Effect of sugar waste, surfactant waste and paint waste on the degradation of anaerobic bioreactor landfill components

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ABSTRACT

Anaerobic bioreactor landfills are the landfills with an increased moisture content inorder to achieve a better biodegradation. Many Bioreactor landfills accept outside liquid wastes to achieve a higher moisture content . But the effect of these wastes on the degradation of landfill components is not known.

In this study, the effect of sugar waste, surfactant waste and paint waste on the degradation of landfill components was investigated. Sugar waste, surfactant waste and paint wastes in different concentrations were added to the combination of paper, cardboard, office paper and plastic with a total moisture content of 70%. The samples were incubated, sampled and analytical parameters analyzed. Sugar waste having a COD of 250,000 mg/L in a concentration of even 5% of the total weight was found inhibitive due to a drop in pH and accumulation of volatile fatty acids. Reactors with surfactant concentrations ranging from 50 mg/L to 500 mg/L showed that a higher concentration of 500 mg/L or above may be inhibitive in nature and the inhibition increases with increase in the concentration of surfactant. However, paint waste with a concentration of even 7.5% highly inhibited the degradation in the reactors. This could possibly be because of some toxicity.

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CHAPTER 1: LITERATURE REVIEW

1.1 Solid waste and management:

Solid waste consists of domestic waste arising from day to day activities (Tchobanoglous et al., 1993). The Environmental Protection Agency (EPA) defines municipal solid waste (MSW) as "more commonly known as trash or garbage — consists of everyday items such as product packaging, grass clippings, furniture, clothing, bottles, food scraps, newspapers, appliances, paint, and batteries." (http://www.epa.gov/msw/facts.htm). It is a technological challenge to determine a convenient method for the safe disposal of solid waste (Tchobanoglous et al., 1993). Reports show that there is a huge increase in the generation of solid waste in USA between 1960 and 2005 (USEPA, 2005). As per the recent report from EPA, 247.5 million tons of municipal solid wastes were generated in 2005 across the USA. Although there was a reduction of 1.6 million tons from previous year, this is an enormous quantity to be treated and safely disposed.

1.2 Constituents of Municipal Solid Waste:

The EPA, in their recent report reveals that paper and paper board are the major constitutes of the MSW, accounting for about 34% of the total solid waste generated in USA (USEPA, 2005). This is followed by yard trimmings, food waste and then plastics. Yard trimmings account for about 13.1%, food waste for about 11.9% and plastics for about 11.8% of the total municipal waste constituents in 2005 (Figure 1.1). When categorized as products, containers and packaging are the major product categories in

solid waste accounting for about 31.2% followed by nondurable goods accounting for about 25.9% of the total waste generation.

1.3 Management of solid waste:

Integrated solid waste management (ISWM) is defined as employing appropriate techniques and sufficient methods to achieve the specific waste management goals (Tchobanoglous et al., 1993). The EPA suggests four effective methods for solid waste disposal and management. The primary method is source reduction which involves minimizing the usage of material, reuse of products etc. This is followed by recycling which includes the reusage of materials in other possible desired forms. Combustion/incineration with energy recovery is the third preferred method of solid waste management. The fourth preferred method for the solid waste disposal is landfills.
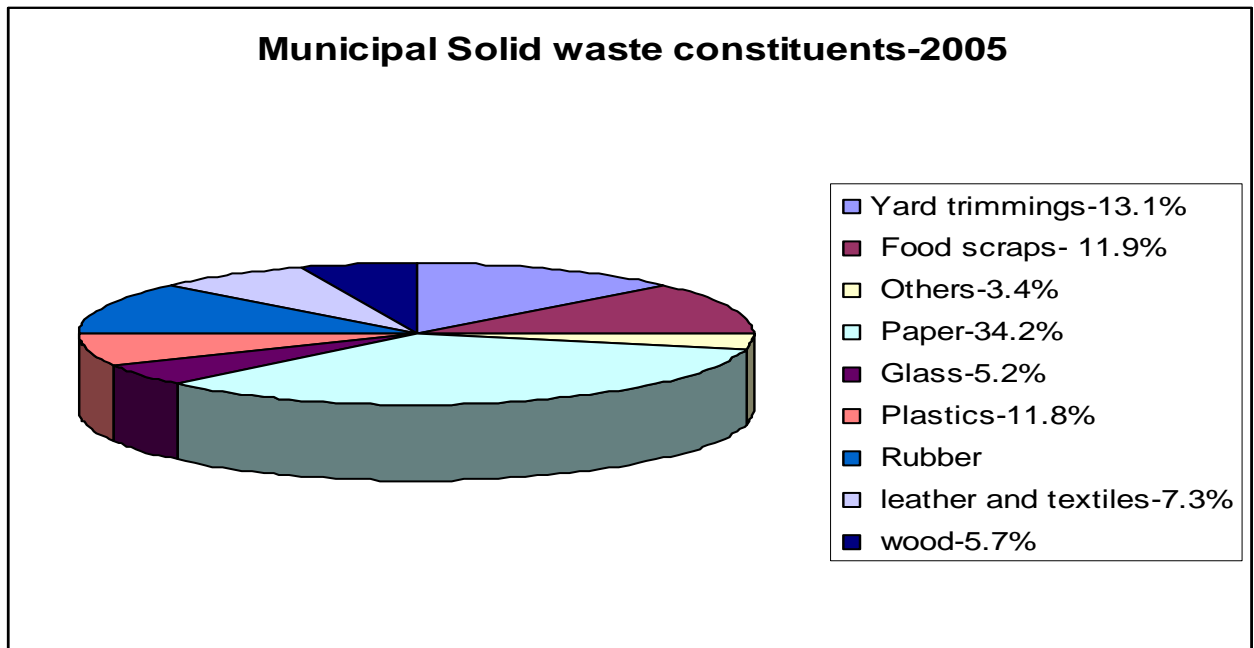
Figure 1.1 Constituents of municipal solid waste in 2005 (adopted from USEPA 2005)

1.4 Landfills:

Landfills are the facilities where the solid waste is disposed on the earth's surface (Tchobanoglous et al., 1993).This is a disposal method for which there is no energy recovery expected. A proper landfilling includes steps such as monitoring the incoming waste, proper disposal of the waste, monitoring and tapping of constituents emerging from the landfill and setting up of control measures needed (Tchobanoglous et al., 1993). During 2005, the quantity of solid waste landfilled accounted for about 54.3% of the total emerged waste (USEPA, 2005). Although the landfill size has increased much, the number of landfills has decreased substantially from 8000 to 1654 over the last 18 year in USA (USEPA, 2005). Different types of landfills include municipal solid waste landfill, bioreactor landfills, construction and demolition debris landfill, industrial landfill etc.

1.4.1 Bioreactor landfill:

Bioreactor landfills are designed for a faster stabilization of solid waste compared to conventional landfills. The moisture content of bioreactor landfill is increased for better microbial activity and hence a better degradation (Bagchi, 2004). This is mainly done by leachate recirculation (Kelly et al., 2006) which ensure a water content above 40% (Bagchi, 2004). It has been shown that bioreactors settle faster and settle 30% more than conventional ones at any given time which gives more room for waste disposal. While the waste in a conventional landfill may take more than 50 years to stabilize, the waste in a bioreactor could be stabilized within 5 years (Kelly et al., 2006). The other advantages of a bioreactor landfill include

- Earlier gas generation

- Quicker leachate stability

- Earlier and more generation of gas compared to conventional landfills

- Quicker settlement of landfill etc.(USEPA, 2002)
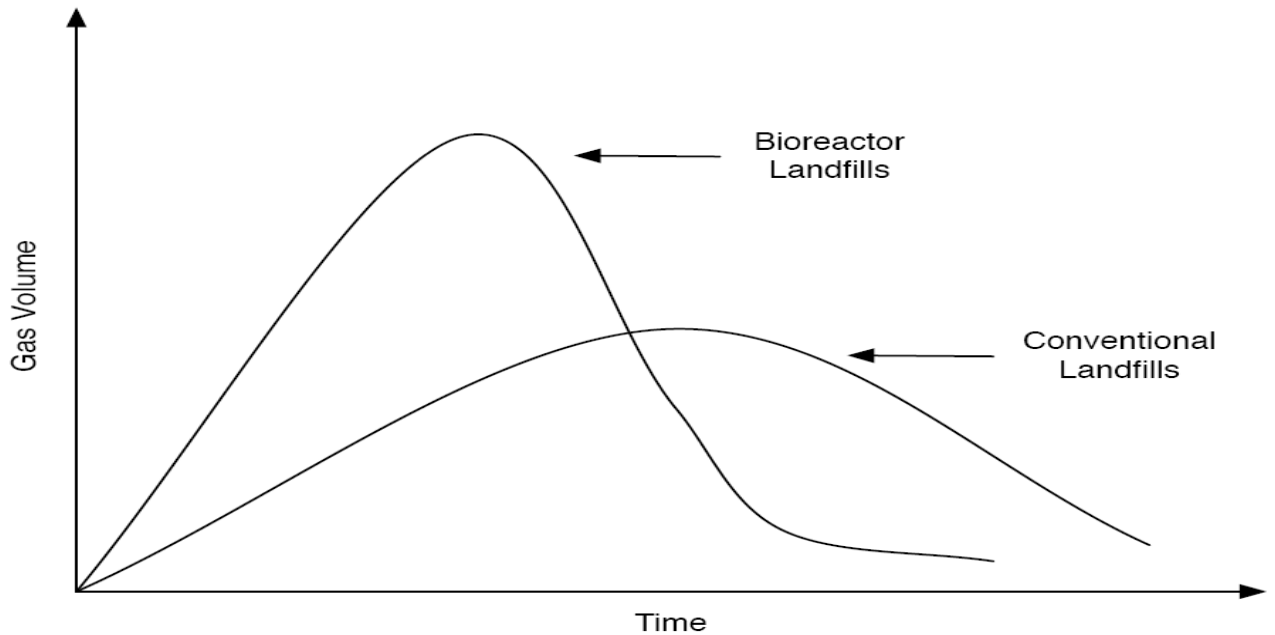
Figure 1.2 Comparison between bioreactor and conventional landfill settlement (adopted from Bagchi 2004)

1.4.2 Types of Bioreactor landfill:

There are mainly 3 types of bioreactor landfills- aerobic, anaerobic and hybrid reactors (Bagchi, 2004).

1.4.2.1 Aerobic reactor:

Aerobic reactors make use of aerobic bacteria in degrading materials in the landfill. Since aerobic bacteria grow quickly than anaerobic bacteria, the degradation in the aerobic reactors is faster (WM). In such type of landfills, aerobic conditions are usually

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maintained by injection of air into them (WM). The main disadvantage of the aerobic reactors is that they are highly susceptible to fires (WM).

1.4.2.2 Anaerobic bioreactor landfills:

In anaerobic bioreactors, the degradation is done by anaerobic bacteria. Although degradation is slower in anaerobic than aerobic landfills, the main advantage of anaerobic landfills is production of methane. The main disadvantage of an anaerobic reactor is that initial cost of setting up is high compared to an aerobic reactor due to the need of more specialized units (Grady et al., 1999).

In hybrid reactors, aerobic and anaerobic conditions are introduced alternatively thereby achieving the advantages of both systems.

1.4.3 Metabolism in an anaerobic bioreactor landfill:

The first step in an anaerobic operation is particulate hydrolysis in which large soluble organic molecules are reduced to smaller size. This is to facilitate the transport of the particles across the membrane of bacteria (Grady et al., 1999). These reactions are catalyzed by a number of extra cellular enzymes which are produced by fermentative bacteria (Grady et al., 1999).

This is followed by acidogenesis in which volatile acids like propionic acid, butyric acid etc. get produced by domain bacteria (Grady et al., 1999). Another peculiarity of this step is the production of direct methane precursors, acetic acid and hydrogen. Hydrogen is formed in this step through 2 different ways- 1) through the fermentative reaction in which dehydrogenation of pyruvate occurs and the quantity of

hydrogen formed in this case is much less and through the oxidation of volatile acids into acetic acid. Another reaction which occurs in the acidogenesis step is the production of acetic acid through a reaction between hydrogen and carbon dioxide by hydrogen oxidizing acetogens (Grady et al., 1999). But, the quantity of acetic acid formed through this reaction is low.
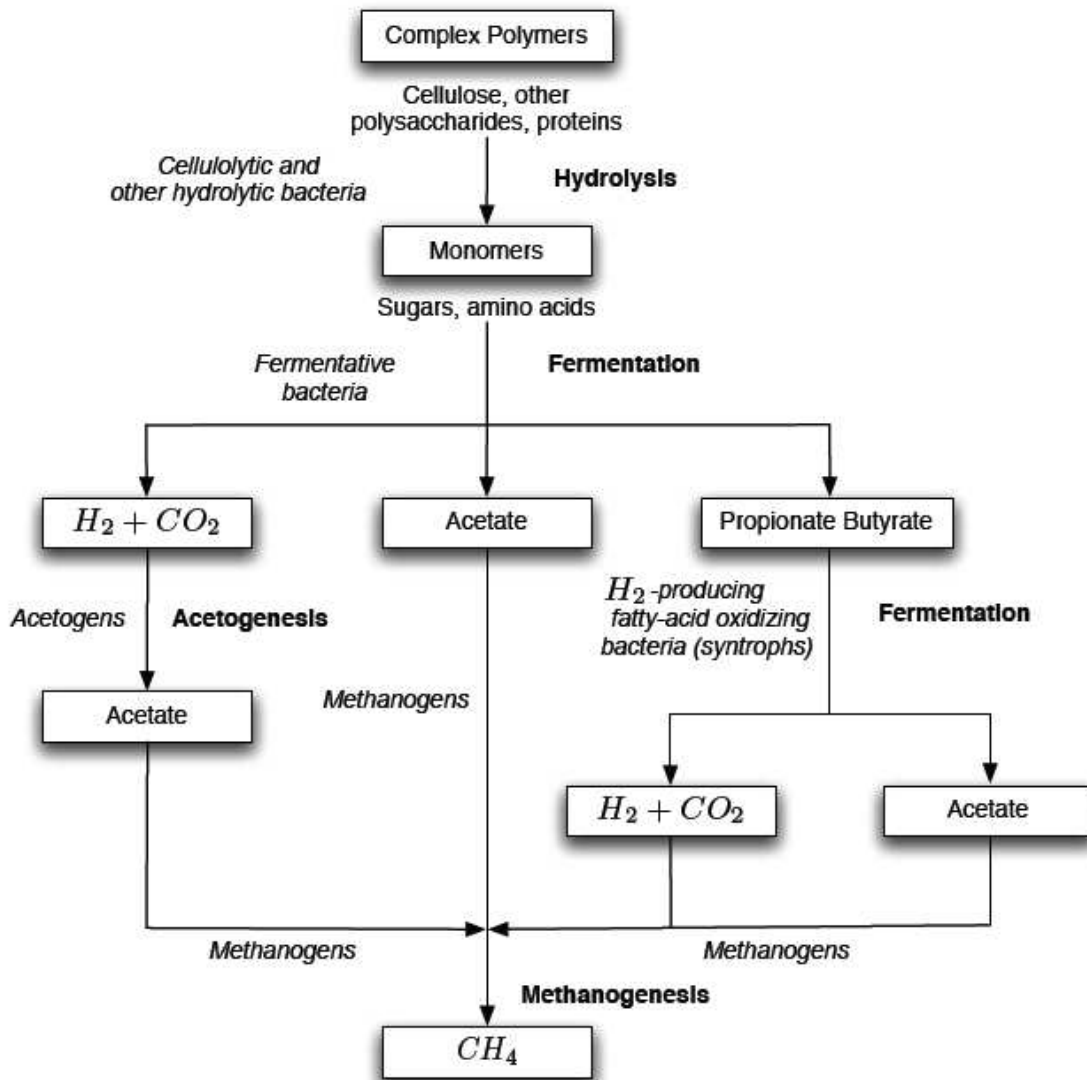
Figure 1.3 Different stages in an anaerobic bioreactor (adopted from Grady et al. 1999)

The third step is methanogenesis in which methanogenic bacteria combine acetic acid and hydrogen gas formed in acidogenesis to form methane gas (Grady et al., 1999). Aceticlastic methanogens are responsible for the production of methane out of acetic acid and hydrogen oxidizing methanogens produce methane by reducing carbon dioxide (Grady et al., 1999). Out of the total methane produced, two-thirds of methane is produced out of acetic acid and the rest from carbon dioxide (Grady et al., 1999).

1.4.4 Decomposition phases in an aerobic bioreactor:

There are 5 widely accepted decomposition phases in an anaerobic reactor process as shown in figure 1.4 (Tchobanoglous et al., 1993; WM).

Phase I is the lag phase in which the moisture content in a landfill gets accumulated (WM). The degradation occurring will basically be aerobic since some amount of air is present and hence no methane will be produced during this phase (Tchobanoglous et al., 1993).

In phase II, the moisture content increases and the oxygen is completely depleted (Tchobanoglous et al., 1993; WM). This phase is a transition from aerobic to anaerobic and hence it is also called transition phase. Another characteristic of this phase is the production of nitrogen gas and hydrogen sulfide, since nitrate and sulfate also serve as terminal electron acceptors as it becomes anaerobic (Tchobanoglous et al., 1993).

In phase III, acidogenesis could occur which results in the production of volatile organic acids as explained above. As a result, this phase is characterized by a decline in the pH. Other characteristics of this phase include high COD levels in the leachate and the solubilization of metals content (WM).

Phase IV is called the methane fermentation phase and this is characterized by the production of methane and carbon dioxide by the activity of methanogenic bacteria (Tchobanoglous et al., 1993; WM). This phase results in the recovery of a neutral pH and hence a reduction in the metal concentration in the leachate (WM).

Phase V is the final phase which occurs as the biodegradable matter completely extinguishes. As a result, gas production also declines and the chemical constituent of leachate becomes constant (Tchobanoglous et al., 1993; WM). This phase is called the maturation phase.
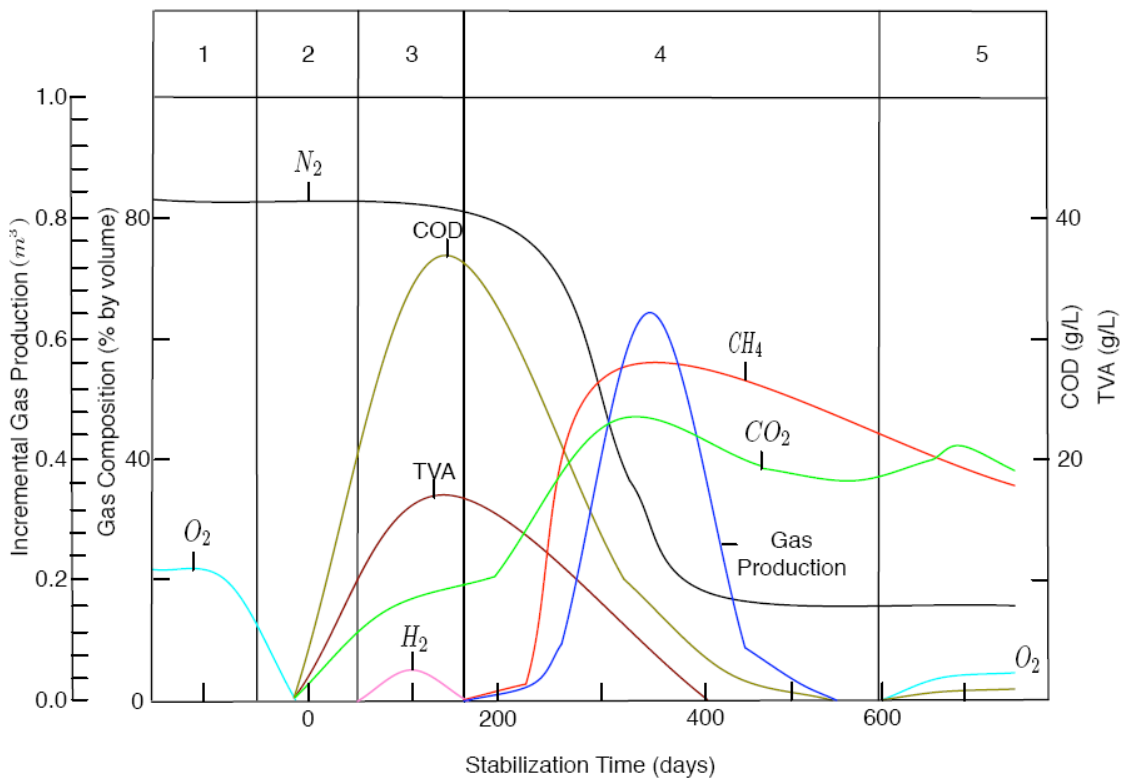
Figure 1.4 Different phases of an anaerobic landfill (adopted from WM)

1.4.5 Major degradable sources of anaerobic landfill materials:

1.4.5.1 Lignocellulose:

Wood contains about 89 to 98% of lignocellulose by dry weight (Colberg, 1988). Since the major constituents of a landfill are comprised of paper and cardboard, wood etc, lignocellulose is the major biodegradable carbon source in landfill materials. It comprises of 3 major components- cellulose, hemicellulose and lignin.

1.4.5.2 Cellulose:

Cellulose is the most abundant material on earth. Cellulose is about 50% dry weight of the solid waste and it has the maximum methane potential among the solid waste components (Table 1). A cellulose molecule is a polymer which contains D-glucose units joined via β-1,4-glycosidic linkages (Colberg, 1988). Glucose is released when cellulose is hydrolyzed completely and serves as a measure of the amount of cellulose present (Colberg, 1988).

1.4.5.3 Hemicellulose:

Hemicelluose consist of pentoses or hexoses and is bonded together with uronic acids of glucose and galactose. The pentoses present are L-arabinose and D-xylose and the hexoses present are D-glucose, D-mannose and D-galactose (Senior, 1990). They account for about 17.1% of total methane potential of the solid waste.

