Assessment of Aerobic Biodegradability for Vegetable Tanning Process Wastewater Generated from Leather Industry

Abirami Balakrishnan, K. Sri Bala Kameswari and Chitra Kalyanaraman

Abstract The most important process in the making of leather is converting raw hides/skins into leather by chrome tanning using basic chromium sulfate or vegetable tanning using vegetable extracts like wattle, chestnut, myrobalan and valonea. Vegetable tanning extracts predominantly contain tannins which bind to the collagen. Vegetable tanning process is usually carried out in tanneries for the production of sole and heavy leathers. In this study, the vegetable tanning wastewater (VTW) was collected from the vegetable tanning bath and was characterized for all physicochemical parameters. The biodegradability assessment was performed using laboratory-scale batch aerobic reactors of 2 L capacity. The results indicated that the VTW had a BOD_5/COD ratio of 0.154 implying that it was not easily biodegradable and 80% of COD was found due to the presence of tannins. The biodegradability test showed an apparent removal of only 24 and 34% of COD, and tannins were observed over a residence time of 24 h. This shows that the efficiency of aerobic microorganisms is affected by the binding of tannins to their cell wall. Supporting data obtained with the help of FTIR is presented in this paper.

Introduction

In leather industries, tanning is the process of converting raw hides or skins into leather. Tannins are water-soluble complex organic compounds that are capable of combining with protein to convert it into a material. The wastewater from vegetable tanning process imparts color and consists of non-biodegradable matter like tannin which persists for long (Dhaneswar 1990). Tannins inhibit the growth of a number of microorganisms, resist microbial attack and are recalcitrant to biodegradation

A. Balakrishnan · K. Sri Bala Kameswari (✉) · C. Kalyanaraman
Environmental Science and Engineering Division, Council of Scientific and Industrial Research - Central Leather Research Institute, Adyar, Chennai 600020, India
e-mail: sribala_k@yahoo.com

V. P. Singh et al. (eds.), *Water Quality Management*, Water Science and Technology Library 79, https://doi.org/10.1007/978-981-10-5795-3_14

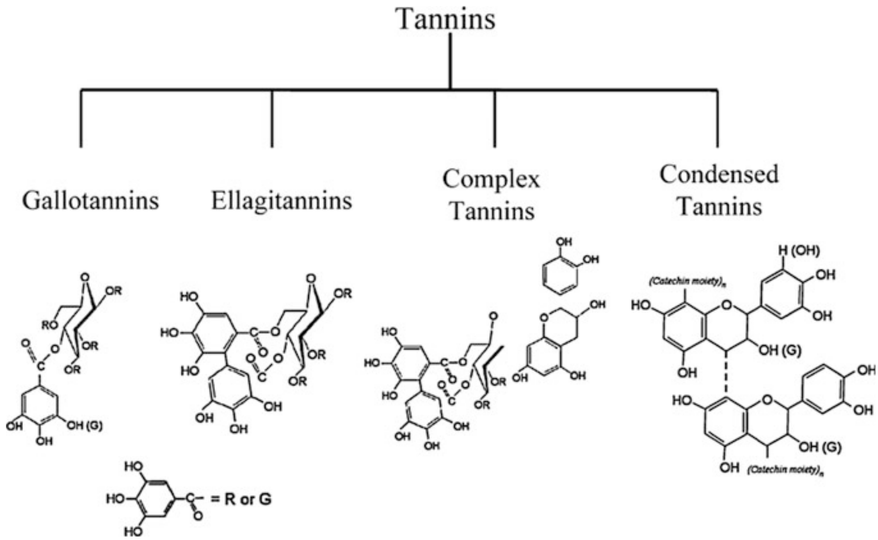

Fig. 1 Classification of tannins (*Source* Aquilar et al. 2007)

(Field and Lettinga 1992). There are two major types of tannins: condensed and hydrolyzable. The classification of tannins is presented in Fig. 1.

Hydrolyzable tannins are composed of esters of gallic acid (gallotannins) or ellagic acid (ellagitannins) with a sugar core which is usually glucose and are readily hydrolyzed by acids or enzymes into monomeric products. Condensed tannins, also known as polymeric proanthocyanidins, are composed of flavonoid units and are usually more abundant in tree barks and woods than their hydrolyzable counter parts (Bhat et al. 1998).

