JOURNAL OF ENVIRON. SCIENCE & ENGG. VOL. 48, No. 3, P. 225 -230, July 2006

Study on Leaching of Pollutants from Vegetable Tanning Residue

DEBABRATA MAZUMDER*+, SANTOSH BISWAS ** AND
PRATIP BANDYOPADHYAY***

The processing of heavy leather employs the vegetable tanning method involving use of tan liquor. The solid residue of this vegetable tanning process aggravates the water pollution by means of leaching of tannin and other associatedpollutants. Tannin is a biologically resistant compound causing several problems in animal body. The present study dealt with the pollution hazard arising out of leaching of pollutants from the open dumped vegetable tanning residue by rainfall washing.The concerned pollutants were pH, Chemical Oxygen Demand (COD), tannin,sulfate and chloride concentration. To explore the possible extent of contamination of these pollutants in the leached water, two different masses (2 kg and 3 kg) of tanning residue were employed. The results of the study showed that there was a continuous release of pollutants from the vegetable tanning residue. Moreover, there was no regular variation in various pollutant concentrations in both the cases solely due to non-homogeneity of the residue.

Key words : *Vegetable tanning, solid residue, run-off washing, leaching of pollutants*

Introduction

Leathers for shoe soles, heavy cases, harnesses and most upholstery applications are prepared by vegetable tanning. However, bottom shoe leather, due to entirely different reasons (poor water-repellent and wearing qualities), is almost given up by the shoe manufacturers, as being no more use in leather trade. When chrome tanning, a type of mineral tanning, was perfected, leather objects before 1886 were probably processed using a vegetable tanning method[2]. Objects tanned by a mineral tanning method are usually lighter-coloured than objects tanned using a vegetable-tanning process[1]. Indeed, vegetable tanning is much advanced today and scope of its further development is full of promise in respect of pollution potential. The principal chemical used in vegetable tanning is tannin extract. Many plant barks contain a bitter ingredient called tannin or tannic acid. It has the property of combining with proteins to form a compound that will not rot or decompose easily. The major sources of tannin are leaves, nuts, bark and woods of hemlock, oak, chestnuts and various other types of trees. Tannins comprise a group of chemical compounds found in many plant materials. The presence of tannins decreases the value of many potential food and forage crops due to the fact that they bind proteins, rendering them indigestible, as well as making the plant unpalatable. One such potentially valuable crop is *Sericea lespedeza*, a legume related to alfalfa, which grows particularly well in the south-eastern United States.

The chemical process of tanning occurs when the tannin molecules bond to the collagen fibrils and separate them[11]. Vegetable tanning is a slow process associated with placing the leather in baths containing the tannin materials. For this reason, vegetable tanned leather can take up to two years to produce. However, it is worthwhile, since it yields a tough, durable, and workable leather[3]. Upon completion of this process, oils and lubricants are applied to the leather to provide flexibility or for further manufacturing processes. The natural colour of vegetable tanned leather prior to finishing ranges from a pale brown to a reddish brown depending on the specific tanning agent used[13]. The overall life of the final product may be related to the tannin used in the processing of the leather. Likewise, the aging characteristics of the leather vary considerably depending upon the type of vegetative materials used[12].

The vegetable tanning is practiced in some tanneries where chrome tanning is not feasible due to various reasons. Although, natural material is used, the process generates a significant quantity of solid residue containing unutilized tannin, COD, etc. Upon exposure in the open environment, this residue is subjected to continuous washing by rainfall that produces a large volume of leachate. Subsequently, the leachate may contaminate the surrounding surface water source or get percolated to the ground water reservoir. It is already established that, tannins induce a negative response on animals when consumed. The effects can be instantaneous like astringency or delayed response like anti-nutritional or toxic symptoms like decrease in feed digestibility. As a whole, tannins have a major impact on animal nutrition on account of their ability to form complexes with numerous types of macromolecules like protein, carbohydrate, etc. Therefore, it is

*Senior Lecturer; **Ex-M.E. Student; ***Assistant Professor, Civil Engineering Department, Bengal Engineering and Science University, Shibpur, Howrah – 711 103 (W.B.), India
+Corresponding Author : E-mail: debabrata@civil.becs.ac.in; dmazumder@hotmail.com

essential to know the extent of pollution hazard caused by the leachate emanated from the vegetable tanning residue and explore a viable methodology for treating the same. The objective of the present study is to determine the pollution profile of the leachate generated from vegetable tanning residue in terms of characteristic parameters like pH, Chemical Oxygen Demand (COD), tannin, chloride and sulfate. With this aim, the present paper encompasses two sets of continuous leaching study carried out on two different amounts of tanning residue for considerable period of time.