1.4.5.4 Lignin:

Lignin is the third most abundant biopolymer on earth. It is an aromatic structure formed by the removal of water from sugars (RPI, 1996). It accounts for about 15.2 % of the percent dry weight of the solid waste (Table 1). On the contrary, it does not contribute much to the methane potential of the solid waste. However, recent studies show that lignin can degrade at higher temperature and possibly can form lignin monomers including ferulic acid, benzoic acid, syringic acid, catechol etc (Miroshnikova, 2006).

1.4.5.5 Other carbon sources:

Other than the above mentioned constituents, other carbon constituents of solid waste include protein, lignin, starch, pectin, soluble sugars etc. But, the contribution of these components, except protein, towards methane potential is negligible.

Table 1.1 Composition and Methane potential of Municipal Solid Waste (adopted from Bagchi 2004).

Chemical Constituent	Percent Dry weight	Methane potential
Cellulose	51.2	73.4%
Hemi cellulose	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

1.4.6 Anaerobic landfill stability parameters:

The degree of degradation of a landfill and subsequent stabilization parameters are not completely defined (Kelly et al., 2006). However, waste composition, leachate quality, gas quantity etc. could serve as important parameters describing the extent of degradation of landfill materials (Kelly et al., 2006). Depending on the constituents and gas composition, certain analytical parameters have been developed for describing landfill stability and the relative efficiency of those parameters in defining the stability of landfill varies (Kelly et al., 2006) which are described below.

1.4.6.1 Lignin:

Lignin is one of the parameter used to describe the degradation of landfills. As indicated earlier, it accounts for about 15.2% of the landfill materials' dry weight. The main problem associated with lignin is that it degrades at a much slower rate than cellulose (Kelly, 2002; Kim, 2004) Also, the method of measurement of lignin does not account for plastics in the sample and hence the value of lignin may include plastics as well unless they are specifically removed (Kelly et al., 2006). Thus, lignin measurements of the samples containing plastics may not indicate the accurate value (Kelly et al., 2006). On contrary, Chandler et al. (2003) have proposed lignin as a predominant indicator of stability, identifying its strong correlation with volatile solids (Komilis and Ham, 2003). Recent studies show that lignin is able to degrade more at an elevated temperature (Miroshnikova, 2006). Also, lignin degradation is greater in a preheated bioreactor than at room temperature (Miroshnikova, 2006).

1.4.6.2 Lignin Monomers:

Lignin is shown to be anaerobically degraded into a series of compounds such as benzoic acid, syringic acid, catechol, vanillic acid, ferulic acid etc (Young and Frazer, 1987). Hence, the degradation of lignin could more easily be identified by the presence of lignin monomers and hence they serve as degradation indicators. Miroshnikova (2006) has shown that lignin could degrade to lignin monomers at higher temperatures and thus the presence of more lignin monomers indicates the degradation of lignin and hence landfill constituents.

1.4.6.3 Cellulose and hemicelluloses:

Cellulose is about 51.2% by dry weight of fresh landfill constituents and has the highest potential for methane production among landfill carbon sources (Bagchi, 2004). Hence, the degradation of cellulose is accepted as a good indicator of landfill stability (Kelly et al., 2006). The most stabilized landfill will achieve a cellulose content as low as 2-5% (Kelly, 2002). Komilis et al. (2003) has reported cellulose degradation up to 91.1%, identifying it as a complete degradation. Hemicellulose is identified as an intermediate in the anaerobic degradation pathway of cellulose and hence the determination of those serves as an indicator of extent of degradation of cellulose (Kim, 2004).

1.4.6.4 Cellulose/lignin(C/L) ratio:

Cellulose/Lignin ratio is another important parameter defined for landfill stability. The ratio is used to distinguish the fresh and mature wastes in the landfill (Komilis and Ham,

2003). A decrease of C/L ratio in a landfill is identified as a sign of increasing stability (Komilis and Ham, 2003). A C/L ratio of 4.04 has been reported for a fresh trash and it decreases and can reach as low as 0.8 which has been reported for a mature landfill (Komilis and Ham, 2003). However, since the lignin has been found to degrade under different conditions and its value is highly variable due to the presence of plastics, the ratio seems to have no advantage in defining the stability of the landfill over cellulose alone (Kelly, 2002; Kelly et al., 2006). Hence, a more nondegradable reference is required in defining the ratio and a weighed amount of plastics seems to serve as a better standard than cellulose in the ratio.

1.4.6.5 Volatile Solids (VS):

Volatile solids is a good parameter in determining the landfill stability (Kelly, 2002). A decrease in the volatile solid content in trash is a good indicator of increasing landfill stability. The ease of determining VS without requiring any expensive instruments add to the preference of this method. But the presence of plastics could make the determination of VS also uncertain and it has to be accounted in when the VS are determined (Kelly, 2002; Kelly et al., 2006). Degradation up to a VS content of 10-20% is accepted as a good indicator of stabilized landfill (Kelly, 2002).

1.4.6.6 Biomethane potential:

Biomethane potential (BMP) is defined as an anaerobic equivalent to BOD (Kelly et al., 2006). This test quantifies the material available for methane production in the municipal solid waste (Kelly et al., 2006). However, the test does not correlate well with cellulose

and VS (Kelly et al. 2006). The main disadvantage of BMP is it is an expensive and time consuming test. The test can serve as a supplement to other stability indicators and could be used as a validation parameter (Kelly et al. 2006). A well stabilized landfill is evaluated to have a BMP of 10-20 ml/g (Kelly 2002).

1.5 Effect of certain liquid wastes on landfill constituents:

1.5.1 Sugar waste:

The sugar industry is a major industry in the United States, producing 80% of the world's refined sugar (Transfairusa, 2007). As a result, many landfills across the country accept sugar waste. However, there are not many records regarding the disposal of sugar waste into landfills and its effect on landfills.

Sugar waste can affect methanogenic activity which inturn could influence processes occurring inside an anaerobic bioreactor. Hutnan et al. (2000) identify sugar waste as a good source for anaerobic digestion. Sugar waste, in an optimal concentration, could give an excellent boost for methanogenic activity, yielding an enhanced biogas production (Hutnan et al., 2000; Knol et al., 1978) . Knol et al. (1978) reports a rapid reduction in the VS content in an anaerobic digestor accepting fruit wastes containing high sugar content.

On the contrary, sugar waste can result in an unbalanced digestion occurring in the anaerobic reactor due to a rapid acidification inside the reactor (Bouallagui et al., 2005; Hutnan et al., 2000; Kelly, 2002; Veeken et al., 2000). Hutnan, N et al. (2000) reports an acidification accompanied by a pH drop to 4.0 within 2 days after accepting sugar beet waste. This includes the progression of anaerobic activity until acidogenesis

and a cessation of the degradation thereafter resulting in the accumulation of volatile fatty acids. This could result in a drop in the pH followed by inhibition in the hydrolysis of particulate organic matter (Bouallagui et al., 2005; Hutnan et al., 2000; Veeken et al., 2000). Although interrelated, recent research suggest the necessity of modeling pH and VFA as a two-phase system since it is difficult to determine which one of the two factors are really inhibitive in nature (Veeken et al., 2000). Veeken et al. (2000) have shown that pH is more important in controlling the methanogenic activity and hence the hydrolysis rate is more dependent on pH than on VFA. Further it is shown that the VFA does not have any effect on hydrolysis rate until the concentration of VFA reaches a value of 30 g/L COD. However, such an unbalanced digestion could be remediated by alkali addition, intermediate interruption or mixing it with nitrogen rich substrates (Knol et al., 1978).

1.5.2 Surfactant waste:

Surfactant wastes are often disposed in landfills. Being valued for about 1.2 billion dollar global market, there are thousands of surfactants used in various industries (Porter, 1994). Surfactants are grouped under xenobiotic compounds and could have potential effects on landfills, when accepted as wastes (Slack et al., 2005). Also, their effect on a landfill vary depending upon the type of surfactant used (Kjeldsen et al., 2002).

Surfactants, above a particular concentration are shown to inhibit the biological activity in the environment (Pennel et al., 2002). Apart from intruding into leachate (Riediker et al., 2000), the presence of surfactants in an anaerobic landfill could affect the degradation of components by influencing methanogenesis. Pennel et al. (2002) suggest

the effect of surfactants on methanogenesis is highly system specific. On addition of the Tween series of surfactants, they had a greater methane production than the control system. In contrast, addition of certain Polyoxyethylene (POE) alcohol surfactants inhibited methanogenic activity considerably resulting prevention of methane production. Anionic surfactants are shown to have a positive effect on biological activity. At a particular concentration, these types of surfactants which include sodium lauryl sulfate and salts of alkyl benzene sulfonates are shown to boost biological activity (Anderson, 1964). It has been further shown that the bacterial group could use the carbon atoms in the straight alkyl chains of the surfactants as a source for their growth (Anderson, 1964). However, the degree of consumption of carbon atoms in a surfactant as substrates decreases as the branching of alkyl chain increases (Anderson, 1964). But at high concentrations anionic surfactants can also be inhibitive to methanogenic bacteria although they are found to be relatively more tolerant to the anionic surfactants than cationic ones (Shcherbakova et al., 1999). The inhibition by surfactants is suggested due to the interaction of those with the bacterial group preventing the transport of essential nutrients into the cells (Gavala and Ahring, 2002). However, the effect of the surfactants specifically in the degradation of landfill constituents and their influence in the landfill stability parameters is not known.

1.5.3 Paint waste:

The Paint industry is one critical field with growth of more than 3% annual sales in the United States (Martens, 1974). Being classified broadly into trade sales and industrial finishes paints (Martens, 1974), different type of solvents and other chemicals are used

by the paint waste industry (Kaelin, 1999). The most common solvents used are petroleum based products such as kerosene, xylene, acetone, ketones etc. and chlorinated solvents like trichloroethene most of which are hazardous (Kaelin, 1999). Although limited by regulations, the EPA strongly suggest the manufacturers of paint to determine whether the waste generated is hazardous (USEPA, 2002). Paint waste itself is generated mainly because of mixing of more paint than needed and then disposing of it when it cannot be used (Kaelin, 1999).

The effect of paint waste on a landfill depends upon the concentration of the constituents inside the waste (Kaelin, 1999; Lambolez et al., 1994). Reports show that paint waste dumped in the landfill has potential effects on both exposed human beings and bacteria inside the landfill. People exposed to sites accepting paint waste have shown a high occurrence of Wilms' tumor (Tsai et al., 2006). Apart from the direct effect, paint waste also produces a very toxic leachate which pollutes the environment (Lambolez et al., 1994; Vaajasaari et al., 2004). Samples from the landfill accepting paint waste show a high concentration of formaldehyde, high TOC and solvent concentrations which inhibit the bacterial activity (Vaajasaari, Kulovaara et al. 2004) and could retard the degradation of waste. Lambolez et al. (1994) had reported severe inhibition caused by the paint waste landfills to algae, photobacterium and other organisms. There is a need for further research in this field for determining the effect of accepting the paint waste on degradation of material in the landfill. Also, the existing physicochemical analyses are not sufficient since they cannot reveal the toxicological effect of chemicals on biological activities (Kelly et al., 2006).

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CHAPTER 2: EFFECT OF SUGAR WASTE, SURFACTANT WASTE AND PAINT WASTE ON THE DEGRADATION OF ANAEROBIC BIOREACTOR LANDFILL COMPONENTS.

2.1 Introduction:

Bioreactor landfills are getting more popular due to their increased and faster degradation (Bagchi, 2004; Kelly et al., 2006). An enhanced degradation is mainly achieved in bioreactor landfills by increased moisture content (Bagchi, 2004; Kelly et al., 2006). It has been shown that while a conventional bioreactor may take 50 years for the stabilization, the same stabilization could be achieved within 5 years in a bioreactor (Kelly et al., 2006)

Many landfills across the country accept a variety of liquid wastes. Apart from the monetary gain from accepting those as wastes, liquids increase the moisture content in landfills thereby aiding in a faster stability. For example, it has been reported that Outer Loop bioreactor, Louisville, Kentucky accepts more than 7 different type of liquid wastes (Hater, ; Novak, 2006). The different wastes accepted include beverage waste, dye water, oily water, surfactant waste and paint waste. But, the effect of all these type of liquid waste on the degradation of landfill components has not been thoroughly studied.

Sugar waste is shown to have an inhibitive effect on anaerobic activity. Above a certain concentration, sugar waste would rapidly decrease the pH of system and causes accumulation of volatile fatty acids, thereby inhibiting the methanogenic activity (Bouallagui et al., 2005; Veeken et al., 2000). Surfactants which are xenobiotic compounds and used in different industries are shown to have varied effects on bacterial

activities and hence on the degradation of materials. Above a particular concentration, they are inhibitive to the biological activity by reducing the transport of essential nutrients into cells (Gavala and Ahring, 2002; Pennel et al., 2002). In contrast, some anionic surfactants at a particular concentration have been shown to have a stimulatory effect on the biological activity by providing carbon atoms of alkyl chains in the surfactants as substrates (Anderson, 1964). Paint waste could be inhibitive to the landfill components because they may contain toxic components. Samples from the landfill accepting paint waste show a high concentration of formaldehyde, high TOC and solvent concentrations which inhibit the bacterial activity (Vaajasaari et al., 2004) and could retard the degradation of waste.

In this study, the effect of sugar waste, surfactant waste and paint waste on the degradation of landfill components was investigated. Sugar and surfactant wastes were synthesized in the laboratory of Virginia Tech while paint waste was shipped by Waste Management, Inc. The different measurements conducted were pH, volatile solids, total solids, methane, carbon dioxide and total gas generation, lignin, cellulose and hemicellulose, volatile fatty acids and lignin monomers. The stability of the landfill components are then analyzed using analytical parameters (APHA, 1998).

2.2 Materials and Methods:

2.2.1 Experimental Setup:

The study was divided into 3 major sections - each dealing with a particular type of waste. The initial set up of the experiment consisted of reactors containing sample mixed with either sugar syrup of 250,000 mg/L as COD, surfactant or paint waste in

triplicate sets at 3 different concentrations. This was termed as phase 1 of the project. A triplicate set of controls were made without adding any of the liquid wastes. Later, an additional 12 reactors were added after the first half of the research was completed and is termed as phase 2 of the project. The actual moisture content of Bioreactor landfills are maintained at 40-50%. Instead, the moisture content of the reactors were kept at 70%, accounting for sugar and paint wastes added as liquids as the case may be. This higher moisture content was used to facilitate the availability of some free liquid in the reactors since the sample was mainly paper and paper products which absorb a lot of moisture.

Since paper and cardboard constitutes major part of the landfill material, the sample used was a mixture of paper, cardboard and office paper. Further, plastic was added for about 10% of the sample by weight. The combined paper and plastic are 30% by weight of the total reactor contents. As a source of bacteria, anaerobic seed from Peppers Ferry wastewater treatment plant for 15% of the total weight of the reactor was added into this.

The different concentration of sugar waste and paint waste used in phase 1 were 30, 22.5 and 15% by weight and the surfactant concentration used were 50 mg/L, 150 mg/L and 250 mg/L. In phase 2 of the project, reactors with 5% and 7.5% sugar wastes, surfactant waste of 1000 mg/L and paint waste of 7.5% were added. Further, tap water was added to increase the total water content (including liquid waste) to maintain 70% of the total weight. When calculating the mass, anaerobic seed and wastes are considered as only liquid and no allowance been given to the solids in them. The experimental matrix for phase 1 is shown in Table 2.1. Similarly following the same matrix except the concentration, the experimental matrix for phase 2 is shown in Table 2.2.

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All reactor set ups were done in a glove box, purging with ultra pure Nitrogen gas in order to assure complete anaerobic condition. The reactors were then closed air tight to insure that no air is intruded and the reactor was connected to a Tedlar bag through an opening at the top. All connections were prior checked for leaks and the reactors were then incubated at 35°C temperature.

Table 2.1 Experimental Matrix for phase 1

	Control	Sugar waste			Surfactant waste			Paint waste		
Number of reactors	3	3	3	3	3	3	3	3	3	3
Sample+ Plastic	30%	30%	30%	30%	30%	30%	30%	30%	30%	30%
Water content	55%	25%	32.5%	40%	55%	55%	55%	25%	32.5%	40%
Sugar waste added	X	30%	22.5%	15%	X	X	X	X	X	X
Surfactant waste added	X	X	X	X	50 mg/L	150 mg/L	250 mg/L	X	X	X
Paint waste added	X	X	X	X	X	X	X	30%	22.5%	15%
Anaerobic seed	15%	15%	15%	15%	15%	15%	15%	15%	15%	15%

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Samplings were conducted once in every 15 days for the first 13 samplings and then monthly once afterwards. Since the pH dropped under normal in sugar waste reactors, they were brought up to neutral on the sampling in 150th day using $NaHCO_3$.

Table 2.2 Experimental Matrix for phase 2

	Sugar waste		Surfactant waste	Paint waste
Number of reactors	3	3	3	3
Sample+ Plastic	30%	30%	30%	30%
Water content	45%	50%	55%	55%
Sugar waste added	10%	5%	X	X
Surfactant waste added	X	X	500 mg/L	X
Paint waste added	X	X	X	7.5%
Anaerobic seed	15%	15%	15%	15%

2.2.2 Materials:

2.2.2.1 Reactor:

Reactors used were 1L PTFE Nalgene bottles from Fischer scientific. These are attached to a 1 L tedlar bag from Fischer scientific to collect gas emerging from the reactor.

2.2.2.2 Sample:

The sample used was 50% newspaper, 25% office paper and 25% cardboard. To assure consistency, the newspaper used was the Collegiate Times, office paper was generated by environmental engineering wing of CEE department of Virginia Tech and cardboard was packing from Fischer Scientific. These were cut down to approximately 1 inch squares. Plastics added were 1" strips of black trash bags and were thoroughly mixed with the sample and weighed. The total sample in each reactor was about 30% by weight of the total reactor content.

2.2.2.3 Seed:

The anaerobic seed from the Pepper's Ferry, an anaerobic digester is used as the source for methanogenic bacteria.

2.2.2.4 Wastes:

As indicated ealier, since it was not possible to procure sugar waste, it was artificially synthesized in the laboratory. For this Pepsi was used. Pepsi was continuously distilled in the laboratory till it reached a COD of 250,000 mg/L. Chemical oxygen demand (COD) tests were conducted periodically on the solution and the distillation was continued till a value of 250,000 mg/L was obtained. The solution was then cooled and used as waste.

Surfactant waste was also synthesized by mixing surfactants in the laboratory. The surfactants chosen for this were sodium salt of dodecyl benzene sulfonate and sodium lauryl sulfate from Sigma Aldrich Ltd. Both are anionic surfactants and are used in

detergents, textile and metal industries and would best represent the surfactant wastes delivered to some landfills.

Paint waste was delivered to the laboratory by Mr. Gary Hater of WM, Inc. and had a total solids content of 153 g/L.

2.2.3 Sampling:

The reactors were sampled once in every 15 days till the 13th sampling (195 days) and once in every month after that until 240 days (15th sampling) in phase 1 reactors. Paint waste reactors were started 45 days after the sugar and surfactant waste reactors and hence have 3 fewer samplings. Phase 2 reactors which were started after 9 samplings of phase 1 were sampled once in every 15 days for first 6 samplings and once in every month after that. During samplings, for a short while, the reactors were taken out into a glove box at room temperature. After purging with ultrapure nitrogen gas, the reactors were opened and 10-15 mg of the sample were quickly transferred to a loaf pan. Four to five ml of leachate were collected from each reactors and were transferred to a 15 ml centrifuge tube and centrifuged to remove solids. The reactors were then sealed and were transferred back to 35°C temperature incubation. The leachate was frozen and stored for further analysis.

Plastics were removed manually from the samples and were weighed. Samples were then dried at 105°C for 24 hours and were milled using a Wiley mill using a mesh of 10mm size. This ground powder was used for further analysis.

2.2.4 Analytical methods:

2.2.4.1 pH:

Samples were mixed with 50/50 distilled water and were kept for 5 hours to equilibrate. pH was then measured using a pH meter.

2.2.4.2 Total Solids (TS) and Water content:

Total Solids were measured using Standard method 2540G (APHA, 1998).

2.2.4.3 Volatile Solids (VS):

Volatile Solids were measured using Standard method 2540G (APHA, 1998).

2.2.4.4 Gas generation, methane and carbon dioxide generation:

The gas generated from reactors was collected in tedlar bags. These bags were detached at the time of sampling and were measured using a syringe. Total gas was expressed in milliliters. The carbon dioxide content and methane content in percentage in the gas were measured using a Shimadzu GC 14A with thermal conductivity detector, injecting 0.5ml of the gas. Calibration graphs were made out of different concentrations of 99.9% methane and carbon dioxide for the analysis of gas samples. Multiplying total gas with the percentage gave the total CO_2 and CH_4 generation out of the reactors.

2.2.4.5 Lignin, Cellulose and Hemicellulose :

The lignin, cellulose and hemicellulose were determined as per ASTM E 1758-95[e1]. Three hundred mg of the sample taken in a 16 mL vial was hydrolyzed using 3 mL of

72% H_2SO_4 and was kept in water bath at 30^0C for 2 hours. The sample was then transferred to a 250 mL bottle and diluted using 84 mL of nanopure water, taking care to completely transfer the hydrolyzed particles. The samples were then autoclaved on 1 hour wetcycle at 15 psi and 121^0C. These were then filtered through a TSS glass standard filter. Filtrates were neutralized using $CaCO_3$ till it reached a pH between 4-6 and then analyzed using a high performance liquid chromatograph with a HPX-87C carbohydrate column (*Biorad*) and a refractive index detector. The filter was then weighed after cooking at 105^0C and then weighed again after heating at 550^0C for 20 minutes. The difference between the weights gave the lignin content. Standard lignin and cellulose from Sigma Aldrich were also analyzed in the same way to determine the percentage recovery. Allowance for the percentage recovery as measured n each case was made in all calculations of lignin and cellulose.

