Co-digestion of tannery wastewater and *phragmites karka* using a laboratory scale anaerobic sequencing batch reactor (ASBR)

Andualem Mekonnen[1]*, Seyoum Leta[2]** and Karoli Nicholas Njau[3]

[1,2] Center for Environmental Science, College of Natural Science, Addis Ababa University, Addis Ababa University, P.O.Box 33348, Addis Ababa Ethiopia
*E-mail: andumk21@gmail.com ** E-mail: letaseyoum@yahoo.com
[3]The Nelson Mandela African Institute of Science and Technology, P.O. Box 447 Arusha, Tanzania.
Email: knjau30@yahoo.com
*Corresponding Author

Abstract: This study was investigated co-digestion of tannery wastewater and *phragmites karka* using a laboratory scale anaerobic sequencing batch reactor (ASBR) at mesophilic temperatures. The co-digestion experiment was conducted at four different mixing ratios (100:0, 75:25, 50:50 and 25:75) of tannery wastewaters to *phragmites karka* by volume. The digestion of tannery wastewater without *phragmites karka* showed the maximum COD (88.9%) and VS (94.1%) removal efficiency. The mixture containing 25% *phragmites karka* produced the highest average methane content (71%) and methane yield (0.26L/g COD removed) while showing the second highest COD and VS removal efficiency. On the other hand, the mixture containing 50% and 75% phragmites showed the lowest biogas production rate and removal efficiency. The methane content and yield were also the lowest. The results of this study showed that co-digestion of tannery wastewater with *phragmites karka* up to 25% improve the quality and the production rate of the biogas than digestion tannery wastewater alone under mesphilic temperature condition.
[Andualem Mekonnen, Seyoum Leta and Karoli Nicholas Njau. **Co-digestion of tannery wastewater and *phragmites karka* using a laboratory scale anaerobic sequencing batch reactor (ASBR).** *N Y Sci J* 2016;9(1):9-14]. ISSN 1554-0200 (print); ISSN 2375-723X (online). http://www.sciencepub.net/newyork. 2. doi:10.7537/marsnys09011602.

Keyword: ASBR, COD, methane yield, phragmites karka and tannery wastewater

1. Introduction

Tanning processes while converting raw hide and skin to leather produce wastewater, solid waste and air emissions (UNIDO, 2000). However, wastewater is by far the most important environmental challenge because it causes very high pollution load in the environment. The wastewater is characterized by substantial organic matter content (COD and BOD_5), high total suspended solids content (TSS), total nitrogen (TN) and salinity (Seyoum Leta *et al,* 2004). The wastewater discharges vary greatly between tanneries based on the processes involved, raw materials and products (Wiegant *et al.,* 1999; UNIDO, 2000).

Integrated anaerobic-aerobic system coupled with constructed wetland treatment system has shown proven success on a pilot scale as demonstrated at Modjo tannery in Modjo, Ethiopia. The constructed wetland unit is planted with phragmites karka and employed to carry out wastewater polishing activities particularly nutrients. Phragmites karka is one of the most widely distributed wetland plant genera worldwide. It is a highly productive grass (Poaceae) with an above-ground net primary production ranging from 3 tone ha-1 y-1 to 30 tone ha-1 y-1 (Kobbing *et al.,* 2014). It is promising emergent macrophytes for sustainable use in wastewater treatment due to its rapid growth (Verma *et al.,* 2014). The operation of the constructed wetland may include regular harvesting and management of phragmites biomass to maintain the wetland hydraulic characteristics.

Anaerobic digestion of the harvested biomass is cheap means to manage the biomass while extracting usable energy in the form of biogas. It combines waste treatment and energy production which can simultaneously improve sanitation and enhance energy availability.

Anaerobic digestion (AD) is a complex biological process in which organic materials are converted to biogas. The biogas production occurs in sequence of four steps involving fermentative bacteria, acidogenic bacteria, acetogenic bacteria and methanogenic bacteria (Abbasi *et al.,* 2012; Kashyap *et al.,* 2003). The biogas contains a mixture of methane (50–75%), carbon dioxide (30–40%) and traces of other constituents (Abbasi *et al.,* 2012). Co-digestion of two or more types of substrates in the same digestion unit generate higher methane yield.

