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Comparative account of Batch Reactor and Anaerobic Baffled Reactor in Methanogenesis of Spent Chrome Liquor

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ABSTRACT

*Tannery effluent contains large amount of biodegradable organics, which can be degraded easily by methanogenic bacteria. The high content of COD, BOD, Total solids, Total suspended solids etc. indicate its potential for methanogenesis. The biological treatment of the spent chrome liquor through Batch reactor (BR) and Anaerobic baffled reactor (ABR) reduces the highly toxic content of total chromium to 99.9%. The present study emphasizes on the degradation of organic matter along with decrease in the load of pollutants to considerable extent by both the reactors. After 55 days of operation COD, Total Chromium, Chloride, Total solid, Sulphate reduction of 83.5%, 99.9%, 66%, 90% and 59% respectively were achieved in Batch reactor in comparison to 91%, 99.9%, 70%, 93% and 71% respectively in ABR. Besides this biogas yield with methane gas %(v/v)in Batch reactor and Anaerobic baffled reactor were 0.165*m^3*/kg COD removed with 57-59% and 0.186*m^3*/kg COD removed with 60-63% respectively.*

Keywords: BR, ABR, COD, BOD, DSS, GNSP.

INTRODUCTION

One of the serious threats to environment is the pollution caused by indiscriminate disposal of industrial effluents. These effluents contain a large amount of toxic metal ions and appreciable organic matter posing serious environmental and health risks. Tanneries are classified under the category "Red most pollution industry" whose waste is ranked the most polluting of all other individual wastes [1]. It is probably the first industrial waste problem of mankind. Most of the tanneries in India are located near the river banks of the Ganga river system in North India because leather processing requires large amount of water. Indian tanneries process sheep and goat skin, cow and buffalo hides using both vegetable and chrome tanning process. About 80% of tanneries uses chrome tanning process as it provide superior finish and luster to the leather. Spent chrome liquor contains organic and inorganic matter both in solution and suspension forms composed of flesh, lime, protein, sulphides, fatty materials, salts etc [2]. In addition to this, high content of total solids, total suspended solids, total dissolved solids, chloride, sulphate and highly toxic chromium (in trivalent and hexavalent forms) are also present. High level of chromium in plants inhibits seed germination and subsequent seedling growth. Visual symptoms of chromium toxicity in plants are stunted growth, poorly developed root system, curled and discolored leaves [3], leaf chlorosis, narrow leaves [4] chlorotic bands on cereals [5], yield reduction [6-7]. Chromium in hexavalent form is extremely toxic, carcinogenic and may cause death to humans and animals. The discharge of tannery effluent into the Ganga river at a current rate will be serious threat to human life and aquatic ecosystem[8]. The maximum acceptable chromium concentration for agricultural soils in many different European countries is in the range of 50-200 mg kg^{-1}[9]. Various low cost natural adsorbents have shown their potential to reduce the toxic content of chromium. In this present study, Groundnut shell power (GNSP) has been used, which reduces the chromium content to a certain extent as well as other pollutants present in spent chrome liquor. As tannery effluent has large amount of biodegradable wastes, its generation and disposal without adequate treatment results in widespread environment pollution. In comparison to aerobic treatment, anaerobic digestion proves to be more advantageous due to its high efficiency, capacity to attain high organic loading rate as well as potential energy saving. Interest in biomethanation as an energy saving waste treatment has led to the development of wide range of anaerobic reactor designs. These includes Upflow anaerobic sludge blanket reactor, Hybrid reactor, Anaerobic fluidized bed reactor, Anaerobic filter reactor, Expanded granular sludge bed reactor, Upflow Anaerobic fixed film reactor etc.

In the present investigation Batch reactor and Anaerobic baffled reactor has been used for anaerobic treatment of spent chrome liquor.