2.2.4.6 Volatile fatty acids:

Leachate from the reactors was analyzed for acetic acid, butyric acid, iso butyric acid, heptanoic acid, hexanoic acid, propionic acid, valeric acid, isovaleric acid and caprionic acid. Frozen leachates were thawed and filtered using 0.2 m, 0.45 μm filters after centrifuging for 10 minutes. 0.99 ml of the filtrate is then added to a 2ml vial containing 0.01ml of 30% phosphoric acid to acidify the solution. These were then analyzed using a Shimadzu GC 14A with a flame ionization detector. Five standards were made out of standard volatile fatty acid from Supelco. Standards and blanks made out of nanopure water were also treated the same way and analyzed. Blank values were deducted to avoid any seed interference.

2.2.4.7 Lignin Monomers:

Lignin monomers including ferulic, syringic, benzoic, cinnamic, vanillic acids and catechol were analyzed using the method adopted from Colberg and Young (Colberg and Young, 1985) and then modified by Miroshinkova, O (Miroshnikova, 2006). Two milliliters of centrifuged and filtered samples in an 8 mL vial was acidified with 2 drops of 50% H_2SO_4. One ml of methylene chloride was added into this solution and shaken vigorously. The sample was then allowed to separate between water and methylene chloride. Two hundred μL of methylene chloride was carefully taken and transferred into a 2mL vial. Two hundred μL of Regisil RC-2 (Bis(trimethylsilyl)trifluoroacetamide +1% Trimethylchlorosilane) from Regis Technologies Inc. was added into this solution followed by 200 μL of acetonitrile from Fisher Scientific, Inc. Vials were mixed thoroughly for 20-30 seconds using a vortex mixer and were kept in a water bath at 60^0 C for 10 minutes for complete formation of trimethyl silyl derivatives (Veeken et al., 2000). The samples were then allowed to cool and were analyzed using a Shimadzu GC 14A with a flame ionization detector. Standards were made using lignin monomers from Fischer scientific and blanks with nanopure water. Both standards and blanks were treated the same way as samples and analyzed using GC. Blank values were then deducted from the sample values to account for seed interferences.

2.3 Results and discussion:

2.3.1 Control gas:

The control gas generated is shown in Figure 2.1. Both the carbon dioxide and methane curves were similar to the one representing an ideal bioreactor (Figure 1.4) and hence it could be concluded that the performance of reactors containing only paper, water and seed was satisfactory.

2.3.2 Sugar waste:

It can be seen in figure 2.2 that the pH in sugar waste reactors went drastically down and was below 4.0 within 100 days whereas the control pHs were near neutral for the whole experiment period. The pH decrease in the sugar waste reactors most likely occurred as a result of volatile fatty acids accumulation. At day 150, the pH was raised to neutral using $NaHCO_3$ to assess the performance.

The gas concentration generated from the sugar waste reactors was much less than that of the controls (Figure 2.3), even after the pH was raised. The maximum cumulative gas emerged in the control reactors was about 16700 ml whereas the maximum cumulative gas in the reactors containing sugar waste was 5700 ml and was obtained from the reactors containing 22.5% sugar waste. All other sugar waste reactors had cumulative gas production less than that of 22.5% with the 30% sugar waste reactors comparable to that of 22.5%. Carbon dioxide emission also followed the same trend. There was not any appreciable gas or carbon dioxide production after 75 days and was almost stagnant for the whole experiment period (Figure 2.4). No specific trend can be drawn for gas accumulation in reactors containing 5% and 10% sugar waste since there

was not as much data available. Methane production in the reactors was also consistent with the sugar concentration in the reactors (Figure 2.5). While the reactors with 5% sugar waste had a better methane production, the least methane was produced in sugar waste reactors with 30% sugar content. How ever, the maximum methane production in the sugar waste reactors was even less than 7% of the maximum methane production in the control reactors. This suggests a strong inhibition in the reactors containing sugar waste, consistent with the amount of sugar in the reactors.

The reason for the inhibition in the reactors containing sugar was likely due to the volatile fatty acid accumulation resulting in the inhibition of methanogenic activities (Veeken et al., 2000). This is validated by determining the volatile fatty acid concentrations in the reactors (Figure 2.6). The maximum total VFA in the sugar waste reactor was found in the reactors containing 30% and 22.5% sugar content. The VFAs were about 4 times higher than the maximum VFA content in the control reactors. The VFA contents in the other sugar reactors were less, mostly consistent with the order of decreasing sugar content. The minimum VFA concentration in the 5% and 10% sugar waste reactors was almost equal to the maximum concentration in the controls at the initial stages of the control operation. The high amount of the VFA in the controls could be due to the acidogenesis happening at the initial stages (Figure 2.6) and a subsequent decrease in the VFA concentration afterwards due to the progress of anaerobic digestion to further steps.

The breakdown of individual VFA was also analyzed (Figures 2.7, 2.8, 2.9, 2.10). It was seen that out of the four prominent VFAs- acetic acid, propionic acid, butyric acid and valeric acid, the maximum concentration of acetic acid and propionic acid were

found in sugar waste reactors of 30%, whereas the concentrations of valeric and butyric acids were maximum in 22.5% reactors. However, there was not much difference in the VFA breakdown concentration in the reactors containing 30%, 22.5% and 15%. The VFA breakdown concentration in 10% and 5% sugar reactors were much less than high sugar reactors, but was more than the control reactors. The control reactors contain a higher amount of all VFAs in the first few samplings and then decreased gradually because of the above explained reasons.

Further analysis of the degradation of sample was done using analytical parameters for landfill stability. An examination of the volatile solids (VS) of sugar waste reactors and controls indicated that the decrease in VS concentration in the controls was about 9% higher than any of the sugar waste reactors (Figure 2.11). There was not much difference between the degradation trend of the VS among reactors containing 30%, 22.5% and 15% sugar waste. The VS degradation in the sugar waste reactors for 30%, 22.5% and 15% reactors were 6, 5 and 4% respectively whereas that of the control reactors was about 9%.

An examination of lignin values revealed that lignin did not degrade much in any of the sugar waste reactors and controls (Figure 2.14). The maximum lignin percentage in control was found to be about 21%. A degradation of 4% lignin was observed in control reactors during the experiment while a degradation of about 2% was observed in reactors containing 30%, 22.5% and 15% sugar content. Although there was a decrease in lignin content in reactors with 5 and 10% sugar content, the trend was not clear due to the lack of sufficient data.

Cellulose degradation was found to be a maximum in the control reactors compared to sugar waste reactors (Figure 2.12). A maximum degradation of 18% is found in control reactors (from 59% to 41%) while sugar waste reactors with 30% sugar show a cellulose degradation of about 9%. Both the reactors containing 22.5% and 15% show a maximum cellulose degradation of 12%. Both the sugar waste reactors containing 10% and 5% sugar show a cellulose degradation of 9 and 10% respectively within the 120 days of observation. Over the same time period, the control reactors had shown a cellulose degradation of 13% while the 30% sugar waste reactors had shown a cellulose degradation of only 5%.

The main hemicellulose content in all the reactors was xylose. Hemicellulose accounted to a maximum of about 23% of the total components in the control reactors (Figure 2.13). This was degraded to a maximum of 10% within 240 days while the reactors containing 30% sugar degraded from 24% to about 13%. Reactors with sugar content of 22.5% and 15% witnessed a degradation of hemicellulose content of about 10 and 9% respectively. Within 120 days of observation, the hemicellulose in 10% and 5% sugar content reactors degraded to about 5% and 6% respectively which was 10% in the control reactors for the same time period.

Cellulose/Lignin (C/L) is a good parameter to explain the landfill stability (Kelly et al., 2006). In view of the degradation of cellulose, plastic could serve as a better datum and the ratio of Cellulose/Plastic (C/P) as a stability parameter was also examined. Plastics were manually removed during the sampling and were weighed. The C/L value for control had decreased to 2.2 whereas the reactors with 30%, 22.5% and 15% sugar content had a minimum value of 2.6, 2.85 and 2.7 (Figure 2.15). It had been reported that

a most stable landfill will have a C/L of 0.23 (Kelly et al., 2006) which suggests that degradation in all reactors was incomplete.

C/P curves of sugar waste reactors and control does not have any specific implication (Figure 2.16). The reason for that might be an uneven manual picking of plastics during sampling.

2.3.3 Surfactant waste:

The surfactant waste pH curves are shown in Figure 2.17. As seen, the pH of all surfactant reactors is fairly neutral between 7.0 and 8.0. There are not much difference between the pH of any of the surfactant reactors and control.

The Figure showing cumulative gas from the reactors (Figure 2.18) containing surfactants indicated that the gas from the surfactant reactors was less compared to control reactors. While the control reactors had a mean maximum cumulative gas release of about 17,000 ml, the average maximum cumulative gas generated in all surfactant reactors was about 10,000 ml. The CO_2 gas release curves also followed the same trend (Figure 2.19). The gas generated in all the surfactant reactors was less than that of the control with no much difference in the gas release between the surfactant reactors. The total methane generated in the control reactors was about 8000 ml whereas the reactors with surfactant of 150 and 250 mg/L showed a cumulative methane production of 5000 ml (Figure 2.20). The reactor containing 50 mg/L surfactant was almost identical to the control reactors with comparable amounts of methane release in both of them.

The pH of surfactant reactors between 7.0 and 8.0 suggest that there was no excess accumulation of acids inside the reactors. Further, although less than control

reactors, the gas release in the surfactant reactors was also fairly good which indicate no inhibition of methanogenic activity inside the reactors. This was in accordance with the volatile fatty acid data (Figures 2.21, 2.22, 2.23, 2.24, 2.25). The Figure showing volatile fatty acid in the surfactant reactors indicate fairly low VFAs in surfactant reactors. Although curves show a small amount of VFA in the initial stages of the research, it was dropped down during the further stages of the decomposition period due to the progression of anaerobic digestion.

An examination of different analytical parameters for landfill stability revealed more about the degradation in the reactors. The VS data for the surfactant reactors was consistent with the amount of surfactants in the reactors (Figure 2.26). The control reactors had shown a degradation of about 9% VS. The 250 mg/L surfactant reactors had a maximum VS content of about 4% less than that of the control reactors. The trend of different curves showed that the VS degradation in the surfactant waste reactors was less than that of the controls and less degradation was achieved as the concentration of the surfactant increased.

Cellulose degradation in the surfactant reactors also showed a less degradation compared to that of controls (Figure 2.27). It was also consistent with the concentration of surfactants in each reactor. The 250 mg/L reactors showed the least degradation with 12% while controls showed a degradation of 18% of cellulose.

The degradation of hemicellulose also followed the same trend as that of cellulose (Figure 2.28). The trend in the degradation of hemicellulose was comparable to the degradation attained for cellulose. The main hemicellulose was xylose and the maximum

degradation obtained in the surfactant reactors with 50 mg/L was 10% and that in the control was 15%.

Lignin had shown a degradation of 5% in the reactors containing surfactant of 50 mg/L while reactors of 150 mg/L and 250 mg/L showed a degradation of 4% (Figure 2.29). Although the trend could not be set in the case of surfactant reactors with 500 mg/L, the degradation attained in 120 days in 500 mg/L reactors was 2% while the control had an average lignin degradation of more than 3% within the same period.

The C/L in the surfactant reactors did not show a high variation compared to the control reactors (Figure 2.30). The value of C/L for all reactors was between 2 and 3 for all surfactant reactors. Compared to the value of 0.23 for the most stabilized anaerobic landfills, suggests a higher potential for degradation in the reactors. C/P curves (Figure 2.31) for reactors containing surfactants also implied no specific trend.

2.3.4 Paint waste:

As explained earlier, the paint waste concentrations chosen were 30%, 22.5% and 15% in phase 1 reactors and 7.5% in phase 2 reactors. Phase 1 paint waste reactors were established 45 days after the starting of phase 1 sugar and surfactant waste reactors. The experiments carried out for the paint waste reactors were the same as that of the sugar and surfactant waste reactors.

The pH of all the paint waste reactors was fairly neutral in between 7.0 and 8.0 (Figure 2.32). Occasionally, the value of some reactors went above 8.0 and below 7.0. But most of the times they were in a range between 7.0 and 8.0 and no specific difference are shown between the pH of any of the paint waste reactors.

The gas emission in the paint waste reactors show a high inhibition compared to that of the control. This was consistent in the case of total gas, CO_2 and methane generation (Figure 2.33, 2.34, 2.35). The total gas generation in all of the reactors was stagnant about 6000 ml. The inhibition of gas generation was irrespective of the concentration of paint waste in the reactors. CO_2 generation in the reactors showed a maximum of 2000 ml and was almost flat in the following stages possibly due to some inhibition. The maximum methane generation in the paint waste reactors was about 4000 ml occurring in 22.5% paint waste reactors. All other paint waste reactors had a total methane generation less than that.

It was evident from the gas emission curves that the paint waste reactors were inhibited. It could not be because of acid accumulation since the pH did not decrease. This was consistent with the volatile fatty acid results. The volatile fatty acids in the paint waste reactors did not show much difference either among the difference paint waste reactors or compared to the controls (Figure 2.36, 2.37, 2.38, 2.39, 2.40). The VFA was high in the initial stage in paint waste reactors as controls and it decreased as it went further down through the different stages of anaerobic digestion.

The stability parameters were also examined as in the case of any other reactors. An examination of the volatile solids revealed less degradation in the paint waste reactor compared to controls (Figure 2.41). This was mostly consistent with the concentration of the paint waste in the reactors. Maximum degradation was attained in the paint waste reactor with 7.5% and the degradation decreased as the concentration of paint waste increased. The 7.5% paint waste reactors showed a degradation of 6% within 120 days.

The maximum degradation of VS in the paint waste reactor was less by 7% compared to the control.

This was consistent with the cellulose and hemicellulose degradation in the reactors (Figures 2.42, 2.43). The maximum degradation of cellulose was almost 5% less than that obtained in the control reactors. The 30% and 22.5% reactors showed less degradation by 8% compared to the control.

The control hemicellulose showed a minimum content of 10% after 200 days. The degradation in the hemicellulose content in the paint waste reactors was inhibited by more than 4% compared to control reactors. The minimum degradation was obtained in 30% sugar waste reactors with a degradation of 10% while the 22.5% reactors and 15% reactors showed more degradation which was consistent with the amount of paint in the reactors.

One noticeable point was the high content of lignin in the paint waste reactors compared to controls (Figure 2.44). The paint waste reactors showed a maximum lignin content of 34% in 30% reactors and the lignin content determined showed a variation which is consistent with the concentration of the paint in reactors. This high content of lignin as determined could possible due to the paint content in the reactors with the same effect as that of plastics in determining the lignin content (Miroshnikova, 2006). It could thus be concluded that the paint content in the reactors changed the lignin determination and did not reflect the actual lignin content.

The C/L showed a lower value between 1.5 and 2.0 for all the paint waste reactors compared to a value in between 2.0 and 3.0 for the controls (Figure 2.45). This lower value was due to the high lignin content and is not reflective of the actual stability in the

paint waste reactors. The C/P did not show any trend due to the inappropriateness of the determination of plastic as explained above (Figure 2.46).

No appreciable amount of lignin monomers were detected in any of the reactors except a very small amount in the controls during the last phase of the study. This suggest that a lignin solubilization is mainly occurs in high temperature condition only (Miroshnikova, 2006).

2.4 Summary and Conclusions:

As explained above, this study could mainly be divided into 3 sections- effect of a) sugar waste, b) surfactant waste and c) paint waste in anaerobic bioreactors.

2.4.1 Sugar waste:

The sugar waste reactors showed a high inhibition even at a concentration of 15% sugar content. The 10% and 5% sugar content also seem to be inhibitive, but much less compared to 15% sugar content and above. The inhibition is mainly due to the accumulation of VFA and this was validated by the volatile fatty acids data and the pH drops inside the reactors. Inhibition in the sugar waste reactors had an immense influence on the degradation of the organic components in the sugar reactors. Buffering of pH in the reactors also did not seem to help in achieving a better degradation. It was seen from the pH data that 30% reactors had a drop in pH following the buffering also whereas 22.5% and 15% sugar content reactors were having a flat pH after that, suggesting there were no anaerobic activities happening in 22.5 and 15% reactors after buffering. Hence the possibility of a rapid and better buffering of the reactors to resume the anaerobic

activities should be investigated to help in resuming the different anaerobic activities for a better degradation in the sugar waste reactors.

2.4.2 Surfactant waste:

It could be noted that all the surfactant reactors had good degradations. This was irrespective of the concentration of the surfactant. However, the reactor with 500 mg/L surfactant consistently shown a less degradation compared to other concentration which suggest that a concentration above 500 mg/L could be inhibitive. Reactors with 50 mg/L were similar to the control in all measures suggesting no inhibition in the reactors with 50 mg/L surfactants. It should also be noted that the surfactant concentration of 150 mg/L and 250 mg/L were less inhibitive than 500 mg/L in many measures. Hence, it could be concluded that the surfactant concentration in the anaerobic bioreactors could be inhibitive at a very high concentration above 500 mg/L and the inhibition should increase with increase of the concentration of surfactants in the reactor. However, this cannot be generalized for all surfactant types.

2.4.3 Paint waste:

It is evident from the different data that paint waste show a high inhibition even at a concentration of 7.5%. There was a high inhibition in both the degradation of components and the gas release which suggest that the paint waste is highly inhibitive. There was not much difference between the degradation in the reactors with different concentration suggesting that the concentration of 7.5% even was highly inhibitive. The volatile fatty acid and pH data suggest that the inhibition was not due to the volatile fatty

acid accumulation, but due to some other toxicity. Also, lignin measurement was highly influenced by the paint content inside the reactors, the same way it is influenced by plastics and the manipulation due to the paint content was consistent with the paint concentration in the reactors. These suggest the manipulative nature of paint content and the usual laboratory method is probably not an appropriate method to determine the lignin content of the samples containing paint.

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Figures and Tables:

CONTROL PERCENTAGE GAS
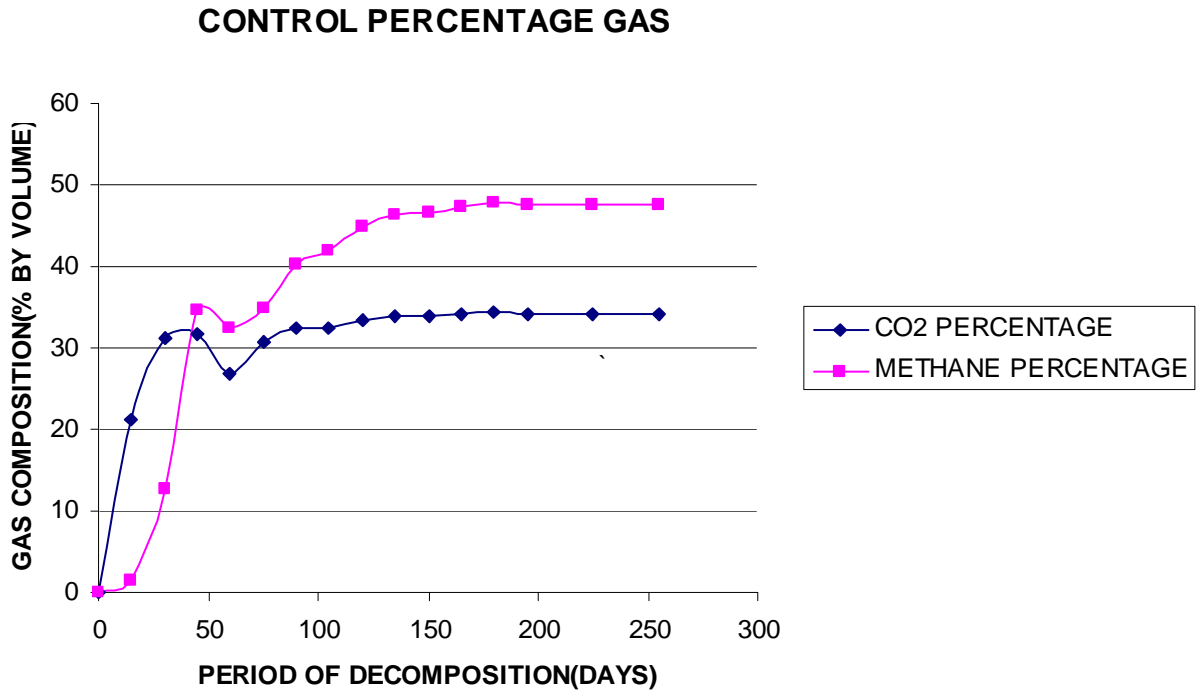
Figure 2.1: Control Percentage gas expressed by total gas volume