Co-digestion dilutes toxic compounds and improves nutrient balance. This enhances high volume of biogas production with high methane content (Minale and Worku, 2014; Patil *et al.*, 2014). Different studies have shown the co-digestion of various types of wastes including potato waste and sugar beet waste (Parawira et al., 2004); fruit, vegetable and abattoir wastewater (Bouallagui *et al.,* 2009); cattle dung and olive mill waste (Goberna *et al.,* 2010); olive mill wastewater and swine manure (Azaizeh and Jadoun, 2010), water hyacinth and beverage wastewater (Lay *et al.,* 2013) and water hyacinth and sheep waste (Patil *et al*., 2014).

However, there is no research result on the co-digestion of tannery wastewater and *phragmites karka.* Hence, the objective of this study was to investigate the co-digestion of tannery wastewater with *phragmites karka* at four different mixing ratios in laboratory scale Anaerobic Sequencing batch Reactor (ASBR).

2. Material and methods

2.1. Experimental set up

Bench scale anaerobic digesters were prepared using 1.5L amber glass bottles. The bottles were sealed with rubber stoppers to maintain anaerobic condition. The rubber stopper has connected with two hose gas pipes each have 8mm internal diameter and 1m length. One of the hose gas pipes was used to feed tannery wastewater and discharge the treated supernatants after five days. The other hose gas pipe was used to collect the biogas produced during anaerobic digestion. At the top of the second hose, there was a plastic bag which was used to collect the produced biogas and it as two valves; they were closed only for the period of measuring the biogas which was produced during operation. The temperature of the digester was maintained at 37^0C using water baths.

Figure 1: picture of the experimental setup.

2.2. Collection of plant

The plant (***phragmites karka***) used in this experiment was collected from constructed wetland at Modjo town in Ethiopia. The wetland is part of the integrated treatment system that is used to treat tannery wastewater. The harvested plant was cut by scissors to pieces.

2.3. Experimental Design

The co-digestion experiment was conducted in four different mixing ratios of *phragmites karka* and tannery wastewater. The mixing ratios used were 100:0, 75:25, 50:50 and 25:75 tannery wastewaters to *phragmites karka* by volume. The tannery wastewater was stored in a refrigerator at 4^0c until used for feeding. All the four digestion bottles were fed tannery wastewater once in every five days. The biogas content was periodically measured using biogas meter. The reactor was operated at mesophilic temperature (37^0c).

2.4. Analytical methods

The characteristics of influent and effluents in terms of chemical oxygen demand (COD), total nitrogen (TN) were measured colorimetrically using spectrophotometer (DR/2010 HACH, Loveland, USA) according to HACH instructions. Total solid and volatile solid were also measured according to the methods described in standard methods (APHA, 1998). pH of tannery wastewater was measured using a pH meter (CON, 2700). The biogas production was measured using wet gas meter and the biogas composition was determined using biogas meter (Biogas meter Geotechnical instruments, UK, England).

2.4. Statistical Analysis

Statistical analysis was performed using EXCEL and Origin 8.0 software. Mean, Standard deviation and Analysis of Variance (ANOVA) were analyzed using Excel statistical package. The graphs were drawn using Origin 8.0 software. The comparison between mean was performed at 95% confidence interval.

3. Results and Discussion

3.1. Physiochemical characteristics of tannery wastewater and phragmites Karka

The physiochemical characteristics of tannery wastewater and *phragmites karka* are shown in Table 1. The tannery wastewater were characterized by high alkalinity content with a resulting pH value of above 9.4 and this could be due to the chemicals used in leather processing. The total Solid (TS) and volatile solid (VS) level were 4.7 ± 0.43% and 78 ± 0.23%, respectively, whereas COD, total nitrogen and total phosphorus were 3860±458, 450±24.8 and 24.4 ± 2mg/L, respectively.

Table 1. Physiochemical characteristic of tannery wastewater and *phragmites karka*

Parameters	Tannery wastewater		*Phragmites karka*	
	unit	value	unit	value
pH		9.4±0.16		
TS	%	4.7±0.42	%	47.7±0.1
VS	Based on TS (%)	78±0.23	Based on TS (%)	82.7±0.84
OC	-	-	Based on TS (%)	45.7± 0.28
COD	mg/L	3860±458	-	-
TN	mg/L	450±24.8	Dry wt. bases %	1.76± 0.21
TP	mg/L	24.4 ± 2	Dry wt. bases %	0.16±0.04
C/N	COD/TN	8.5	(OC/TN)	25.4

The total solid (47.7±0.1%), volatile solid (82.7±0.84%) and organic matter content (45.7 ± 0.28%) of the phragmites were high while total nitrogen (1.76 ± 0.21%) and total phosphorus (0.16±0.04%) content was small. The carbon to nitrogen ratio value in the phragmites is important factors for anaerobic digestion. The ratio was 25.4 which were within the optimum recommended range for anaerobic digestion. The optimum C:N ratio for anaerobic digestion are between 25:1 and 30:1(Zhong *et al.,* 2012).

