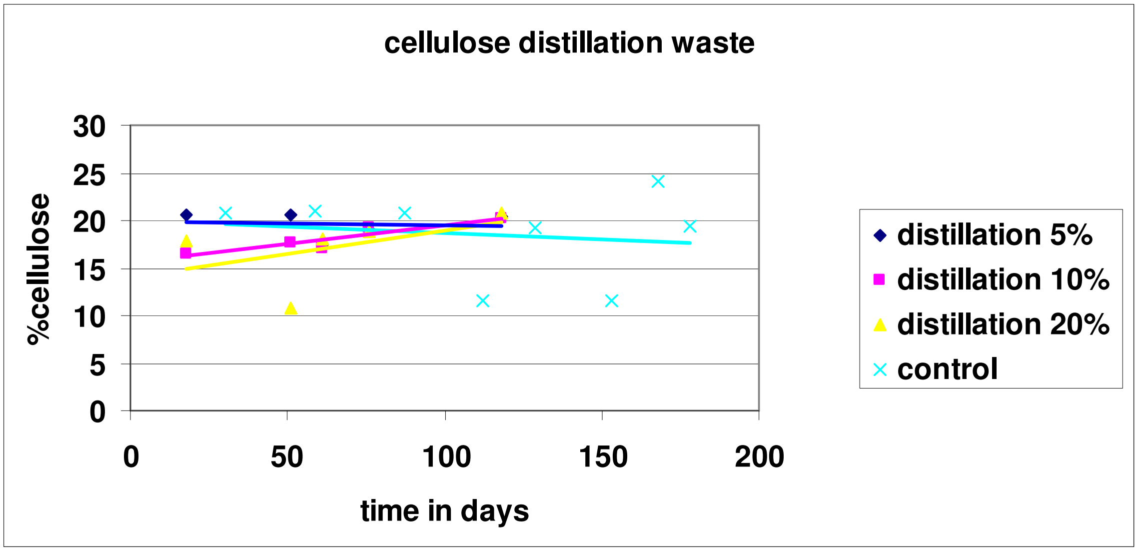

Figure 2.37: Percentage cellulose content in control and distillation waste reactors

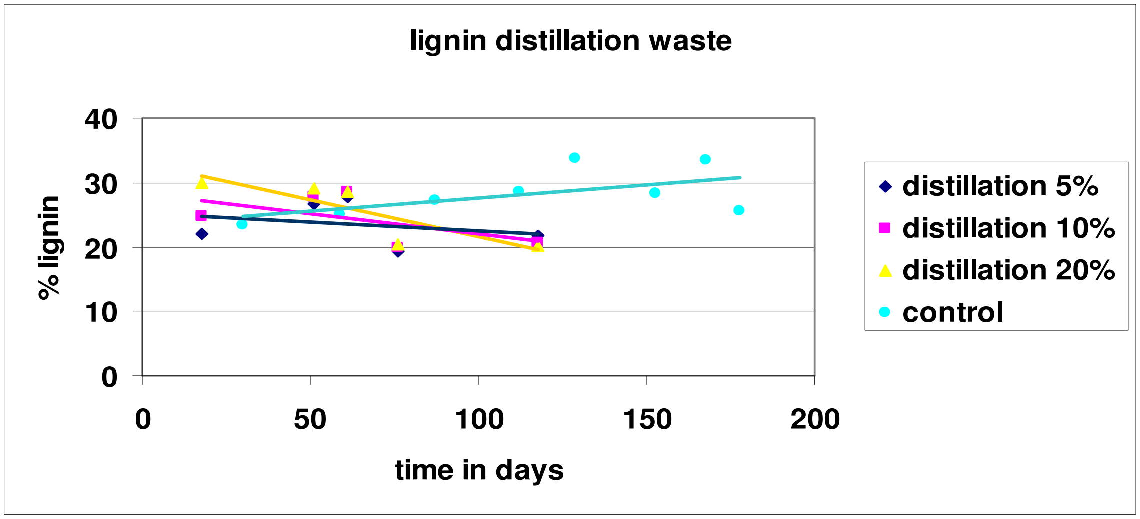

Figure 2.38: Percentage lignin content in control and distillation waste reactors

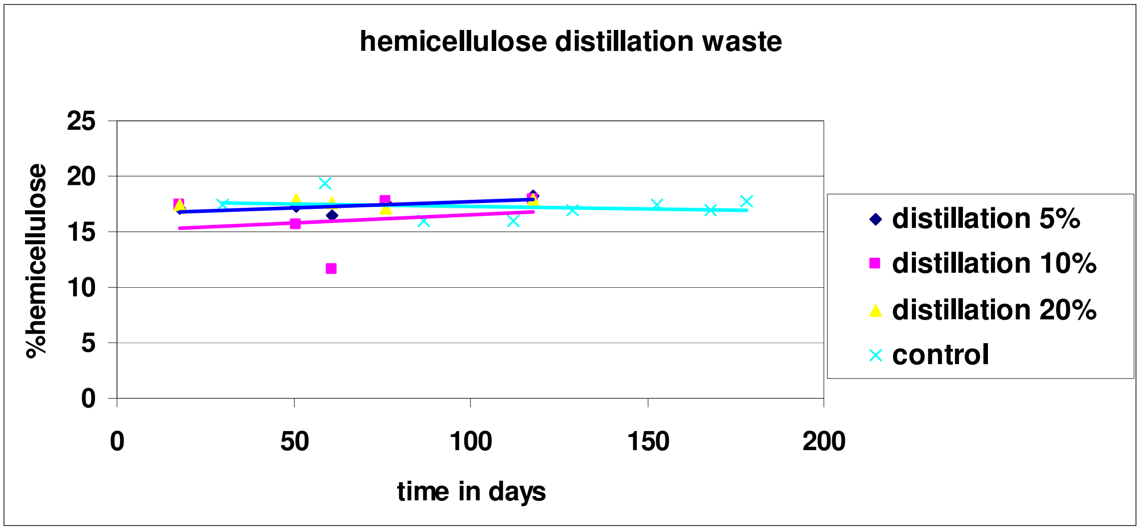

Figure 2.39: Percentage hemicellulose content in control and distillation waste reactors

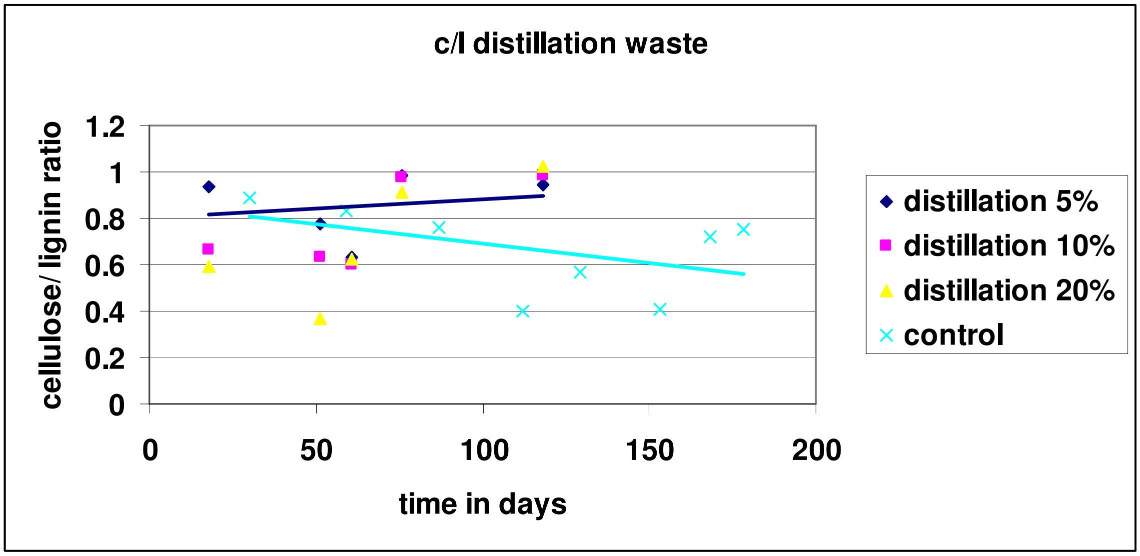

Figure 2.40: Cellulose to lignin ratio in control and distillation waste reactors

