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Temporal Evaluation of Biochemical Properties in Chemically Amended Wastewater Derived Biosolids

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ABSTRACT: The objective of this research is to investigate the effect of four additives including iron slag (IS), works debris (WD), fly ash (FA), and lime kiln dust (LKD) on the biochemical properties of biosolids produced at Mangere Wastewater Treatment Plant (MWWTP), Auckland, New Zealand. All these additives are homogenously mixed in the laboratory with biosolids at various percentages with and without lime. All these prepared amendments are compacted into polyvinyl chloride (PVC) tubes for curing durations of 2 weeks, 4 weeks and 8 weeks. Water content (WC), volatile solids (VS), pH, total organic carbon (TOC) concentrations, proteins, carbohydrates, lipids and VFA's (volatile fatty acids) are determined for all the samples. These parameters are analyzed initially and after 2, 4 and 8 weeks for every PVC tube. Results indicated that when biochemical changes occurred within biosolids, all of these parameters results are affected. After comparing results of all the amendments it is concluded that FA 50% with lime 20% inhibited most of the biological activities and maintained pH of biosolids at elevated level of 12 or above for 8 weeks and thus can be applied to biosolids for stabilization before land filling. FA 50% with lime 20%, like all the other additives, is added to wet biosolids on the basis of dry weight. Solid content of biosolids is around 25% so the addition of even 70% additive to wet biosolids on the basis of dry weight is very less in amount.

Key words: Bio solids, Landfill, Proteins, Lipids, Carbohydrates

INTRODUCTION

Biosolids is an organic waste which is the end product of municipal wastewater treatment processes worldwide. Wastewater contains various kinds of different pathogens that come in the excretion by disease carrying humans and animals (Wen *et al.*, 2009). After purification of the wastewater the water is disposed off into marine environment. The remainder sludge contains concentrated chemical and biological constituents that are source of pollutants when biosolids is disposed off or reused (Escudey *et al.*, 2007). A high moisture content and high content of volatile solids in the biosolids is critical to cope with before land filling of this hazardous material (Wang *et al.*, 2008). Pathogens and vector attractions are major concerns during the final disposal of biosolids after waste stabilization (Hong *et al.*, 2004). Mangere Wastewater Treatment Plant (MWWTP) which is owned by Water care Services currently produces 300 wet tonnes per day (108,000 tonnes per year) of biosolids. The biosolids currently are stabilized with approximately 33% of lime on the basis of dry weight then mixed with oxidation pond sludge (OPS) from the Mangere upgrade area, prior to deposition at the landfill. Lime stabilization initially maintains the required pH of 12 at the site but then decreases gradually due to biological activity over time. A study by O'Kelly (O'Kelly, 2006) found the alkalinity of biosolids to reduce slightly due to ongoing biodegradation and bioactivity. This biological activity results in the release of methane gas in high amount, cracking of the surface, and a lowering of the strength. The solution to decrease this gas production and to reduce the surface cracked is important as the landfill will be build into recreation area after closing. Without proper stabilization of biosolids before deposition at the landfill can cause poor dewatering characteristics that will lead to meet higher chemical requirements in biosolids stabilization. Finally, higher operation and disposal costs are required due lower quality of final processed product (Ayol, 2005). Managing these mushy biosolids after lime addition is being very critical to deposit at the landfill and also to be taken care of later on. For depositing these type of biosolids which have high water content, rafts are used as construction vehicles cannot drive directly onto biosolids that increases cost of deposition. Besides, bulk quantities of the biosolids are left behind after

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efficient cleaning of the discharged water due to improved quality restrictions of water discharges into the sea. The disposal of such large quantities of biosolids is critical. The interest for the development of techniques that reduce biosolids volume along with reduction in mass by reducing biological activity is presently increasing (Laurent, 2009; Yoon, 2004).

First factor to identify in this research is the additive that could inhibit biological activity as effectively as possible. That additive at the same time should be less costly or available for free to the MWWTP facility owners. Alkaline stabilization (lime addition) can improve structural characteristics of biosolids and reduce pathogens and odours. Besides lime, different industrial waste by-products are used as additives and mixed with the raw biosolids from the MWWTP. These mixtures of additives and biosolids then called amendment are tested for their biochemical properties to finally conclude that which additive along with biosolids i.e. which particular amendment could achieve better strength and higher pH of biosolids. The four chosen alkaline additives for this research are namely, lime kiln dust (LKD), fly ash (FA), works debris (WD), and iron slag (IS). At the same time problem of disposal of these waste materials for their respective facility owners could be solved. This research focuses on the change in biochemical parameters taking many additives at a same time into consideration by mixing them with biosolids and investigating at various curing durations of 2 weeks, 4 weeks and 8 weeks.

MATERIALS & METHODS

Biosolids samples are collected from MWWTP before the final lime stabilization of biosolids. These samples are collected in air tight 10 liters plastic containers. Lime (CaO) is picked from the MWWTP. It is the lime that is used to stabilize biosolids prior to land filling. Iron slag or smelter slag (IS) is picked up from NZ steel from big pile lying at the side. Slag is the by-product of smelting ore to purify metals. Works debris (WD) is collected from a stockpile area from Pacific Steel. It is generated as a by-product of the steel making process at Pacific Steel where scrap steel is refined. Fly ash (FA) is obtained from Huntly Power Station, Waikato. FA is the residue of the combustion of coal. It is carried up out of the boiler with the exhaust gases flow collected using electrostatic precipitators (ESP) from stack gases (9). Lime kiln dust (LKD) is obtained from MacDonald Lime, Otorohanga. A lime kiln is a kiln used to produce quicklime by the calcinations of calcium carbonate (limestone). The by-product of this reaction is LKD.

PVC (polyvinyl chloride) tubes with 60mm diameter and 300 mm length are used for curing of biosolids samples. There are total of four additives that are mixed homogenously with and without lime with biosolids namely FA, IS, LKD, and WD. The mixtures are such that, LKD 50% on the basis of dry weight of biosolids is added to biosolids, making first amendment. Then LKD 50% with lime 10% on the basis of dry weight is added to biosolids, making second amendment. Also, LKD 50% and lime 20% is third amendment. A single amendment is compacted into three tubes for 2 weeks, 4 weeks and 8 weeks data. Similarly, three LKD amendments are prepared using LKD 30% instead of 50%, also compacted for above mentioned durations. All the rest of the amendments are prepared similar to LKD using FA, IS and WD. All these percentages of additives are added on the basis of dry weight of biosolids. Each of the above mixtures i.e. amendments are compacted into PVC tubes at a density of $1.1 g/cm^3$ which is the in-situ density at the MWWTP treatment plant. So, there are 6 tubes for a single additive with various amendments for 2 weeks tests. Similarly, 6 tubes for 4 weeks and 8 weeks tests are prepared respectively. That made a total of 18 tubes for a single additive with various amendments. As there are 4 additives, so there are total of 72 PVC tubes. There are also controlled PVC tubes samples with raw biosolids and biosolids with 10% and 20% lime for 2 weeks, 4 weeks and 8 weeks tests. Lime is also added on the basis of dry weight of biosolids. That made a total of 9 tubes for controlled samples. All these combinations made a total of 81 PVC tubes samples.