3.2. pH, total dissolved solids and salinity

Anaerobic digestion process is sensitive to pH change because each of the microbial groups involved in the reactions has a specific pH range for optimal growth and the optimum pH range is 6.0-8.0 (Acharya *et al.,* 2008). pH was between 6.2 and 7.36 in all the digesters during the course of this study. All the digesters were within the optimum pH values. The minimum pH was observed in digester four and this could be due to the accumulation of volatile acids. Digester D1 (7.57) showed the highest pH followed by digester D2 (7.36). These two digesters are slightly alkaline and methanogenesis appears to be an alkalizing step that consumes hydrogen and H_3O+ ions (Acharya *et al.,* 2008; Patel and Madamwar, 2000).

The average EC value in the digesters was in the range between 7.259 to 10.53mS and TDS and salinity were also ranged between 7.06 to 8.2g/l and 8.178 to 9.2g/l, respectively. All the parameters were lowest in digester D1 followed digester D2. The highest were observed in digester D4 followed by digester D3. The value of all the parameters was high in all the digesters. The high value of EC and salinity in the digester is due to the higher concentration of total dissolved solids (TDS) which resulted from lime and other chemicals used in the tanning process (Lefebvre *et al.,* 2006). High salinity (mainly the cations) content in the waste strongly inhibits anaerobic digestion process. Studies indicated that methanogenesis process is highly inhibited with sodium concentration greater than 10 g/L (Sunny and Mathai, 2013: Lefebvre *et al.,* 2006).

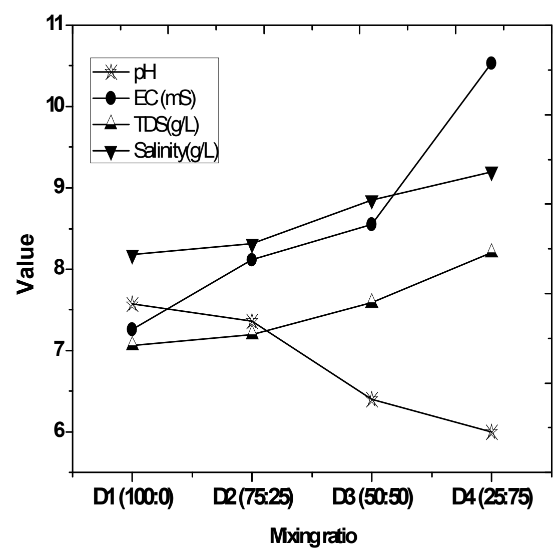

Figure 2: variation of pH, EC, TDS and salinity

3.3. Biogas production

The trends of cumulative biogas production of the entire four digesters (D1-D4) are shown in Fig.3. As shown in the figure, all the digesters started gas production in the 5^{th} days and showed similar trends until the 15^{th} days of the experiment. The biogas production was slow at the beginning of the experiment and this is mainly due to the lag phase of microbial growth. Biogas production rate in batch condition is directly equal to specific growth of methanogenic bacteria.

After the 15^{th} day, digester one started to show variation in the biogas production. This variation is mainly resulted from the difference in the amount of tannery wastewater used in the feeding. Digester one was fed twice in every five days while the feeding for the other three digesters remained the same. Similarly, digester two has shown significant difference in biogas production from the other two digesters after the 35th day ($p<0.05$). This increment in biogas production may attribute to the exponential growth of methanogens and the hydrolysis of the wetland plants. The other two digesters showed similar biogas production throughout the experiments with average gas production rate of 200ml/day. Digester one showed the highest cumulative biogas production with an average gas production rate of 352.9ml/day followed by digester two with average gas production rate of 305.9ml/day. On the other hand, digester three (D3) and four (D4) showed significantly lower gas production rate than digester D1 and D2 ($p<0.05$) while, the biogas production rate in digester D3 was not significantly different with digester D4 ($p=1.0$). This low production of biogas might be resulted from the high load of plants biomass. Plant biomasses in dry weight contain cellulose, hemicelluloses and lignin up to 90% (Sidik *et al.,* 2013). Phragmits karka contains 50.55±0.4% α-cellulose, 25.12±0.54% hemicelluloses and 22.00±0.32% lignin (Kumar, 2013). In the anaerobic digestion of feeding materials with high level of lignin shows recalcitrance against the hydrolysis process because of the high stability of the material to bacterial attacks (Taherzadeh and Karimi, 2008). Hence, this increase the hydraulic retention time and reduces the gas production. The other factor could be the accumulation of volatile fatty acid can lead to a drop in pH and the continual drop in pH inhibits the methanisation process (Carucci *et al.,* 2005).