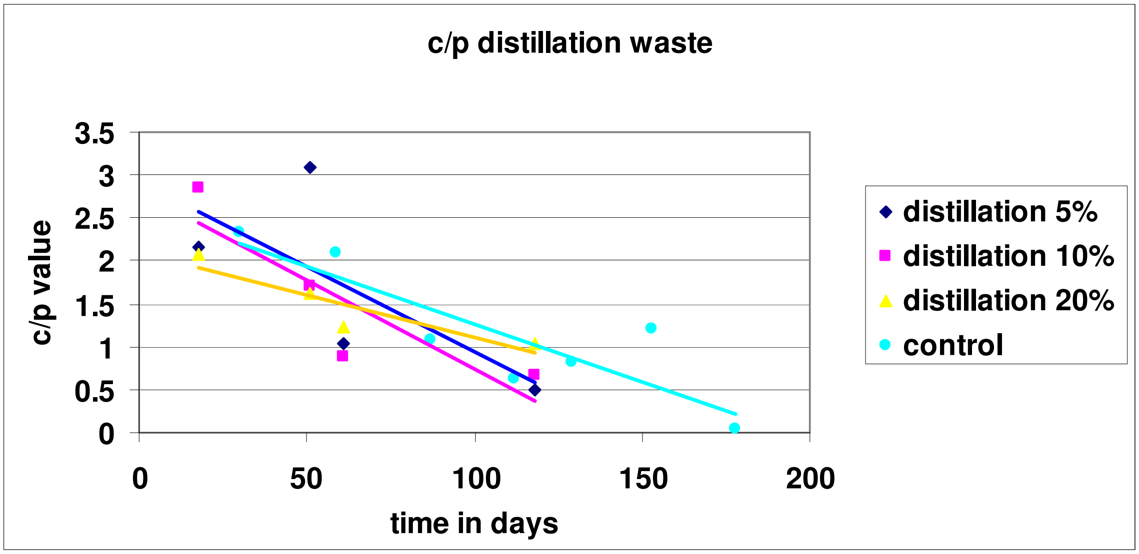

Figure 2.41: Cellulose to plastic ratio in control and distillation waste reactors

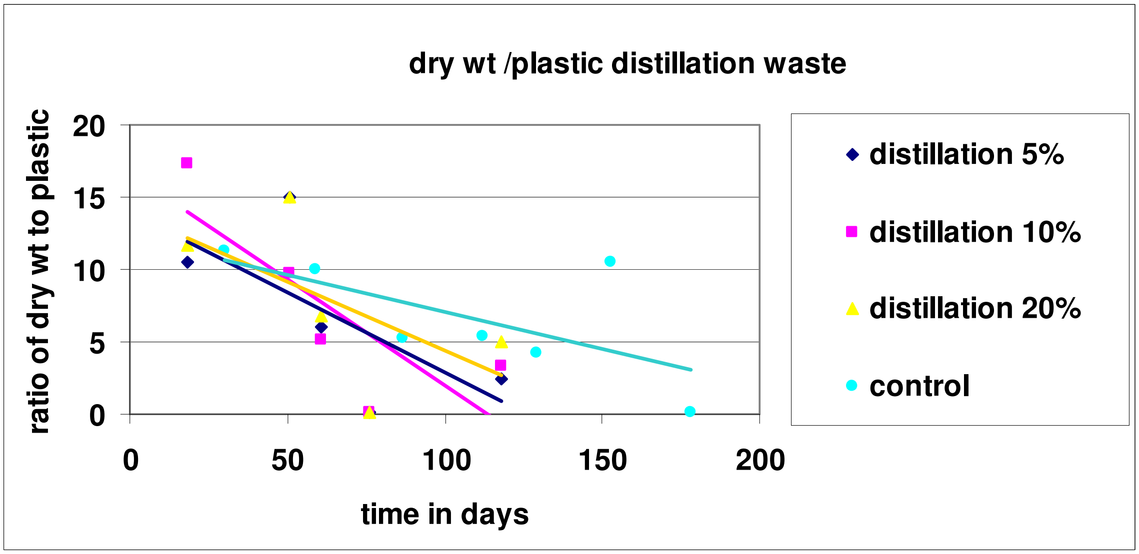

Figure 2.42: Dry weight to plastic ratio in control and distillation waste reactors

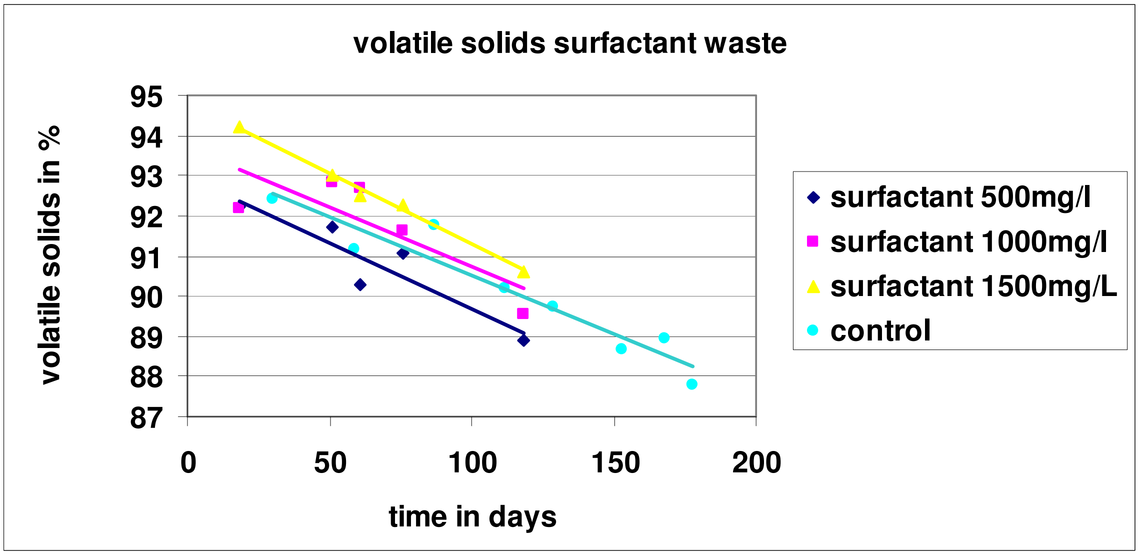

Figure 2.43: Volatile solids in control and surfactant waste reactors.

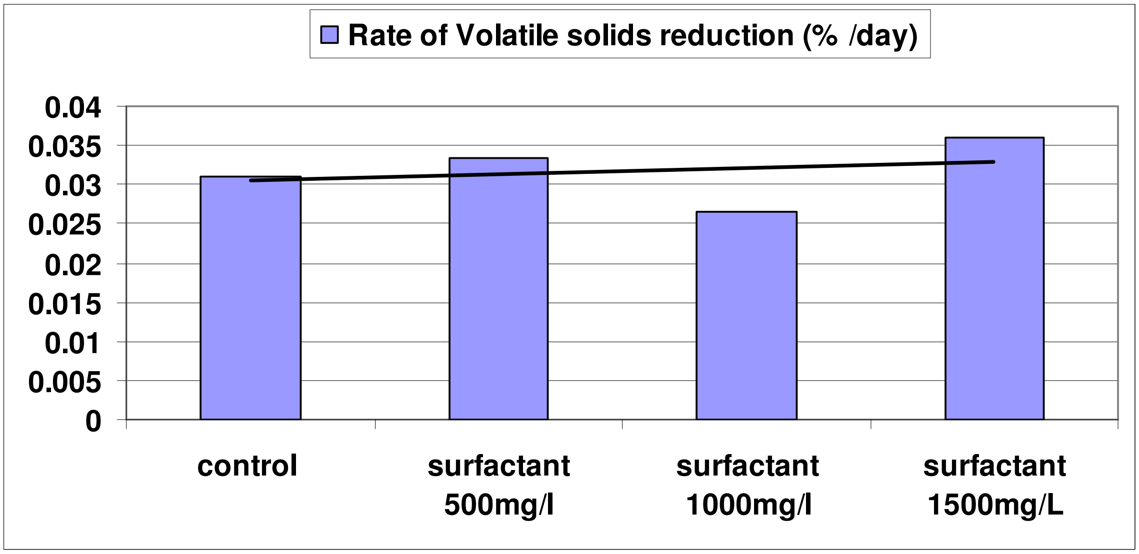

Figure 2.44: Volatile solids comparison surfactant waste reactors.