The parameters are investigated for all of the PVC tubes after each curing period of 2 weeks, 4 weeks and 8 weeks. These parameters are also determined initially as soon as the amendments are prepared. The parameters that are analysed are, pH, water content (WC), volatile solids (VS), carbohydrates, lipids, proteins, total organic carbon (TOC), and volatile fatty acids (VFAs). The pH of biosolids is measured in solution using a pH meter (NZS, 1986). Solution is prepared by stirring biosolids in deionised water using a magnetic stirrer. Water content (WC) is measured by oven drying method at 105 ^{0}C overnight to constant weight (Gravimetric Analysis - (NZS, 1986)). Volatile solids (VS) are measured by igniting samples in furnace at 550 ^{0}C for 30 minutes (loss on ignition). Total organic carbon (TOC) is analysed by using a TOC analyzer (Shimadzu-V_{CSH}). For TOC analysis, biosolids samples are oven dried overnight at 105^{0}C, and then powdered using manual grinding mortar. After calibration curves are prepared, required amount of sample is weighted directly into the sample boat. The samples are analysed in duplicates and the average reading is noted. For carbohydrates extraction, biosolids are firstly hydrolyzed in 72% H_2SO_4 for 2 hours at 30 p C in the

incubator (ASTM, 2007). The samples are then autoclaved at 'ster/dry cycle' at 121 ^{0}C for 45minutes. The samples are then filtered using filter paper of 10µm pore size. The filtrate now had extracted carbohydrates from the biosolids. 6N NaOH is added to this filtrate and left aside for 30 minutes Anthrone reagent is then added to the filtrate solution then it is heated for 7 minutes at least and the concentration of carbohydrates are determined by colorimetric method using HACH DR 2700 spectrophotometer (Loewus, 1952; Jermyn, 1975). Lipids are extracted by Soxhlet extraction apparatus at a rate of 20cycles/h for 6 hrs according to standard methods for the examination of water and waste water using n-hexane as a solvent (AWWA, 1995; Czechowski *et al.*, 2006). The apparatus is fixed on heating equipment called digester at a temperature of 130^{0}C. Proteins are first extracted from the biosolids by the procedure of cooking biosolids in 1N NaOH in the boiling water bath (Matthew *et al.*, 2004; Meya *et al.*, 2008). After cooking, the samples are first vortexed at 2000rpm for 1 minute then centrifuged at 4000rpm for 15 minutes. The supernatant is again centrifuged at 40000rpm so that there is no solid particle remaining in the supernatant and there is a solid pellet formed at the bottom of the centrifuge tube. The supernatant is taken out from the tube without disturbing the pellet. Protein assay is then carried out by standard BCA™ (bicinchoninic acid) Total Protein Assay kit using micro titre plate method and then absorbance is read at 562nm in the U Quant BIOTEK plate reader. BSA (bovine serum albumin) is used as standard to prepare calibration curve. VFA's are extracted after soaking in diluted HCL and then the solution is vortexed at 2000rpm for 1 minute and then centrifuged at 4000rpm for 15 minutes.

The supernatant is then filtered by 0.45µm filter paper using vacuum suction filtration unit. The sample is then filled into 1.5ml GC (gas chromatography) sample vials 1.5ml from Agilent technologies with teflon/silicon septor caps. The sample is filled into 2 vials for duplication. Then VFAs concentrations are determined using a gas chromatograph (HP 6890 Series). The column used is Zebron ZB-FFAP (Nitroterephthalic acid modified polyethylene glycol 30m x 320µm x 0.25µm). The FID (Flame Ionization Detector) detector is used at a temperature of 350^{0}C. Injection volume is 1.0ul, split 100:1. The inlet temperature is 250^{0}C. Flow rate of helium onto the column is 1.69 ml/min. The oven is at 100^{0}C held for 2 minutes, ramped 8^{0}C /min to 180^{0}C. Then 20^{0}C / min to 240^{0}C and held for 2 min. FID temperature is 350^{0}C, H_2 flow rate is 45ml/min and air is 400 ml/min for the detector. VFA's standard ACCU FAMQ-004 is used to prepare calibration curve. Volatile acid standard solution is with 10mM each in water: MeOH (98:2). Four points calibration is done with the standards of 10mg/l, 5mg/l, 2 mg/l and 1mg/l.

RESULTS & DISCUSSION

The results suggest that all the parameters are affected by the addition of different additives. When TOC starts degrading, VFAs start increasing simultaneously with the same rate of the degradation of TOC. Similarly, as carbohydrates and lipids decrease, proteins are increased. With the amendments that had IS in those, TOC degraded at faster rate and VFAs production is largest as compared to other amendments except raw biosolids. This suggest that IS doesn't have any effect on the biological activities. All the amendments with FA in those especially along with lime, inhibit biological activity to quite a large extent. The pH remains high throughout in biosolids amended with FA and lime suggesting lesser bioactivity. LKD and WD also have some minimizing effect on biological activity.

Considering all the amendments, initial concentration at the time of filling the PVC tubes is from 26ppm to 30ppm. The TOC concentration decreased with time but less decreased with lime addition and with higher amount of additive. The maximum concentration of TOC with respect to all amendments after 8 weeks is with FA 50% with lime 20% which is 24 ppm. This showed that FA 50% with lime 20% allowed minimum biological activity and thus less degraded material over time. Raw biosolids showed maximum degradation and thus least concentration of TOC after 8 weeks i.e. 9ppm. With respect to all amendments, the minimum concentration of TOC after 8 weeks is with IS 30% without lime, which is 10ppm. This indicated that IS without lime allowed maximum biological activity easily as compared to other amendments. Thus more degraded material over time is there. Fig. 1 shows the degradation of TOC with respect to maximum amount of amendments over time to show how maximum amounts are inhibiting biological activity.