Vegetable tanning waste management - Indian scenario

The tan liquor, tan sludge arising out of vegetable tanning can be made into solid or powder that can be further used as a reducing agent in the preparation of chrome tan liquor. It may also be used in anti-rusting, boiler cleaning and oil drilling compounds. The waste tan bark can be used for the purification of water, for the preparation of brown papers, chip boards, card boards and for fuel. The tan bark may also be mixed with crude oil or coal dust and thereby made into briquette to evolve heat energy. There is a possibility of using the tan bark by mixing with bitumen and then applying as the roofing material. Oxalic acid can be extracted from tan bark. The tan bark is also used in the field of white lead industry[5]. Rao and Dasnurkar (1968) applied alum and ferric chloride for the chemical treatment of vegetable tan liquor. Considerable good removals of COD and tannin were observed using alum, but were not comparable with the removals obtained in the ferric chloride treatment.

Mahajan (1985)[4] also supported that the vegetable-tan solids and sludge can be segregated and used as fuel in the recovery of furnace. Moreover, in vegetable tanning, an improved process like "pit tan" can be adopted to reduce the pollution load, which is found to be rapid and efficient. Pandey and Carney (1989)[6] stated that vegetable tan bark can be used as a fuel and the vegetable tan sludge may act as fertilizer and soil conditioner. Vegetable tanned shavings are also utilized for the manufacture of leather boards and allied products. Vegetable tanning sludge is sometimes dewatered and incinerated with other solid wastes.

Presently, the tanning industries are going for a tanning system associated with natural products like vegetable tan liquor. But, the vegetable tanning process contributes significant organic load, which is difficult to degrade. Therefore, several methods have been explored to treat the effluent liquor containing myrobalan, a widely used hydrolyzable tannin[9]. In this study, two methods have been adopted to reduce the pollution load of myrobalan liquor. The first method is applied to break down the vegetable tannins to simpler compounds by oxidative degradation using hydrogen peroxide. The second method facilitates precipitation of vegetable tannins using zinc sulfate as a precipitant. A 28% COD reduction was observed for the effluent liquor treated with H_2O_2 in the presence of Zeolite-Iron catalyst at 50ºC. When myrobalan liquor is precipitated with zinc sulfate at pH 10, COD reduction of 74% was obtained. By adopting precipitation followed by oxidative degradation in presence of Zeolite-Iron catalyst, additional COD reduction was observed resulting in total COD reduction of 96%.

Pickle-less vegetable tanning becomes vital to the tanners on account of environmental problems. An investigation was conducted to tan goatskins using commercially available vegetable tanning agent (wattle) at pH 8.0 – 8.5 (Saravanabhavan *et. al.*, 2004)[8]. To make a comparison, a partial pickling to pH 4.5 was also accomplished as control. In this study, no surface deposition of vegetable tannin in the leather was observed although tanning was carried out at higher pH. However, the exhaustion of vegetable tannin was observed to be higher in case of experimental process. The processed leather also showed slight improvement in hydrothermal stability in comparison to the conventionally processed leather. The performance of the leathers was observed to be at par with the conventionally treated leathers through physical and tactile evaluation. The process performance also revealed that the reduction in total solids, chloride and COD load of 73, 97 and 19 % respectively is possible from the identified waste streams.

Investigation of the tannery unit

A small vegetable tannery unit, situated near Park Circus, Kolkata was visited for studying the processes and sources of wastewater generation, and subsequent characterization. This tannery unit processes buffalo hides to make heavy leather for shoe soles or other similar uses. Presently, it produces about 10 – 12 Nos. of heavy leather per day. After conducting the usual processes up to deliming and bating, the hides are tanned with the babul-bark extract, as the tan-liquor. The tanning process generates a solid residue, which is dumped successively over the ground. Though all the processes have been looked upon, the sample was collected from this vegetable tanning residue to examine the pollution potential.