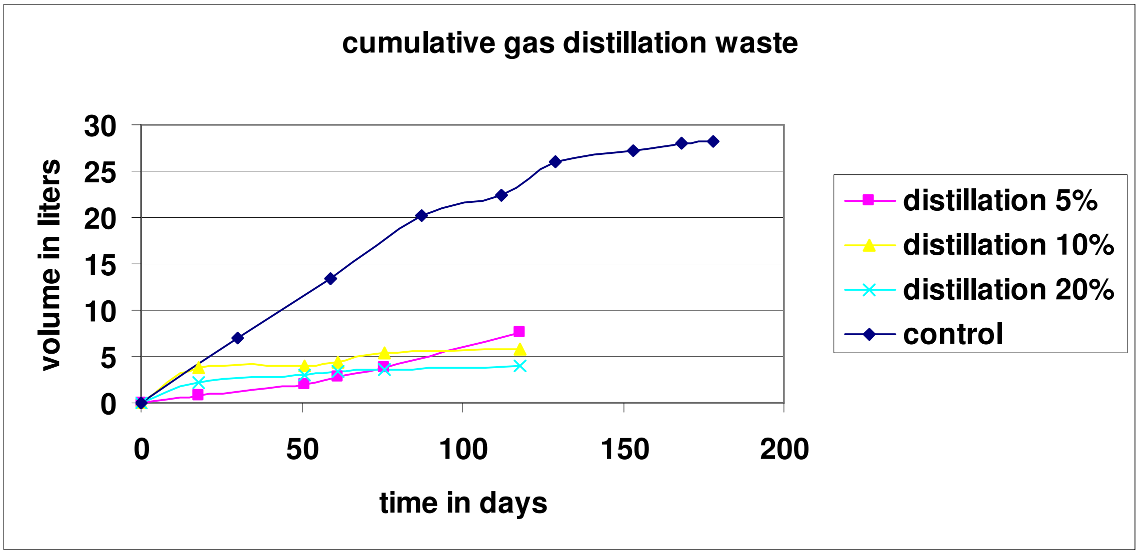

Figure 2.45: Cumulative total gas in control and surfactant waste reactors

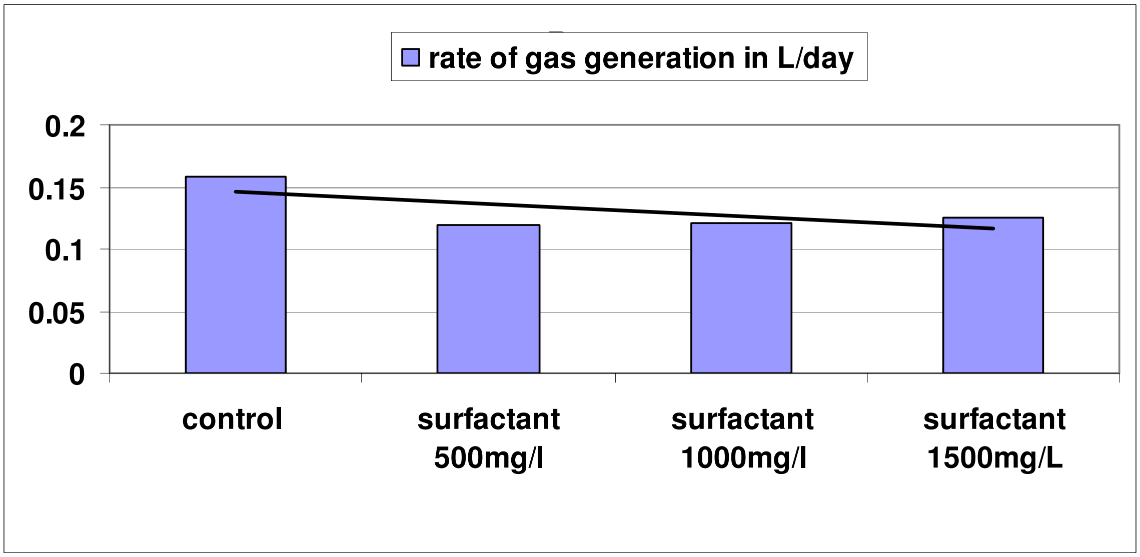

Figure 2.46: Rate of total gas generation in control and surfactant waste reactors