Carbohydrates keep decreasing with time throughout the experiments. With the influence of lime and other additives, the rate of decreasing is slow down. The maximum concentration of carbohydrates with respect to all amendments after 8 weeks is with FA 50% with lime 20% which is 2.6 carbohydrates mg / g dry biosolids. This narrated that FA 50% with lime 20% allowed minimum biological activity and thus lesser amounts of carbohydrates are utilized over time. The minimum concentration of carbohydrates with respect to all amendments after 8 weeks is with IS 30% which is 0.9 carbohydrates mg / g dry biosolids. This showed that IS without lime allowed maximum biological activity easily as compared to other amendments. Additive in fewer amounts and without lime allowed more biological activity so more

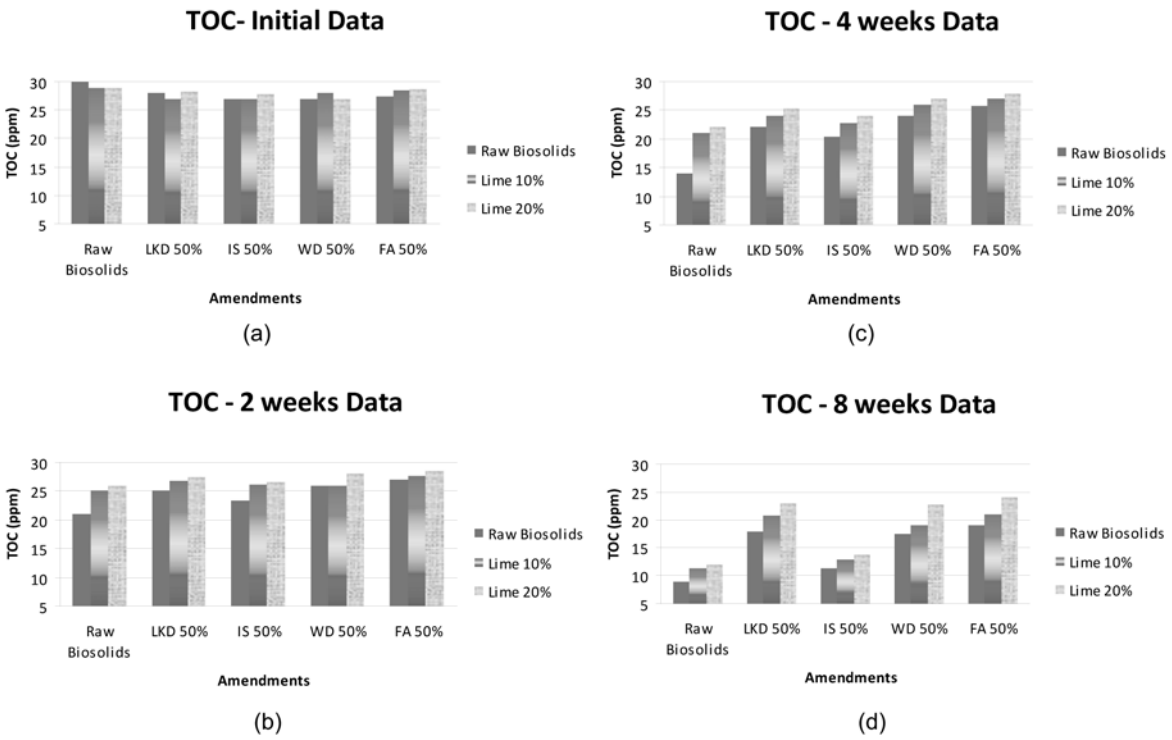

Fig. 1. TOC degradation in raw biosolids LKD 50%, FA 50%, WD 50% and IS 50%

carbohydrates are utilized over time as compared to those samples that had lime in them. It can be analyzed that as the amount of additive and lime increased, the biological activity decreased over a period of time. Table 1 shows this behaviour of carbohydrates utilization with respect to different amendments.

Lipids which constitute an important fraction of bio solids (Reveille *et al.,* 2003) start decreasing as soon as biodegradation starts (Amira *et al.,* 2008). Initial percentage of lipids on basis of dry weight in all samples is around 12% lipids. Amount of lipids decreased with time but less decreased with lime addition and with higher amount of additive. The maximum concentration of lipids with respect to all amendments after 8 weeks is with FA 50% with lime 20% which is 9.7%. This suggested that FA 50% with lime 20% suppressed most of the biological activities and thus less degraded material over time. The minimum concentration of lipids with respect to all amendments after 8 weeks is with IS 30% which is 5.1%. This manifested that IS without lime allowed maximum biological activity easily as compared to other amendments. Fig. 2 shows this behaviour of lipid change within biosolids.

Considering all the amendments, initial amount of proteins at the time of filling the PVC tubes is around 6mg/g dry biosolids. Amount of proteins increases with time but less increases with lime addition and with higher amount of additive. The maximum concentration of proteins with respect to all amendments after 8 weeks is with IS 30% without lime, which is 14.1 mg/g dry biosolids. This shows that IS 30% without lime, permits maximum biological activity and thus more forms of proteins are formed over time. The minimum concentration of proteins with respect to all amendments after 8 weeks is with FA 50% with lime 20%, which is 7.5 mg/g dry biosolids. This indicates that more amount of FA with lime inhibits biological activity as compared to other amendments. Thus, fewer forms of proteins are formed over time. Table 2 shows all proteins values. A study by Verma et al. (Nitin *et al.*, 2006) found that proteins released during anaerobic digestion of various sludge is strongly correlated with volatile solids removal. A strong relation between pH and VS is found in the current research as per discussion in (Nitin *et al.*, 2006). As pH is increased TOC increased also in (Batziaka *et al.*, 2008) which is proved by this research. Results of present study are very much similar with these investigations.