MATERIALS AND METHODS

The spent chrome liquor used for methanogenesis process was procured from leather complex Jalandhar, Punjab (India) at their common disposal site. The sample was collected three times within two hours interval in 15L capacity of plastic cans and stored in refrigerator. The composite spent chrome liquor was analysed for its physiochemical characteristics. All the Analytical grade chemicals were used for measuring waste water parameters. Century digital pH meter (model CP901) was used to record the pH of the effluent and influent at various stages. The procedure of APHA[10] was followed to find out various parameters such as COD, BOD (3days) Total dissolved solids, Total suspended solids [10], Chloride, Sulphides, Sulphate and Total chromium [11].

Groundnuts were collected from local market. Their shell was removed and powdered to obtain particle mesh size of 36 British standard sieve (BSS). Digested Sewage sludge (DSS) was obtained from Municipal sewage wastewater treatment plant Okhla, New Delhi and screened through 2 mm sieve before use. The total suspended solids (TSS) and volatile suspended solids (VSS) in the DSS were found to be 30 g/l and 9 g/l respectively.

Batch Reactor (BR)

A 6L capacity aspirator bottle having a mouth and small opening at bottom through cork was selected as a batch reactor. There was also the arrangement of feeding the influent and extraction of the treated influent attached to the peristaltic pump.

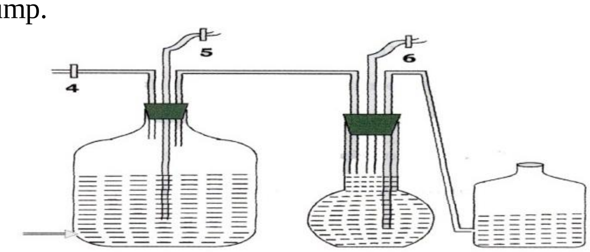


Fig 1. Batch Reactor

1. Aspirator bottle
2. Gas collecting bottle
3. Displacement reservoir
4. Influent pipe

5. Effluent pipe
6. Gas exit

Corks were fitted at top and bottom through which glass tubes were tapped. To prevent gas leakage and to maintain anaerobic conditions, the opening of reactor was sealed by m-seal. The volume of the gas was measured by methyl orange solution displacement method. The gas collection unit consisted of 3.5L capacity bottle which was connected with aspirator bottle. The gas collecting bottle was initially filled with methyl orange solution completely. As the gas produced enters in the gas collecting unit, it displaces the methyl orange solution. This displaced solution was collected in measuring jar which was kept open to atmosphere to maintain the pressure in jar and aspirators bottle same as atmosphere pressure. The schematic configuration of batch reactor is given in Fig.1.

Anaerobic Baffled Reactor (ABR): A laboratory scale anaerobic baffled reactor was fabricated using Plexiglass. ABR consists of 3 chambers and each chamber was separated by a vertical baffle. The working volume of the reactor was 10L (l 38 cm; b12 cm; h 29.5 cm). The three chambers represents three different stages of anaerobic treatment i.e. hydrolysis, acidogenesis and methanogenesis. On one end there is a hole at the bottom for the introduction of influent into first chamber. The treated effluent comes out of the methanogenic chamber on the other end from third chamber.

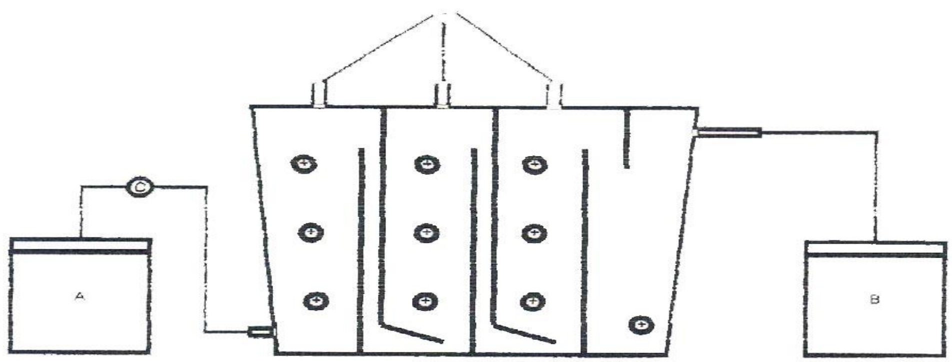
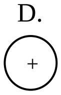


Fig 2: Anaerobic Baffled Reactor

A. Influent.
B. Effluent.
C. Peristaltic pump.
D. Gas outlets.

 Sampling port.