Shoe soles, brief cases, luggage and belts are made by vegetable tanning process. On the other hand, shoe uppers are tanned by chrome tanning process. However, most of these chrome-tanned products are later re-tanned with vegetable tannins.

Owing to the presence of tannins, the wastewater is usually highly colored, which is very difficult to be removed by conventional treatment methods (Etiegni et al. 1999). In addition, tannins can inhibit growth of microorganisms and inhibit the efficiency of the biological treatment process. This negative effect can be observed when tannin-containing wastewater is biologically treated in wastewater treatment plants (Ren 2004). Methods such as adsorption (Liao and Shi 2005; Marsal et al. 2003), photocatalytic and sonochemical process (Arana et al. 2001; Svitelska et al. 2004), membrane filtration (Cassano et al. 2003; Scholz and Lucas 2003) and Fenton and ozonation (Kalyanaraman et al. 2015) have been explored to treat tannin-containing wastewaters by various researchers.

Even though anaerobic digestion is a preferred process, problems of high toxicity and inhibition of biodegradation have been encountered (Beccari et al. 1996). This is because methanogens are sensitive to the organic compounds present, especially the phenolic compounds like tannin, thus limiting the performance of anaerobic digestion process (Hamdi 1992). A concentration of tannins higher than 0.2 g/L inhibits the anaerobic digestion process (Gupta and Haslam 1989), while 2 g/L of tannin will completely inhibit the process as reported by Munz et al. (2009).

Several studies were conducted to study the biodegradability of tannin wastewater (Routh 2000; Tramsek et al. 2006; Banu and Kaliappan 2007). In a study by He et al. (2007), when the tannin content of the wastewater was 4,900 mg/L, only 34.7% of biodegradation extent was reached in 14 days of incubation. On the other hand, when the tannin content was 490 mg/L, the COD and tannin removals reached 51.3 and 45.1% respectively in 6 days.

Aerobic biodegradation of VTW was performed to find out how tannin influences the conventional aerobic treatment process efficiency. The results of removal of COD and tannin after aerobic treatment were assessed, and validation of degradation through FTIR analysis was described in detail in this paper.

Materials and Methods

Analytical Methods

Characterization of Vegetable Tannin Wastewater

During vegetable tanning operation, a mixture of condensed tannins and hydrolyzable tannins were used based on the nature of the final product. Vegetable tanning process wastewater (VTW) was collected from a commercial tannery and characterized for physicochemical parameters, viz. pH (Part 4500-H + method B), chemical oxygen demand (COD; Part 5220 method C), biochemical oxygen demand (BOD as BOD_5 at 20 °C; Part 5210 method B), sulfates (SO_4^{2-}; Part 4500 method E) and suspended solids (total suspended solids dried at 103–105 °C; Part 2540 method D), and tannin content was measured by Folin–Ciocalteau phenol method (tannin and lignin; Part 5550 method B) as per standard methods 20th edition (APHA 1998). Samples were analyzed in triplicate, and the average values with standard deviation are reported. The aromaticity of the wastewater due to the presence of aromatic compounds in terms of UV_{280} measurements, before and after treatments, was determined by UV-2450 Shimadzu spectrophotometer using a 1-cm quartz cell.

Aerobic Biodegradation of Vegetable Tanning Wastewater

Batch experiments were conducted in 2 L reactors with working volume of 1.5 L. The initial biomass and COD were kept to maintain an F/M ratio of 0.15 as suggested in CPHEEO manual (1993) for extended aeration process. Aquarium air pumps and microporous air diffusers were adopted for aeration. Studies were carried out for a period of 72 h, and the samples were collected at intermittent time intervals for analysis.

Fourier Transform Infrared Spectrometry Analysis

Fourier transform infrared spectrometry (FTIR) analysis was carried out in order to assess the functional groups present in the VTW before and after aerobic treatment. The samples were filtered through 0.45-mm filter paper and dried and were pelletized with potassium bromide (KBr) in the ratio of 1:50. The pellets were subjected to FTIR analysis using transmission mode. The measurements were carried out in the mid-infrared range from 4000 to 500 cm^{-1}, with Thermo Scientific make Nicolet iS5 model FTIR.

Results

Characterization of Vegetable Tanning Process Wastewater

Vegetable tanning process wastewater (VTW) collected from a commercial tannery was characterized for pH, COD, BOD, tannin, sulfate, sulfide, suspended solids and dissolved solids as per the procedures given in standard methods (APHA 1998). The results are presented in Table 1.