The processes

The buffalo hides are received in the tanneries in wet salted or dry salted condition to avoid bio-degradation. Then are subjected to the following process operations sequentially.

(i) *Washing and soaking* : In this process, hair, dart, salt, insecticides, blood and non-fibrous protein of the salted hides are removed and the moisture is lost during preservation and storage is restored.

(ii) *Liming and unhairing* : Unhairing is accomplished by the use of lime along with sodium sulphide . Thus, the effluent contains hair, high pH and high content of sulphide and sulphite.

(iii) *Fleshing* : In this process, the loosened hair, fat and flesh are removed by mechanical means resulting in "pelt". Proper conditioning of the pelt at this point is essential to obtain the desired characteristics in the final leather. The time duration varies depending on the batch load.

(iv) *Deliming and bating* : After the fleshing operation, deliming and bating are carried out to reduce the swelling and remove the protein degradation products, thus making the hide ready for tanning.

(vi) *Vegetable tanning* : The method followed in this unit is popularly known as "Bag Tanning". Here the hide coming out of delimimg and bating is stitched to make a bag, with an opening at top and suspended from a pole or a branch of a tree. Crushed vegetable tanning material (babul bark dust) is stuffed inside and filled with water. The tan liquor is gradually extracted from the babul bark dust and diffuses into the hide to fix-up the protein materials. At the same time, leaching of tan liquor also takes place due to fluid pressure, which is collected in a mud pit underneath the bag. A portion of this leached liquid is transferred to the bag, after every few hours. This operation is continued for one or two days and then the bag is made inside out releasing the tanning residue. The bag is now filled with babul bark dust and water again to tan the inside portion for another one day. After removal of residue, the bag is hanged-off and unstitched followed by putting the hide into the sunlight for drying.

(vii) *Finishing process* : In this process, a mixture of finishing agents (commonly known as "Naspal /Hara + Radhi Oil + Gur") is spread over the hide and rolled properly for 5 to 8 hours. Again the hide is put into the sunlight for final drying and pressed to convert into the leather. The process flow sheet is shown in **Fig. 1.**

Materials and methods

The leaching study was accomplished to find out the pollution hazard caused by washing out from the vegetable tanning residue. It was also aimed to explore the residence period of different pollutants in the leachate, i.e. how long time any pollutant takes to come out from the tanning residue. At the same time, efforts were made to estimate the total volume of water to be passed through a specific amount of residue for achieving pollutant free water. Therefore, parameters like pH, Chemical Oxygen Demand (COD), tannin, chloride and sulfate concentration were measured at various time intervals, i.e. at different discharge volumes. Subsequently, a concentration profile was drawn for each parameter to express the leaching of pollutants with the progress of time.