pH: control and sugar waste
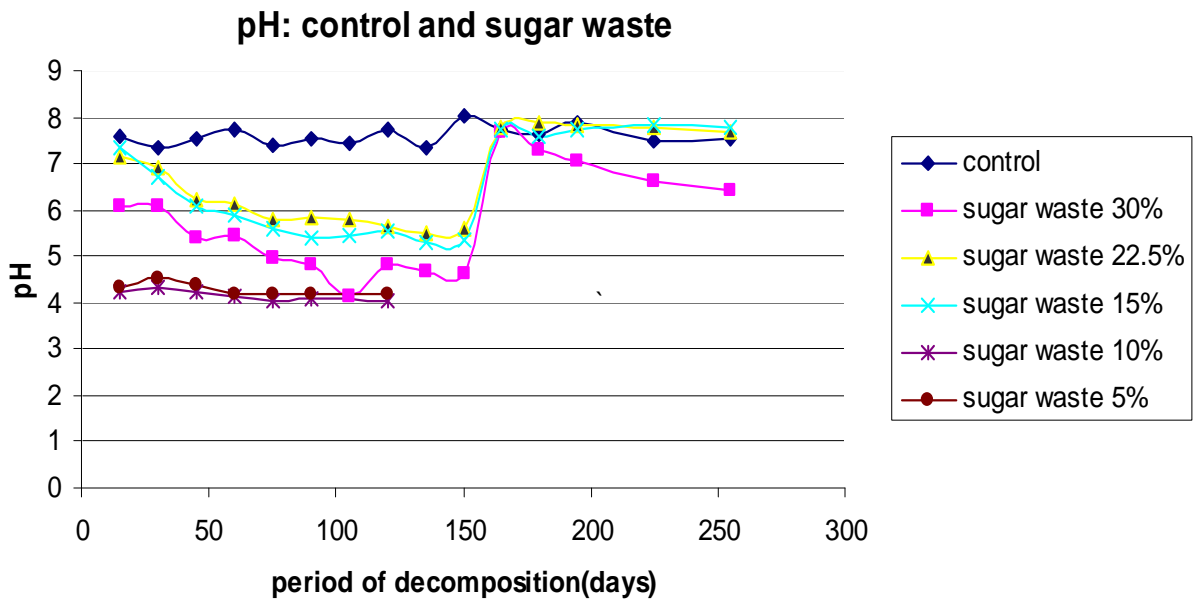
Figure 2.2: pH of control and sugar waste reactors
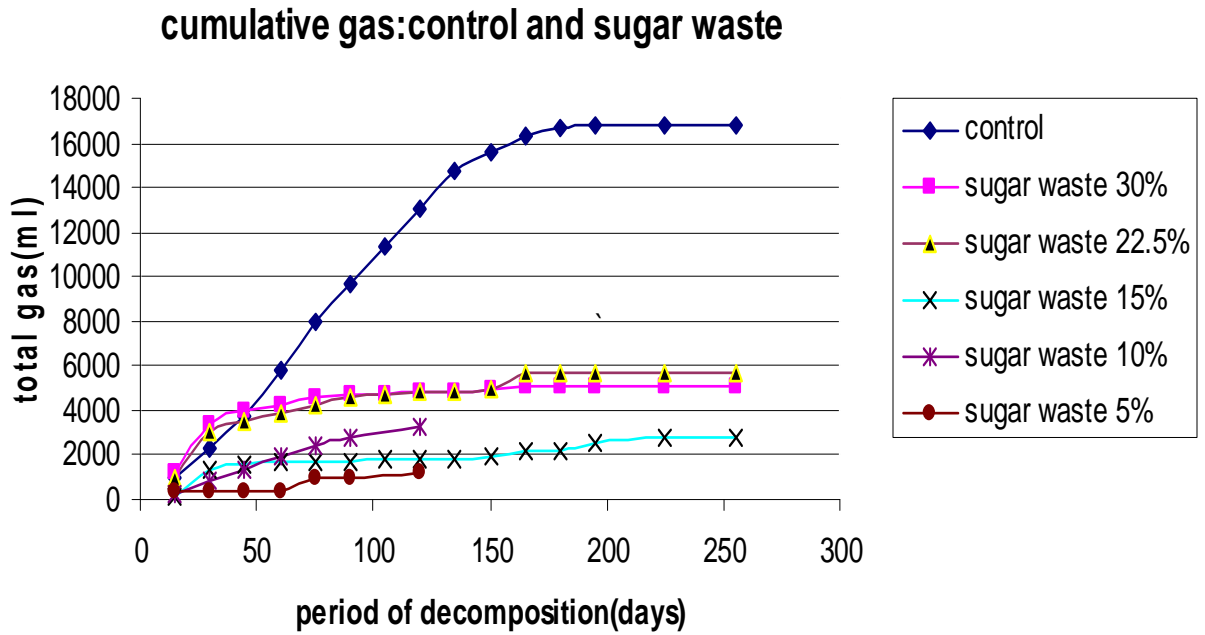
Figure 2.3 Cumulative gas release from control and sugar waste reactors
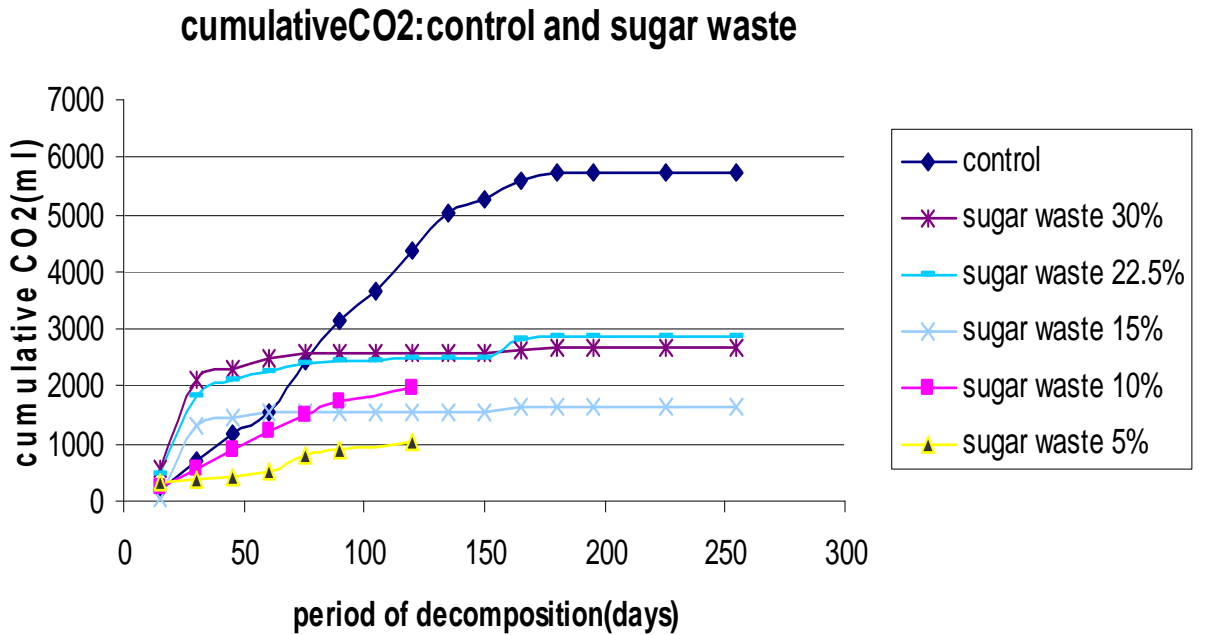
Figure 2.4 Cumulative CO₂ release from control and sugar waste reactors

cumulative methane:control and sugar waste
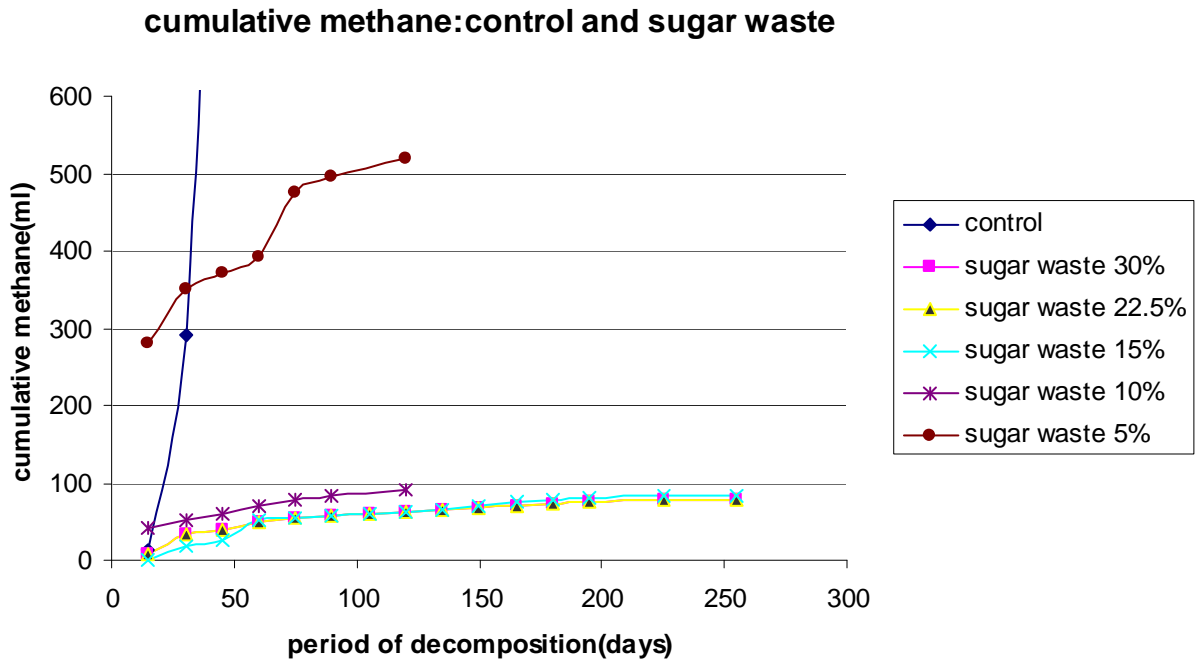
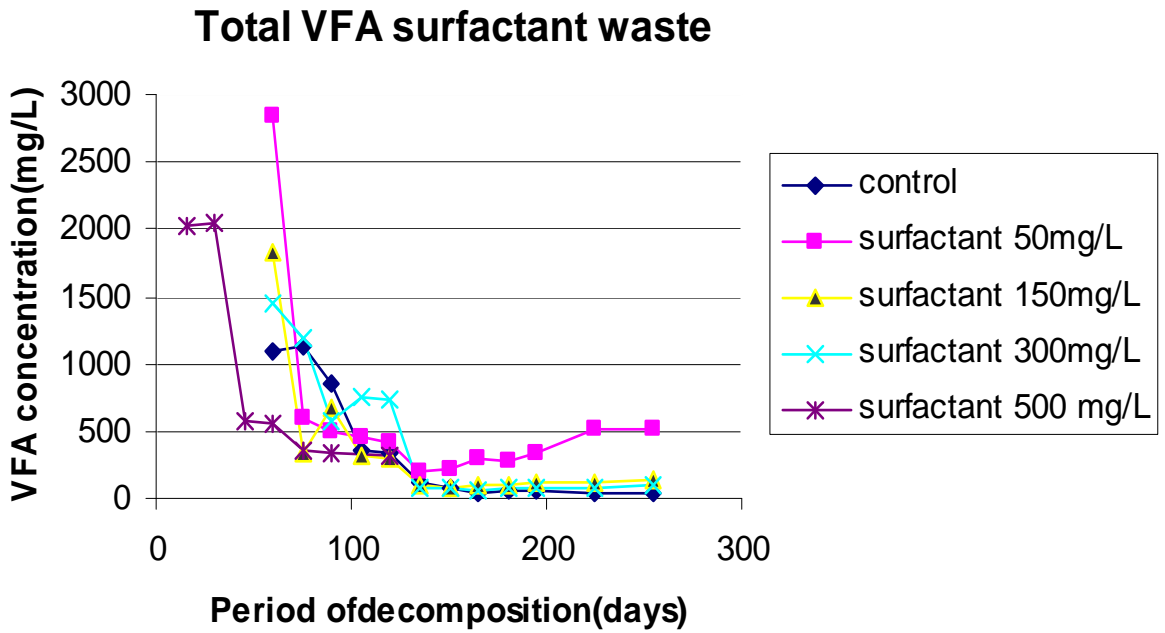*Figure 2.5 Cumulative methane release from control and sugar waste reactors*

Total VFA sugar waste
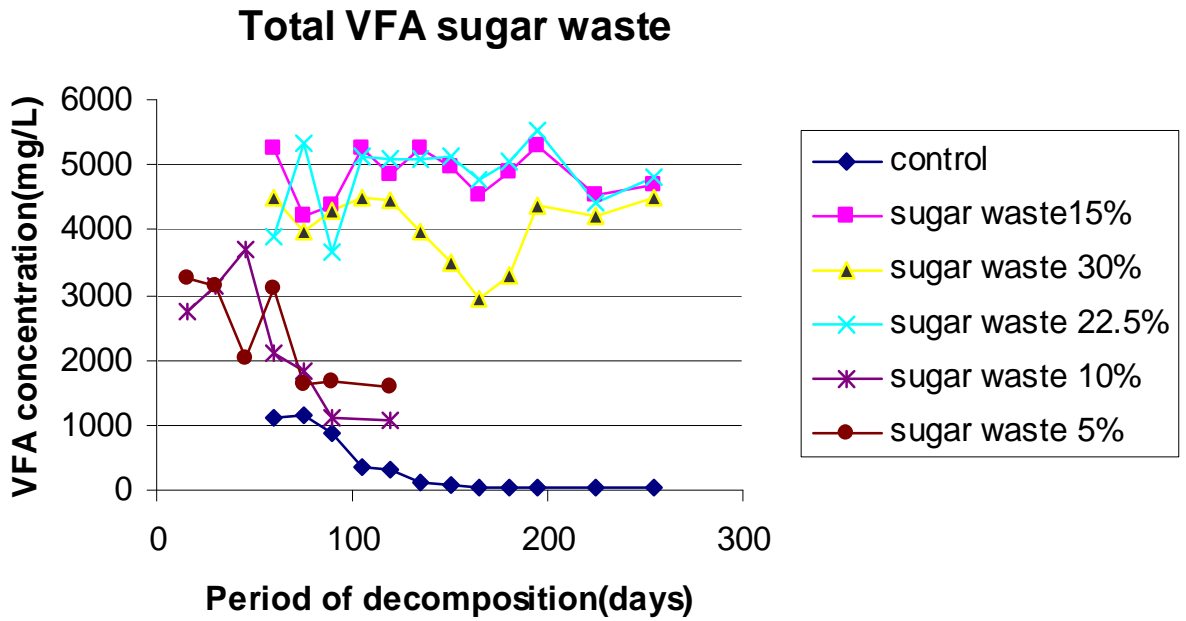
Figure 2.6 Total VFA in control and sugar waste reactors
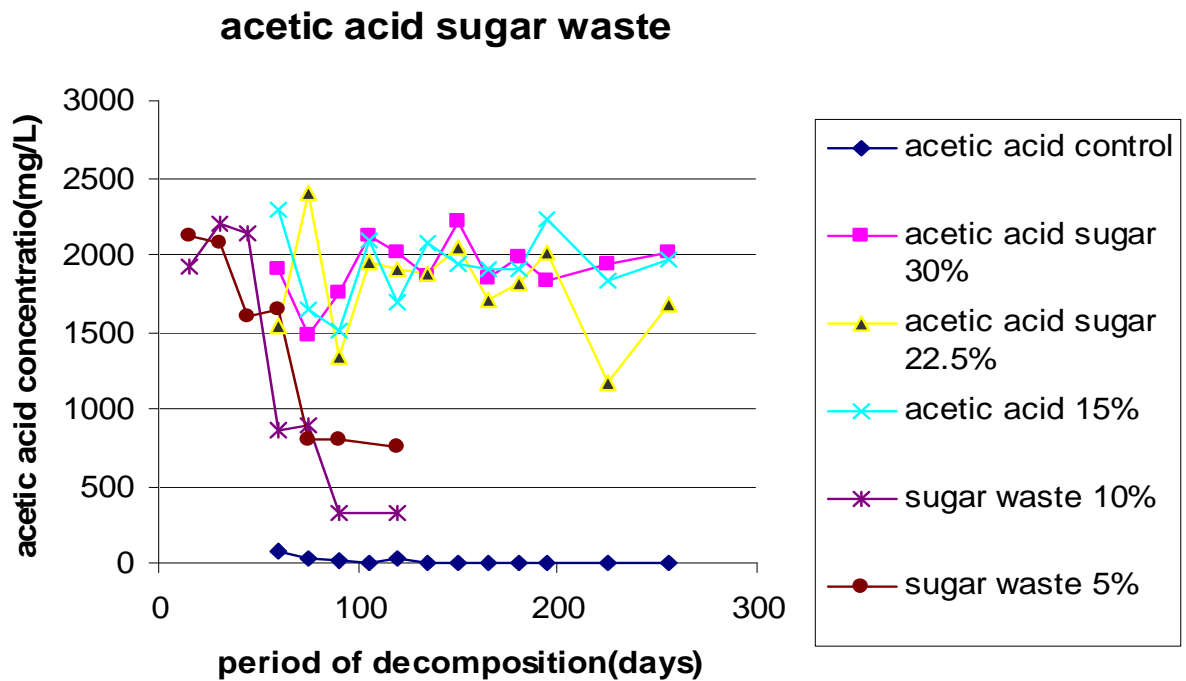
Figure 2.7 Total acetic acid in control and sugar waste reactors
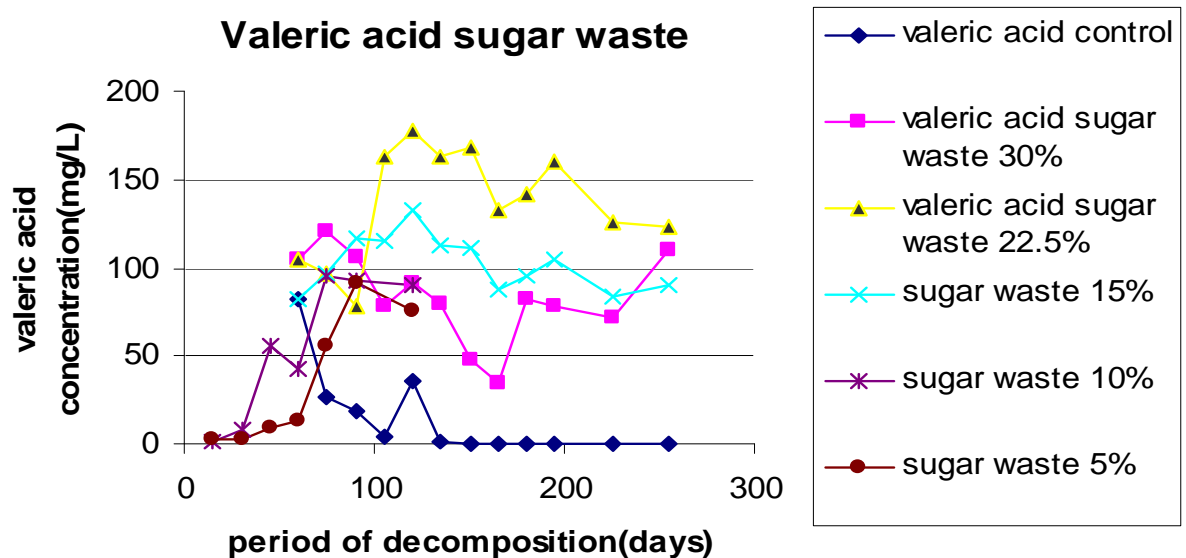
Figure 2.8 Total valeric acid in control and sugar waste reactors

butyric acid sugar waste
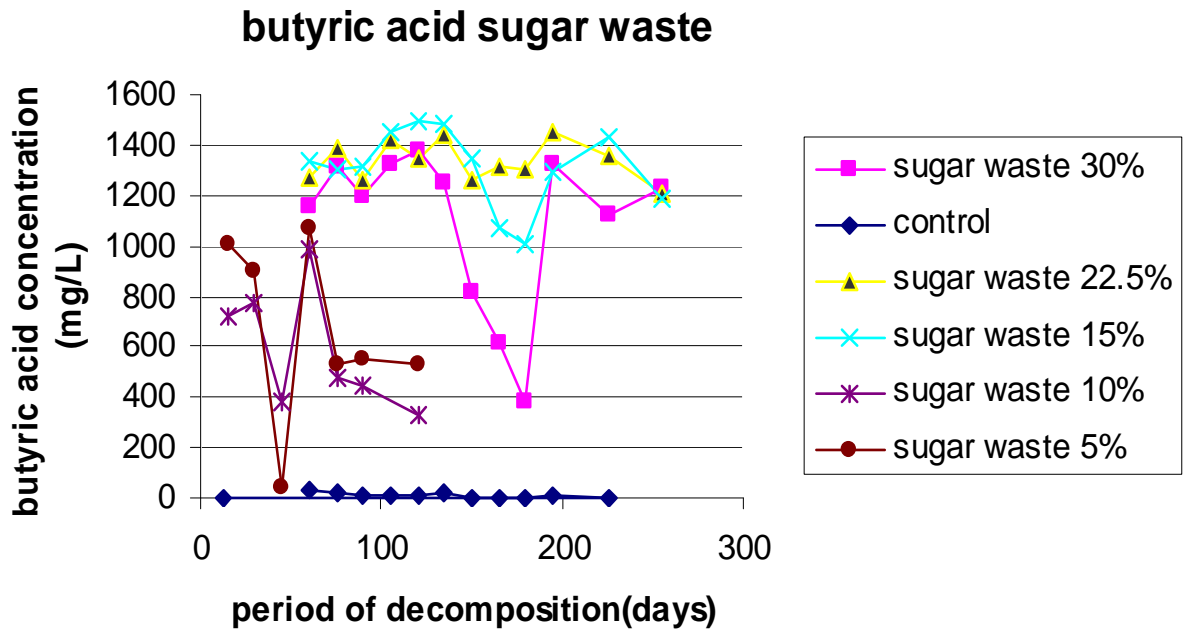
Figure 2.9 Total butyric acid in control and sugar waste reactors