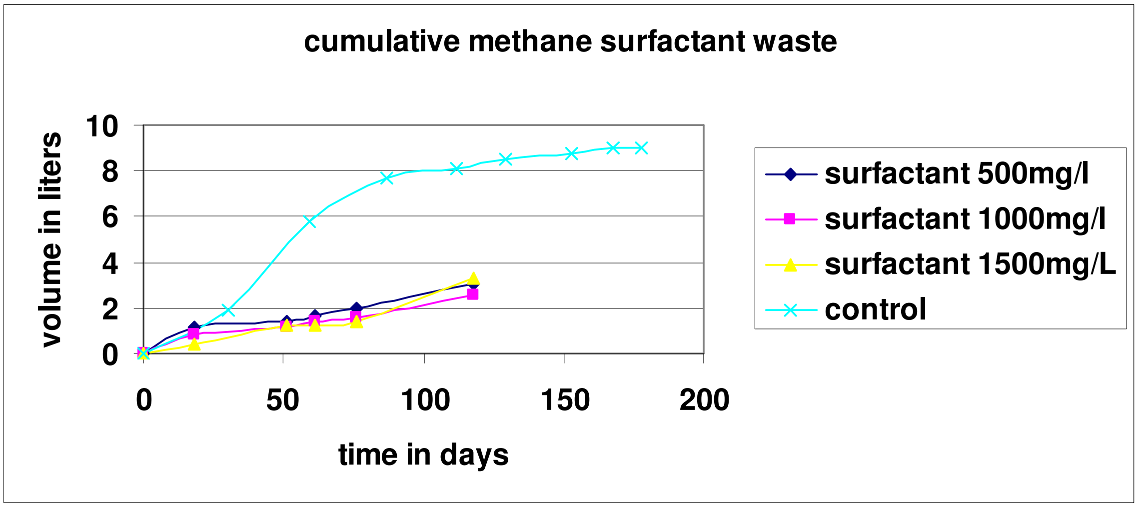

Figure 2.47: Cumulative methane in control and surfactant waste reactors

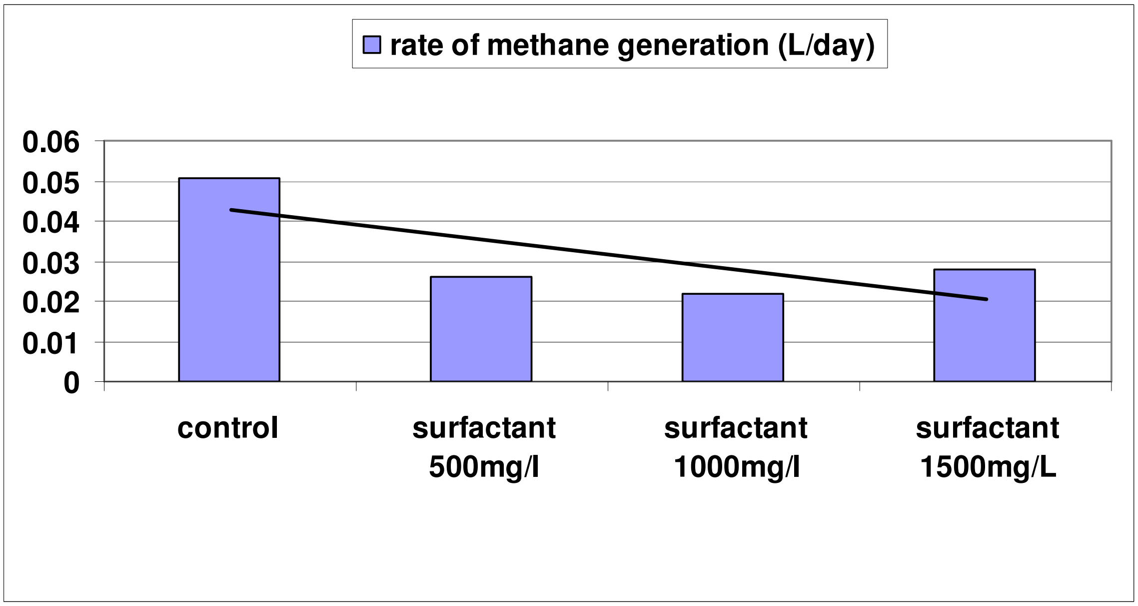

Figure 2.48: Cumulative methane comparison surfactant waste

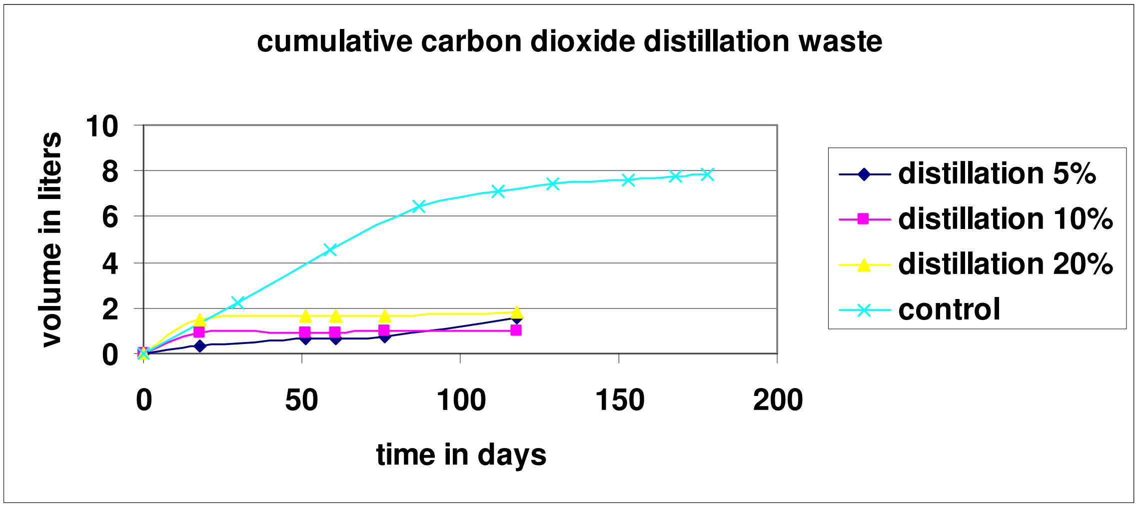

Figure 2.49: Cumulative carbon dioxide in control and surfactant waste reactors

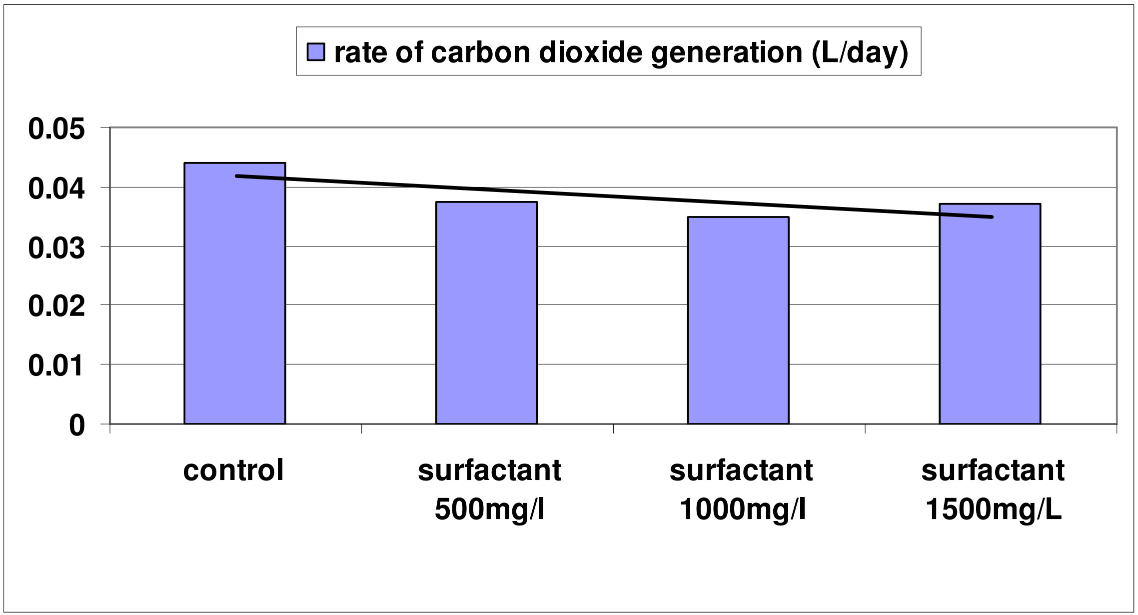

Figure 2.50: Cumulative carbon dioxide comparison in control and surfactant waste reactors

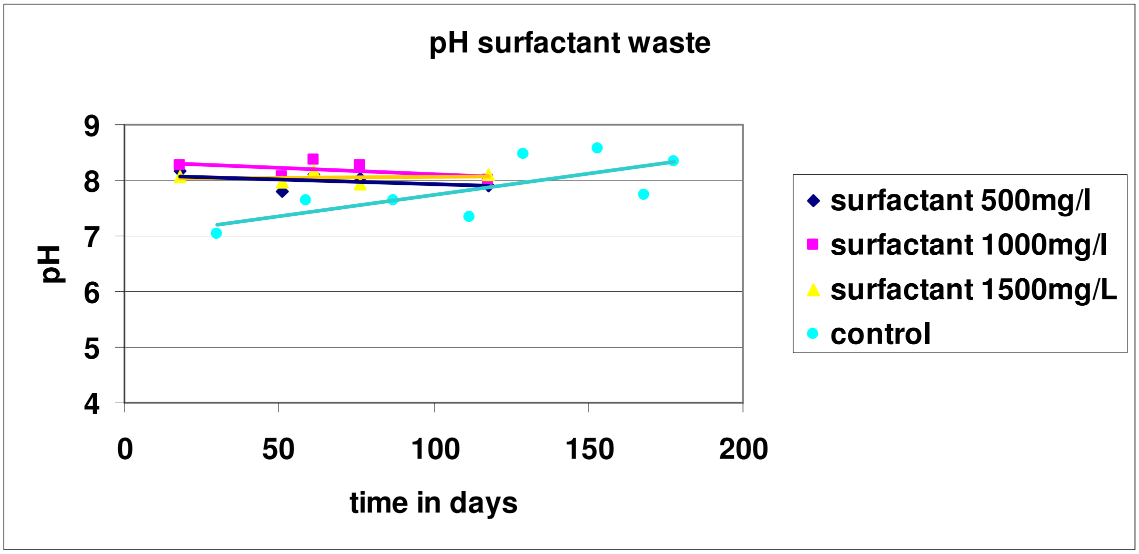

Figure 2.51: pH in control and surfactant waste reactors

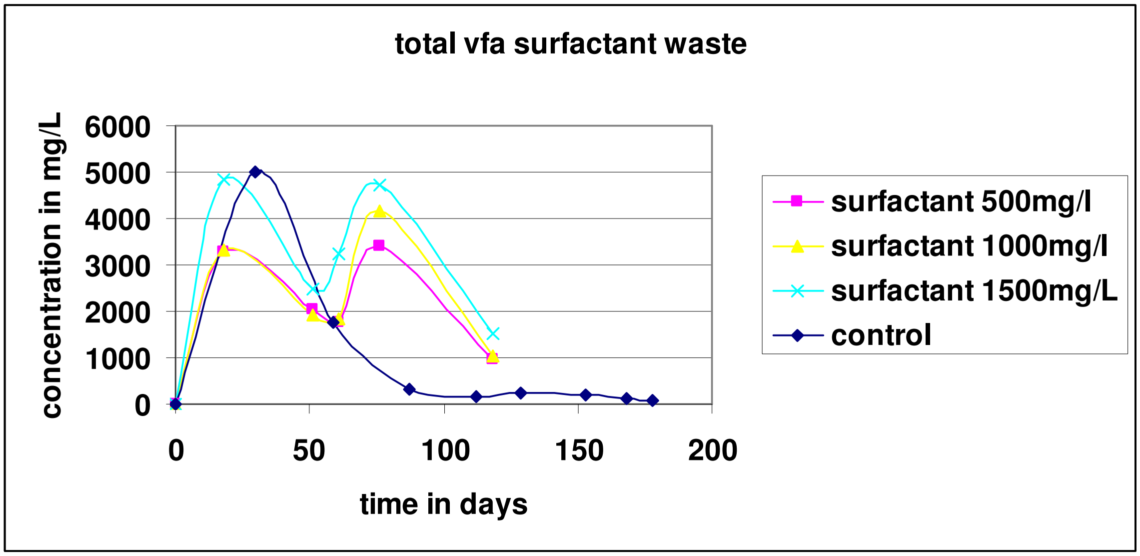

Figure 2.52: Total volatile fatty acids concentration in control and surfactant waste reactors