Vegetable tannin wastewater was acidic in nature. The pH was always found to be around 3.5 because of the acids used in pre-tanning process like in pickling of hides. The BOD_5/COD ratio was 0.154, indicating that the VTW is not easily biodegradable. It was observed that almost 80% of the COD was found due to the presence of tannins. The BOD was always found to be about 15–20% of COD of the VTW. This is because of the polyphenolic nature of the tannin, which is

Table 1 Characteristics of vegetable tanning process wastewater

S. No.	Parameter	Average value ± standard deviation
1	pH	3.3–4.2
2	Chemical oxygen demand (COD), (mg/L)	23,140 ± 250
3	Biochemical oxygen demand (BOD_5), (mg/L)	3577 ± 150
4	Total tannin content (mg/L)	19,640 ± 300
5	Sulfates (mg/L)	7526 ± 100
6	Suspended solids (mg/L)	3670 ± 50
7	BOD_5/COD ratio	0.154

composed of complex organic constituents. This contributes to the non-biodegradable nature of VTW. The presence of sulfates can be attributed due to the addition of sodium sulfate salts during the pre-tanning process of liming. Spectrophotometric analysis at 700 nm for the presence of tannins and for identification of functional groups FTIR analysis was carried out. UV–visible and FTIR spectra are presented in Figs. 2 and 3.

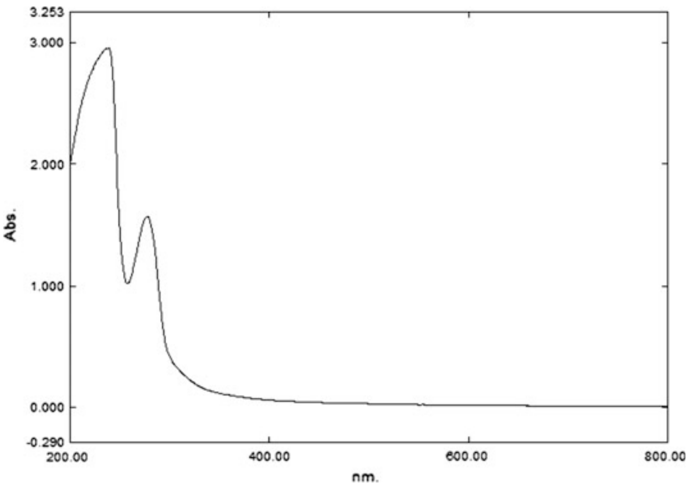

Fig. 2 UV visible spectrum of vegetable tannin wastewater

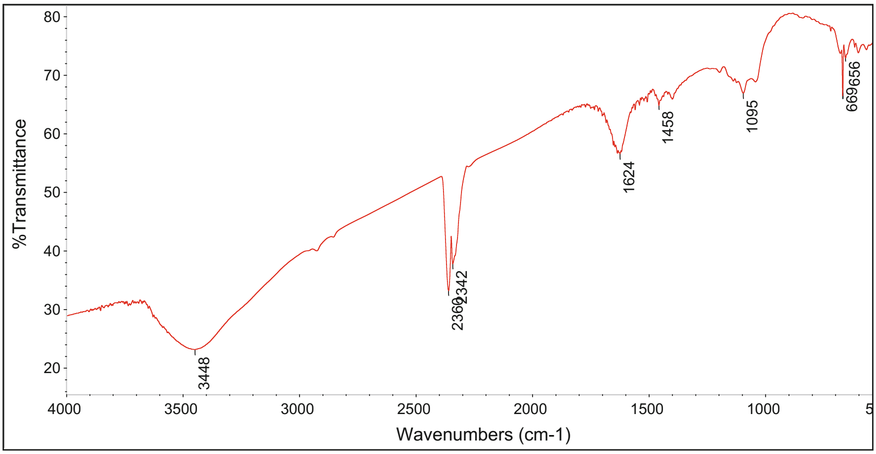

Fig. 3 FTIR spectrum of vegetable tanning wastewater

The UV–visible spectra of VTW showed two peaks at around 220 and 280 nm. The 280-nm peak corresponds to aromatic ring groups which are the predominant groups present in tannin. The 220-nm peak corresponds to amino groups. The presence of aromatic rings in tannin makes it resistant to biodegradation.