propionic acid sugar waste
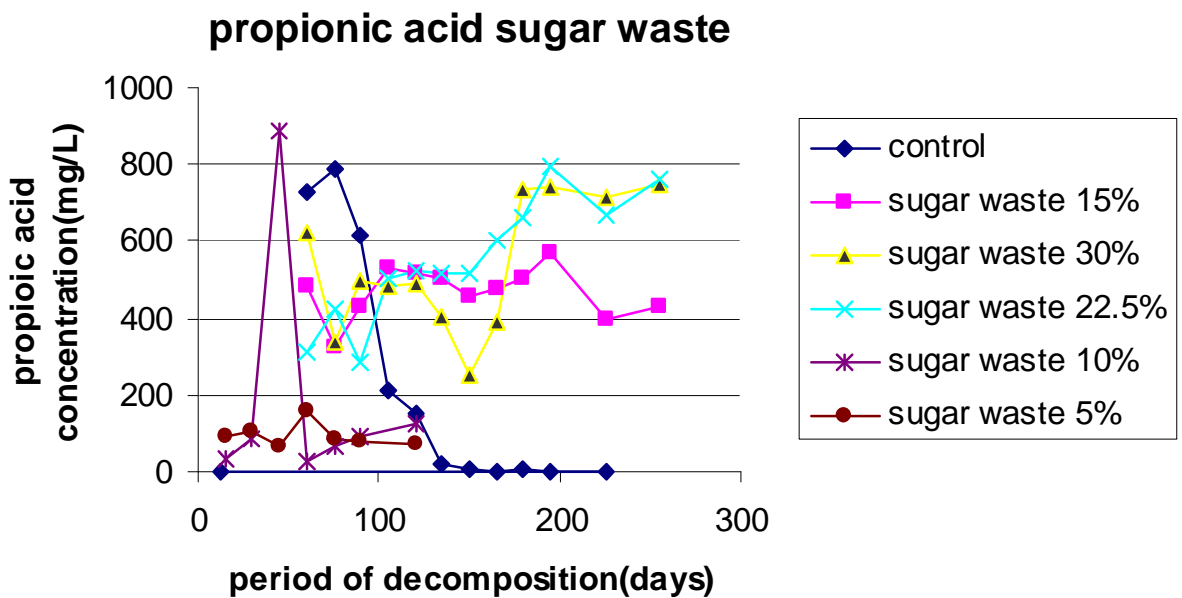
Figure 2.10 Total propionic acid in control and sugar waste reactors
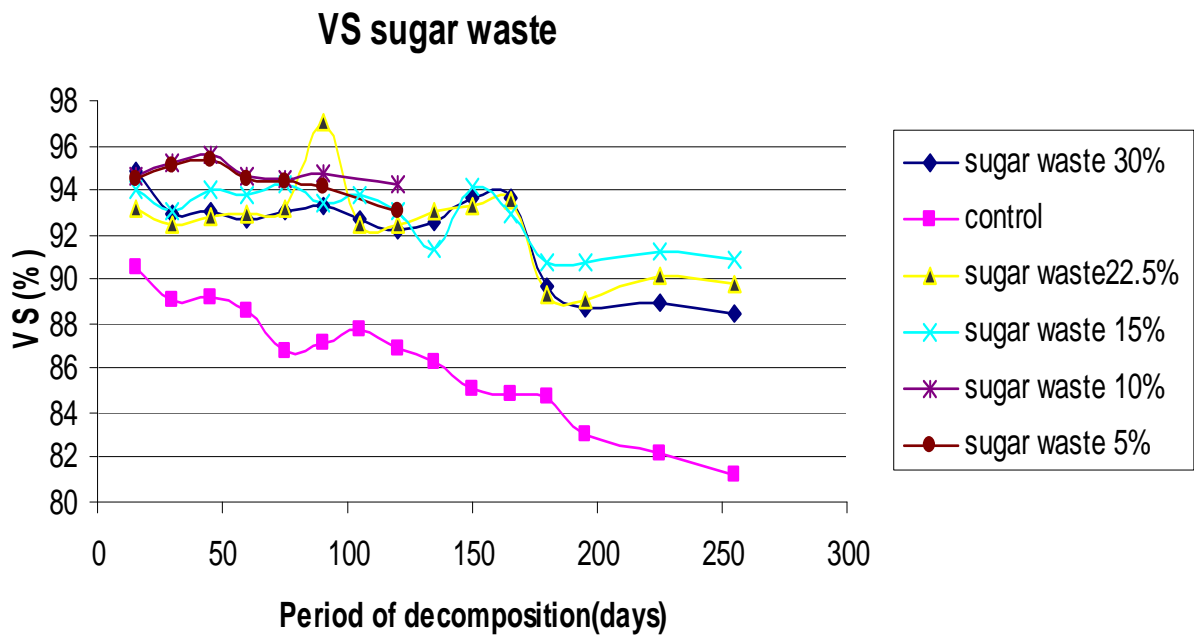
Figure 2.11 Volatile solids in control and sugar waste reactors
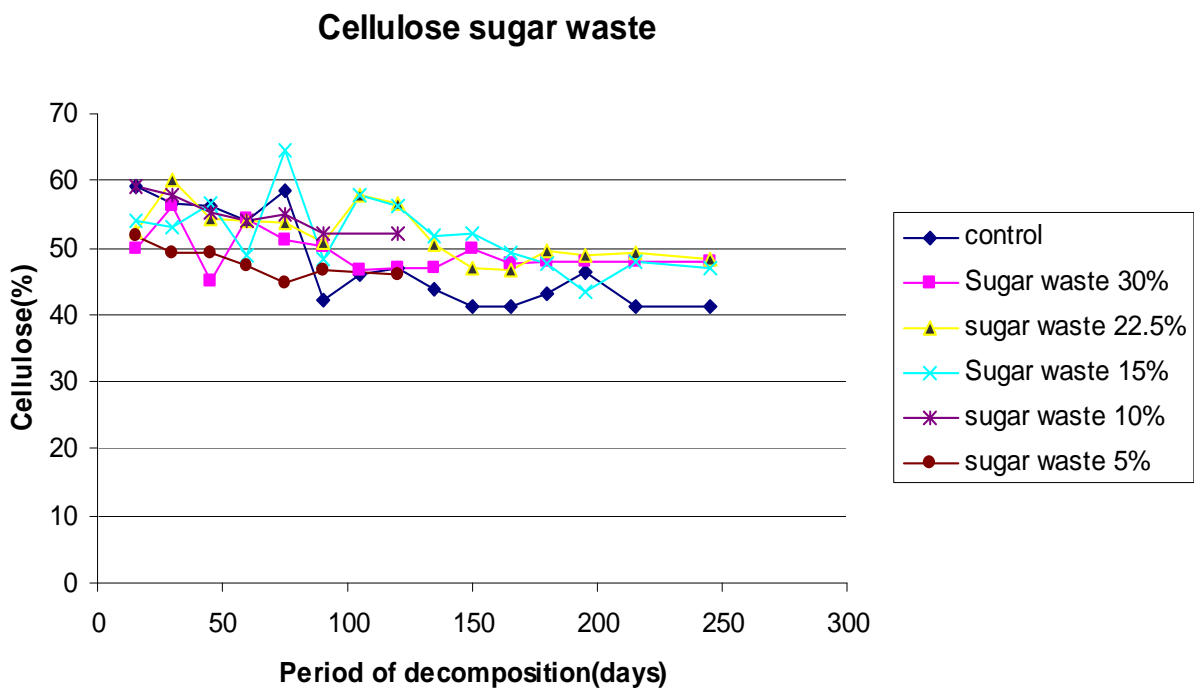
Figure 2.12 Cellulose in control and sugar waste reactors

Hemicellulose Sugar waste
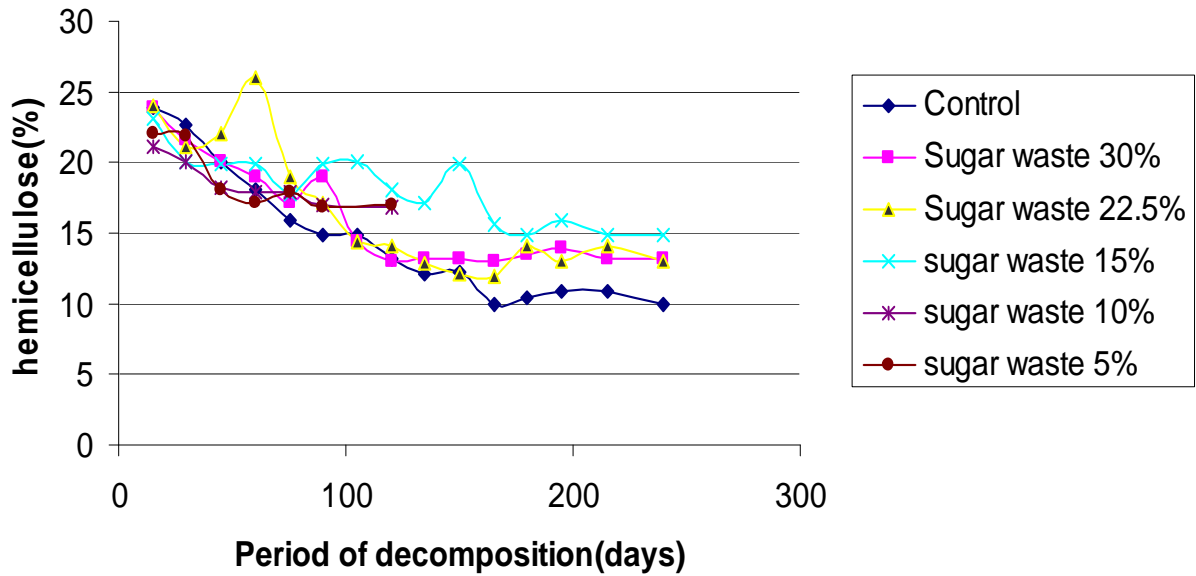
Figure 2.13 Hemicellulose in control and sugar waste reactors

Sugar waste and control lignin
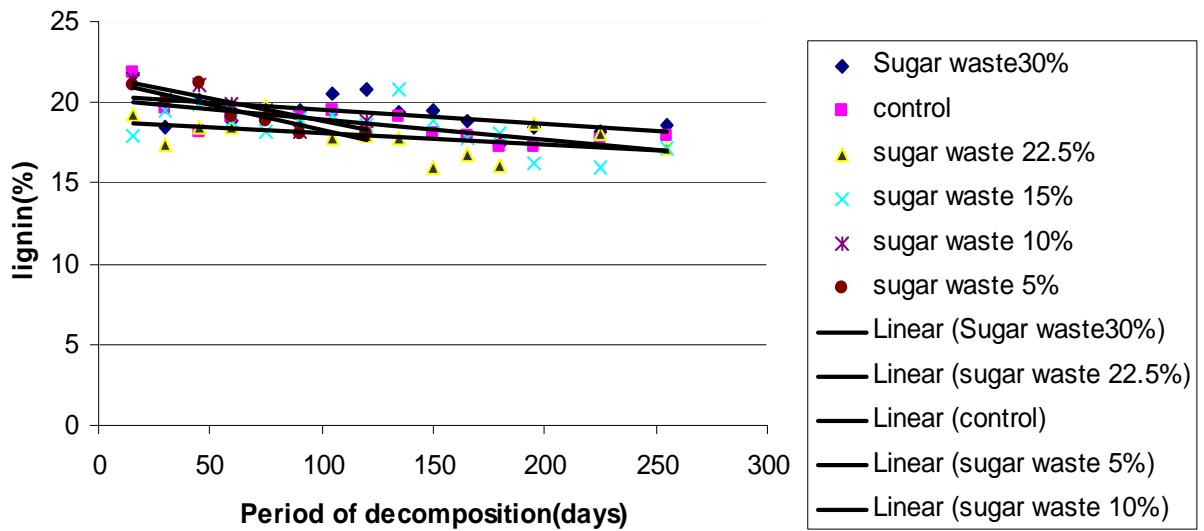
Figure 2.14 Lignin in control and sugar waste reactors
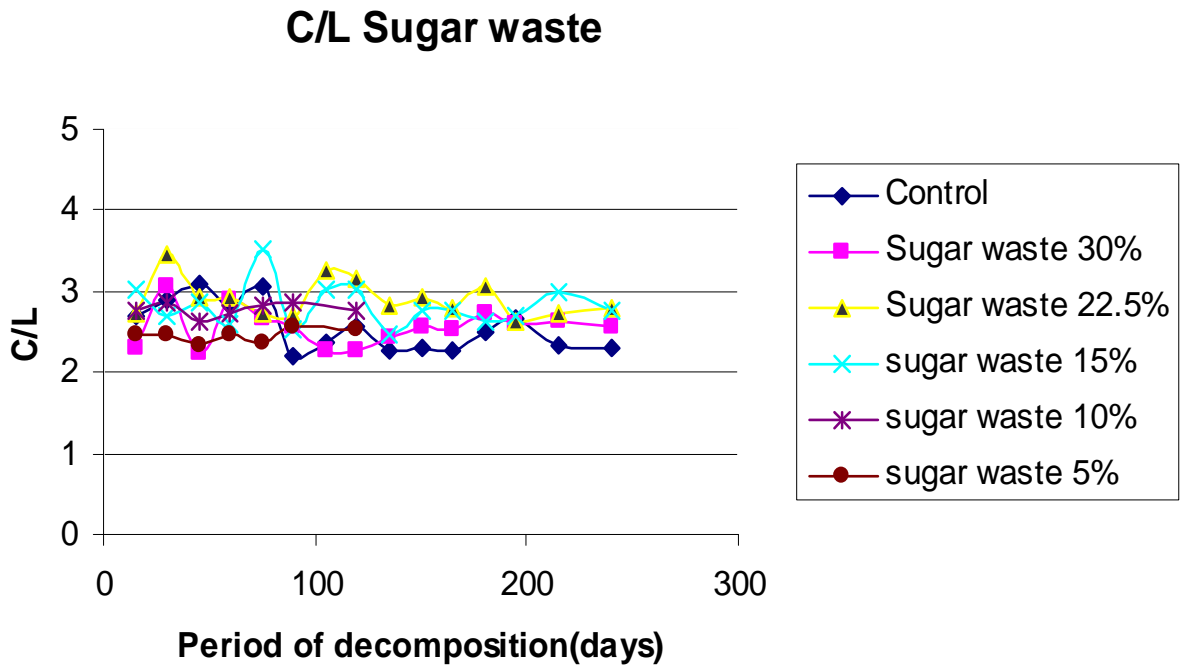
C/L Sugar waste

Figure 2.15 C/L in control and sugar waste reactors
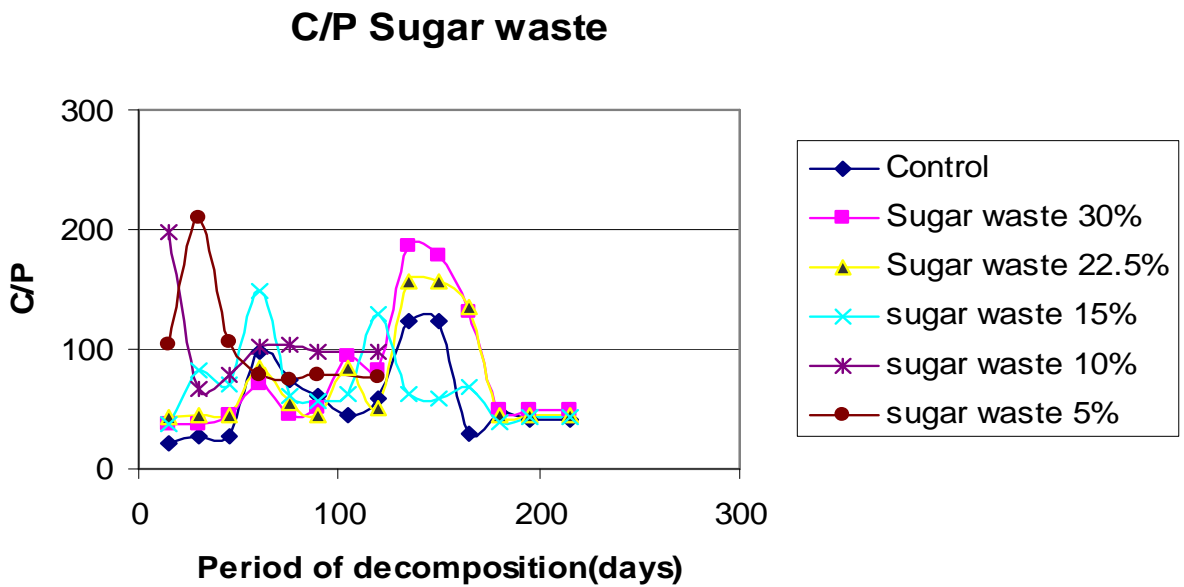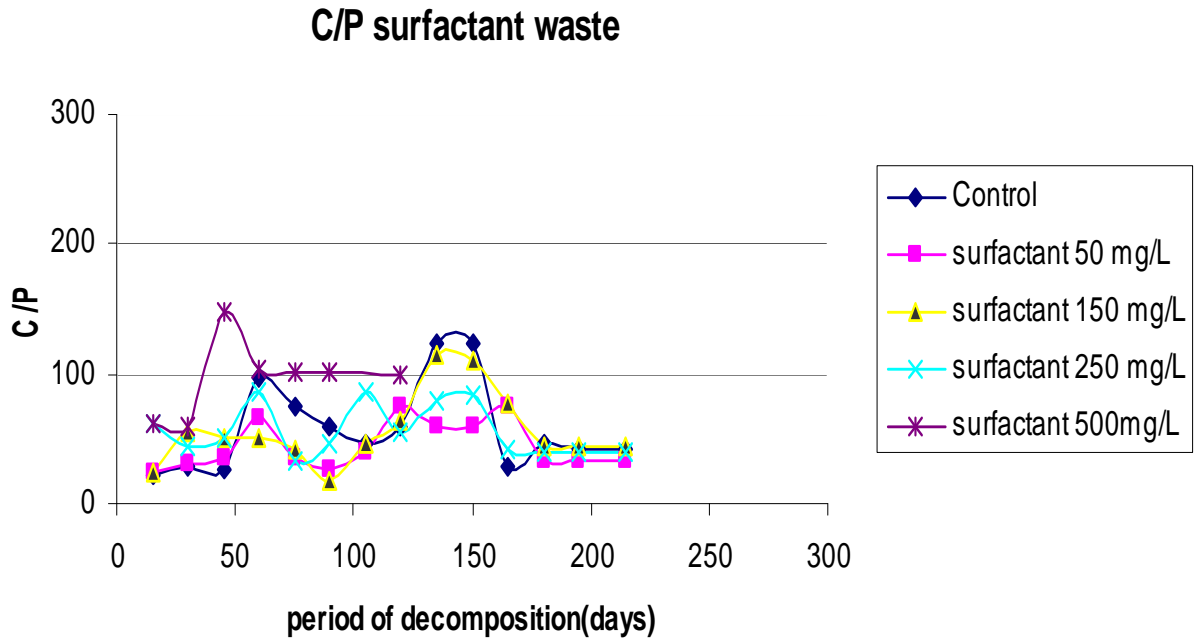
C/P Sugar waste