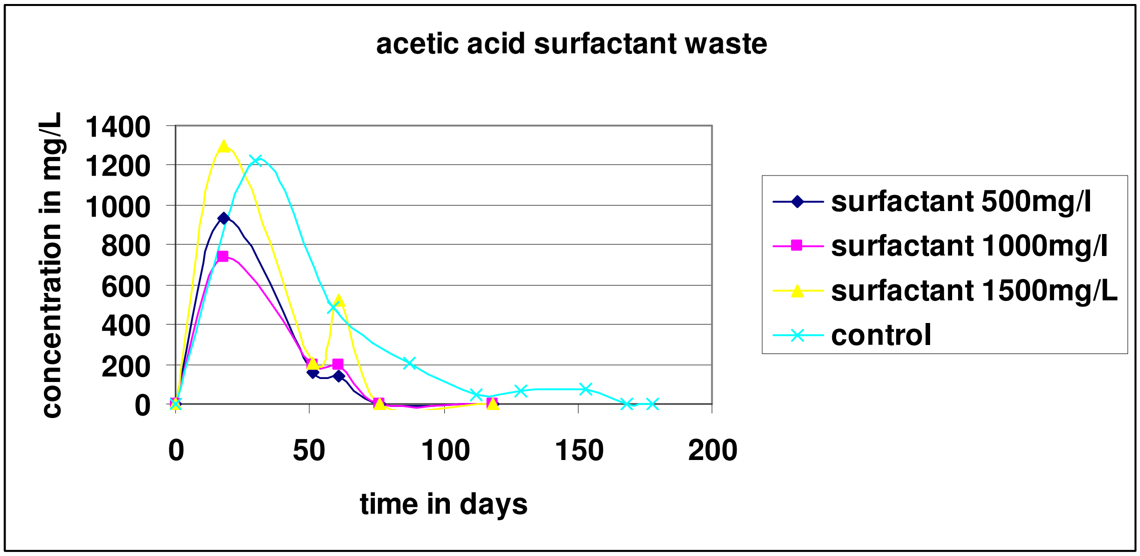

Figure 2.53: Acetic acid concentration in control and surfactant waste reactors

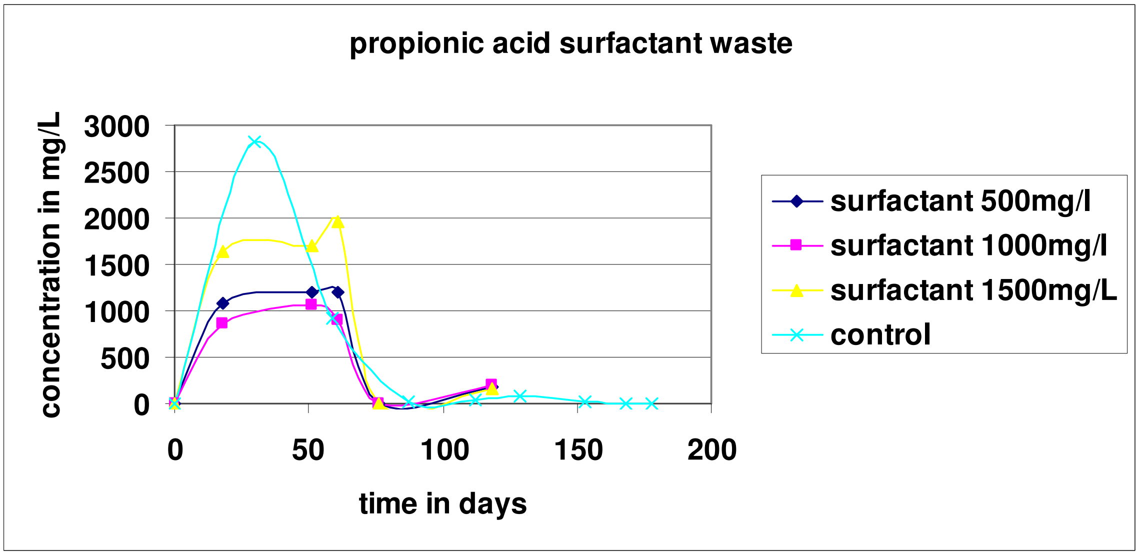

Figure 2.54: Propionic acid in control and surfactant waste reactors.

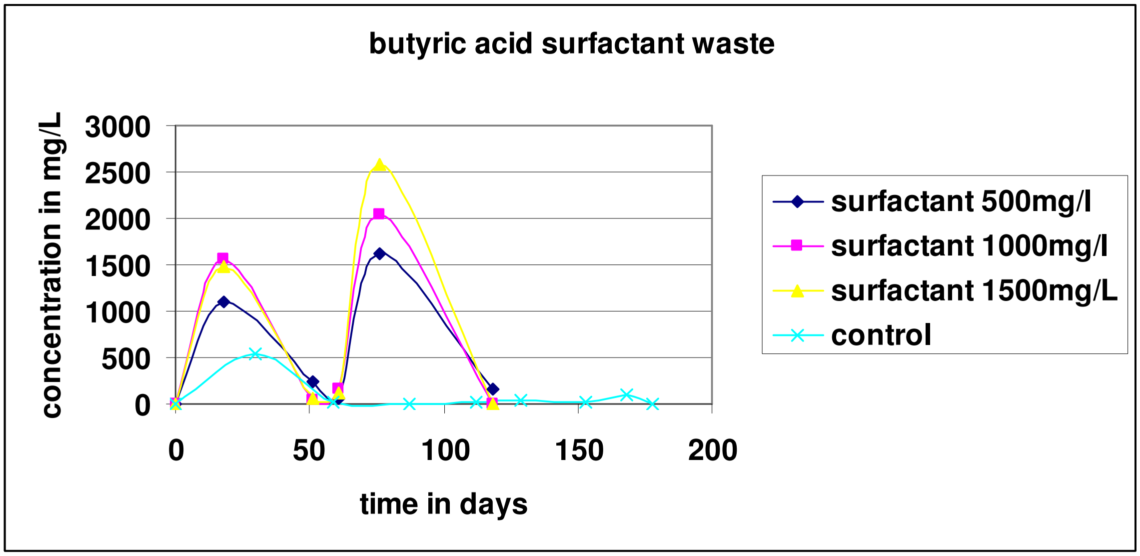

Figure 2.55: Butyric acid in control and surfactant waste reactors.

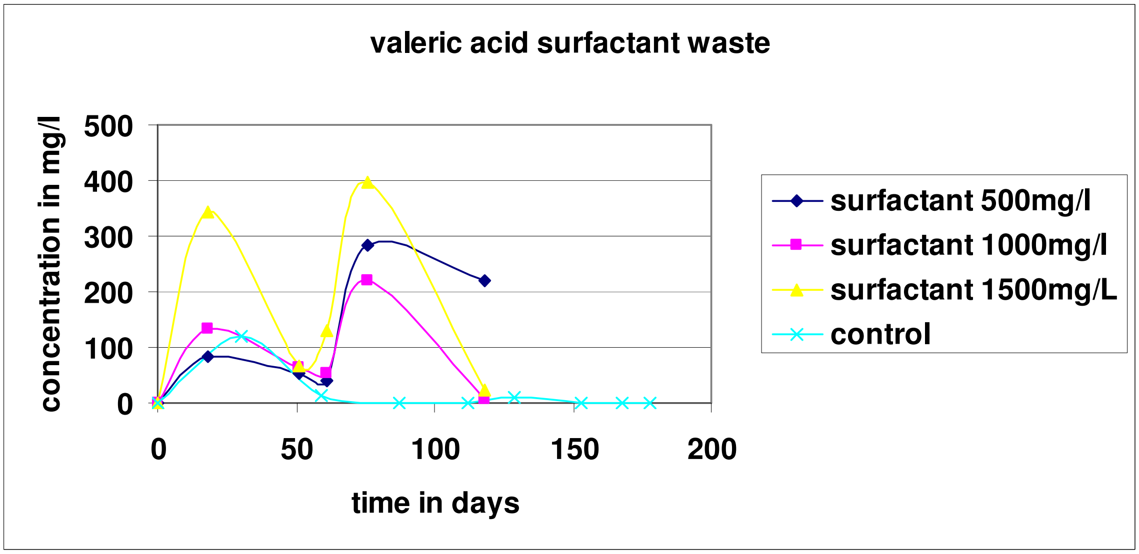

Figure 2.56: Valeric acid in control and surfactant waste reactors.

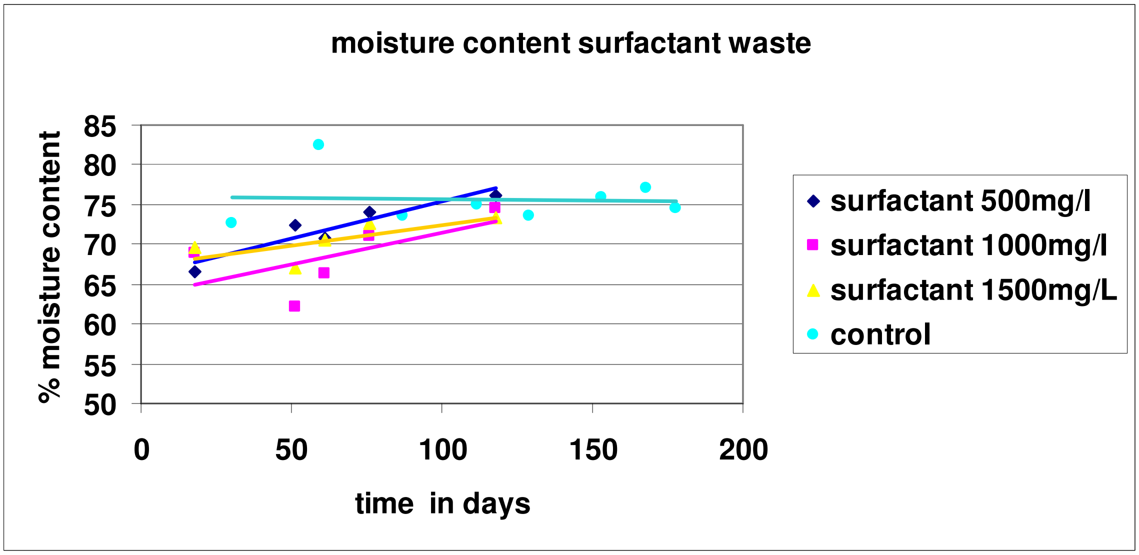

Figure 2.57: Percentage moisture content in control and surfactant waste reactors