In the FTIR spectrum of VTW, the broad absorption band around 3400 cm^{-1} was due to O–H stretching and C–H stretching vibrations. The FTIR spectrum of VTW shows the peaks at 1624 and 1457 cm^{-1} which denotes C=C stretching vibrations present in alkenes and aromatics. CO stretching of carboxylic acid was observed at 1624 cm^{-1}. Peak due to O–H stretching was observed at 3448 cm^{-1}. Peak at 1095 cm^{-1} showed the stretching of C–O–H bond. Peak observed in the region of 2342 cm^{-1} was characterized by dissolved CO_2.

Aerobic Treatment of Vegetable Tanning Wastewater

The seed sludge used for aerobic process contained 7500 mg/L of mixed liquor suspended solids. Based on this, an F/M ratio, i.e., BOD/MLSS = 1125/7500 = 0.15, was maintained. Before adding to the sludge, the initial COD and tannin content of VTW were found to be 5000 and 3000 mg/L, respectively. The contribution of COD and tannin by the sludge was detected by using a control reactor with only the seed sludge. The efficiency of the aerobic treatment was monitored. The percentage removal of tannin and COD is presented in Fig. 4.

From the removal efficiency graph, it was seen that only 8 and 14% of tannin and COD removal occurred at the end of 4 h. After 24 h, it increased to 24 and 35% reduction in tannin and COD. It did not decrease to any significant level even after 72 h aeration. This is due to the binding of tannin to the cell wall of sludge microbe. Tannins cannot be removed through biodegradation since they are recalcitrant to microbial action. Generally, a residence time of 24 h is maintained in the aerobic

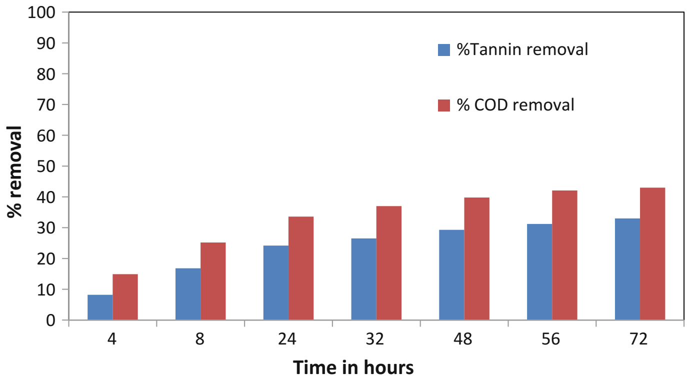

Fig. 4 Removal efficiency of tannin and COD

treatment units for the tannery wastewater in CETPs and ETPs. But in this case of non-biodegradable nature of wastewater, only 24 and 34% removal of tannins and COD was observed for 24 h. By further increasing the contact time, no substantial increase in the removal of tannins and COD was observed. Tannins present in VTW are composed of flavonoid units and are difficult to degrade by the aerobic microorganisms (Danhong et al. 2008). Tannins form strong cross-link with the cell membranes of microorganisms during their biodegradation process, which is responsible for their low biodegradability.

FTIR Analysis of VTW Before and After Aerobic Treatment

FTIR spectrum of VTW before and after aerobic treatment is shown in Figs. 5 and 6. The FTIR spectra of tannins showed transmittance in the range 1500–800 cm^{-1}, known as the “finger print” region. There was a prominent absorption band around 3400 cm^{-1} in all the spectrum of VTW. It can be associated with O–H stretching of intra-molecularly hydrogen bonded polymeric compound (Mistry 2009). The peaks around 1635 and 1400 cm^{-1}, in the fingerprint zone, could be due to C=C–C aromatic ring stretching.

After aerobic treatment, VTW showed that almost all the compounds present in it were not degraded effectively. The presence of aromatic ring stretching was still observed in the fingerprint region. In particular, the intensity of both the peaks 1635 and 1400 cm^{-1} due to aromatic ring remained the same in the treated effluent, indicating that the degradation was not efficient. These results clearly indicated that tannins should be made biodegradable so that the aerobic microorganisms are not hindered to carry out efficient biodegradation.