Figure 2.16 C/P in control and sugar waste reactors
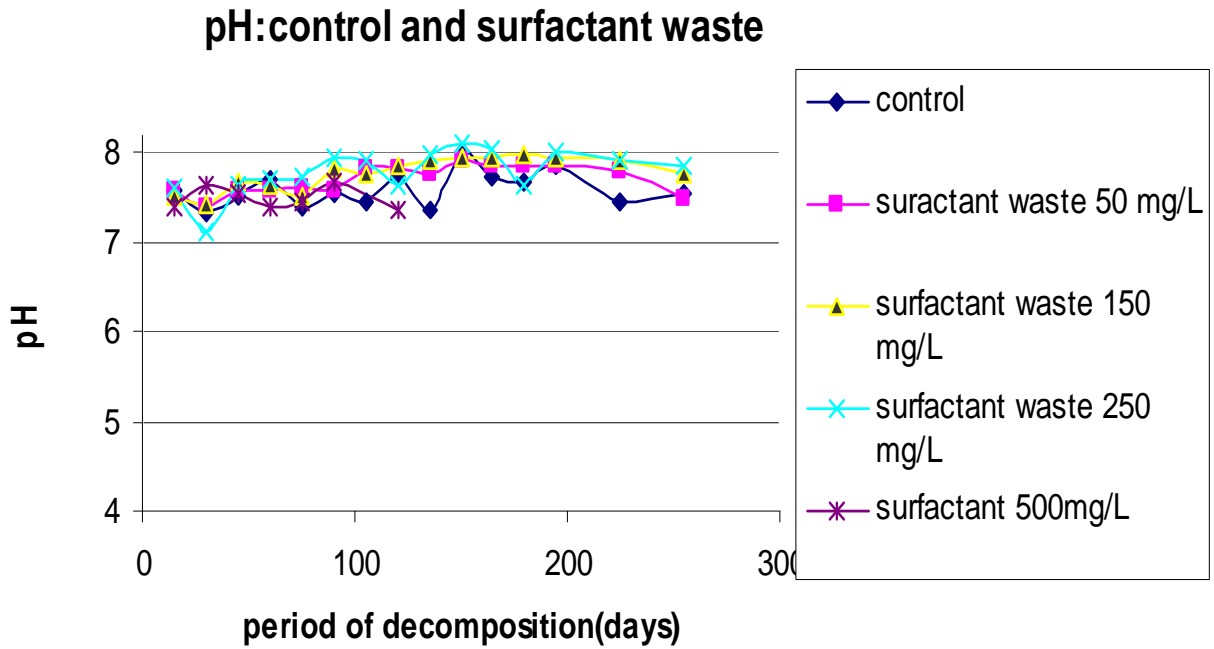
Figure 2.17: pH of control and surfactant waste reactors
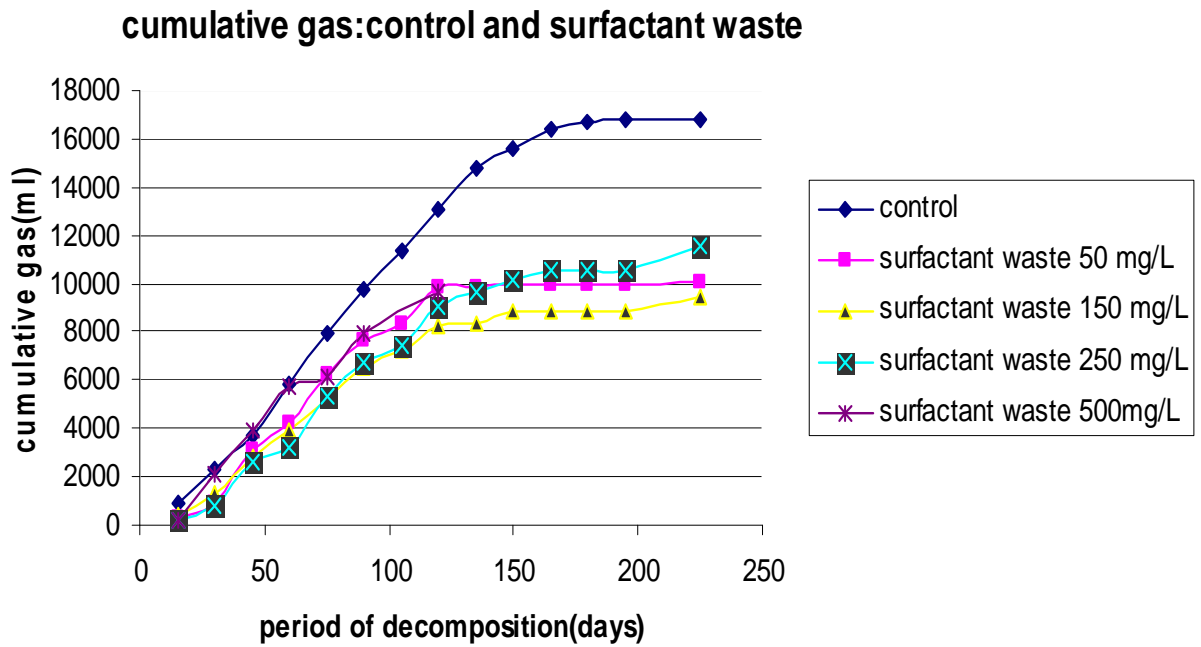
Figure 2.18 Cumulative gas release from control and surfactant waste reactors
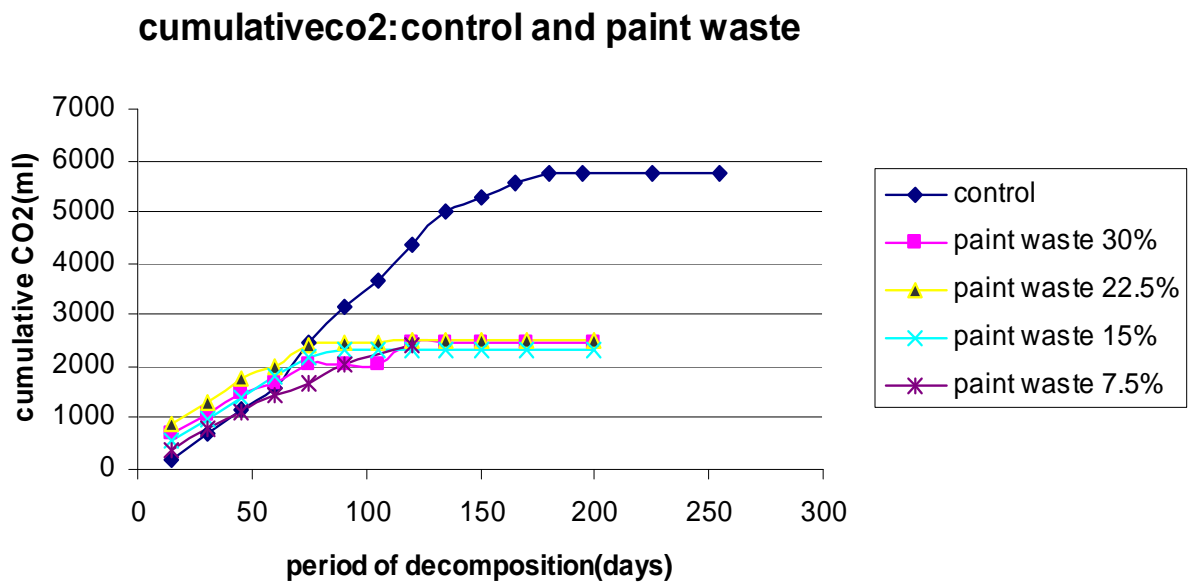
cumulative co2: control and surfactant waste
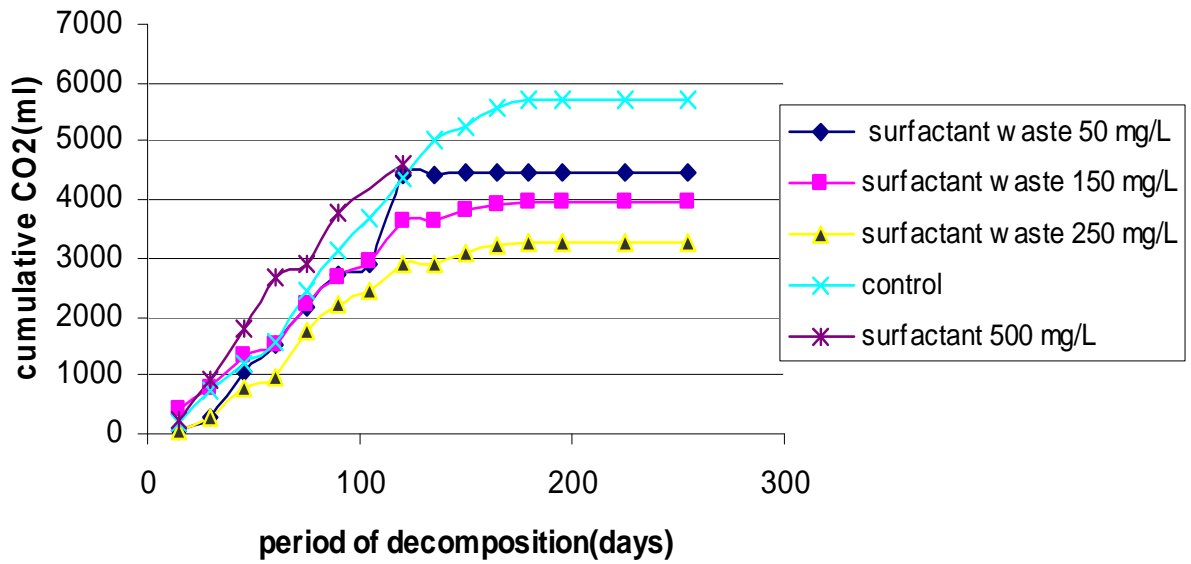
Figure 2.19 Cumulative CO₂ release from control and surfactant waste reactors

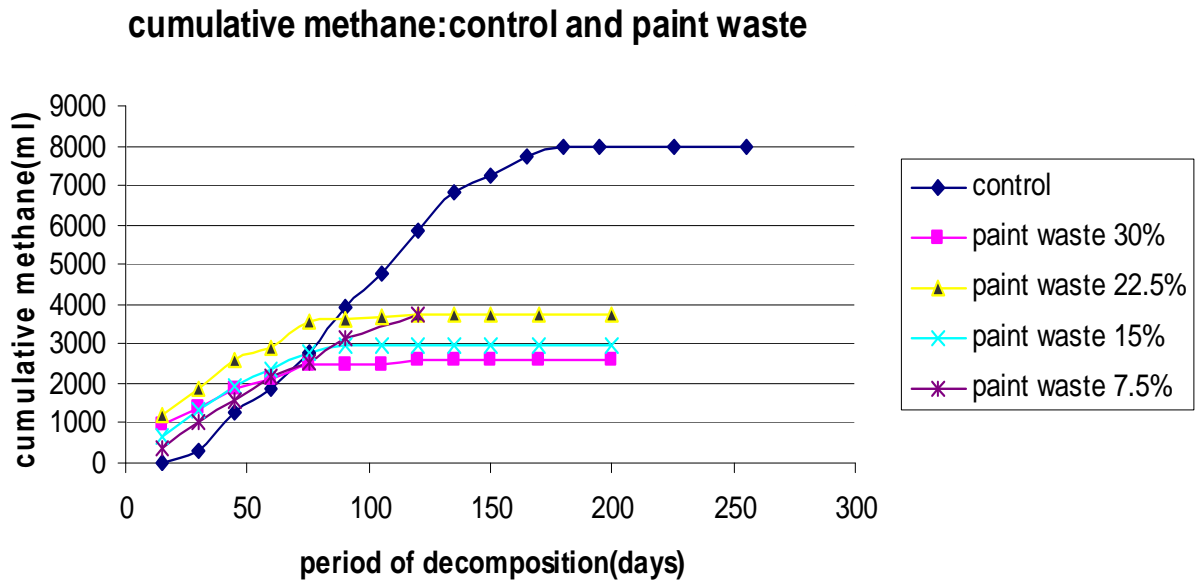# cumulative methane:control and surfactant waste
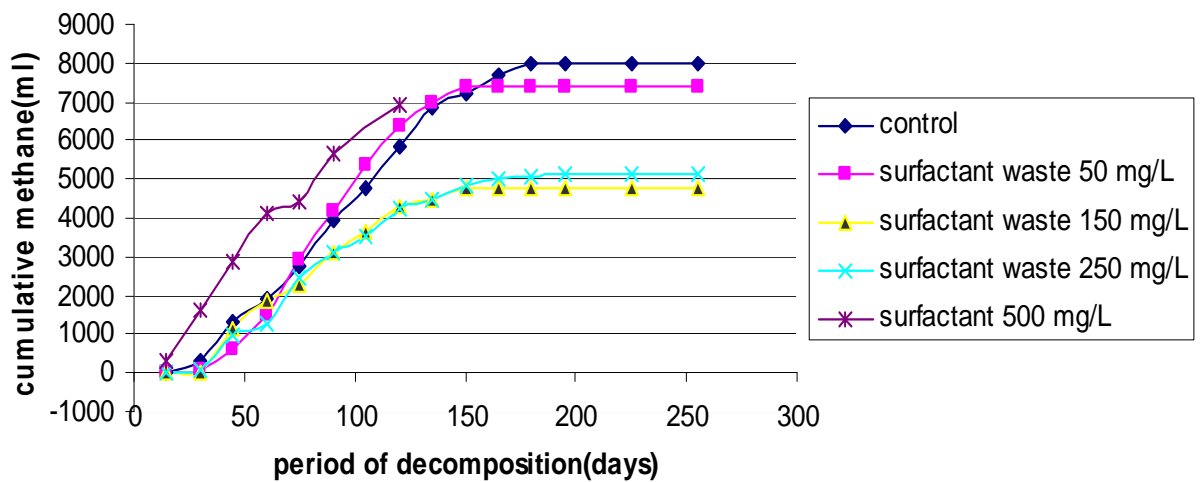
Figure 2.20 Cumulative methane release from control and surfactant waste reactors

Figure 2.21 Total VFA in control and surfactant waste reactors
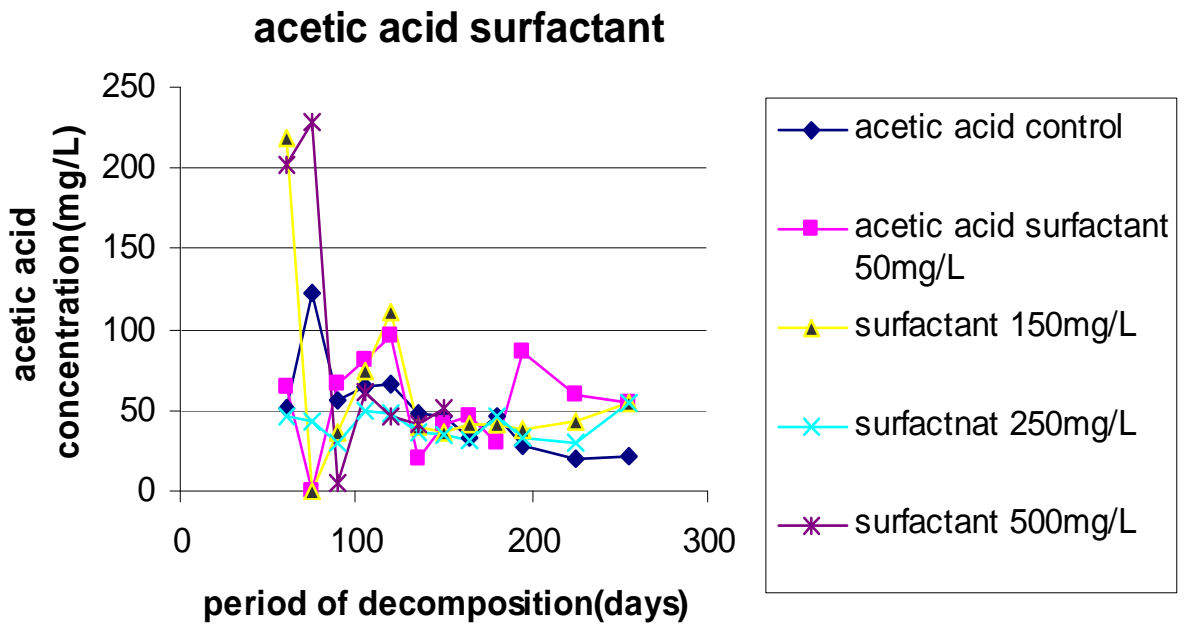
Figure 2.22 Total acetic acid in control and surfactant waste reactors

valeric acid surfactant
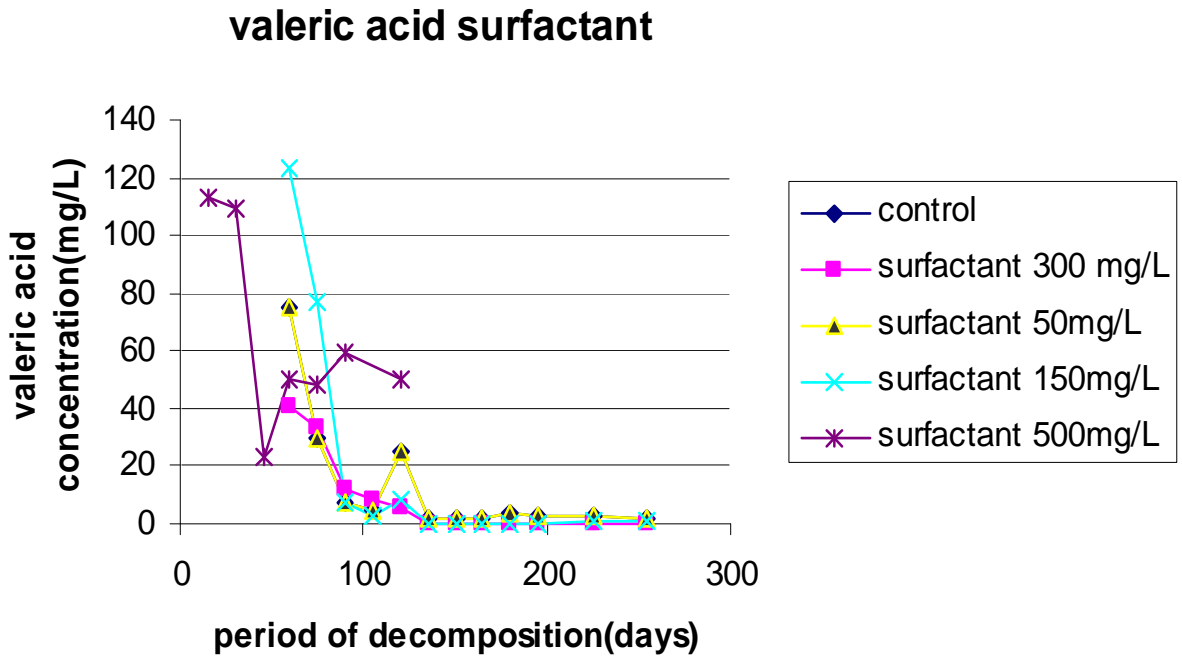
Figure 2.23 Total valeric acid in control and surfactant waste reactors

butyric acid surfactant waste
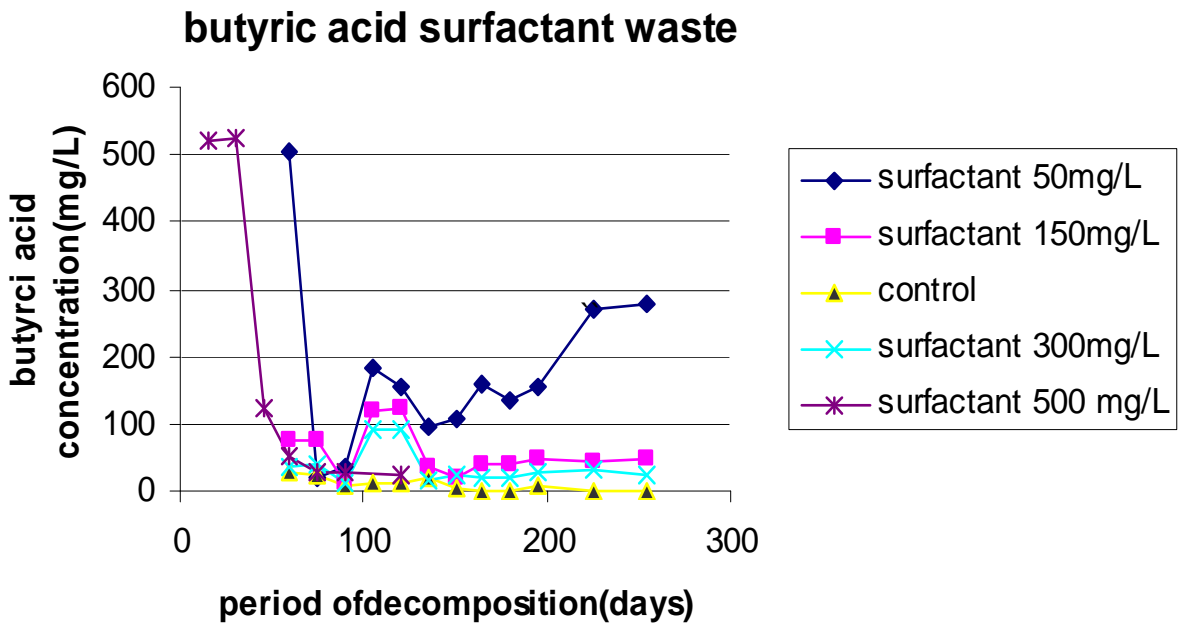
Figure 2.24 Total butyric acid in control and surfactant waste reactors

propionic acid surfactant waste
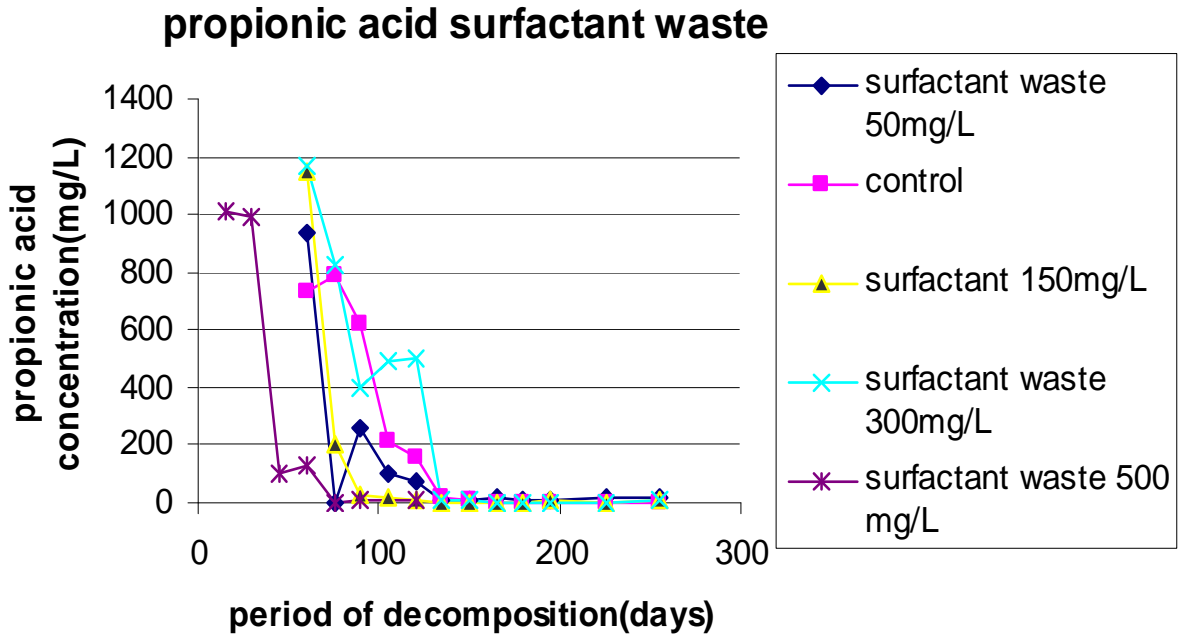
Figure 2.25 Total propionic acid in control and surfactant waste reactors