Considering all the amendments, initial concentration at the time of filling the PVC tubes is from 4.6 to 4.7 mg VFA/mg dry solids. VFA's concentration increases with time but less increases with lime addition and with higher amount of additive. The maximum concentration of VFAs with respect to all amendments after 8 weeks is with IS 30% without

Table 1. Changes in Carbohydrates Mass. All Values in Carbohydrates mg / g Dry Biosolids

Carbohydrates		Lime %		
AMENDMENT	weeks	0	10	20
Raw Biosolids	0	2.9	3.0	3.0
	2	2.0	2.4	2.4
	4	1.3	2.0	1.8
	8	0.5	1.2	1.2
30% LKD	0	3.0	3.1	3.2
	2	2.6	2.1	1.7
	4	3.2	2.6	2.3
	8	1.5	1.7	1.9
50% LKD	0	3.0	2.9	3.0
	2	1.8	1.5	1.6
	4	2.5	2.8	1.9
	8	1.6	2.0	2.0
30% IS	0	3.2	2.7	2.3
	2	2.7	2.4	1.6
	4	3.6	3.5	2.8
	8	0.9	1.2	1.3
50% IS	0	2.7	2.4	2.5
	2	2.5	2.0	1.9
	4	3.3	2.5	2.0
	8	1.2	1.2	1.7
30% WD	0	3.0	3.0	3.2
	2	2.5	2.5	2.7
	4	2.0	2.0	2.4
	8	1.3	1.6	2.2
50% WD	0	3.1	3.1	3.0
	2	2.7	3.0	3.0
	4	2.4	2.6	2.7
	8	1.8	1.9	1.9
30% FA	0	3.1	3.2	3.0
	2	2.3	2.5	2.7
	4	2.0	2.2	2.5
	8	1.4	2.3	2.6
50% FA	0	3.2	2.9	2.8
	2	3.0	2.6	2.8
	4	2.7	2.3	2.7
	8	2.0	2.4	2.6

Table 2. Changes in Protein Mass over Time. All Values in Protein mg/g Dry Biosolids

Proteins		Lime %		
AMENDMENT	weeks	0	10	20
Raw Biosolids	0	6.2	6.0	6.2
	2	9.1	7.6	7.0
	4	12.2	8.2	8.2
	8	16.0	13.8	13.0
30% LKD	0	6.1	6.1	6.0
	2	8.1	7.9	7.7
	4	10.1	8.8	8.3
	8	12.9	12.0	11.9
50% LKD	0	6.4	6.0	6.0
	2	7.9	7.8	7.2
	4	9.1	8.2	8.0
	8	12.0	11.1	11.0
30% IS	0	6.5	6.4	6.3
	2	8.0	7.1	6.5
	4	11.0	9.6	9.1
	8	14.1	12.0	11.4
50% IS	0	6.3	6.1	6.4
	2	6.5	6.6	6.5
	4	8.8	8.4	8.3
	8	12.2	11.0	10.5
30% WD	0	6.1	6.1	6.0
	2	8.0	7.9	7.0
	4	10.5	10.2	9.9
	8	13.0	12.2	11.1
50% WD	0	6.1	5.8	6.0
	2	7.9	7.6	6.5
	4	10.0	9.0	8.0
	8	12.8	12.0	11.1
30% FA	0	6.5	6.4	6.3
	2	8.0	7.9	7.1
	4	8.4	8.0	7.5
	8	9.7	9.0	9.1
50% FA	0	6.3	6.1	6.2
	2	6.6	6.6	6.5
	4	7.9	7.0	6.9
	8	9.0	8.1	7.5

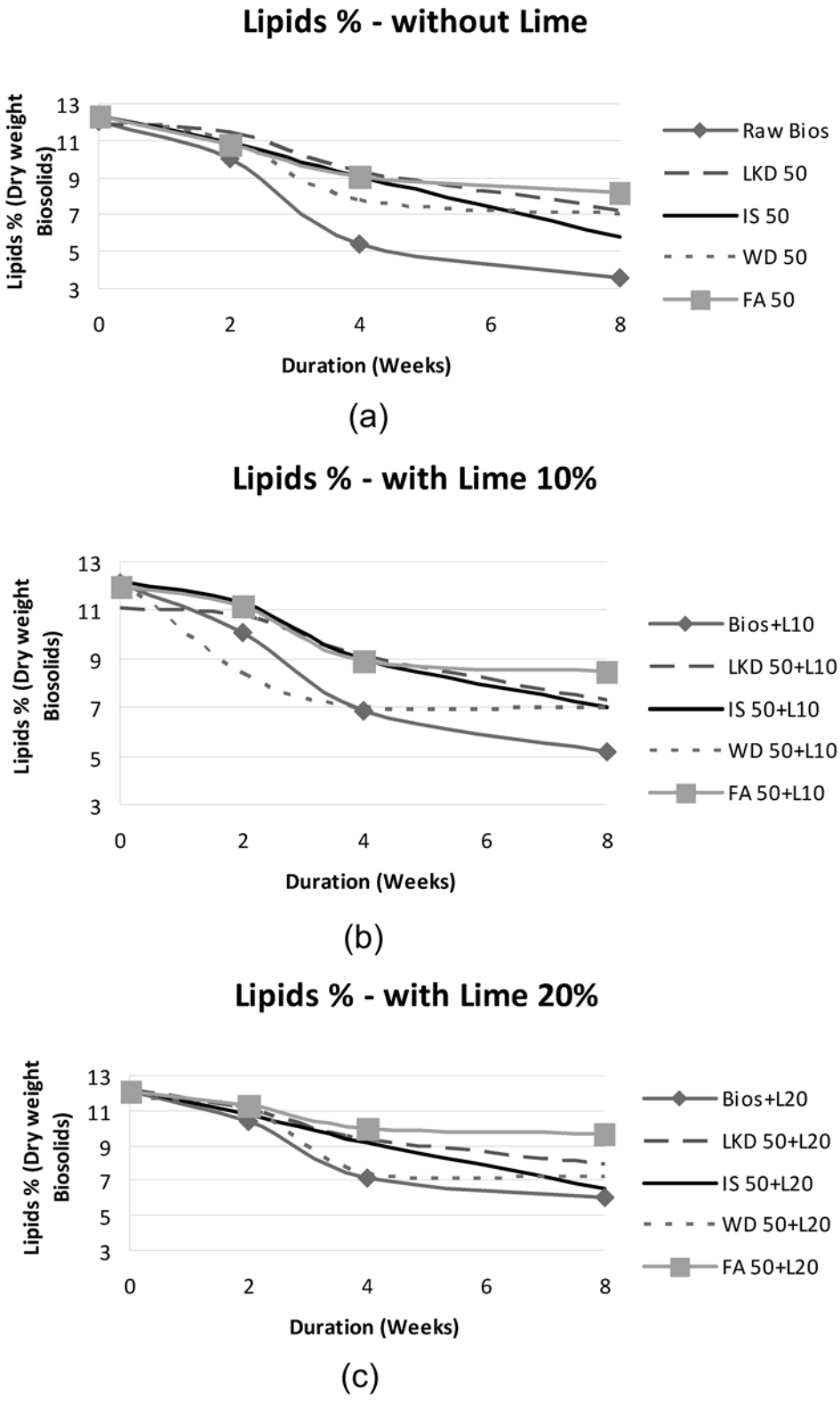

Fig. 2. Changes in lipids percentage in raw biosolids, LKD 50%, FA 50%, WD 50% and IS 50%

lime which is 18.1 mg VFA/mg dry solids. This indicates that IS without lime allowed maximum biological activity and thus more degraded material over time. The concentration of VFAs of raw biosolids after 8 weeks is 19 mg VFA/mg dry solids which is larger than VFAs of IS 30% without lime. The minimum concentration of VFAs with respect to all amendments after 8 weeks is with FA 50%, lime 20% which is 6.5 mg VFA/mg dry solids. This gives evidence that FA along with lime does not allow biological activity easily as compared to other amendments. Thus less degraded material over time is there.