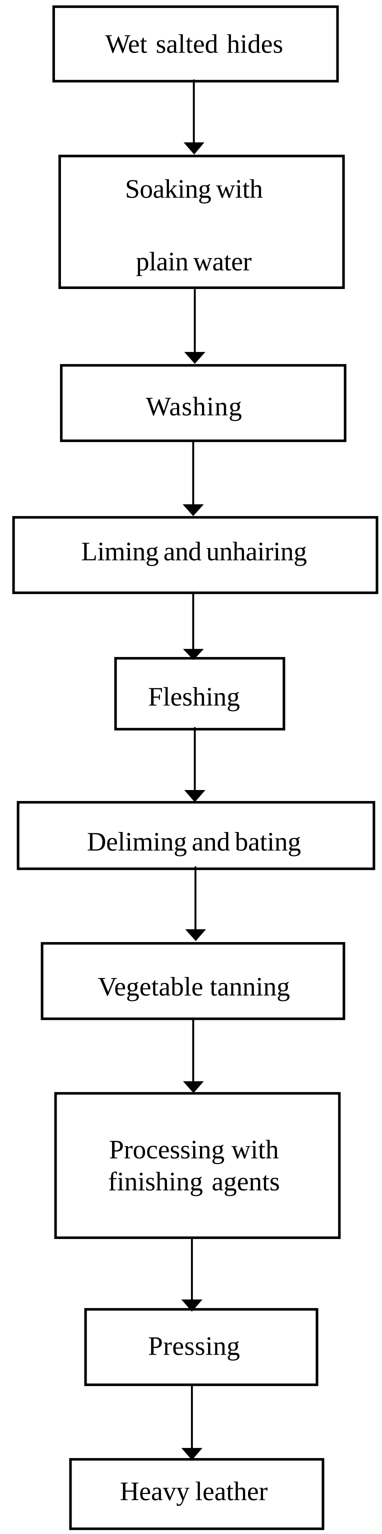

Fig.1 : Various processes involved in the vegetable tannery unit

Vegetable tanning residue

The vegetable tanning residue was collected from the open dump in the tannery unit visited during the present study. The colour of the residue appeared to be medium brown. The residue was taken in wet form and the moisture content was measured as 38%. After bringing it to the laboratory, the moisture got loosened. Subsequently, the field capacity (the maximum moisture content the sample can retain) was also measured as 63%. The specific gravity of the residue was measured as 1.22 by means of simple water displacement method. Before loading to the column reactor unit, homogenization was done on the entire residue content by hand mixing.

Leachate generating reactor unit

The leaching test was done on a column reactor unit made up of PVC and with a diameter and height of 100 mm (I.D) and 810 mm respectively. The bed volume of the column reactor unit was 6.11 L.The reactor was arranged with flow control system in both the inlet and outlet. One screen was wrapped around the inner part of the inlet to prevent entry of coarser particles to the unit. The system was entirely closed in such a way that both the upflow and downflow movement of water can be attained. The reactor unit was supported on a metallic tripod base. The water was allowed to flow by means of a tullu pump with a revolutionary speed of 25 rpm. The leachate sample was collected on a bucket placed below the outlet pipe. The bucket was graduated and therefore the volume of water passed was measured at different time periods. The set-up with column reactor unit is shown in **Fig. 2**.

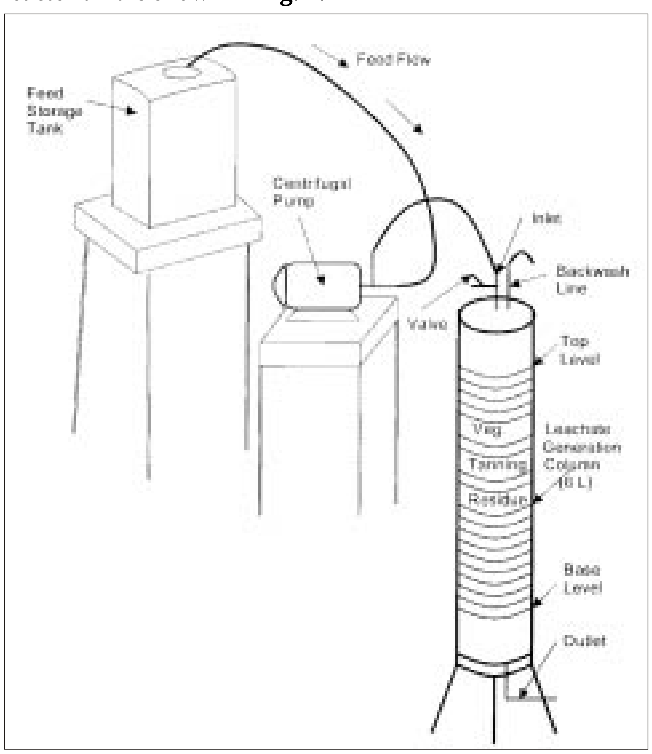

Fig. 2 : A schematic diagram of the reactor set-up

Leaching study

The leaching study was performed by passing about 250 and 570 L of water through the bed of 2 and 3 kg dry tanning residue respectively. Due to percolation of water with a rate of about 0.25 L per minute, different pollutants were washed out and their concentrations varied in the effluent. After a long time or passing of a large volume of water, the concentration of a pollutant was reducing gradually. Since, the flow rate might have changed due to clogging within the column, total volume of water was considered as a governing parameter. One simulation was made that if there is an average rainfall over a catchment area under consideration, causing a definite run-off and percolating through a pit comprising of tanning residue, then it would derive a pollutant concentration as obtained from the concentration profile. Therefore, it would be possible to determine the time of targeted washout of a pollutant, if the intensity of rainfall is known.