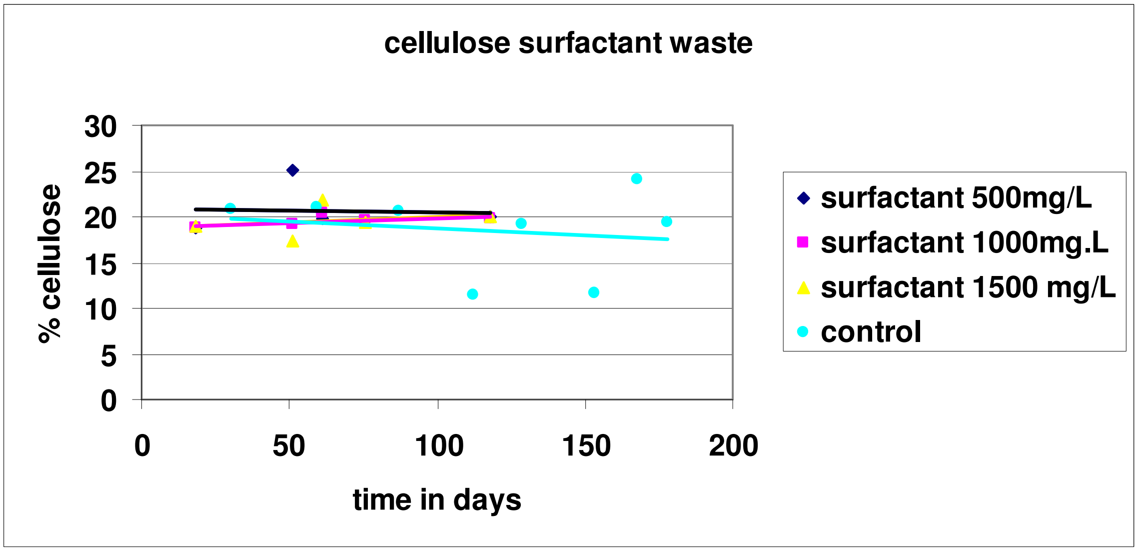

Figure 2.58: Percentage cellulose in control and surfactant waste reactors

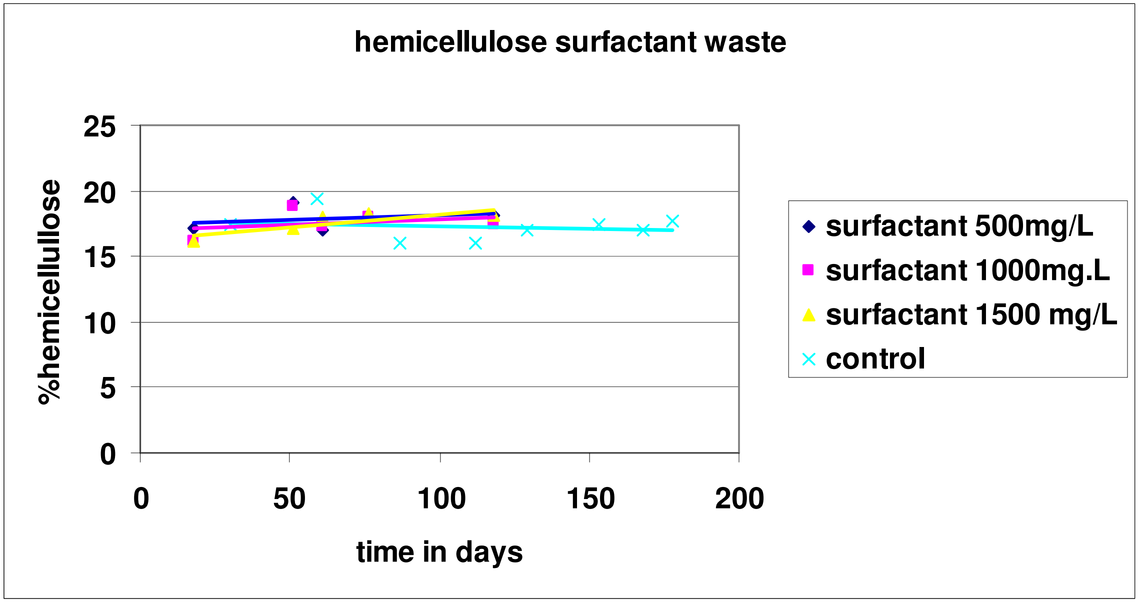

Figure 2.59: Percentage hemicellulose in control and surfactant waste reactors

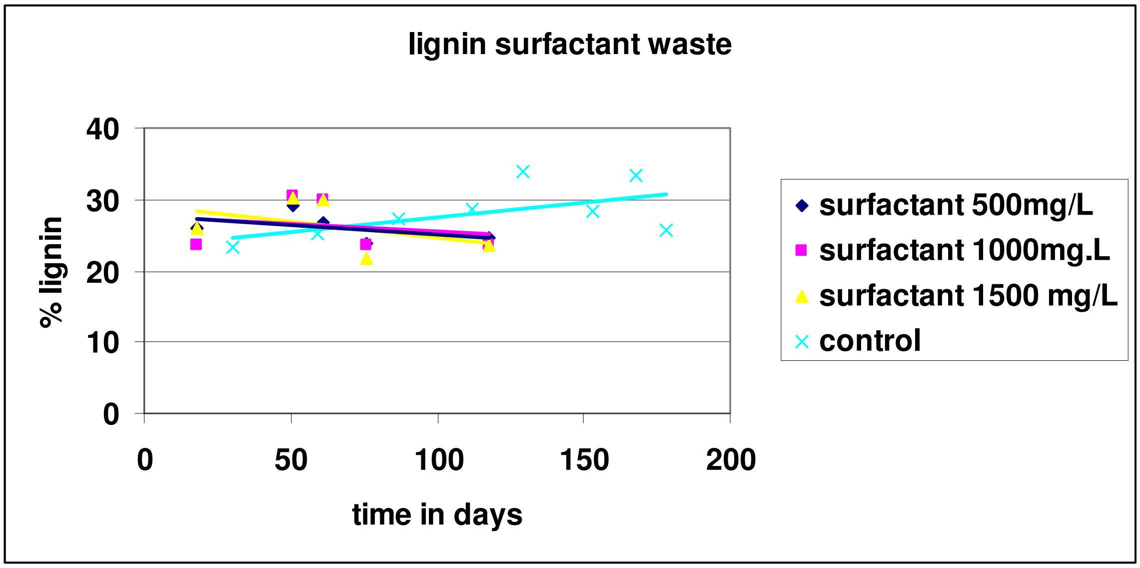

Figure 2.60: Percentage lignin in control and surfactant waste reactors

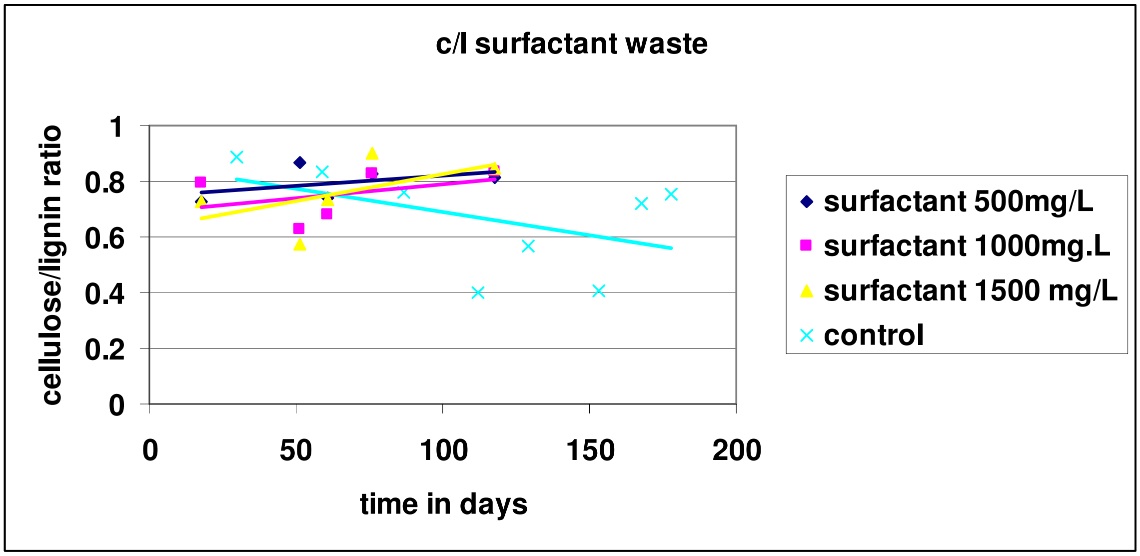

Figure 2.61: Cellulose to lignin ratio in control and surfactant waste reactors.

