Composting and Beneficial Use of Tannery Wastewater Treatment Sludges

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Abstract

The treatment sludges from leather industry contain high levels of biomass which has a potential to be applied to arid and/or agricultural areas. However, the soluble carbon in sludge is a limiting factor for its direct use as a soil conditioner as well as its salt and pathogen content. The high levels of Cr^{+3} in the sludge can be another handicap if wastewaters carrying Cr^{+3} are not separately treated.

Since the leather industry consumes high amounts of water, the amount of sludge generated from biological treatment plants (TP) create problems related with its disposal. Composting is listed as one of the best available techniques for tannery TP-sludges.

Here, the composting of tannery biological TP-sludge is studied and the beneficial use of the product is evaluated. The sludge is co-composted with i) sole and vegetable leather shavings, ii) yard waste, iii) protein from fleshings recovery and iv) tobacco leaves waste. Four different mixes were investigated for compostibility and 50-60% of TP-sludge was used in recipes.

The mixes were composted in aerated reactors and the temperature, volume and organic matter content reductions, changes in soluble carbon and water content were monitored during the composting period. Two best recipes were selected and tested in pilot scale. The combination resulted with optimum C/N ratio and E. Coli reduction was chosen to be used for industrial scale. Further investigation on agricultural use of the product was also conducted and it is recommended to be used in soil mixtures up to 25% for horticulture and ornamental plants.

Keywords: Tannery sludge, compost, recovery, waste, biostabilization, legislation

Introduction

There is a vast production of wastewater treatment sludge above 9.8 million tons worldwide (Zupancic and Jemec, 2009) with a substantial contribution of the tanning industry including leading leather producers of the European Union countries. A survey conducted in 2001 revealed that in 1998 there were around 3000 tanneries in Europe. Italy is the major leather producer in EU and producing 190 million m^2 of leather per year. (Zupancic and Jemec, 2009) But, it has been estimated that the majority of the 900,000 tons of sludge generated annually in the EU, including the sludge from leather processing, is deposited in landfills.

Since the sludge from the tanneries has high levels of biodegradables, it is aimed to be diverted from the landfills in EU. Therefore, direct landfill of biodegradable sludge will probably be banned completely in Europe and Turkey in forthcoming years (Milleu Ltd.,2010, Turkish M.O.E.F, 2010). However, some newly member countries still heavily or entirely use landfilling for sludge disposal (Milleu Ltd., 2010). In addition, it is known that, there is also an issue of treating the leachate generated from sludge landfill sites which is a real handicap both environmentally and economically. According to Zgajnar et al.(2009), raw tannery landfill leachate contains high level of contaminants including COD (3400 mg/l), N-NH_4^+ (2792 mg/l), and Cl^- (3500 mg/l). It is also reported in this study that i) the landfill leachate is toxic to aqueous organisms according to the tests conducted with daphnia magna and vibrio fischeri, and ii) the results showed that the leachate samples has very low biodegradability.

Because of the handicaps mentioned above, the avoidance of sludge landfill had spread in the world. Recently, the application of available techniques for reducing tannery sludge's organic content and/or valorization of its biomass content is at the top of the agenda of the related countries and the leather manufacturers.

Various techniques can be used for the processing of tannery sludge for decreasing its organic content and stabilizing the material, such as; incineration, anaerobic digestion and composting.

Incineration is one of the conventional techniques for disposal of tannery sludge and there are some studies about its applicability and side effects such as evaporation of chromium vapors during incineration. As reported in Ping et al. (2008) H_3PO_4 pretreatment of sludge is required in order to control heavy metal emissions in the process of tannery sludge incineration. However there are numerous incineration plants which are processing tannery sludge without pre-treatment causing hexavalent chromium emissions. One other disadvantage of incineration of tannery sludge is the moisture content of dewatered sludge, which can be up to 75 % (Kilic et al., 2011) which results with very high operational costs due to the energy requirement for the drying of the material (Kilic et al., 2011).