Parameters measured

In the present study, following relevant parameters were measured : (i) pH, (ii) Chemical Oxygen demand (COD), (iii) sulfate (SO_4^{-2}), (iv) chloride (Cl^-) and (v) tannin concentration. pH, Chemical Oxygen Demand, Cl^-, SO_4^{-2} and tannin concentration were regularly monitored in the leaching study. All the parameters were measured as per the methods illustrated in the Standard Methods (1989)[10].

Results and discussion

The leaching study was conducted with 2 kg and 3 kg of tanning residue and the relevant parameters like pH, COD, tannin, chloride and sulfate concentration were measured along the volume of water passed. The variation of pH with respect to the volume of water passed is shown in **Fig. 3**. The COD concentration was measured in the effluent for 2 kg and 3 kg of tannin residue at regular time interval and plotted in **Fig.4**. Similarly, the variation of tannin in the effluent from both 2 kg and 3 kg of tanning residue is shown in **Fig. 5**. Besides, sulfate concentration in the effluent was also measured and plotted with respect to the volume of water passed as shown in **Fig. 6**. Finally, chloride concentration in both the effluents was plotted with respect to the volume of water passed as shown in **Fig. 7**.

The results of analyses indicated that the pH values of the leachate samples varied from slightly acidic to slightly alkaline in nature (**Fig. 3**). At the beginning, it was acidic and subsequently it became almost 7.0 with the progress of time in both 2 kg and 3 kg of tannin residue. The COD concentrations in both the cases were found to fluctuate abruptly at the initial stage, but after a number of cycles, these showed a steady-state value (**Fig. 4**). For example, in case of 3 kg of tannin, the COD value reached to a constant level after passing water volume of about 540 L, whereas for the second case (2 kg of

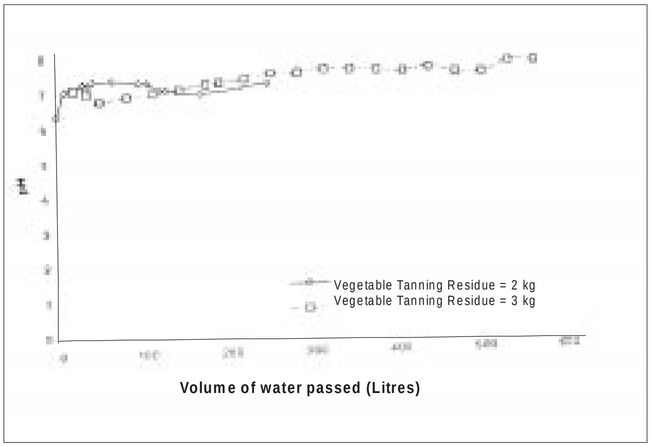

Fig. 3 : Variation of pH in the leachate for different amounts of tanning residue

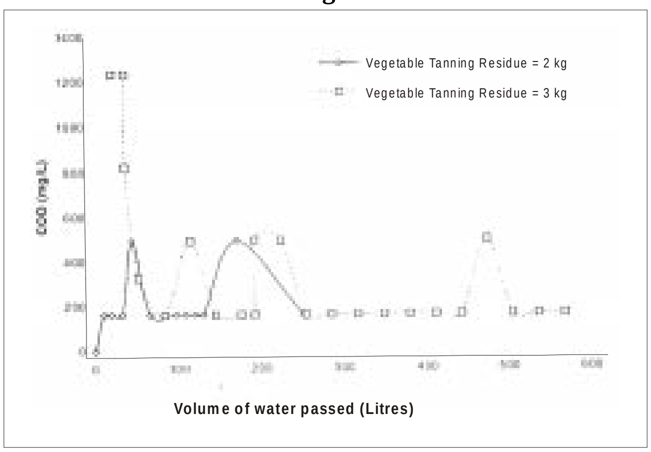

Fig. 4 : Variation of COD in the leachate for different amounts of tanning residue