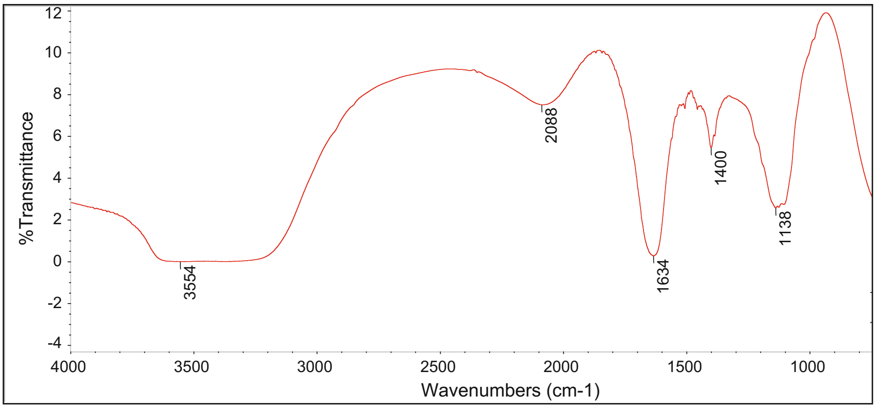

Fig. 5 FTIR spectrum before aerobic biodegradation

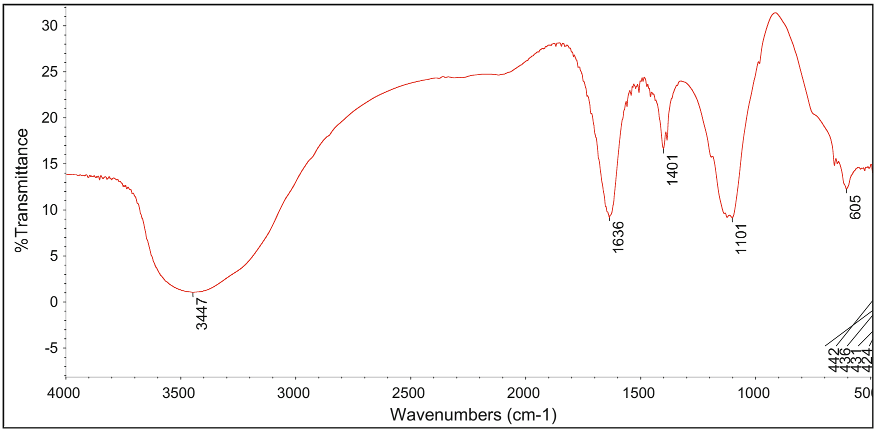

Fig. 6 FTIR spectrum after 24 h of aerobic biodegradation

Owing to the aromaticity/polyphenolic nature of tannin, the aerobic microorganisms are inefficient to degrade tannin completely. In order to change the nature of the compound, appropriate pre-treatment is necessary to increase the biodegradability of VTW.

Conclusion

Vegetable tannin wastewater (VTW) predominantly contains tannins which are recalcitrant to biodegradation. This VTW is characterized by high COD and color. Almost 80% of COD is due to the presence of tannins. The aerobic treatment studies show that the COD and tannin removal is not very significant even after 72 h of treatment. Only 24 and 34% removal of tannin and COD, respectively, was observed. The low removal efficiencies of COD and tannins are mainly due to binding of tannins over the cell wall of the aerobic microorganisms. The FTIR spectrum also revealed that there was no change in the 1635 and 1400 cm^{-1} aromatic stretch peaks before and after aerobic treatment.

It is therefore necessary to treat the VTW before aerobic biodegradation, using appropriate pre-treatment technologies such as application of advanced oxidation process or enzyme application, in order to increase the biodegradability. From this study, it is evident that there is no significant removal of COD and tannin by aerobic biodegradation process. This was attributed to the toxic effect of tannin toward the aerobic microorganisms.

Acknowledgements The authors wish to thank the Department of Biotechnology (DBT), New Delhi, for funding the research project. The authors also thank the Director, CSIR–Central Leather Research Institute (CLRI), Chennai, India, for permitting to publish this work. This research work was carried out as part of the PhD programme of the candidate Ms. Abirami Balakrishnan registered under Anna University, Chennai. Ms. Abirami Balakrishnan, Senior Research Fellow, would like to express her gratitude and thanks to DBT for funding this research project.