Anaerobic digestion is also a technique which is commonly used to process municipal sludges, but its use on tannery sludge should be assessed. Zupancic et al. (2009) has reported two major concerns in anaerobic treatment which are the salt and the chromium content of the sludge. As also stated by Altas (2009), the inhibitory concentrations of Cr in the range of 27 to 3000 mg / l can cause 50% reduction in the cumulative methane production. Considering the trivalent Cr content of tannery sludge which may vary between 350 to 64000 ppm (Haroun et al. 2007; Paverill et al. 1999), it is unlikely to conclude solely tannery sludge as a valuable material for anaerobic digestion. In addition, long retention times may be in the range of 12 to 45 days depending on the process type, result in large digester volumes which increases both the investment and operational costs of these systems. Another common problem observed in anaerobic digesters is unstable digestate which needs additional expenses for its stabilization. It is also known that anaerobic bacteria are more sensitive to the chemicals, and even low concentrations of some chemicals used in tannery processing may be inhibitory to the bacterial culture in the digesters. For preventing this inhibition, pretreatment of sludge is necessary in most cases.

Compared to these techniques, composting offers a more economic and efficient way to process tannery sludge by means of dewatering, stabilizing and recycling. High nitrogen content of tannery sludge is around one percent and this value offers a preferable raw material for composting (Haroun et al., 2007). As studied by Haroun et al. (2007), tannery sludge can be composted with various admixtures such as chicken manure, sawdust, and green waste. Also overall heavy metal concentrations in compost were found in compliance with the standards of the Canadian Regulation Limits which offers a compost suitable for marketing as a soil conditioner.

While tannery sludge composting is as possible as it seems, its effect on plant growth must be taken into consideration before applied to soils. A different approach is present by Krzystof (2008) on tannery sludge composting by using earthworms and the effects of this vermicompost were investigated. In the study, several vermicompost recipes have applied to maize, rape, sunflower and oat plants with various admixtures and the product was investigated for growth and chromium bioaccumulation in plants' lower and upper structure. Results had shown a considerable difference on the growth of plants compared to the control (no compost application to the soil) and very low metal accumulation on top parts of the chosen plants (Krzystof, 2008)

In the scope of this study, the compostibility of tannery sludge generated from treatment of the vegetable and chrome tanning processes effluents was investigated in laboratory scale and the lab-scale results were validated by using the data obtained from the industrial scale trials. Here, the major findings and the remarks from the study are presented.

Material and Methods

The main material used in this research is the wastewater treatment sludge generated from the effluent treatment plant of Sepiciler Caybasi Tannery, Turkey. Tannery's process consists of two different tanning types; chrome tanning (50% of the total production) and vegetable tanning (50%). Wastewater treatment plant has physical treatment, aeration, chemical sedimentation, biological activated sludge and secondary gravitational sedimentation units with a belt press sludge dewatering system. Investigated sludge is generated in belt press unit and has 75 % water content. Following admixtures are used in preparation of compost mixtures: vegetable tanned leather shavings and dust & shavings generated from the vegetable section of tannery, solid protein waste generated by the centrifugation process in fleshing waste recovery plant in the tannery and tobacco leaves waste supplied from a nearby facility.

The study has two major steps. The first step was conducted in lab-scale in order to define the sludge's availability for composting. In lab-scale, the various admixtures are prepared to observe the sludge co-composting process by using the above mentioned materials produced in the tannery. The initial water content, organic matter content, dissolved organic carbon (TOC_d), and dissolved nitrogen (TN_d) levels of the materials were initially determined according to the standard analytical methods. Four different admixtures were prepared for this purpose and the components in the mixtures are presented with Table 1. As can be seen from the table, the major component of the mixtures is tannery sludge. Vegetable leather shavings were used to obtain available porosity in the mixture and also the bacterial community, tobacco leaves were used to arrange C/N, and solid protein from fleshing treatment is used to obtain i) fresh bacterial population which is necessary to start the aerobic decomposition and ii) triglycerides which is controlling the occurrence and loss of ammonia.

