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REMOVAL OF NATURAL TANNIN FROM TANNERY WASTEWATER USING SEQUENCING BATCH REACTOR

KANCHANABHAN, T.E., ARUTCHELVAN, V., SEKARAN, G. AND ABBAS MOHAIDEEN

Dept. of Civil Engineering, Annamalai University
Annamalai Nagar- 608 002, India
Dept. of Environmnetal Technology, Central Leather Research Institute, Adyar, Chennai- 600 020, India
Dept. of Chemical Engineering, Sathyabama Institute of Science and Technology, Jeppiarnagar, Chennai- 600 119, India

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ABSTRACT

The present study was concerned with the biological treatment of tannery wastewater. The treatment of tannin laden wastewater in Activated Sludge Process of low residence time (36 hours) does not yield the desired results. Hence mere has been a search for the development of methodology for the elimination of tannin under elongated periods of aeration. Sequencing Batch Reactors (SBR) is a unique method of biological treatment plant, which is essentially a modified form of activated sludge process, *Jn* the present investigation, a Sequencing Batch Reactor (SBR) of 5 litre capacity was fabricated and used The reactor treated high strength wastewater and the cumulative COD and Tannin removal efficiency was 77 % and 88 % respectively. The removal efficiency of tannin and COD in wastewater were controlled by tannin concentration, hydraulic residence times, micro and macronutrients. The degradation of tannin was confirmed through the enzyme assay test.

INTRODUCTION

Tannins are naturally occurring plant polyphenols. Their main characteristic is mat they bind and precipitate proteins. The word tannin is very old and reflects

atraditional technology. 'Tanning" (waterproofing and preserving) was the word used todescribe the process of transforming animal hides into leather by using plant extractsfrom different parts of different plant species. Tannins also occur in vascular plant tissues such as leaves, needles, bark, heartwood, grasses, seeds and flowers (Haslam, 1989).

Tannins exist primarily in Condensed and Hydrolyzable forms. Historically, interest intannins has stemmed from industrial uses (the tanning of hides or as an ingredient in adhesives) and impacts (wine, tea and feed quality). In recent decades, tannin research has expanded to natural products (where much progress has been made in terms of tannin structure and taxonomic surveys) and in a much more limited fashion to forestry. Vegetable tanning is the process of converting putrescible hides and skins into imputrescible leather using naturally occurring plant phenolics known as vegetable tannins. Various types of leather such as Sole, Kattai and Bunwar are using vegetable tannins. Of the total vegetable tannins available, 90 % are accounted for leather industry and in this 65 % goes to heavy learner production. These vegetable tannins are water soluble polyphenolic compounds and are mostly amorphous, astringent and feebly acidic in nature.

Activated sludge process is the most widely used biological wastewater treatment process in treating sewage and a variety of industrial wastewaters. During the early development of the activated sludge process in the United Kingdom by Adera and Lockett around 1914, plants were operated using Fill and Draw or interrupted batch feed methods. The concept of operation is that of a single reactor basin using repetitive cycles of aeration, settlement and discharge of treated effluent. By the late 1970s, the generic SBR was well established and many small plants were in operation. A major development took place in 1978 with the incorporation of a pre-react zone within the SBR to control filamentous sludge bulking. In me late 1980's the suspended growth treatment process were used in the treatment of land leachates and industrial discharges, which contained high levels of hazardous waste, hi 1985, the focus shifted to on site and in situ bioreclamation of soil contaminated with petroleum hydrocarbons, phthalates, trinitrotoluene etc. In the 1990's emphasis is on projects for the biological treatment of ground water contaminated with benzene, toluene, trichloroethylene etc. All these effects used periodic process. The SBR was adopted for the work, since all the operations like fill, react, settle and draw can be carried out in a single tank. Also it would be more suitable in areas where flow is fluctuating in quantity. The SBR with its many merits would be a good option among other conventional methods of treatment like extended aeration since it would require less area. It could be used as system for treating tannery effluents.

MATERIAL AND METHOD

SBR Reactor

Acrylic material was used for the fabrication of SBR of volume 5 litres. The reactor was provided with a sludge settling zone, clear water zone, outlet port

and sludge with drawl port The oxygen needed for the oxidation of organics in wastewater was provided in the form of air supplied from the bottom of the reactor through spargers (5 numbers) at a pressure of 0.5 kg/cm^2.

Wastewatcr

The wastewater used in the present study was transported from a leather industry engaged in processing raw to El leather. The wastewater collected from the industry was transported to the laboratory immediately hi refrigerated vessels. The wastewater was screened to remove coarse floating solids and fine grit like sand. The settled wastewater was fed to the SBR through a peristaltic pump to avoid shock load to the microbial mass.

Start up of SBR

The sludge required for the seeding of the reactor was organized from the activated sludge process employed for the treatment of wastewater discharged from an industry processing raw goat/sheep skins to E.I leather. The sludge was acclimatized to the wastewater hi stage wise addition of tannin concentration of 50 mg/L- After the tannin concentration had reached the required level, the wastewater was applied as a bulk with the required addition of micro and macronutrients.