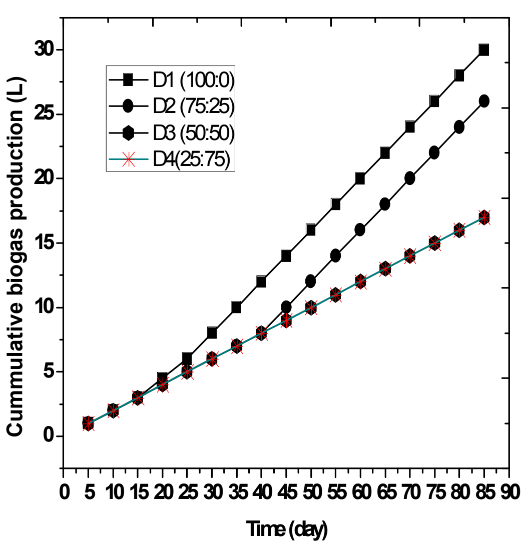

Figure 3: Cumulative biogas production

3.4. Methane content

The methane content of the biogas produced in all the digesters are illustrated in Fig 4. As it is shown in the figure, the methane percentage was low in all the digester at the beginning of the experiment. This could be due to the low acclimatization of methanogenic bacteria.

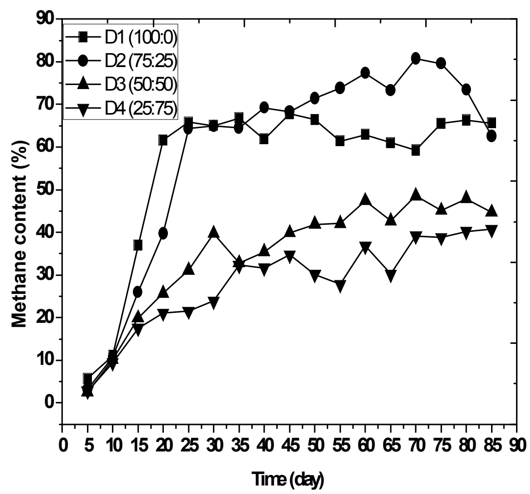

Figure 4: methane percentage with respect to different mixing ratio

After the 20th days, the methane content in the biogas produced in digester D1 was stable around 59–67% during most of the experimental period. Similarly, digester D2 showed stable biogas production after the 25th days with an average content of 71% and maximum content of 80%. The biogas produced in digester D3 was stable around 31-48% after 25th days with an average content of 41.5%. The biogas produced in digester D4 was also in between 27.8% to 40% starting from the 35th days of the experiment. The methane content was low in both digesters D_3 and D_4 throughout the experiment. This is mainly due to the accumulation of volatile acids. At high organic loading rate, the overall growth rate of acidogenic bacteria proceeds faster (10- fold) than that of methanogenic bacteria and inhibitory products such as volatile fatty acids and H_2 accumulate in the reactor, which slows slow down the entire process (Ronnachai *et al*., 2007).

3.5. Methane yield (per COD removed)

The variations of methane yield during the experiment are shown in Fig.5. It is expressed in terms of liters of methane produced per gram of COD removed. Methane yield was low in all the digester until 15th days. This could be due to the low acclimatization of methanogenic bacteria.