Table 1. Components of lab-scale admixtures

Components	Component Distribution in Compost (%)			
	Mixture I	Mixture II	Mixture III	Mixture IV
Tannery Sludge	60	60	50	60
Vegetable Tanned Leather Shavings	40	20	10	25
Solid Protein From Fleshings Treatment	-	10	20	5
Tobacco Leaves Waste	-	10	20	20
TOTAL	100	100	100	100

The lab-scale composting studies were conducted in a 28 days period by forming waste piles with the height of 0.75 m and the width of 1.2 m. The wastes were mixed for homogenization prior to the pile forming and the aeration was obtained by mixing the piles with manpower. The initial water content in the waste mixtures were arranged as 75% and was not allowed being below 45% in the first 20 days.

Field scale trials were decided according to the results from the lab-scale studies. In field scale, the height of the pile was 1.5 m and the width was 2.7 m with a trapezoidal cross section. Approximately 10 tons of waste mixture was used for field scale trials. Since the lab scale trials were resulted with achievement in the mixtures having high levels of tannery sludge, the ratio of tannery sludge in field operation was increased. The sludge content was 80% in field scale, where tobacco leaves waste was 10%, vegetal shavings was 8% and protein waste was 2%. This recipe was also much more suitable to the waste production rates of the tanning facility. The waste piles were mixed by man power in the initial phases of the field trials, but then a compost turn over machine, which was accelerated by a truck, was obtained since the results were satisfactory. The pile temperature was also followed during the field trials of composting and the final product properties were analyzed at the end of the process.

Results and Discussion

The moisture content, organic matter content, dissolved organic carbon and nitrogen levels of the studied waste materials are presented in Table 2.

Table 2. Initial waste properties

Waste Description	Moisture Content (%)	Organic Matter (% d.m)	Total Organic Carbon (ppm d.m.)	Total Nitrogen (ppm d.m.)
Tannery Sludge	73	96	8220	1370
Vegetable Tanned Leather Shavings	54	87	31778	4546
Solid Protein From Fleshings Treatment	57	76	119200	4900
Tobacco Leaves Waste	12	53	160000	6000

The initial properties of the waste admixtures used in compost mixtures are also determined and given in Table 3.

Table 3. Initial properties of waste admixtures

Mixture Number	Moisture Content (%)*	Organic Matter (% d.m)	Total Organic Carbon (ppm d.m.)	Total Nitrogen (ppm d.m.)	C/N Ratio
I	75	92.4	17643	2640	7
II	75	67.4	39208	2821	14
III	75	82.4	63128	3320	19
IV	75	82.8	50837	3404	15

* Moisture level of all mixtures is set to 75 %

The temperature profile of the waste piles in lab-scale studies are given in Figure 1 for 28 days of composting period.