Aeration Exptfimcnt

The wastewater was adjusted to the neutral pH and tho acccgsafy»mioro and trace- -elements were added to avoid the nutrient limitation during the course of the aeration process. Aliquot of samples had been withdrawn through me sampling ports at regular time interval and the samples were analyzed for COD, tannin, pH, and BOD to assess the performance of the SBR. At the end of the set HRT the samples were withdrawn and analyzed for COD, BOD, pH and tannin etc.

Polyphenol Oxidase

Tannin the macro molecular compound present in the wastewater was metabolized by the organism intra cellular. Hie poly phenol oxidase concentration was determined at regular interval of time. Hie poly phenol oxidase* was determined in accordance with the following procedure.

*** Substrate - DOPA**

1. Preparation of 8 mflB molar solutions

Weight of DOPA Powder = volume * molecular wt of DOPA * molarity /1000.
If SO ml of solution is needed men (Depending on the no of samples to be tested) Volume = 50 ml.
Molecular wt of DOPA = 197.19mg.

Molarity =8xlO~^{3}.

Weight of DOPA Powder = 50 x 197.19 x 8 x 10 ~^{3} /1000

=0.0788 g

2. Calibration of Spectrophotometer

Table - 1
A- HRT- 32 Hours

Characteristics	Initial	3 hrs	6 hrs	24 hrs	28 hrs	32 hrs
pH	7.6	8.0	7.6	8.24	7.9	8.0
SVI	24	21	21	21	21	21
Tannin	117.88	42.85	30.85	29.64	20.00	13.21
COD	558.8	264.8	176.40	98.0	58.82	58.83
Polyphenoloxidase (u/m)		388	118	488	202	

Table - 2
HRT- 24 hrs

Charactristics	Initial	2.5 hrs	21.5 hrs	24 hrs
pH	8.19	8.84	8.81	8.84
SVI	20	18	18	19
Tannin	90	40	32.16	32.16
COD	529.18	235.29	196.07	156.86
Polyphenol Oxidase (u/ml)		312	238	144
BOD	200.8			58

C- HRT- 16 hours

Charactristics	Initial	16 hrs
pH	7.6	8.0
SVI	20	21
Tannin	132	67.80
COD	578.8	289
Polyphenol oxidase (u/ml)	470	50
BOD	224	108.37

D- HRT - 8 hours

Charactristics	Initial	2 hrs	4 hrs	6 hrs	8 hrs
pH	7.14	8.10	8.18	8.38	8.17
SVI	26	26	27	27	27
Tannin	166.42	119.26	94.28	85	69
COD	764.7	647.05	588.23	529	529
Polyphenoloxidase (u/ml)	173	213		134	156
BOD	286.60				194

All units except pH and polyphenol oxidase are in mg/l.

Distilled water was taken in a cuvette and the absorbance of spectrophotometer was calibrated to zero. 2.5 ml of DOPA was taken in cuvette and was also calibrated to zero.