There are also present three sampling ports in each of the chambers through which treated wastewater can be withdrawn at any time. The gas produced in the methanogenic chamber enters into gas collecting unit throuh the outlet. The schematic configuration of ABR is given in Fig 2.

RESULTS AND DISCUSSION

Characteristics of spent chrome liquor: Spent chrome liquor from common disposal site contained lesser amounts of chromium and sulphate as compared to those present in the effluent of individual unit. This was because of the lime treatment given to the effluent so as to settle chromium and other contents as flocculent. The collected sample showed a great variation in its physicochemical characteristics, and has to be characterized every time. Various parameters in spent chrome liquor are given in Table1.

Table 1. Characteristics of Composite Spent Chrome Liquor

pH	7.30-8.20
COD	8000-12000
BOD_3	1100-1300
TSS	10000-13000
TDS	11000-12000
TS	21000-25000
Chloride	6500-7500
Sulphide	80-100
Sulphate	3200-3500
Ammonical Nitrogen	110-140
Protein Content	45-65
Alkalinity	6000-8000
Total Chromium	200-225
Phosphate	Nil
Volatile fatty acid	1130

All parameters are in mg L^{-1} except pH

Treatment of spent chrome liquor using low cost natural adsorbent GNSP: In order to combat the hazards of chrome liquor as well as its suitability for anaerobic degradation, it was subjected to treatment with low cost biosorbent, Groundnut Shell Powder (GNSP). From the results, it was seen that the concentrations of highly toxic total chromium and sulphate were reduced by 63% and 77% respectively. This might be due to adsorption site provided by the adsorbent to the adsorbate. The COD of the spent chrome liquor increased to approximately double of its initial amount because leaching of water soluble organic compound such as proteins, fats, soluble sugars, etc. All of these materials contain carbon than can be converted to carbon dioxide biologically, thus exerting an oxygen demand[12]. Total solids were also increased by 12-18% of its initial amount. The increase in total solids were due to slight increase in leaching as compared to decrease in the content of sulphate, chromium etc. The chloride level also decreased by 27-31%. The pH of the GNSP treated effluent (7.48) was also suitable for the growth of anaerobes in the methanogenic process. The results of GNSP treatment are given in Table 2.

Table 2. Effects of GNSP Treatment on Composite SpentChrome Liquor

Parameters	Before Treatment	After Treatment
pH	7.70	7.48
Total Chromium	216	80
Chloride	6800	4700-5000
Sulphate	3500	800
COD	8000-12000	18000-22000
TS	24500	27440-28910

All parameters except pH are in mg L^{-1}.

Setting up of Batch reactor and Anaerobic baffled reactor: The treated effluent was diluted and mixed with Digested Sewage Sludge (DSS) in the ratio of 3: 2.5 (v/v)[13] so as to have resultant COD of 2000 mg L^{-1}[13]. The acclimatization of the DSS was done in three reactors separately under batch condition. The three reactors were sealed and their gas outlets were clipped. The pH was maintained in the range of

6.8-7.3. This process took 45 days to reach steady state. After reaching steady state, feed solution was prepared by adding 200 mg L^{-1} urea and 200 mg L^{-1} ammonium ortho-dihydrogen phosphate into both the reactors with COD equivalent to approximately 2000 mg L^{-1} at retention time of 5 days. The conditions of setting up of Batch Reactor and Anaerobic Baffled Reactor is given in Table 3.