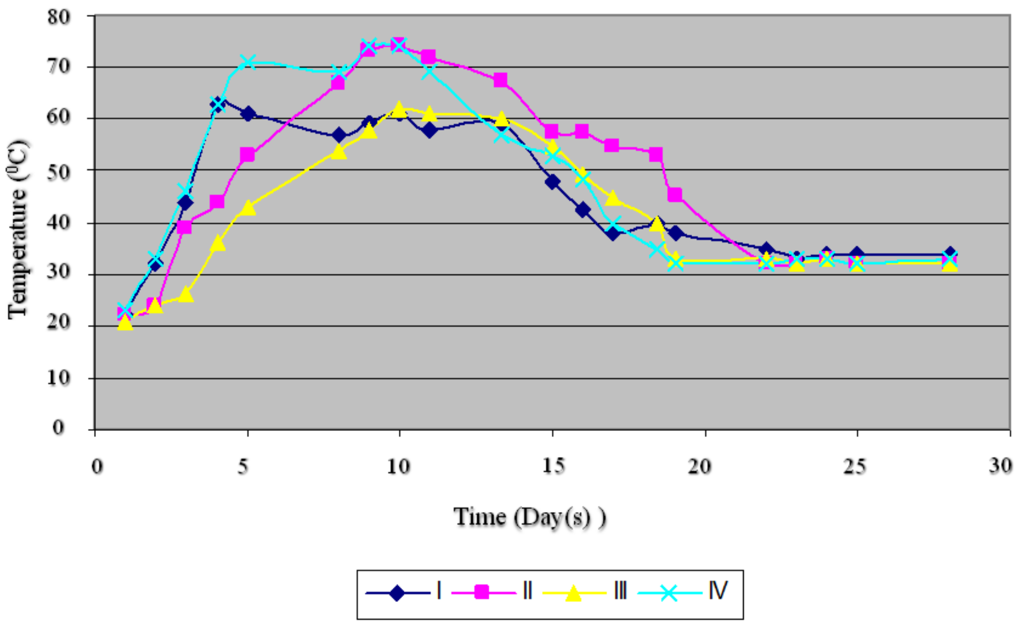

Figure 1. The temperature profiles in lab-scale composting piles

As can be seen from Fig.1, the pile temperatures instantly raised and exceeded the pasteurization threshold of 60°C in the first week of the study, except for Mix III. It is important to emphasize that the system temperatures decreased with the drop in water content. Therefore, the humidity of the piles was kept under control during the first 20 days of composting. Two important factors effecting the composting period were found as available C/N ratio and presence of sufficient initial microbial consortium. Although the initial C/N ratio in Mix I was lower than Mix III, the higher tobacco leaves waste ratio (which is substituted to vegetal shavings) in Mix III could not supply enough microbial support and the temperature raise was not rapid in Mix III. On the other hand, high microbial population in Mix I resulted with early ending of the process even though the water content were kept around 60%. Therefore, it is hard to accept the presence of dissolved carbon stabilization in the pile of Mix I. In addition, Mix III, which has better C/N ratio than the other mixes, cannot develop by means of microbial consortium and relatively low temperatures were observed. Better temperature profiles were seen in Mix II and Mix IV. In these mixes, the positive effects of protein waste and tobacco leaves waste have seen. It was also concluded that, in Mix II and Mix IV, the microbial consortia supplied by vegetal waste is sufficient. However, longer stabilization period obtained by Mix II is much preferable for efficient TOC_d stabilization. The final C/N ratio and the water content of the products obtained at the end of the composting period are given in Table 4.

Table 4. The final product properties of the lab-scale composting studies

Mixture Number	Product Moisture Content (%)	Product C/N Ratio
I	43	7
II	27	9
III	34	16
IV	29	11

As it was mentioned before, sludge content was 80% in field scale trials, where tobacco leaves waste was 10%, vegetal shavings was 8% and protein waste was 2%. In field trials, temperature and humidity is also constantly monitored during the composting process. Significant increase in pile temperature was observed and its variation is showed in Fig 2.

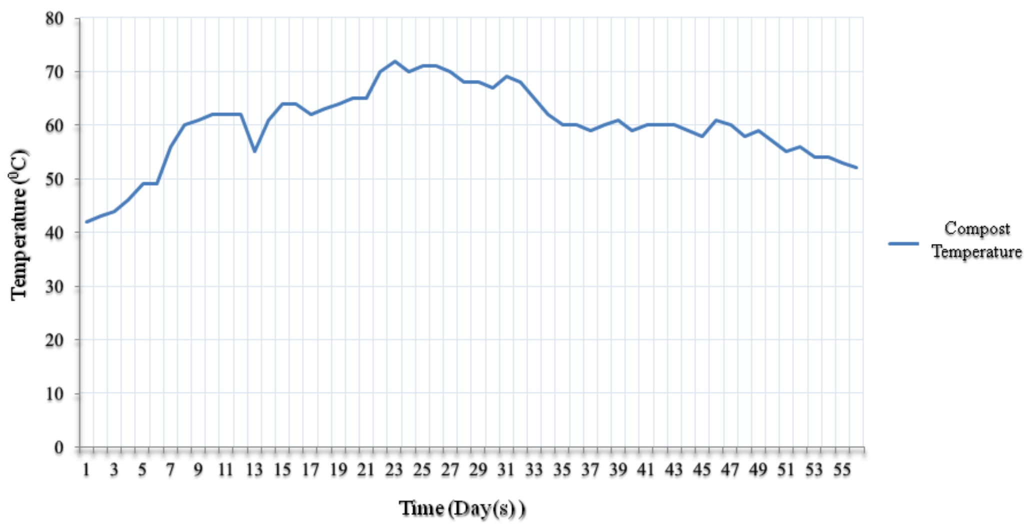

Figure 2. Temperature variation in windrows during the field scale compost trials

As can be seen from the figure, the temperature had risen up to 72 ^{0}C during the process which enables the microbial stabilization of the material. It is also favorable to keep the windrow temperature over 50 °C for 58 days of composting, which was maintained by systematical aeration by turn over machine and sufficient humidification of the piles which allowed the stabilization of dissolved carbon.