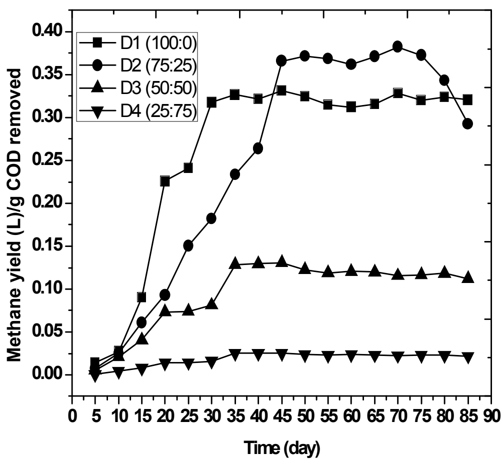

Figure 5: Methane yield with respect mixing ratio

The methane yield in the first digester (D1) showed increasing trends up to the 25th day and remained stabile around 0.24 to 0.32L/g COD removed on the remaining days of the experiments. The methane percentage in the second digester have shown continuous increment until 45th day and remained stable in between 45 to 70th days of the experiment. After the 70th day, the methane yield showed continuous reduction. This reduction in methane yield might attribute to the reduction of the *pharagmites* level in the digester. On the other hand, digester D1 and D2 showed the lowest methane yield form the entire four digesters. In comparing the digesters, the average methane yield of the first digester (0.26L/g COD removed) was not significantly different from the second digester (0.25L/g COD removed). The methane yields in both digesters D1 and D2 were significantly higher than the third digester (0.10 L/g COD removed) and the fourth digester (0.08L/g COD removed) ($p<0.05$).

3.6. Removal efficiency of COD, TS and VS

The average removal efficiency of organic matter, total solids and volatile solids are shown in Fig.6. The COD removal efficiency observed was in the range of 62.4 to 88.9 % in all the four digester. The COD removal efficiency in the digester D1 (88.9%) was significantly greater than the D2 ($p<0.05$). This is contrast to the observed methane yield and methane content of the two digesters**.** The second digester was also showed significantly higher COD removal efficiency than the other two digesters ($p<0.05$) while, the COD removal efficiency in digester D4 was significantly lower than the removal efficiencies of all the digesters ($p<0.05$).

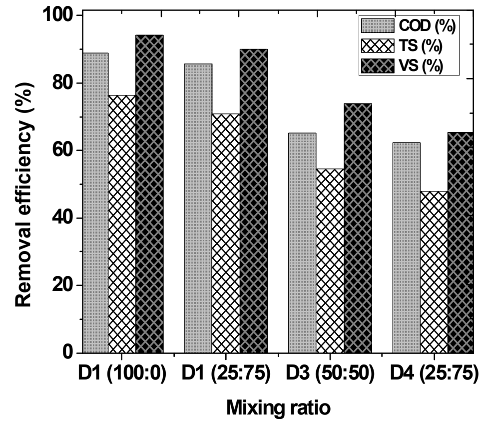

Figure 6: Removal efficiency of COD in all mixing ratio

There was also variation of TS and VS removal efficiencies with variation of mixing ratio of tannery wastewater to *phragmites karka*. The removal efficiencies of TS and VS were varied in the range of 48 to 76.3% and 65.3 to 94.1%, respectively with variation of mixing ratio. The removal efficiencies of TS and VS in digester D1 (100: 0) were significantly higher than the other three digesters ($p<0.05$). Similarly, digester D2 (75:25) showed significantly higher TS (70.8%) and VS (90%) removal efficiency than the other two digesters ($p<0.05$) while, the removal efficiencies TS (48%) and VS (65.3%) in digester D4 was much significantly lower than the removal efficiencies of all the digester ($p<0.05$). In all the digesters, the removal efficiency of TS was significantly lower than VS removal efficiency ($p<0.05$). This higher removal efficiency of VS than the TS might be due to the high uptake rate of the organic fraction of total solids by methanogenic bacteria.

4. Conclusion

The biogas production from biomass is of growing importance as it offers considerable environmental benefits. In this study co-digestion of tannery wastewater and *phragmites karka* was investigated at different mixing ratio. The results showed that the removal efficiencies of COD, TS and VS decreased as the proportion of *phragmites karka* increased from 25% to 75% in the feeding substrate. Similarly, the biogas production rate and methane content showed reduction with increasing of phragmites proportion. The mixture containing 25% *phragmites karka* produced the highest average methane content (71%) and methane yield (0.26L/g COD removed). Hence, the co-digestion of *phragmites karka* up to 25% with tannery wastewater enhances the quantity of methane yield and the quality of biogas. Co-digestion of *phragmites karka* with strong wastewater offers a reliable way of recycling after it is used in tannery wastewater treatment.

Acknowledgment

This research work was supported by the Swedish International Development Cooperation Agency (SIDA) through Bioresources Innovations Network for Eastern Africa Development *(Bio-Innovate)* program.