VS surfactant waste
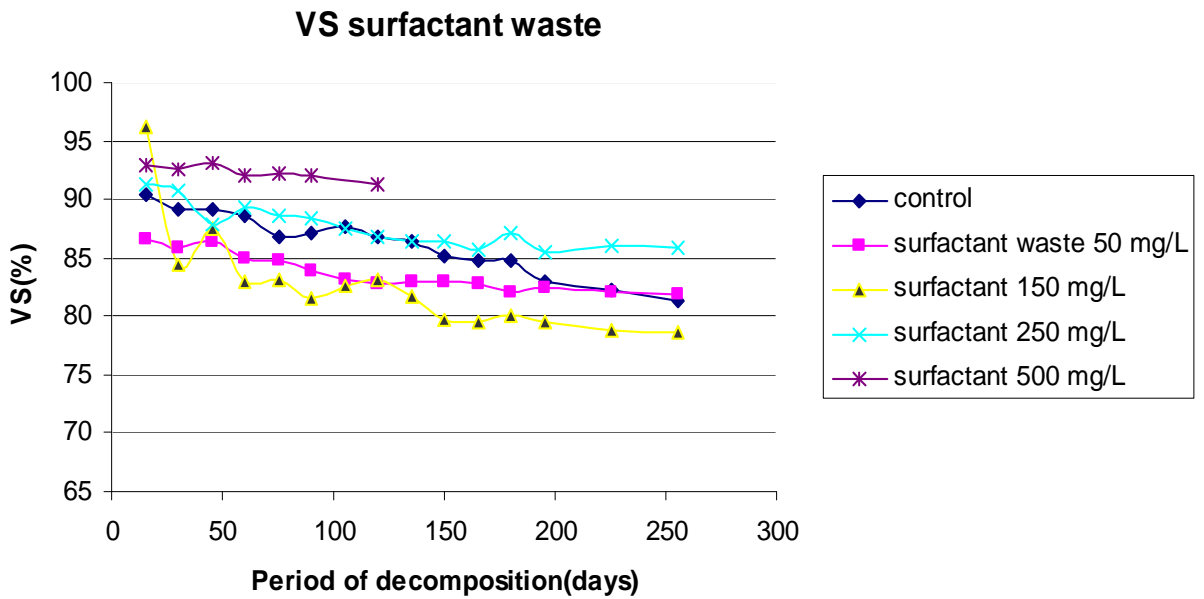
Figure 2.26 Volatile solids in control and surfactant waste reactors

cellulose surfactant waste
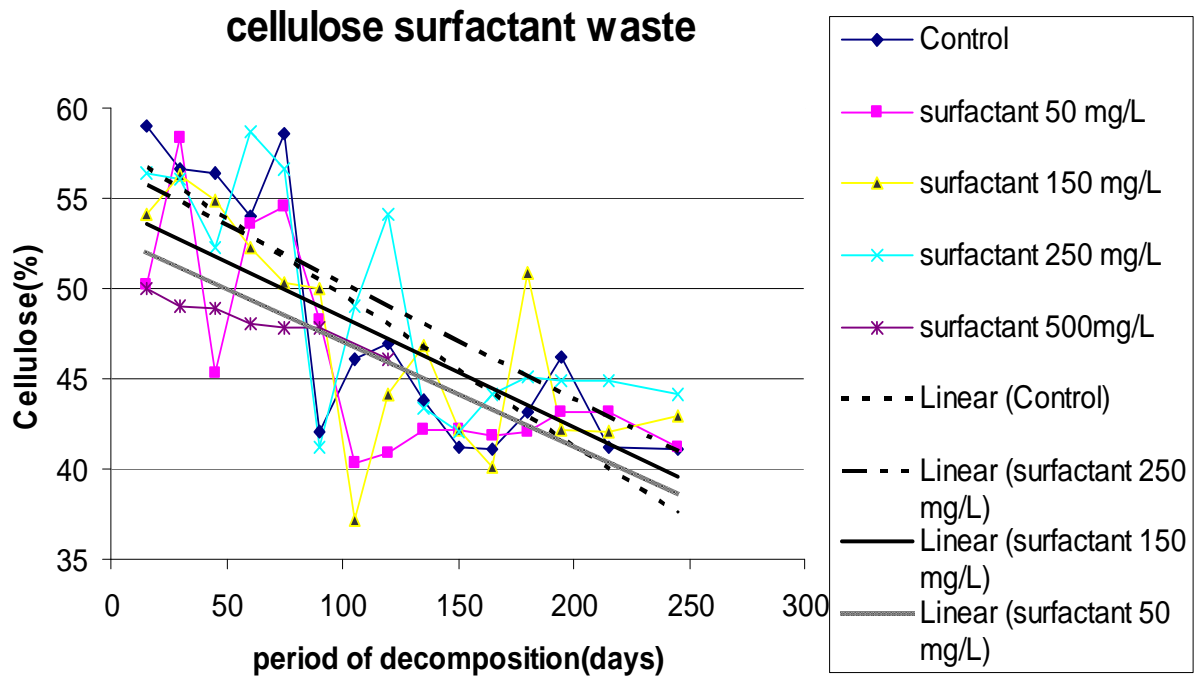
Figure 2.27 Cellulose in control and surfactant waste reactors

Hemicellulose surfactant waste
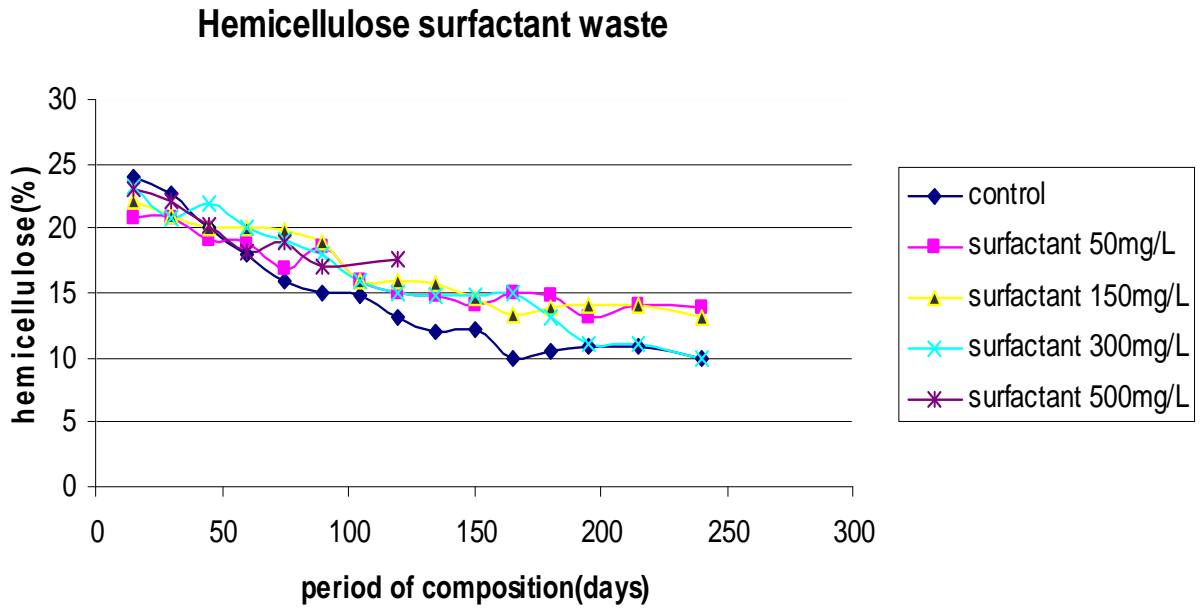
Figure 2.28 Hemicellulose in control and surfactant waste reactors

Surfactant and control lignin
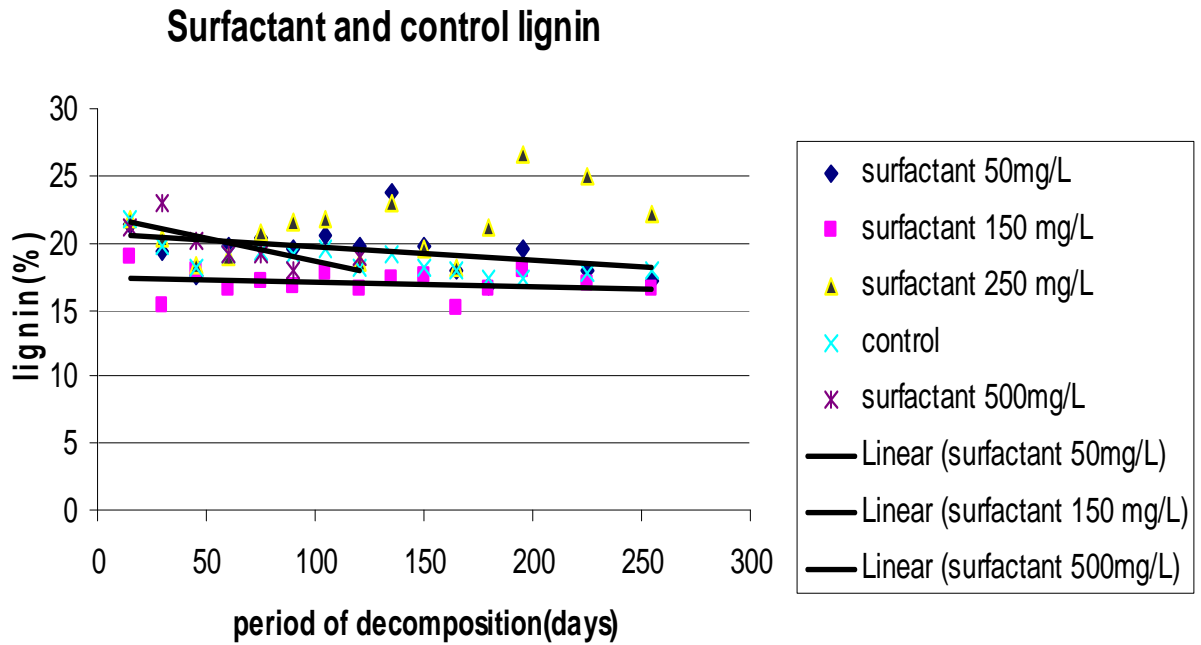
Figure 2.29 Lignin in control and sugar waste reactors

C/L surfactant waste
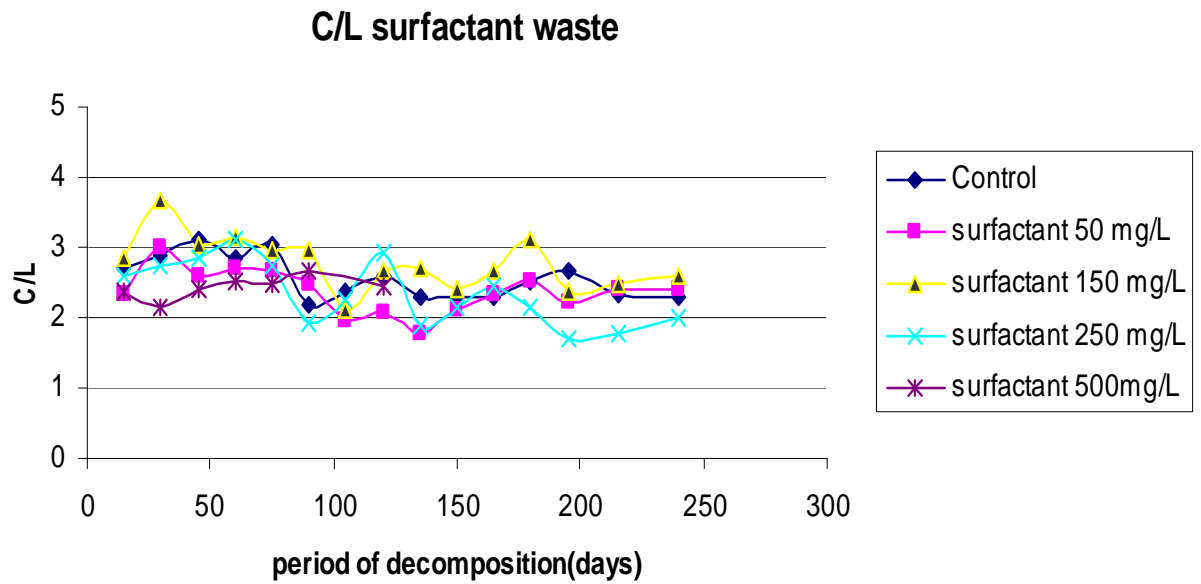
Figure 2.30 C/L in control and surfactant waste reactors

C/P surfactant waste

Figure 2.31 C/P in control and surfactant waste reactors

pH:control and paint waste
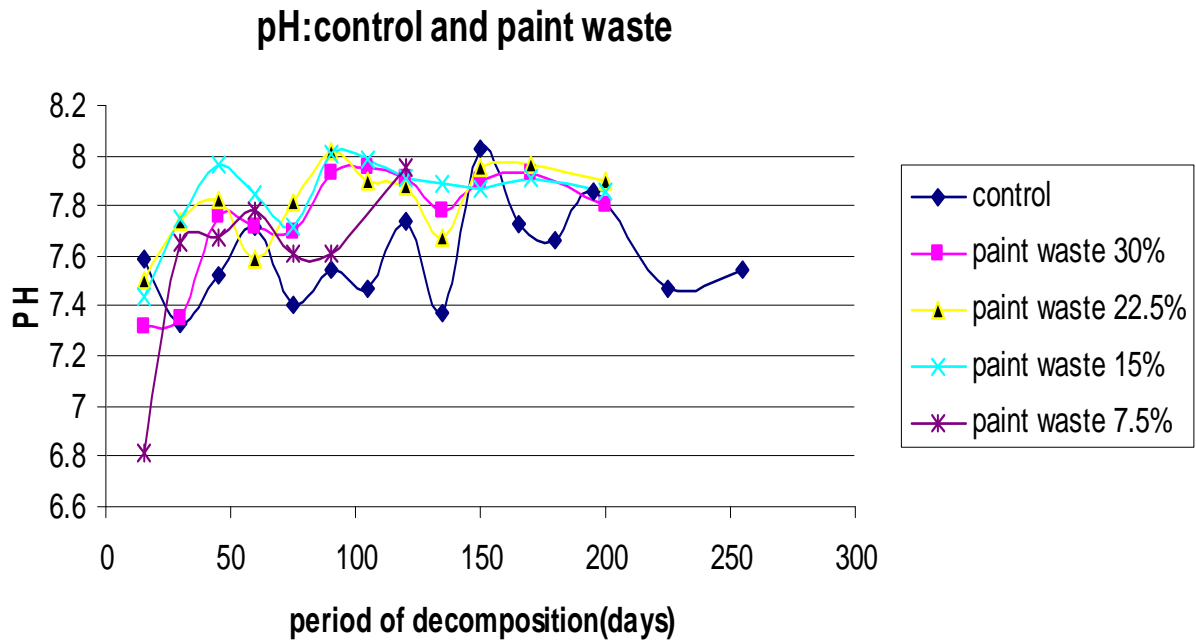
Figure 2.32: pH of control and paint waste reactors
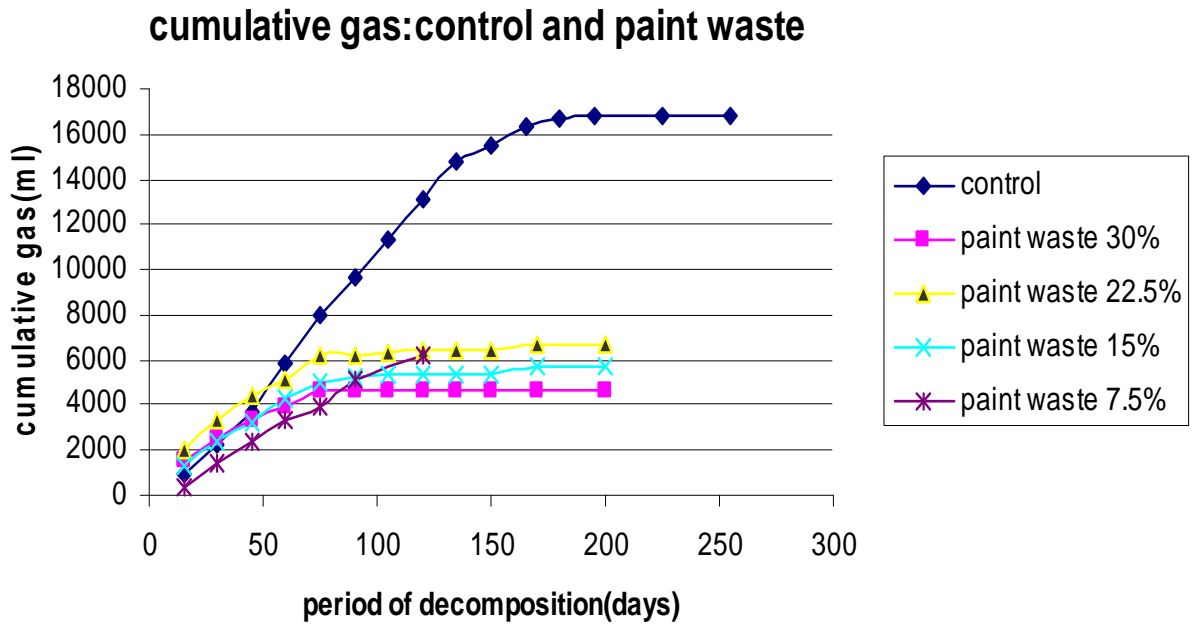
Figure 2.33 Cumulative gas release from control and paint waste reactors

Figure 2.34 Cumulative CO$_2$ release from control and paint waste reactors

Figure 2.35 Cumulative methane release from control and paint waste reactors
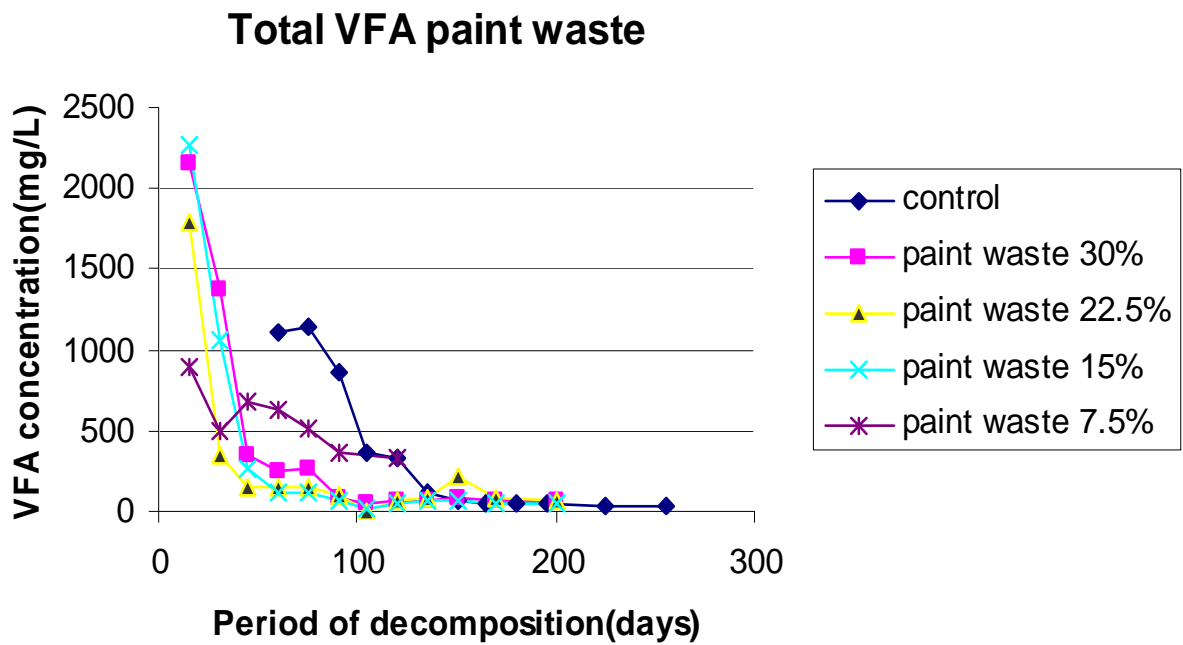
Figure 2.36 Total VFA in control and paint waste reactors
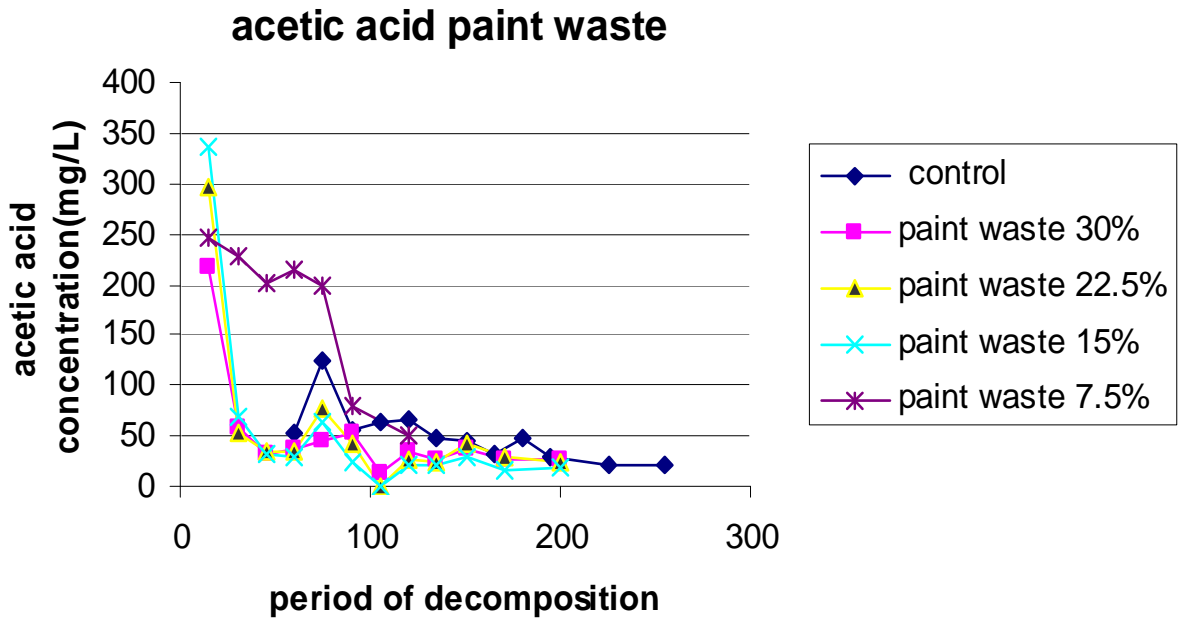
Figure 2.37 Acetic acid in control and paint waste reactors