VFAs are analysed with all the maximum percentage of amendments to show that how the formation of these acids can be inhibited. The results are then compared to raw biosolids over a period of 2, 4 and 8 weeks. The results indicate that initial amount of VFAs are almost same in raw biosolids and biosolids with all the amendments. VFAs increase sharply in raw biosolids and in biosolids amended with IS (with and without lime). After 8 weeks the amount of VFAs after of FA amended biosolids is not much as compared to its initial amount. This indicates that FA can maintain pH of biosolids at elevated level for a longer period of time as compared to other amendments. It is obvious from the results that lime addition especially with FA is greatly inhibiting biological activity. Fig. 3 shows VFAs data details in raw biosolids, LKD 50%, FA 50%, WD 50% and IS 50%, all with and without lime.

VFAs are composed of acetic, propionic, isobutyric, butyric, isovaleric, valeric, isocaproic, caproic, and heptanoic acids. After looking at results of VFAs composition it is concluded that acetic, butyric, valeric and heptanoic acids are dominant with in VFAs. The results show that all of these follow same trend of increment as total VFAs. Results also suggest that all the compositions of VFAs effect on biosolids as the total parent VFAs.

The pH of FA 50% with lime 20% after 8 weeks is 12.3 which is the second highest pH value among all the amendments. The pH = 12.3 doesn't allow most of the biological activities to occur. So FA 50% with lime 20% can be chosen as a priority amendment. From Chaurhuri et al. (2003) work it can be analyzed that pH had effect on the other biochemical parameters of bio solids (Chaudhuri *et al.*, 2003). So it is an important parameter to be investigated closely.

Taking water content into consideration, water content of FA 50% with lime 20% after 8 weeks is 181.2% which is lower than water content of all the amendments. The higher the WC, higher is the biological activity and lower the WC lower the biological activity. WC results also support that the amendment FA 50% with lime 20% is better than other amendments.

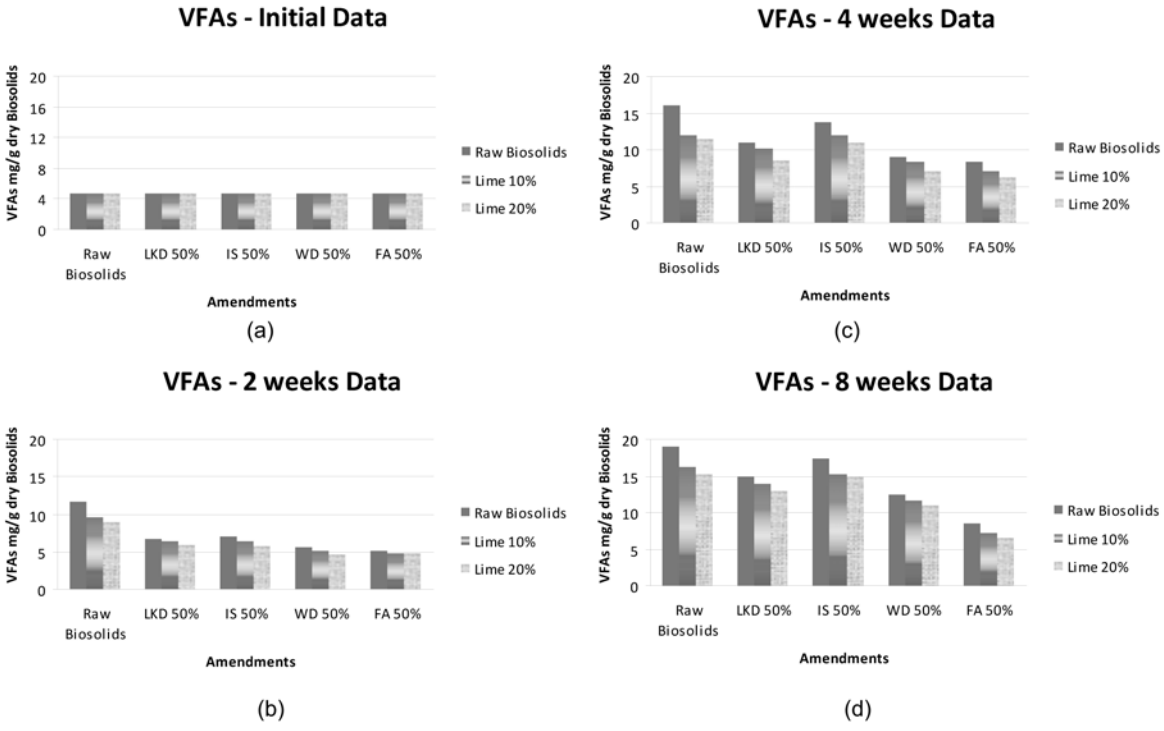

Fig. 3. VFAs increment in raw biosolids, LKD 50%, FA 50%, WD 50% and IS 50%

VS of IS 30% after 8 weeks is 49.9% which is the highest among all the amendments. High VS means that there is more biological activity taking place with this amendment as compared to other amendments. VS of FA 50% with lime 20% after 8 weeks are 36.9% which is lower than VS of many of the amendments. This value is not the lowest but itself this value proved that there is not much biological activity taking place with this amendment. So FA 50% with lime 20% can be chosen as a good amendment to inhibit biological activity.