References

Aguilar CN, Rodríguez R, Gutiérrez-Sánchez G, Augur C, Favela-Torres E, Prado-Barragan LA, Ramírez-Coronel A, Contreras-Esquivel JC (2007) Microbial tannases: advances and perspectives. Appl Microbiol Biotechnol 76:47–59

APHA, AWWA, WEF (1998) Standard methods for the examination of water and wastewater, 20th edn. American Public Health Association/American Water Works Association/Water Environment Federation, Washington, DC, USA

Arana J, Tello RE, Dona RJM, Herrera MJA, Gonzalez DO, Perez PJ (2001) High concentrated phenolic wastewater treatment by the Photo-Fenton reaction—mechanism study by FTIR-ATR. Chemosphere 44:1017–1023

Banu JR, Kaliappan S (2007) Treatment of tannery wastewater using hybrid upflow anaerobic sludge blanket reactor. J Environ Eng Sci 6:415–421

Beccari M, Bonemazzi F, Majone Mand Riccardi C (1996). Interaction between acidogenesis and methanogenesis in the anaerobic treatment of olive oil mill effluents. Water Res 30:183–189

Bhat TK, Singh B, Sharma OP (1998) Microbial degradation of tannins—a current perspective. Biodegradation 9:343–357

Cassano A, Adzet J, Molinari R, Buonomenna MG, Roig J, Drioli E (2003) Membrane treatment by nanofiltration of exhausted vegetable tannin liquids from the leather industry. Water Res 37:2426–2434

CPHEEO (1993) Manual of sewerage and sewage treatment, 2nd edn. Central Public Health and Environmental Engineering Organization, Ministry of Urban Development

Danhong S, Qiang H, Wenjun Z, Yulu W, Bi S (2008) Evaluation of environmental impact of typical leather chemicals. Part II. Biodegradability of organic tanning agents by activated sludge. J Soc Leather Technol Chem 92(2):59–64

Dhaneswar RS (1990) Tannery wastewater treatment and disposal—state of art. J Ind Environ Prot 10:134–141

Etiegni L, Wakoli M, Ofosu AK (1999) Design of an efficient tannin extract effluent treatment system. Water Sci Technol 39:321–324

Field JA, Lettinga G (1992) Toxicity of tannic compounds to microorganisms. In: Hemingway RW, Laks E (eds) Plant Polyphenols: synthesis, properties, significance. Plenum Press, New York, pp 673–692

Gupta RK, Haslam E (1989) Vegetable tannin structure and biosynthesis in polyphenol in cereals and legumes-report. International Development Research Center, Ottawa, Canada

Hamdi M (1992) Toxicity and biodegradability of olive mill wastewaters in batch anaerobic digestion. Appl Biochem Biotechnol 37:155–163

He Q, Yao K, Sun D, Shi B (2007) Biodegradability of tannin containing wastewater from leather industry. Biodegradation 18:465–472

Kalyanaraman C, Kameswari KSB, Rao JR (2015) Studies on enhancing the biodegradation of tannins by ozonation and Fenton's oxidation process. J Ind Eng Chem 25:329–337

Liao XP, Shi B (2005) Selective removal of tannins from medicinal plant extracts using a collagen fiber adsorbent. J Sci Food Agric 85:1285–1291

Marsal A, Garcia EA, Ribosa I, Cot J, Manich A (2003) Removal of vegetable extracts by the use of activated clays. J Soc Leather Technol Chem 87:219–222

Mistry B (2009) A handbook of spectroscopic data chemistry: UV, IR, PMR, cNMR and mass spectroscopy. Oxford Book Company

Munz DG, De Angelis R, Gori G, Mori M, Casarci C Lubello (2009) The role of tannins in conventional and membrane treatment of tannery wastewater. J Hazard Mater 164(2–3):733–739

Ren S (2004) Assessing wastewater toxicity to activated sludge: recent research and developments. Environ Int 30:1151–1164

Routh T (2000) Anaerobic treatment of vegetable tannery wastewater by UASB process. Indian J Environ Health 20:15–123

Scholz W, Lucas M (2003) Techno-economic evaluation of membrane filtration for the recovery and re-use of tanning chemicals. Water Res 37:1859–1867

Svitelska GV, Gallios GP, Zouboulis AI (2004) Sonochemical decomposition of natural polyphenolic compound. Chemosphere 56:981–987

Tramsek M, Gorsek A, Glavic P (2006) The aerobic biodegradation kinetics of plant tannins in industrial wastewater. Chem Biochem Eng 20:285–291