References

1. Abbasi T. *et al*. Anaerobic digestion for global warming control and energy generation-An overview. Renewable and Sustainable Energy Reviews 2012;16:3228- 3242.
2. Acharya B. K., Mohana S. and Madamwar D. Anaerobic treatment of distillery spent wash – A study on upflow anaerobic fixed film bioreactor. Bioresource Technology 2008; 99: 4621-4626.
3. APHA. Standard methods for the examination of water and wastewater, 19th edn. American public Health Association, Washington DC. 1998.
4. Azaizeh H. and Jadoun J. Co-digestion of Olive Mill Wastewater and Swine Manure Using Up-Flow Anaerobic Sludge Blanket Reactor for Biogas Production J. Water Resource and Protection 2010; 2:314-321.
5. Bouallagui H., Rachdi B., Gannoun H.and Hamdi M. Mesophilic and thermophilic anaerobic co-digestion of abattoir wastewater and fruit and vegetable wastein anaerobic sequencing batch reactors. Biodegradation 2009; 20:401- 409.
6. Goberna M., Schoen M.A., Sperl D., Wett W.and Insam H. Mesophilic and thermophilic co-fermentation of cattle excreta and olive mill wastes in pilot anaerobic digesters. Biomass Bioenergy 2010; 34:340–346.
7. Kashyap D.R., Dadhich K.S. and Sharma S.K. Biomethanation under psychrophilic conditions: a review. Bioresour. Technol. 2003;87:147-153
8. Kobbing J.F., Thevs N. and Zerbe S. The utilisation of reed (Phragmites australis): a review Mires and Peat 2014; 13 (1):1-14.
9. Kumar L. Biochemical characterization of thermo-alkalophilic xylanase and its application in bleaching. PhD thesis, Indian Institute of Technology Roorkee, India, 2013.
10. Lay C., Sen B., Chen C., Wu J., Lee S. and Lin C. Co-fermentation of water hyacinth and beverage wastewater in powder and pellet form for hydrogen production. Bioresource Technology 2013;135;610-615.
11. Lefebvre O., Vasudevan N., Torrijos M., Thanasekaran K. and Moletta R. Anaerobic digestions of tannery soak liquor with an aerobic post-treatment. Water research 2006;40:1492-1500.
12. Parawira W., Murto M., Zvauya R. and Mattiasson B. Anaerobic batch digestion of solid potato waste alone and in combination with sugar beet leaves. Renew. Energy 2004; 29:1811-1823.
13. Patel H. and Madamwar D. Biomethanation of low pH petrochemical wastewater using up-flow fixed film anaerobic bioreactors. *World Journal of Microbiology and Biotechnology* 2000;*6:69-75.*
14. Patila J.H., AntonyRaja M.A.L., Shankar B.B., Shetty M. K. and Kumar B.P. P. Anaerobic Co-Digestion of Water Hyacinth and Sheep Waste. Energy Procedia 2014;52: 572 – 578.
15. Ronnachai C., Piyarat B., Poonsuk P. and Sumate C. Effect of organic loading rate on methane and volatile fatty acids productions from anaerobic treatment of palm oil mill effluent in UASB and UFAF reactors. J. Sci. Technol. 2007; 2:311-323.
16. Seyoum Leta, Gumelius, L., FassilAssefa and Dalhammar G. Biological nitrogen and organic matter removal from tannery wastewater in pilot operations in Ethiopia. Appl. Micrbiol. Biotechnol. 2004; 66(3):333-339.
17. Sidik H.U., Razali B. F., Wan Alwi S. R. and Maigari F. Biogas production through Co-digestion of palm oil mill effluent with cow manure. Nigerian Journal of Basic and Applied Science 2013;21(1):79-84.
18. Sunny N. and Mathai L. P. Physicochemical process for fish processing wastewater. International Journal of Innovative Research in Science, Engin and Techn. 2013;2(4).
19. Taherzadeh M.J. and Karimi K. Pretreatment of Lignocellulosic Wastes to Improve Ethanol and Biogas Production: A Review. Int. J. Mol. Sci. 2008;9(9):1621-1651.
20. Verma A., Kumari M., Dhusia N. and Nandkishor. Phytoremediation potential of phragmites karka for arsenic contaminated soil and water. IOSR Journal Of Environmental Science, Toxicology And Food Technology 2014;8(1):84-92.

1/18/2016