Strong relationship between pH decline, VFAs production and increment in water content of biosolids is found out. To test this dynamic behaviour of biosolids, biosolids are tested with all the amendments with maximum percentage of lime i.e. 20% lime. Also, maximum percentage of additives are chosen to judge that if pH decline is deliberately slower down then what would be its effect on VFAs production and WC increment. All these conditions are tested initially and after 2, 4 and 8 weeks. The results give evidence that rate of increase in WC of raw biosolids is highest. WC increases slowly in all the amendments. In those biosolids samples where pH is higher due to lime and/ or additive addition, water content (WC) does not increase much which tells that not much bioactivity is going on (Anne *et al.*, 2001) , (Franco *et al.*, 2003). On the contrary, WC decreases in FA amended biosolids. Fig. 4 shows this phenomenon of changes in pH and its effect on the dynamics of WC and VFAs with in biosolids. The reason being FA contains silicon dioxide (SiO_2) and calcium oxide (CaO). Due to production of VFAs i.e. gelatinous precipitate from SiO_2 forms that declines WC. Besides, CaO (lime) itself does not allow much production of VFAs.

When pH starts declining due to the production of volatile fatty acids, TOCs are also degraded (Saviozzi *et al.*, 1999). After looking at VFA's and TOC results, it can be judged that TOC degradation is directly proportional to the concentration of VFAs and FA 50% with lime 20% that is the best to inhibit biological activity. Considering raw biosolids, the graph shows that initially when the concentration of TOC is maximum, VFAs are minimum but as the concentration of TOC is decreasing with time, VFAs are increasing respectively. When lime is added to raw biosolids, it prevents the production of VFAs and thus TOC is degraded with a slower rate as compared to raw biosolids. When comparing all the additives with each other, IS allows highest production of VFAs in biosolids even when lime is added with IS to biosolids. Initial amount of VFAs in biosolids amended with FA is same as other amendments but after 8 weeks, VFAs are not produced much. It indicates that when FA is added to biosolids especially with certain amount of lime, it resists the production of VFAs and thus maintaining a high pH of biosolids. Fig. 5 shows that how VFAs are increasing at the declining of TOC concentrations.