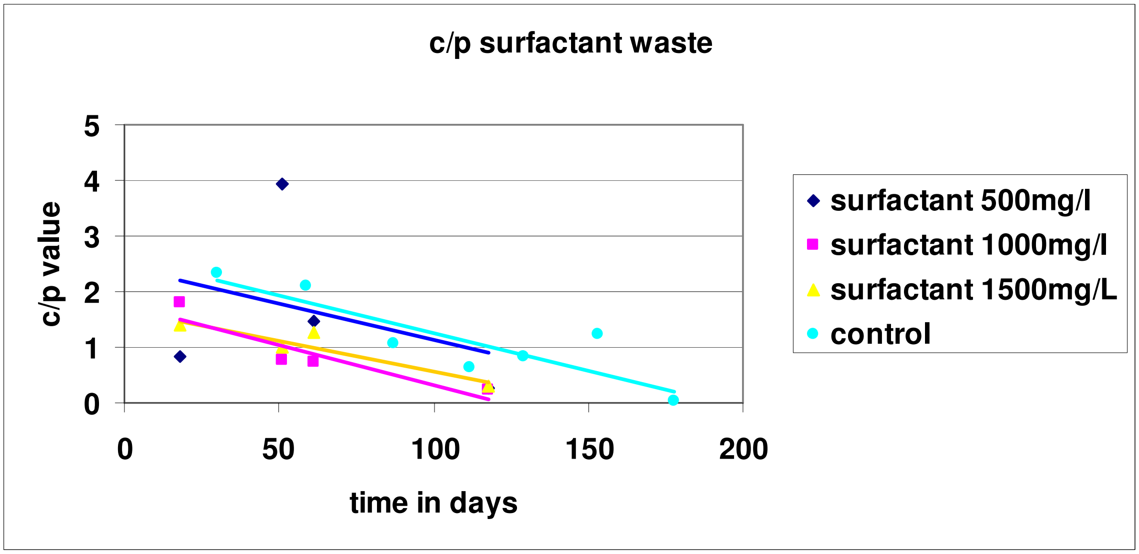

Figure 2.62: Cellulose to plastic ratio in control and surfactant waste reactors.

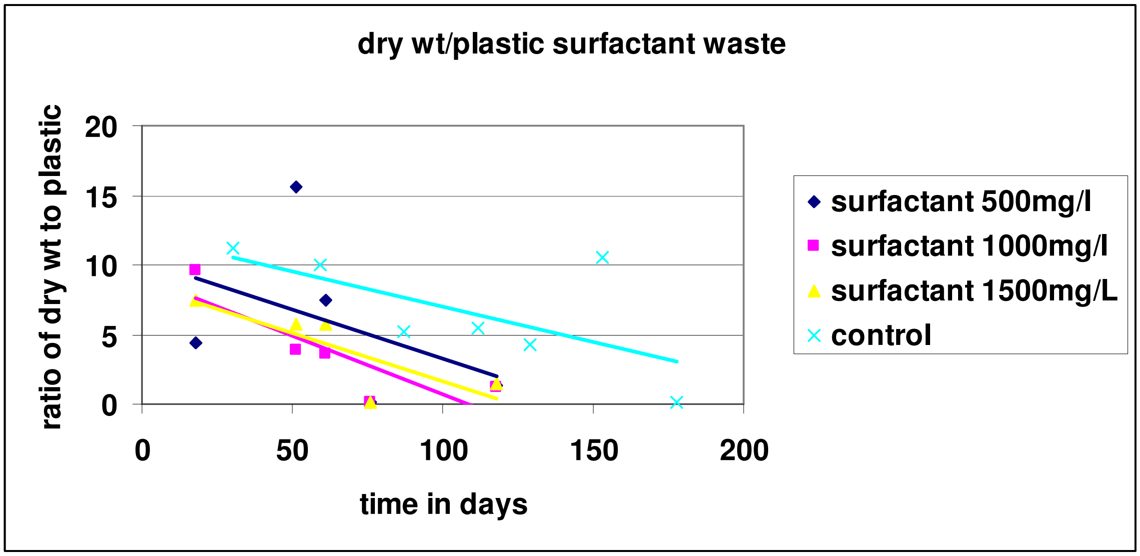

Figure 2.63: Dry weight to plastic ratio in control and surfactant waste reactors.

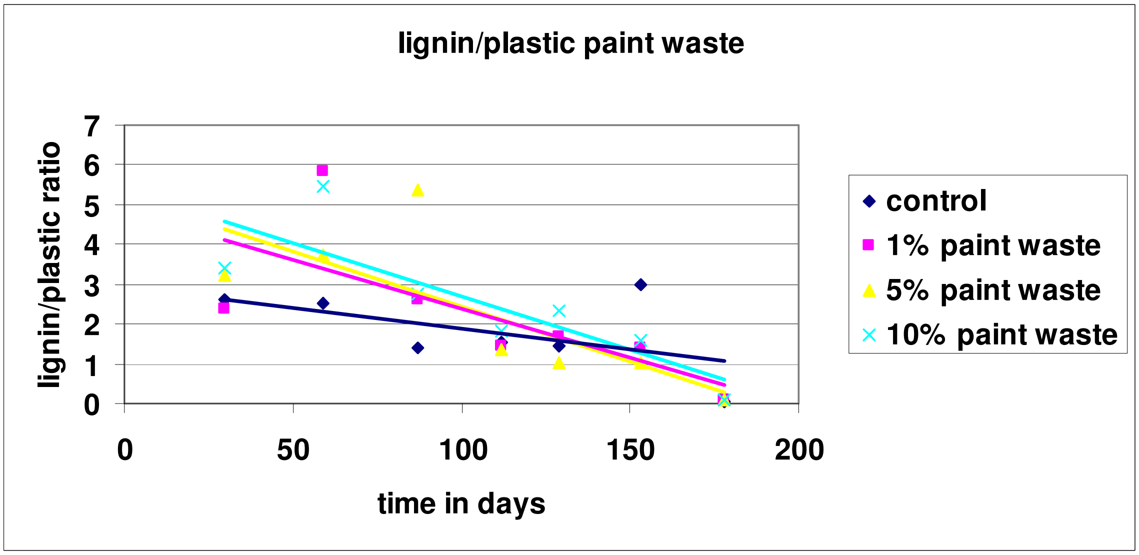

Figure 2.64: Lignin to plastic ratio in control and paint waste reactors.

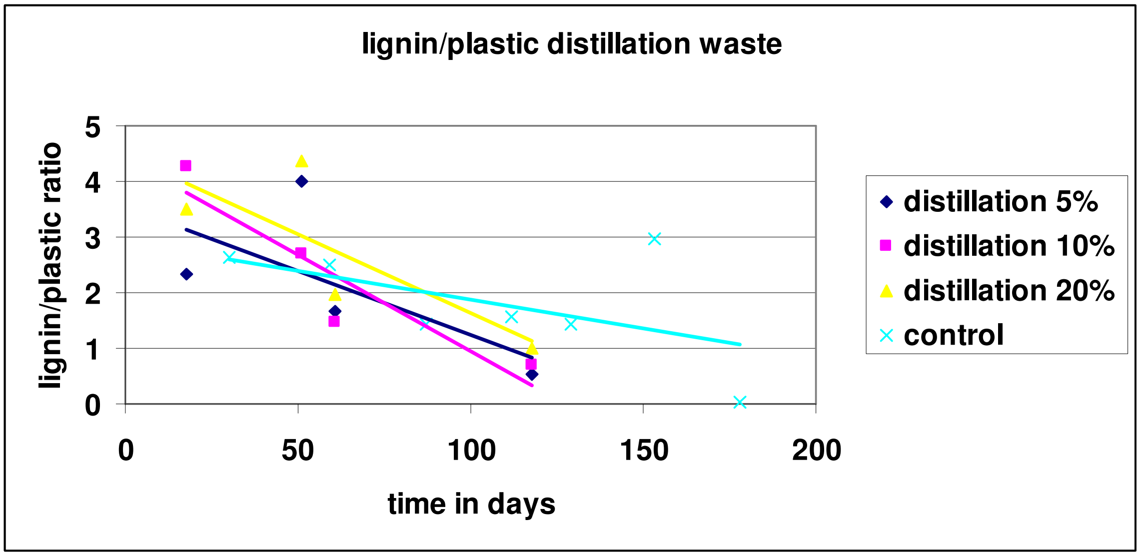

Figure 2.65: Lignin to plastic ratio in control and distillation waste reactors.