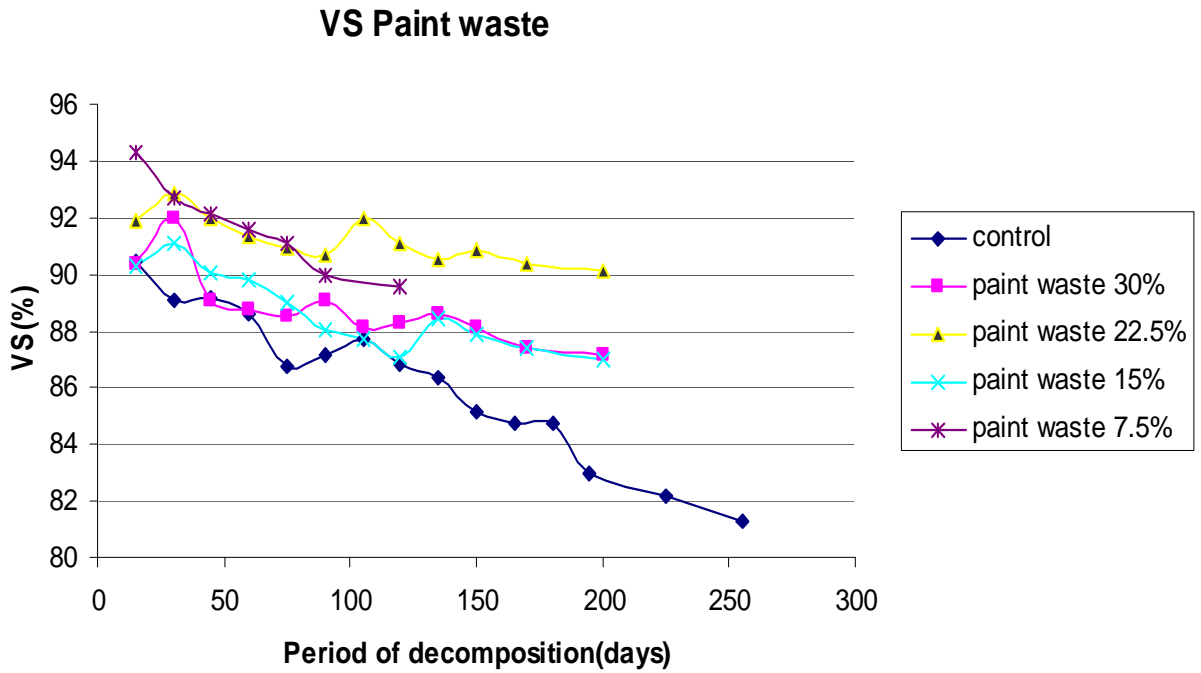*Figure 2.38 Valeric aicd in control and paint waste reactors*
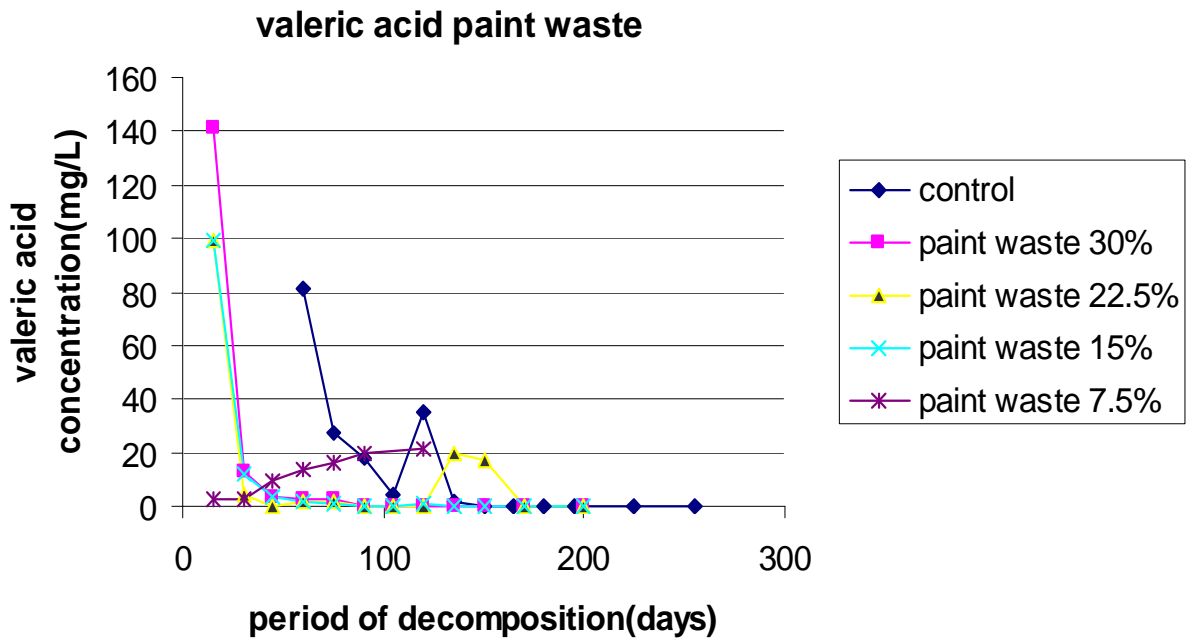
butyric acid paint waste
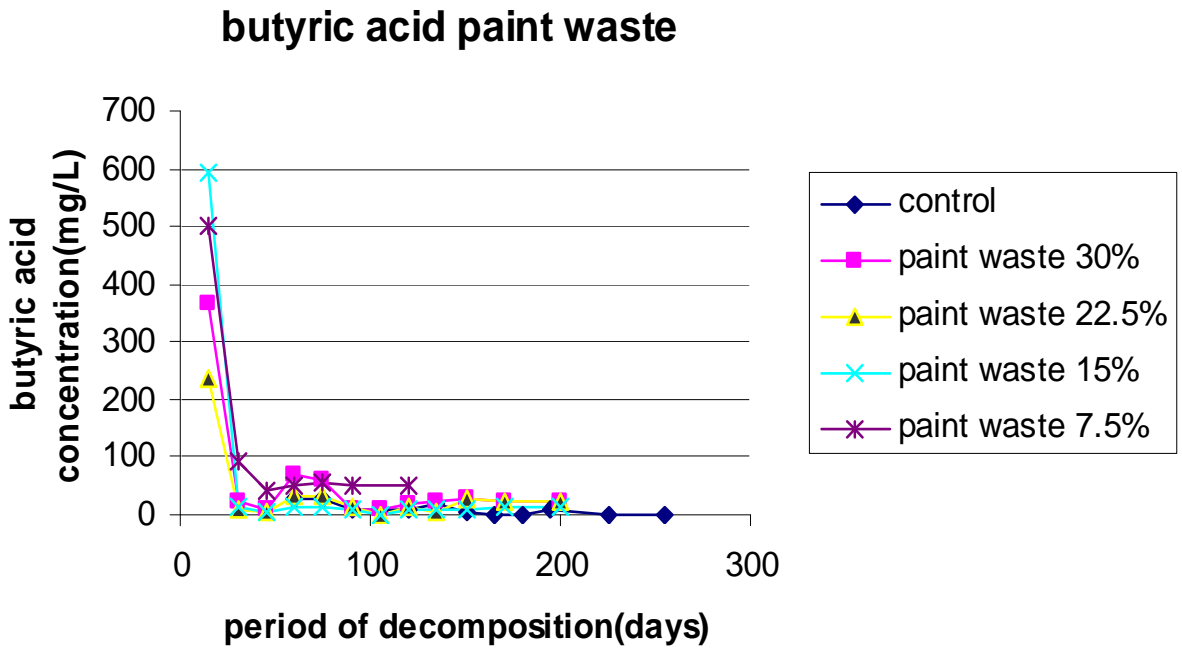
Figure 2.39 Butyric acid in control and paint waste reactors

propionic acid paint waste
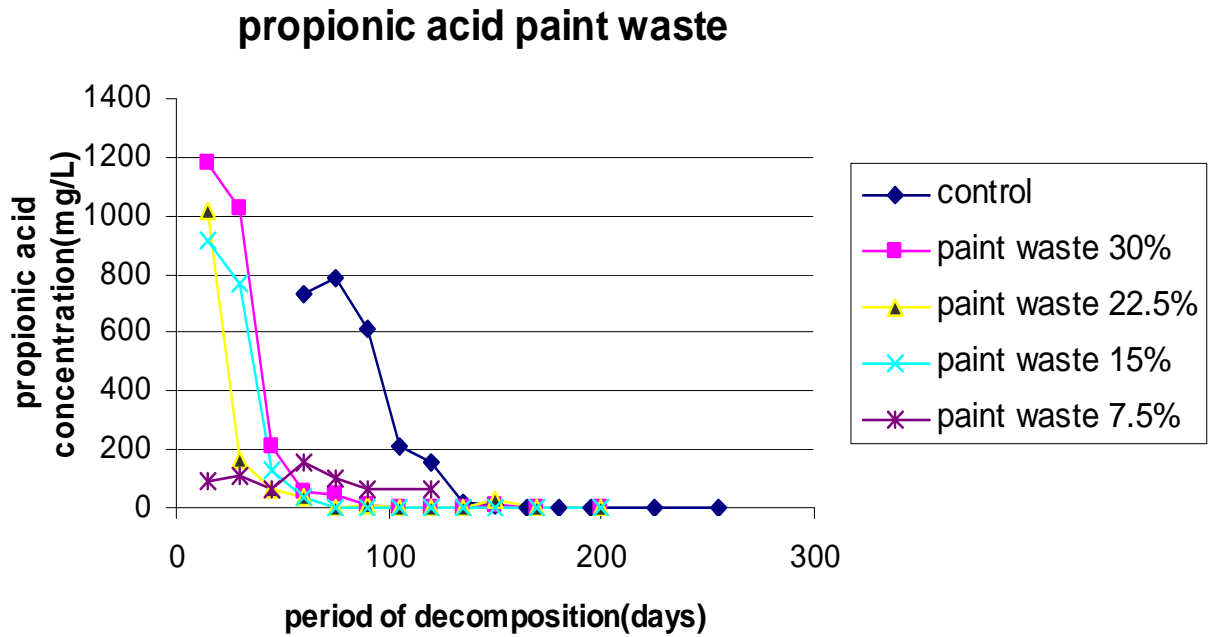
Figure 2.40 Propionic acid in control and paint waste reactors

VS Paint waste

Figure 2.41 VS in control and paint waste reactors

Cellulose Paint waste
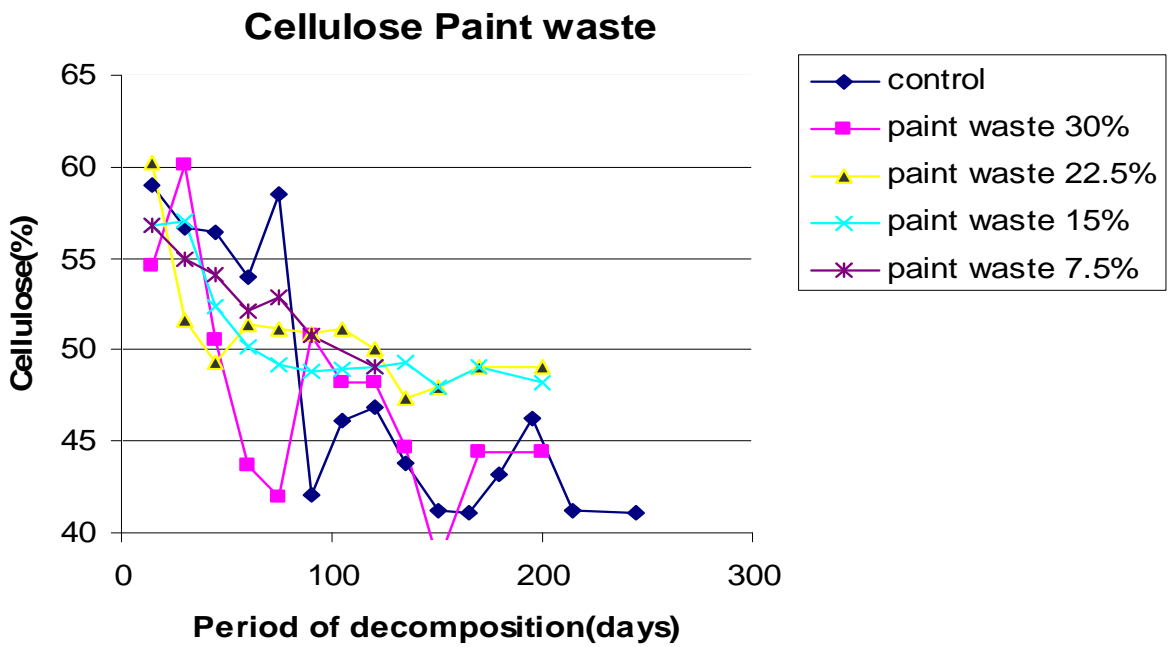
Figure 2.42 Cellulose in control and paint waste reactors
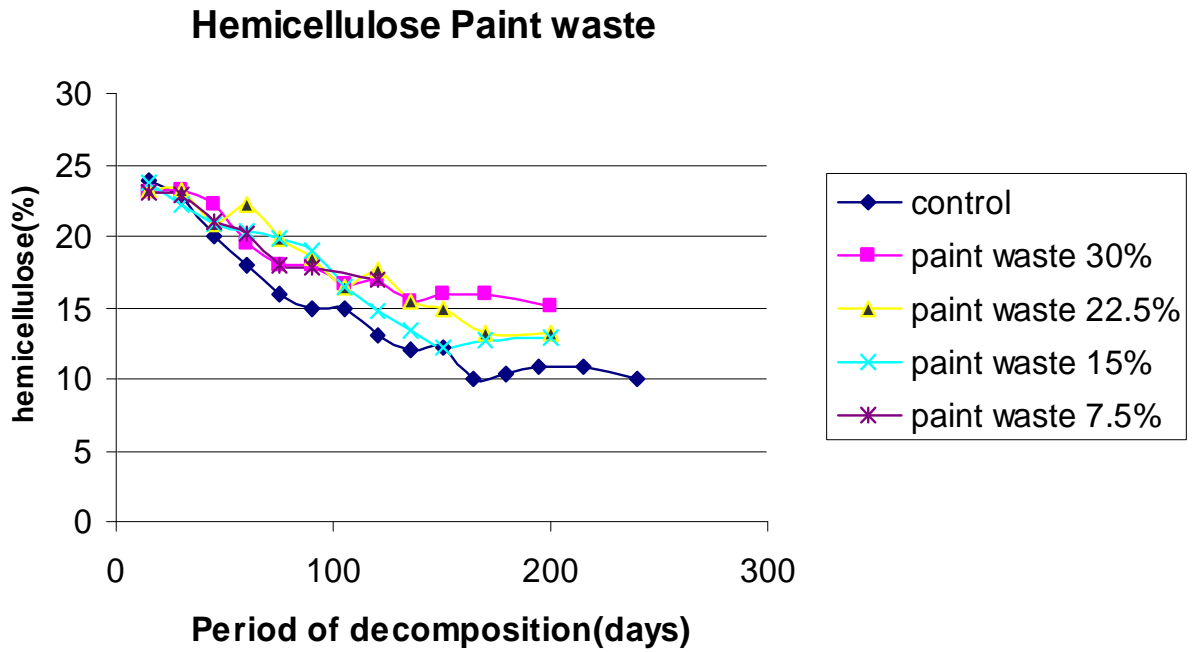
Figure 2.43 Hemicellulose in control and paint waste reactors

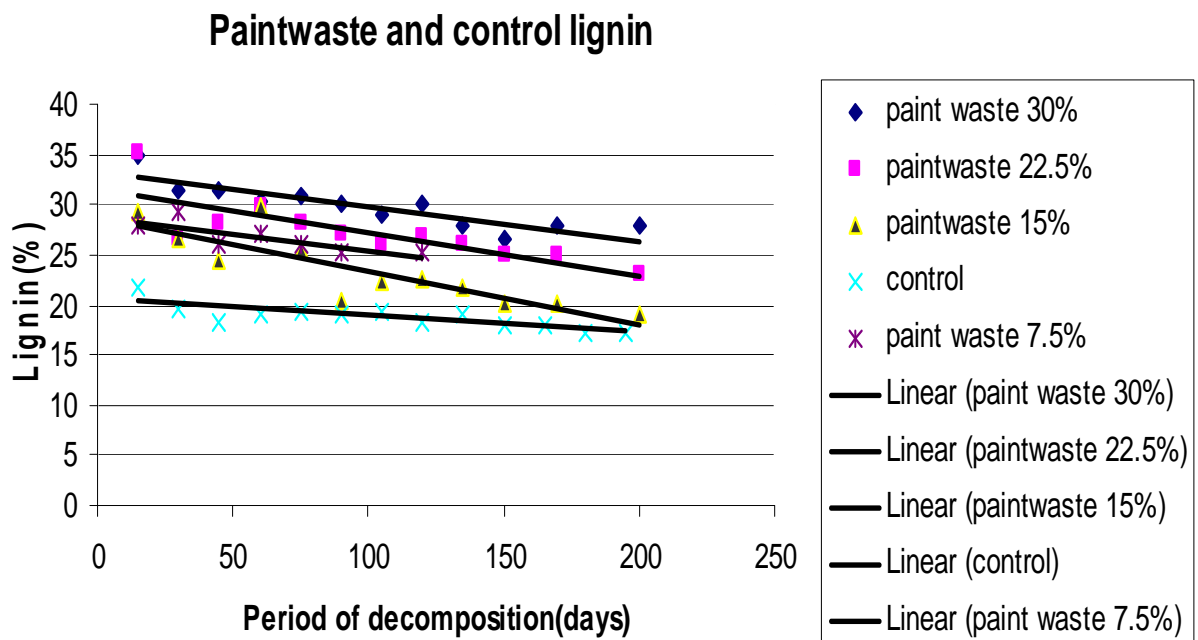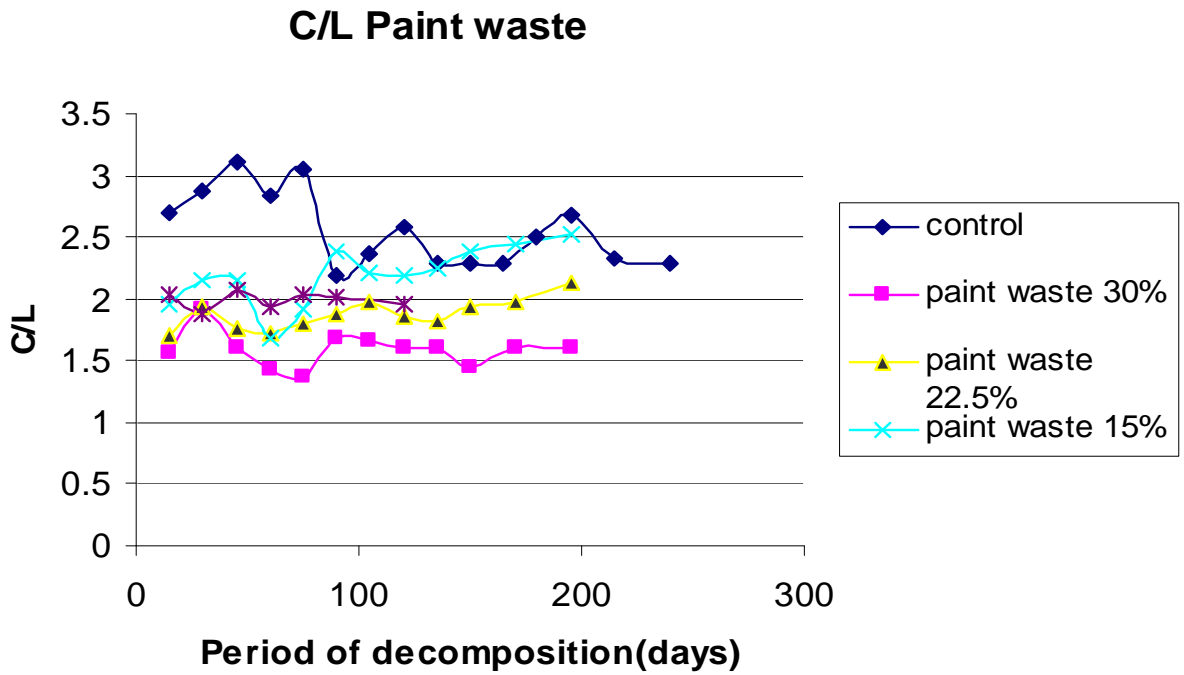*Figure 2.44 Lignin in control and paint waste reactors*

C/L Paint waste

Figure 2.45 C/L in control and paint waste reactors
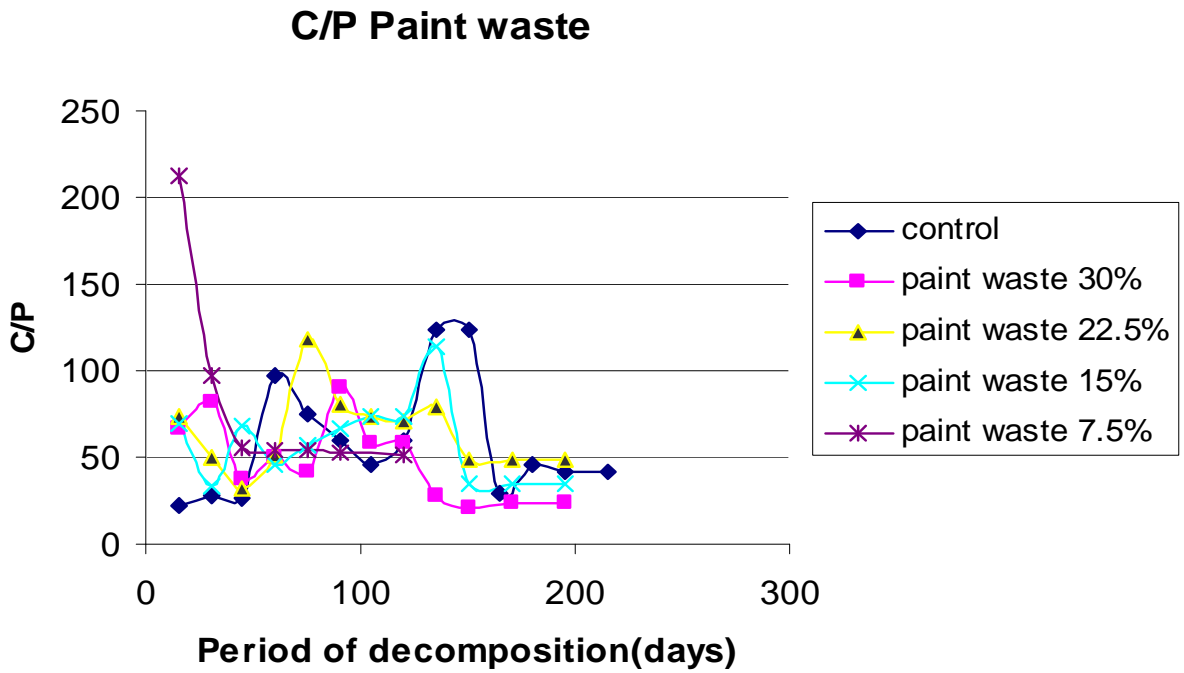

C/P Paint waste

Figure 2.46 C/P in control and paint waste reactors

VITA

Vijesh Karatt Vellatt was born in 1980 at Calicut, Kerala, India. He secured his undergraduate degree in Civil Engineering from National Institute of Technology, Calicut and had worked in Khansaheb Civil Engineering LLC and other companies in Dubai, UAE for about 2 years. He was admitted to the MS in Civil Engineering program to Virginia Tech in August 2005 and received his MS degree in Environmental Engineering by May 2007.