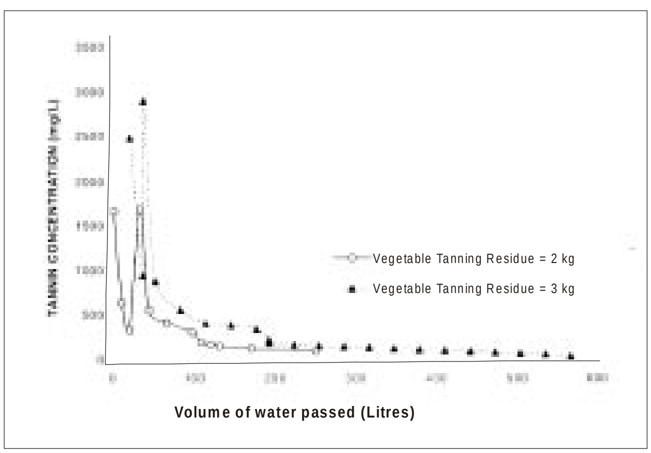

Fig. 5 : Variation of tannin in the leachate for different amounts of tanning residue

tannin residue), the same COD concentration was attained after passing about 250 L of water. In both the cases, the steady-state concentration appeared to be near about 180 mg/L.

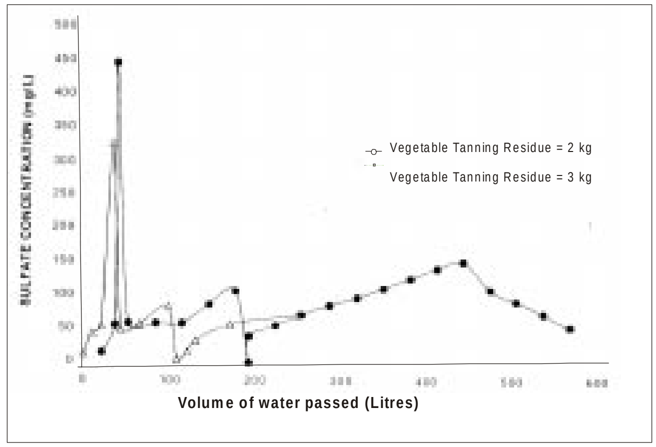

Fig. 6 : Variation of sulfate in the leachate for different amounts of tanning residue

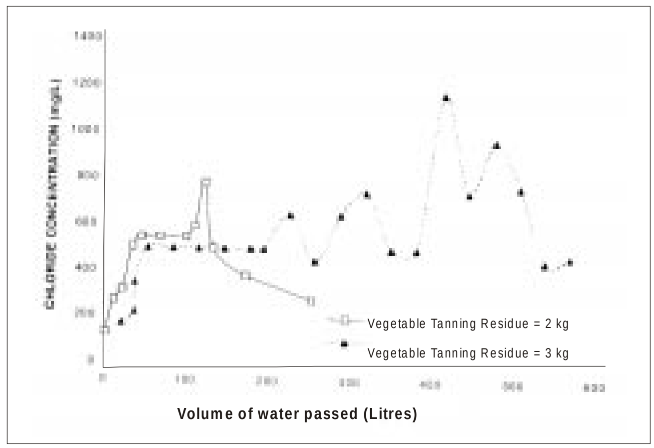

Fig. 7 : Variation of chloride in the leachate for different amounts of tanning residue

Obviously, 3 kg of tanning residue contributed higher amount of COD. But, it sharply decreased to a value of about 190 mg/L after passing about 80 L of water as in case of 2 kg tanning residue. Sudden increase in COD of wash water was envisaged for both the cases, particularly when the continuous operation was resumed after a break. Apart from that the materials became more and more saturated with the progress of time causing change in porosity and thereby lesser volume of water passed per unit time. It was prominently observed for higher amount of tanning residue. Moreover, the initial effluent COD concentrations under 2 kg and 3 kg of tanning residue were nil and extremely high respectively, which revealed that the materials were not uniform over the entire bed.

The effluent tannin concentrations were also varied significantly up to 100 and 200 L of water volume passed under 2 kg and 3 kg of tanning bed respectively (**Fig. 5**). Beyond these values, tanning concentration gradually diminished, producing a long tail in case of 3 kg tanning residue bed. However, long tail was not observed in case of 2 kg tanning residue bed due to limited passing of water over a short period. From the trend of the concentration profile, it appeared that, tannin concentration would be nil after a prolong operation. A wide variation in effluent sulfate concentration was observed under both 2 kg and 3 kg of tannin residue (**Fig. 6**).