It is known that, not only the temperature raise but also the development of a group of gram-positive bacteria, which releases antibiotics, are the reasons of pathogens pasteurization in composting. The presence of actinomycetes was also observed at the crown of the waste piles when a profile was opened in the windrows at the last stage of composting, after the aeration was ceased. To ensure product stabilization, presence of Escherichia Coli in the raw sludge and in the composted material was also analyzed. The colony count in raw sludge is detected as 44 x 10^5± 21 x 10^4 (number of colonies / g) and the colony count in compost is 60 x 10^3± 25 x 10^3. These results showed that the 99% E.coli reduction was achieved during composting. The graphical presentation of E. coli stabilization is presented with Fig 3. The mass reduction during composting process was also measured and found as over 52.5 % which is very beneficial by means of storage of final product.

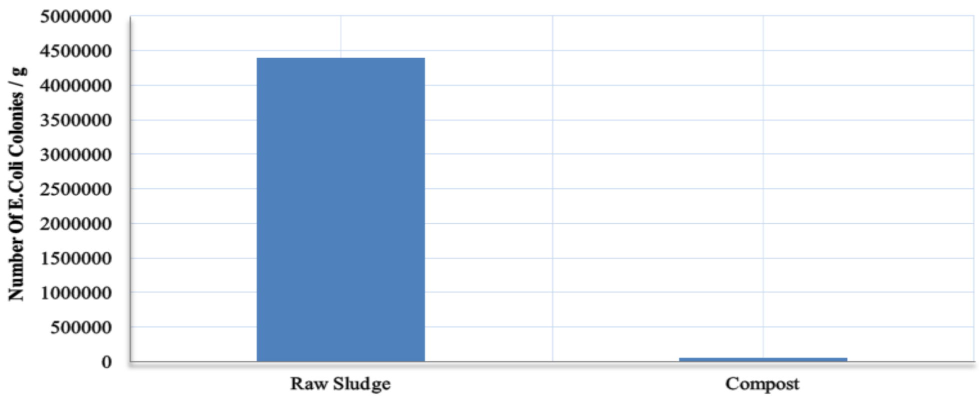

Figure 3. E. coli population in raw sludge and composted material

According to the findings, it can be concluded that the tannery sludge can be successfully co-composted by using the other wastes produced in the facility. The heavy metals in the final product was also analyzed and the results found below the EU 86 / 278 / EEC Directive (European Commission, 1986) Limit Values (Table 5).

Table 5. Heavy metal concentrations in compost and EU Regulatory Limits

Parameters	Concentration in Compost (mg / kg dry matter)	278 EEC Directive Limit Values (mg / kg dry matter)
Cadmium	0.93	20 – 40
Copper	31.1	1000 – 1750
Nickel	27	300 – 400
Lead	19.1	750 – 1200
Zinc	99	2500 - 4000
Mercury	0	16 - 25
Chromium	6270	-

In addition, nutrients were also analyzed and N/P/K was found as 35500/2680/3500 mg/kg d.m. The pH of the final product was 8, electrical conductivity was 31.6 dS/m, water content was 20.04% and the organic matter content was detected as 42.5% in dry matter.

The availability of the product as a soil conditioner will also be investigated in the near future by plant tests. And chromium removal studies will be conducted by modifying the exhaustion level in tanning process.

Conclusion

The outputs of the study can be summarized as follows:

- The tannery sludge can be composted by using other wastes generated in tanneries
- The tannery sludge ratio in the waste mixes can be as high as 80%
- The presence of sufficient initial aerobic bacterial consortia is prerequisite for composting achievement of tannery sludge
- The initial dissolvable C/N ratio is important for the sustainability of the composting process to achieve desired carbon stabilization
- The product quality is satisfactory since the bacterial pasteurization was achieved
- The nutrient levels in the final product are satisfactory

Further studies on the use of compost products as soil conditioner will be conducted by plant trials.

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