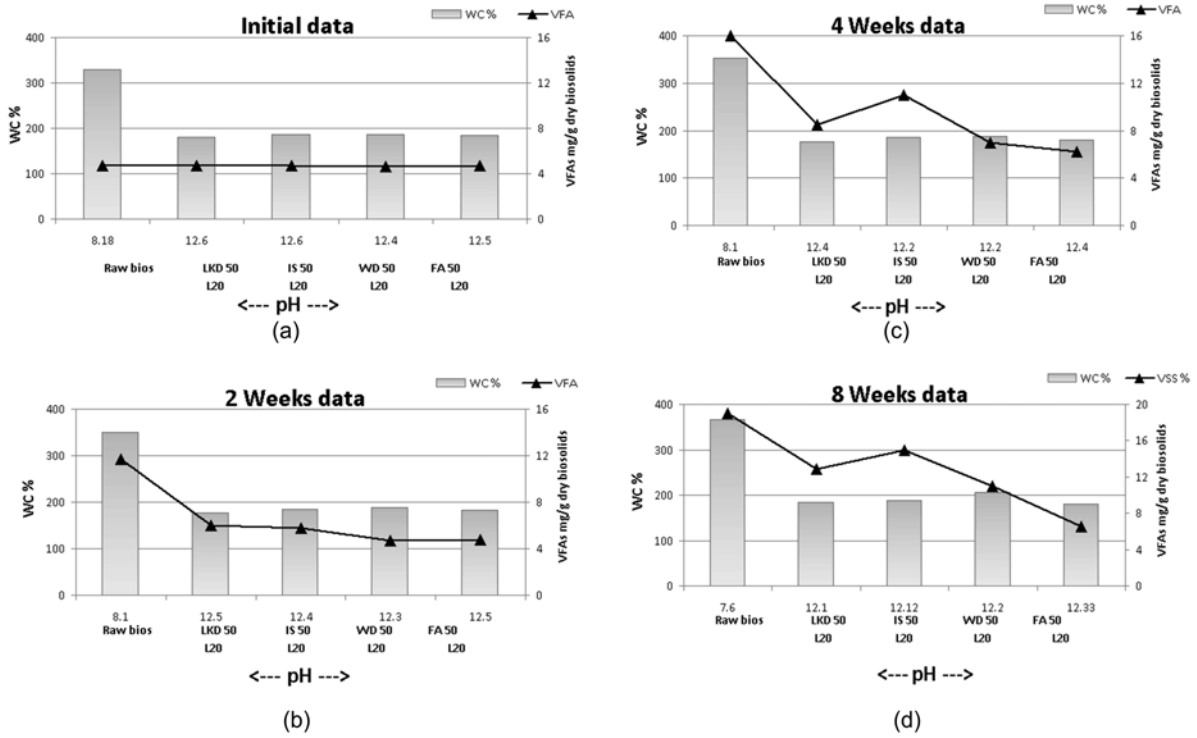

Fig. 4. Effect of changes in pH on WC and VFAs of biosolids

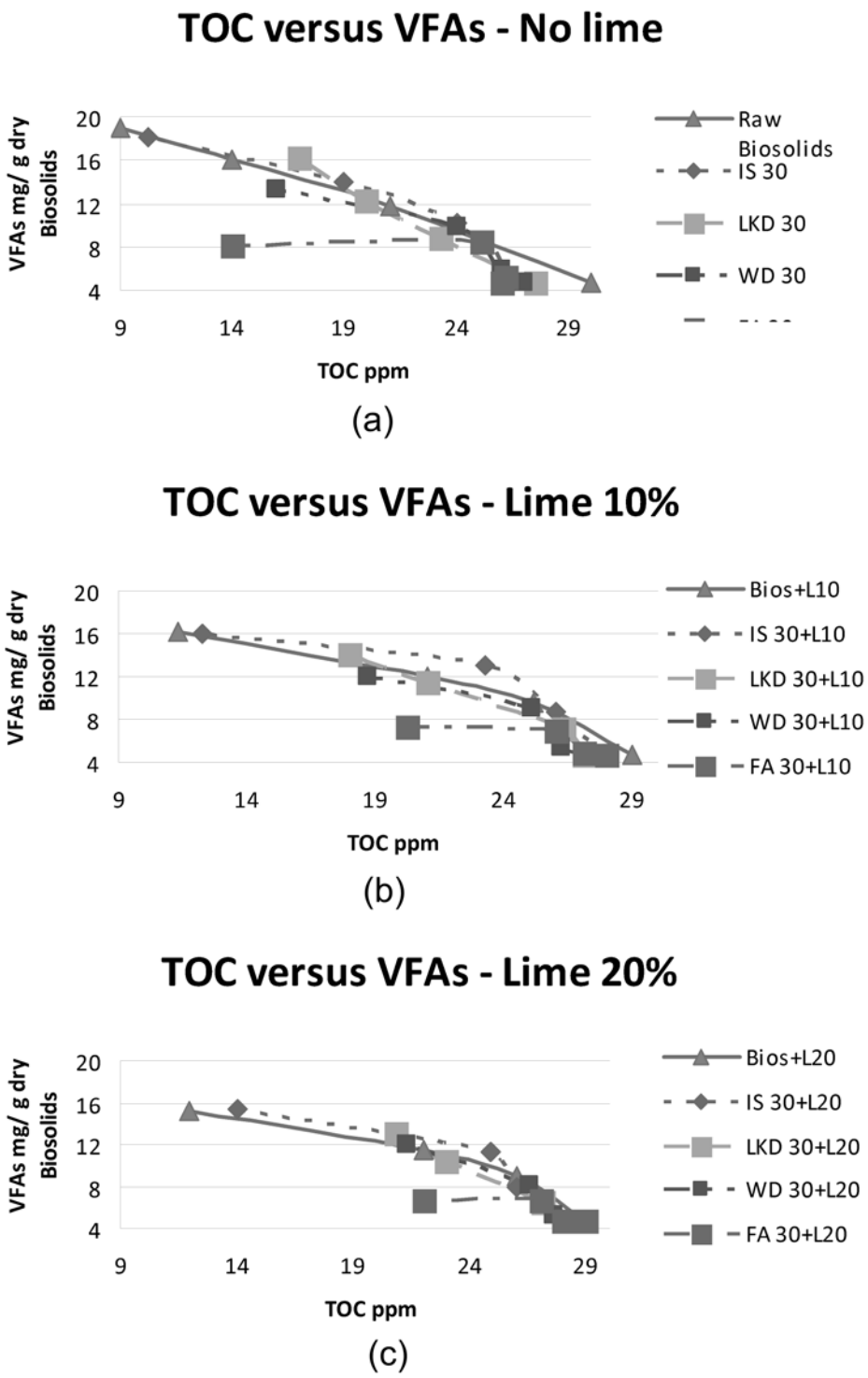

Fig. 5. Relationship between TOC and VFAs

The results of proteins and VS are compared against TOC from initial data to 8 weeks data through all durations. It is found out that TOC decreases substantially in raw biosolids samples from 30ppm initially to 9ppm after 8 weeks. As TOC decreases, %VS also decline but protein mass shoot up from 6.23 to 16 mg/g dry biosolids. Among all the amendments, FA 30 amended biosolids show least decline in TOC and VS from the initial values and least production of proteins. Fig. 6 shows changes in protein and VS with respect to degradation in TOC.

As lipids decrease and fatty acids increase, proteins and water content also start increasing (Czechowski *et al.*, 2006). Proteins and lipids are

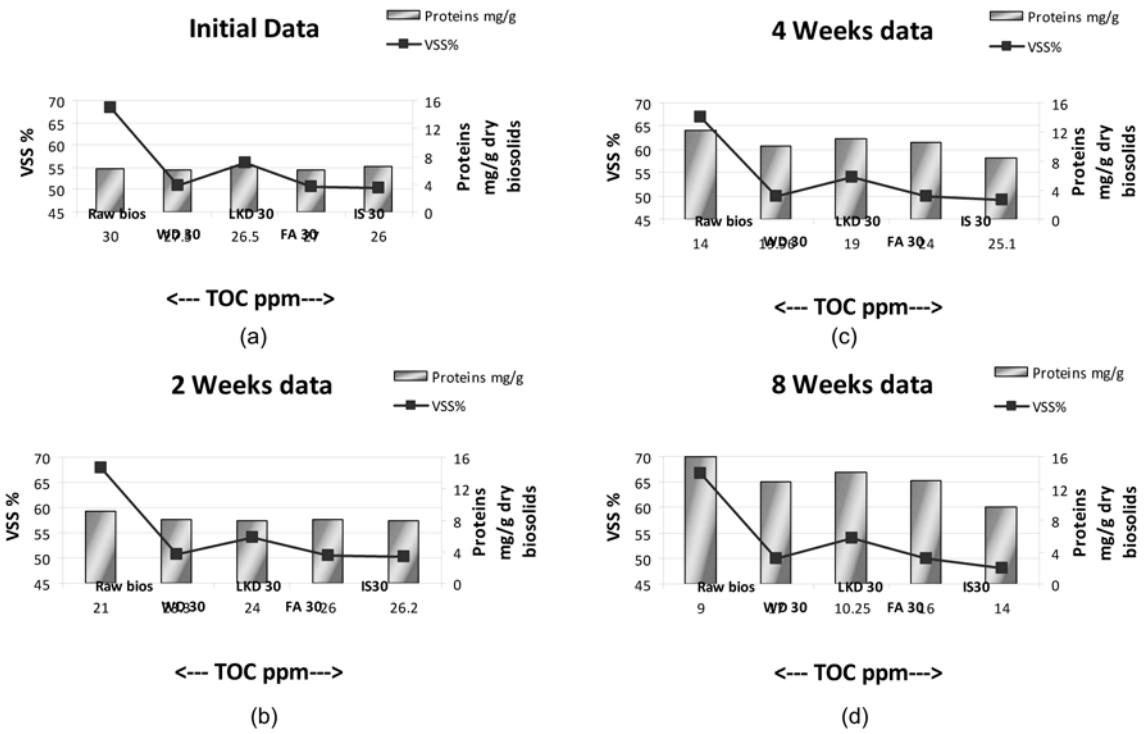

Fig. 6. Changes in Protein and VS with respect to change in TOC

analysed against the carbohydrates for initial data, 2, 4 and 8 weeks data. Besides the controlled sample i.e. raw biosolids, all the amendments without lime are taken into consideration so that the basic dynamic effect of each amendment on each of these parameters could be judged. The rate of degradation of lipids varied with all the amendments with respect to the degradation of carbohydrates. It is no doubt highest in raw biosolids and then in IS amended biosolids. This rate is lowest when biosolids are amended with FA.

As the carbohydrates are degraded or used up, proteins started increasing. Ratio of carbohydrates to protein decreases with time due to biodegradation (Kim *et al.*, 2004). Chemically, carbohydrates are simple organic compounds being used both as an energy source and are the major source of fuel. This role of carbohydrates indicated that as carbohydrates are being used up without resistance, more proteins are generated. The resistance in the form of amendments are provided to biosolids. The results suggested that, FA provided maximum resistance to the usage of the energy and fuel source in the form of carbohydrates. Fig. 7 shows the relationship between the decline in lipids and carbohydrates and increment in proteins.