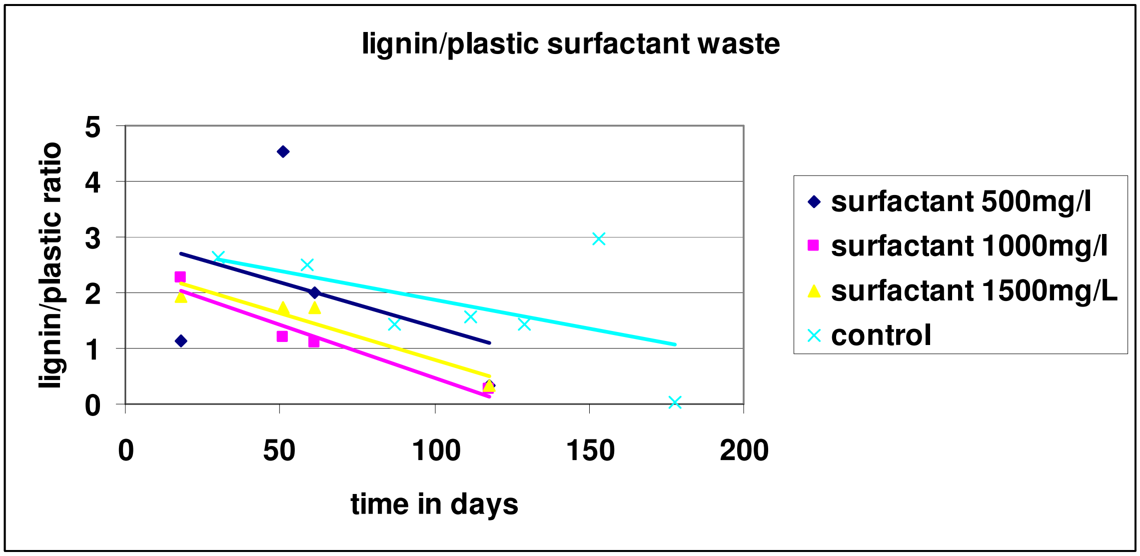

Figure 2.66: Lignin to plastic ratio in control and surfactant waste reactors.

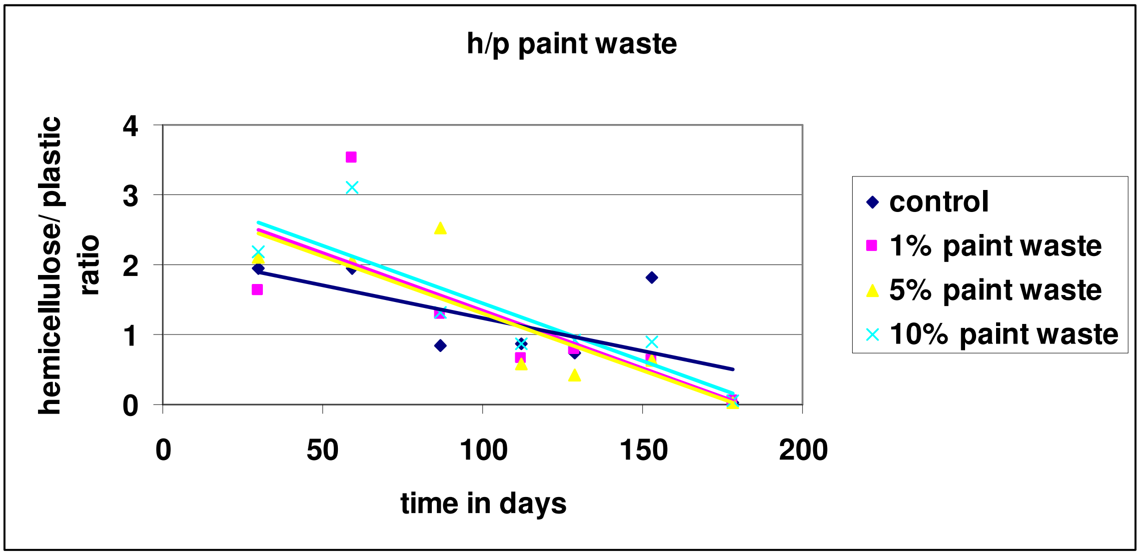

Figure 2.67: Hemicellulose to plastic ratio in control and paint waste reactors.

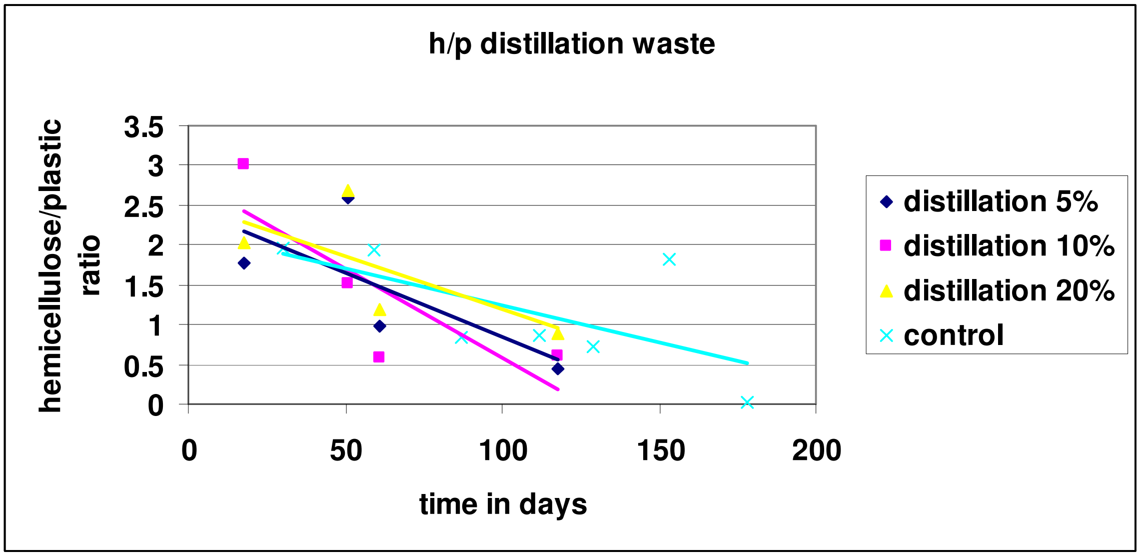

Figure 2.68: Hemicellulose to plastic ratio in control and distillation waste reactors.

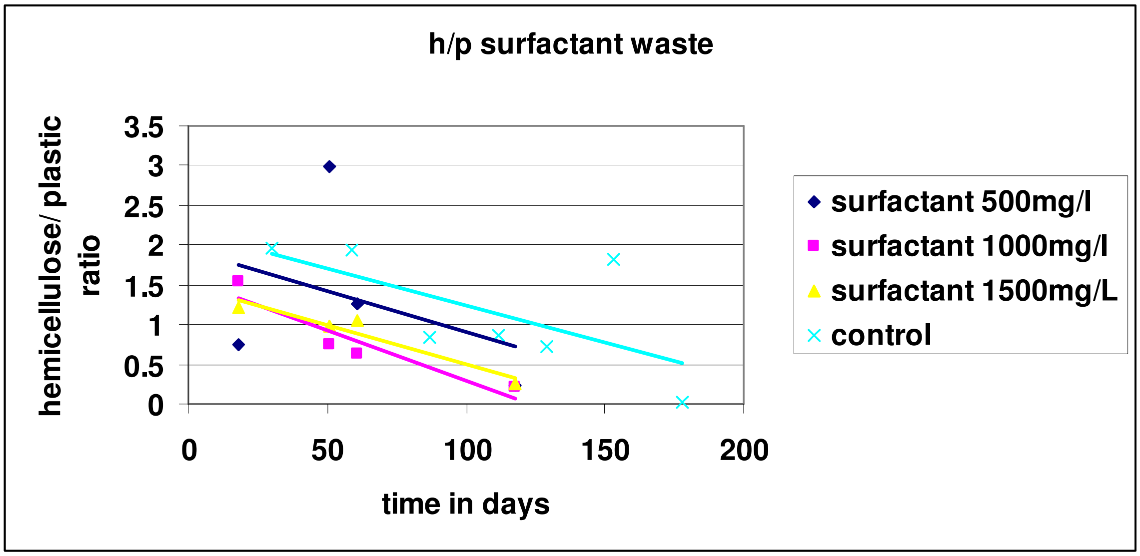

Figure 2.69: Hemicellulose to plastic ratio in control and surfactant waste reactors.