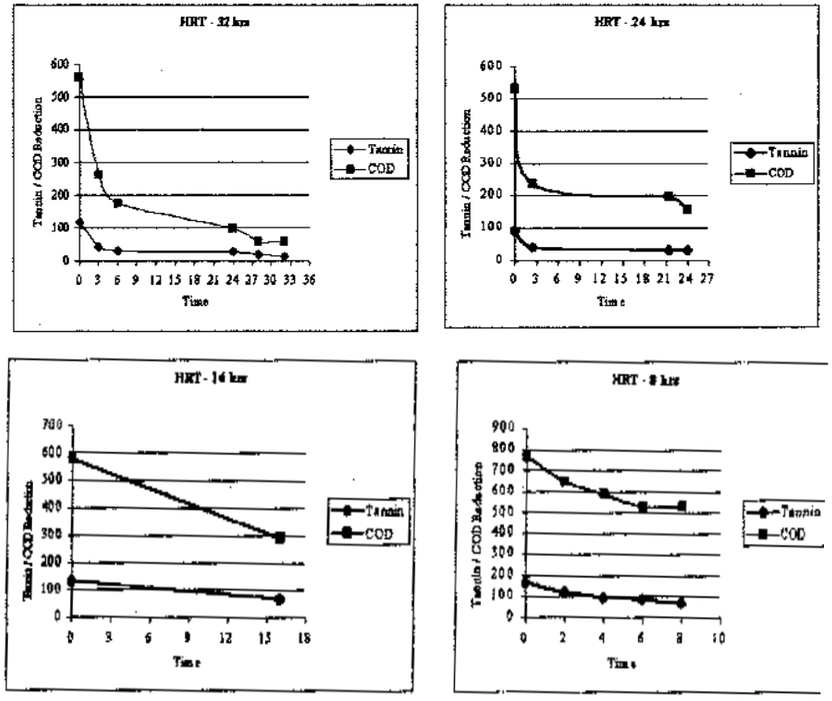

Fig. 1- The reduction of Tannin and COD with respect to various HRT

3. Analysing the solution or sludge.

A known quantity of sample from the reactor was taken and centrifuged at 4000 rpm for 5 minutes. The centrifuged sludge was washed with phosphate buffer, men taken in a beaker and sonicated for 5 to 10 min. The same was centrifuged again and the supernatant was used for analysis as follows: 0.5 ml of supernatant was added to the DOPA taken in the cuvette. The lid was closed and the initial absorbance reading (at zero min.) was noted Then the reading was noted after 1 min, 2min, 3 min, 4 min and 5 min.

4. Enzyme activity

= Change in absorbance (2 min to 1 min.)
(or any minutes depending on value / (0.001 * 0.5) = _____ units /ml

RESULTS AND DISCUSSIONS

Tannin, the polymeric compound having molecular weight in the range 500-3000 mg appeared to be degraded at a very slow rate and the intensity of colour increased with the length of the aeration period The fragmentation of the molecule requires the assistance of the enzymes secreted by aerobic bacteria in the biological unit The activated sludge process was less efficient in controlling

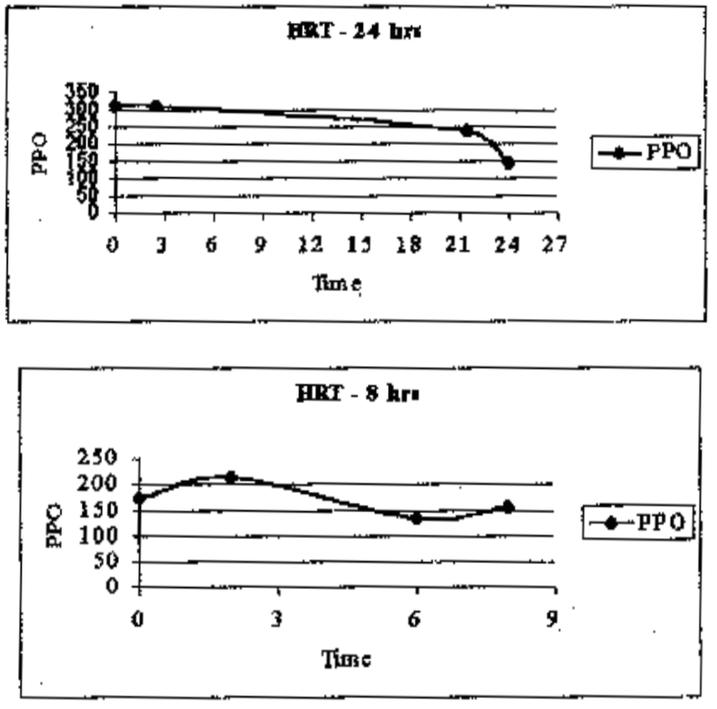

Fig. 2- The Polyphenol oxidase (PPO) concentration for various HRT

the discharge of the tannin in me wastewater because me removal of tannin from the wastewater follows asymptotic approach after certain period of time. Hie volume of the reactor to be provided to match the asymptotic approach was very difficult, which will account for huge investment and maintenance costs. SBR serve to reach (he desired concentration by allowing the degradation to take place in a given reactor, to follow (he linear decrease with time of aeration. Hence, the investment cost towards the aeration equipments and civil structures were decreased considerably.

Fig I Illustrates the removal of tannin and COD over the period time at different hydraulic Retention Time (HRT). The results suggest that the tannin removal was not absolute even after aeration for 32 hours while at HRT 16 hours the pollution parameters had reached the substantial level of reduction. This indicates mat the tannin was hydrolyzed and metabolized to a certain extent and the non-hydrolysable Residual tannin is available.

The fraction of the compound becomes recalcitrant. This was evidenced from the determination of polyphenol oxidase (PPO). Fig fl shows (he variation of polyphenol oxidase as a function of time. The PPO concentration was the maximum in the initial aeration period and becomes very less at HRT Shows and at 16 hours while the same was relatively at higher concentration at HRT

24 hours and 32 hours. The secretion of PPO at elated HRT was considerable while it was repressed at low HRT.

CONCLUSION

Tannin, the poly compounds used considerably in tanning industries pose environmental concern as it affects the ground water quality due to non-degradable fraction of the tannin in the treated wastewater. The accumulation of biological resistant tannin fraction likely to adsorb onto the biomass in the Activated Sludge Process leading to non micro flora could be averted by reducing the HRT and by differentiating extended aeration reactors into SBR. However, SBR show retarded synthesis of poly phenol oxidase responsible for the degradation of tannin at low HRT. These shortcomings may be sorted by integrating SBR with ICR (Immobilised Cell Reactor) of low residence time.

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