CONCLUSION

Fly ash (FA) acted as an excellent additive that can be applied to biosolids for stabilization before land filling. FA shows high efficiency in suppressing biological activities within biosolids, especially when lime is added to biosolids with FA. FA 50% + L 20% on the basis of dry weight of biosolids is found to be the most promising amendment that inhibits biological activities more as compared to other amendments (Lai *et al.*, 2004). For digging up the reasons of the stability of FA against biological activities, the composition of FA is studied. FA includes substantial amounts of silicon dioxide (SiO2) and calcium oxide (CaO). Silicon dioxide is known to have high chemical stability and has been known for its hardness. Due to this chemical stability, FA resists most of the biochemical activities to occur. FA has a fine silty texture and it has less clay content (Mudda *et al.*, 2007). FA contains silty sand which has coal and residues that remains un-burnt which is a non-reactive material and has more than 50% sand sized particles (<4.75 mm). Due to this non reactivity, it stays stable for longer periods. In addition, high salt contents in fly ash (EC 5.12 dS/m) can inhibit biological activity efficiently (Lai *et al.*, 2004). Thus, FA can efficiently be used as stabilizer of biosolids. CaO, which is also present in FA, is used in water and waste water treatment, as a flocculent, to reduce acidity, to harden, and to remove phosphates and other impurities. Calcium oxide or quicklime (CaO) is produced by the burning of calcium carbonate ($CaCO_3$). As soon as CaO is exposed to air after mixing with biosolids, it begins to absorb carbon dioxide (CO2)

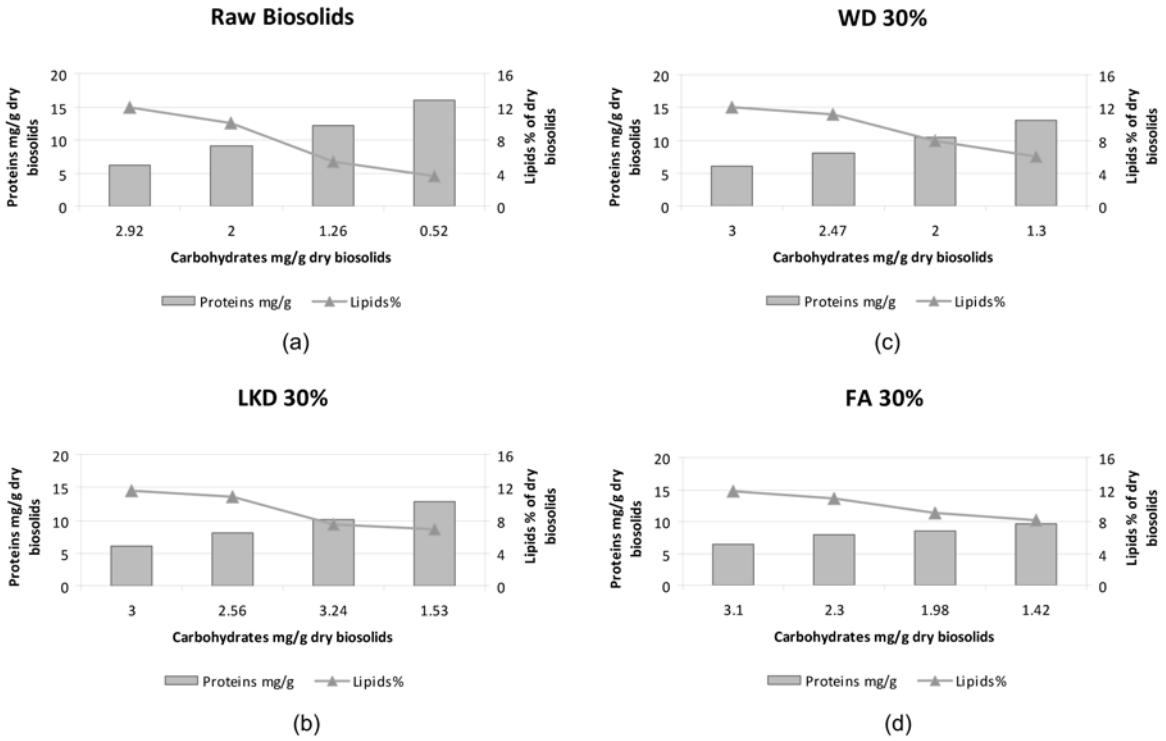

Fig. 7. Changes in lipids and proteins with respect to carbohydrates utilization

from air and ultimately converted back to calcium carbonate ($CaCO_3$). It has the ability to neutralize acids when produced due to biological reactions of biosolids, and thus it maintains high pH. Thus, FA 50% + L 20% can be used at MWWTP to stabilize the bio solids before land filling. There are number of other benefits in using FA. Here, few important ones are discussed. Firstly, worldwide, more than 65% of fly ash produced from coal power stations is disposed off in landfills. Fly ash is one of the residues generated in the combustion of coal. The recycling of fly ash has become an increasing concern in recent years due to increasing landfill costs and current interests in sustainable development. This large quantity of ash requires proper and stable engineering designs for disposal for its long-term environmental performance. If this waste product will be used efficiently in stabilization of biosolids in environment friendly manner then issues of its mere disposal can be minimized giving relaxation to the owners of wastewater treatment plant as well as owners of coal-fired power plants because land disposal of these two materials i.e. biosolids and FA is a major problem as both are hazardous and contains harmful matter (Sajwan *et al.*, 2003). Besides, economical disposal of FA will be achieved (Jala *et al.*, 2006). Secondly, the final chosen additive i.e. FA is competent enough to maintain high pH values with in biosolids as the strength and stability of biosolids at the landfill is very much affected by increasing or decreasing pH values (O'Kelly, 2006) Fly ash has a pH of about 12.5 which is high enough to be used as a liming additive for stabilization of biosolids. At this pH it kills pathogens and reduces metals leaching (Logan *et al.*, 1995). FA due to high pH also promotes the minimization of the bioavailability of toxic trace elements like heavy metals in the leachate by neutralizing acidic organic by-products (Sajwan *et al.*, 2003). With high pH the desired shear strength of 8 to 12 kPa can be achieved which is essential for the biosolids produced at MWWTP to ensure stability. Finally, application of FA to biosolids is a cost effective measurement as it is available at no cost to the facility owners. Thus FA 50% + L 20% can be used at MWWTP to stabilize the biosolids before land filling.

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