Table 3. Setting up of batch reactor and Anaerobic Baffled Reactor

	BR	ABR
pH	7.15	7.15
COD (mg/l)	2000	2000
Working volume (L)	4	10
Diluted effluent: DSS	3:2.5	3:2.5
Urea (mg/l)	200	200
Ammonium othrodihydrogen phosphate (mg/l)	200	
Citrus peels (g) (crude pectin)	50	50 (in methanogenic chamber only)

Comparative account of Batch Reactor and Anaerobic Baffled Reactor in methanogenesis of spent chrome liquor: The performance of the two reactors to treat tannery effluent was assessed. The measurement of reduction in organic load of pollutants and percentage of gas production was done after 35 days and 55 days of operation. The treatment efficiency of three reactors were calculated on the basis of three important parameters

1. Quality percentage of methane gas
2. Biogas yield
3. Reduction in organic matter.

The percentage of methane gas obtained in Anaerobic baffled reactor was 60-63% after 55 days of operation as compared to 57-59% in Batch reactor. This large quantity in ABR might be due to separation of all the three phases of methanogenic activity in ABR so that production of high amount of acid during acid genesis does not hamper the activity of methanogenic bacteria to a considerable extent.

The biogas yield obtained was 0.186 m^3kg^{-1} COD removed in ABR reactor as compared to 0.165 m^3 kg^{-1} COD in Batch reactor respectively after 55 days of operation. The increase in biogas yield may be due to adjustment in the growth of methanogenic bacteria towards shock load by the separation of methanogenic phase from acidogenic phase.

Reduction in the organic matter, particularly in terms of COD is one of the important parameters which would decide the efficiency of methanogenic process. An initial amount of 2000 mg L^{-1} in the influent was reduced to 180 mg L^{-1} i.e. 91% reduction after 55 days of operation as compared to 83.5% in Batch reactor.

Regarding the inorganic constituents, total chromium [Cr(VI) and Cr(III)], both the reactors performed almost to the same extent i.e. the removal of complete chromium below detection limit. This was due to reaction of hexavalent and trivalent ions with the other negative ions and settling down as slats in the sludge[14].

As far as chloride is concerned, the initial chloride content of 1143 mg L^{-1} was reduced to 343 mg L^{-1} i.e. 70% reduction after 55 days of operation as compared to 66% in Batch reactor. This reduction was due to the complex reactions of chloride ions with other anions settling down as sludge[14]. In terms of sulphate, the removal was 71% in ABR as compared to 59% in Batch reactor.

Biodegradability of the effluent depends on the total solids and volatile solid content. Large amount of inorganic constituents contribute to high solid content and these inorganic materials are the major pollutants[15]. A maximum of 93% Total solids reduction was achieved in ABR as compared to 90% in Batch reactor.The results of percentage removal of pollutants and methane content are given in table 4.

Table 4. Comparative account of anaerobic reactors under Similar conditions

Parameters	**Batch Reactor**		**Anaerobic Baffled Reactor**	
No. of Days	35	55	35	55
COD	57%	83.5%	60%	91%
Total Chromium	75%	99.9%	82%	99.9%
Chloride	40%	66%	45%	70%
Total Solids	60%	90%	62%	93%
Sulphate	43%	59%	59%	71%
Biogas yield m^3/kg COD removed		0.165		0.186
Methane gas % (v/v)	57-59%		60-63%	

APPLICATIONS

The present study indicates the efficiency of the treatment of tannery effluent and maximized production of biogas. This treatment could very well be extended for field scale operation in tanning industry.

CONCLUSIONS

From the results, it was concluded that performance of Anaerobic baffled reactor in terms of reduction of organic and inorganic constituent was more than Batch Reactor and hence demonstrated greater potential in reducing the pollution effect of tannery waste water besides generating a fuel in the form of methane. Hence, ABR was selected for the continuous treatment in further study.

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