Sulfate concentrations reached to maximum values of about 325 mg/L and 450 mg/L after passing only 30 and 35 L of water under 2 kg and 3 kg tanning residue respectively. Obviously, the high sulfate concentration was attained after discontinuation of operation for overnight that led to high sulfate yield in the leached water. Surprisingly, no sulfate concentration was traced after passing 100 and 200 L of water under 2 kg and 3 kg of tanning residue respectively. It was observed that the sulfate concentration profiles were almost same in nature for both 2 kg and 3 kg of tanning residue. Higher mass of residue, i.e. 3 kg required more volume of water in turn more time to yield same sulfate concentration in the wash water. For instance, about 75 mg/L of sulfate was detected after passing about 98 and 130 L of water in case of 2 kg and 3 kg tanning residues respectively. A wide fluctuation in sulfate concentration was observed at the initial stage possibly due to non-uniform distribution of sulfate compounds within the residue.

The chloride concentration found to vary to a great extent for both 2 kg and 3 kg of tanning residues (**Fig. 7**). The chloride concentrations gradually increased to steady-state values of 550 and 500 mg/L in case of 2 kg and 3 kg of residues respectively. Subsequently, the chloride concentration reached to maximum values of 800 and 1175 mg/L under 2 kg and 3 kg of residues respectively. It is to note that in case of 2 kg residue, the chloride concentration progressively decreased during the passage of water volume from 100 to 250 L. It appeared to be not matching with that for 3 kg tanning residue for which the extent of fluctuation was remarkable. This is possibly due to intermediate accumulation of chloride salts within the void spaces of the residue mass, which was washed out irregularly. Obviously, the scope of such retention is more in case of 3 kg mass of residue than 2 kg mass due to higher bed depth.

Conclusions

1. The composition of the vegetable tanning residue is not uniform and it requires a better homogenization before planning for any treatment.
2. There is a more or less steady-state condition in terms of chemically oxidizible organic matter, i.e. COD.
3. There is practically no significant chloride contamination from the vegetable tanning residue.
4. There is practically no sulfate contamination from the vegetable tanning residue.
5. The pH contamination from the residue is almost nil.

References

1. Canadian Conservation Institute, Care of alum, vegetable, and mineral tanned leather. *CCI Notes*, **8(2)**, 1-4 (1992)
2. Color Plus, About leather: Why leather goes bad and what to do about it, *Color Plus Web Site* (1997), http://www.colorplus.com/book/book.htm
3. Guldbeck, P. E., Leather: Its Understanding and Care, Nashville : American Association for State and Local History (1969)
4. Mahajan, S.P., Pollution Control in Process Industries, Tata Mc Graw Hill Publishing Company Limited, Fifth Reprint (1985)
5. Naudamma, Y., Wealth from Leather Waste, Proceedings of Symposium on Utilization of Byproducts of Leather Industry, CLRI, Madras (1960)
6. Pandey, G. N. and Carney, G.C., Environmental Engineering, Tata Mc Graw Hill Publishing Company Limited, Sixth Reprint (1989)
7. Prabhakara Rao, A.V.S. and Dasnurkar, D.D., Disposal of Tannery Waste Effluents, JIE (I), Public Health, Vol. 49 (1968-69)
8. Saravanabhavan, S., Thanikaivelan, P., Raghava Rao, J. and Unni Nair, Balachandran, Studies on the Development of Pickle-less Vegetable Tanning, *Journal of the American Leather Chemists Association*, **99(7)**, 281 – 288 (2004).
9. Sharli, A., Madhan, B., Raghava Rao, J. and Unni Nair, Balachandran, An Approach for the Treatment of Vegetable Liquor containing Hydrolysable Tannins, *Journal of the American Leather Chemists Association*, **98(10)**, 381 – 387 (2003).
10. Standard Methods for the Examination of Water and Wastewater, Prepared and Published Jointly by American Public Health Association, American Water Works Association and Water Pollution Control Federation; Sixteenth Edition (1989).
11. Storch, P.S., Curatorial Care and Handling of Skin Materials, Part 1 : Tanned Objects, Conservation Notes, **17**, 1– 4 (1987)
12. Thomson, R. S., A history of leather processing from the medieval to the present time, In : Calnan, C. and Haines, B. (eds.), Leather : Its Composition and Changes with Time. Northampton : The Leather Conservation Center, 12–15 (1991)
13. Waterer, J. W., A Guide to the Conservation and Restoration of Objects Made Wholly or in Part of Leather, New York : Drake Publishers, Inc. (1971)