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Anaerobic Treatment of Rubber Latex Processing Effluent for Energy Production and Pollution Abatement

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A B S T R A C T

Rubber latex processing plants generally produce large quantity of effluents which contains high amount of degradable organic matter characterised by high BOD, COD and TS. The rubber latex processing effluent (RLPE) is often not properly treated in many rubber latex processing plants before discharged to land. This may affect the local environment resulting in adverse effects on public health. Hence adoption of a suitable and affordable technology for waste stabilization and energy generation is needed. In order to develop a suitable anaerobic bioreactor, the biomethanation characteristics should be known and hence such a study was taken up. Even though RLPE was acidic it was found that RLPE could be subjected to biomethanation using cow dung slurry as inoculum. Even at a lower RLPE: inoculum ratio, the system could be started up and yield appreciable levels of biogas coupled with – per cent TS reduction. The use of formic acid for latex coagulation is a better option as the effluent treatment process is trouble free and facilitates anaerobic digestion to produce methane rich biogas to be used to dry rubber sheets

Introduction

Among the plantation crops, rubber holds a prominent position in Kerala and is a main source of livelihood for many farmers of the state (Karunakaran and Vijayan, 2020). Natural rubber is used in diverse applications owing to its many desirable qualities including large stretch ratio and resilience (Chauhan *et al.*, 2020), toughness, minimum hysteresis, elasticity and durability (Jansomboon *et al.*, 2020). Hence, they are of high demand in the automobile industry, preparation of surgical rubber goods and many other goods which have become a daily necessity for people (Guan *et al.*, 2020). Natural rubber consists mainly of cis-1,4-polyisoprene, protein and fatty acids (Azadi *et al.*, 2020). It is mainly harvested by tapping the rubber trees and obtained in the form of a milky colloidal suspension called rubber latex (Kang *et al.*, 2020). Tapping is the process of making incisions manually on the bark of rubber trees using special knives (Kamil *et al.*, 2020). The collected latex mixed with water is coagulated under control conditions using formic acid. The coagulated latex is then allowed to set in a dish. Once the latex is fully set the excess water is squeezed out using pressing rollers so as to convert it into thin sheets. These rubber sheets are then dried by open sun drying or in biomass fired drying chambers, often called 'smoke chambers' (Nhu Hien *et al.,* 2017). The important primary products of the rubber processing industry includes concentrated latex, block rubber and ribbed smoked sheet rubber (Jawjit *et al.*, 2010).

In the light of net zero carbon footprint the natural rubber production is increasing (Tanikawa *et al.,* 2020) but at the same time the rubber latex processing effluents (RLPE) released is causing water, soil and air pollution (Nhu Hien *et al.*, (2017) and Brooks *et al.*, (2017)). The fact that 6-7 m^3 of water is required for processing one tonne of concentrated latex (Jawjit *et al.,* 2013) explains the quantity of effluent disposed by each rubber processing industry. It is estimated that by 2024 an additional plantation of 4.3–8.5 million ha is needed to meet the growing industrial demand (Warren-Thomas *et al.,* 2015). This tells the urgency of solving the environmental problems that can be raised by RLPE. The latex processing effluent mainly contains BOD, COD, NH_3-N, organic nitrogen and phosphate (Jawjit and Liengcharernsit, 2010), in complex mixture form with varying compositions (Arimoro, 2009). The chemicals such as Ammonia and Diammonium phosphate used for latex preservation causes human toxicity and eutrophication respectively (Jawjit *et al.*, 2013) and the H_2S present in RLPE can make river water unsafe for drinking up to several hundred miles downstream from the disposal point (Martinez-Hernandez and Hernandez, 2018). In addition these chemicals on open water bodies causes huge depletion of dissolved oxygen (Atagana *et al.,* 1999; Brooks *et al.,* 2017) thus affecting the related ecosystem components, agricultural activities and human health (Martinez-Hernandez and Hernandez, 2018). Larger processing centers have treatment facilities, but many of the small and medium rubber latex processing units let out these effluents to open lands or water bodies without proper treatment. On open treatment, the degradation of volatile fatty acids can produce greenhouse gases whereas proper bio-methanation can produce energy (Tanikawa, *et al.,* 2020). This emphasizes the need for engineering a sustainable and environment friendly system which can last for a long-term for treating RLPE (Fox *et al.,* 2014).

Kerala state of India, known as 'God's own country' in the world tourism scenario is famous for its natural beauty and earns a significant share of its GDP from tourism (Fenn *et al.*, 2020). Kerala is ranked first in India for annual rubber production of 490460 tonnes in 2018-2019 (MCI, 2019), and there is a serious concern on the environmental problem due to discharge of untreated RLPE. In addition to the pollution due to RLPE, the drying of rubber sheets in biomass fired dryers called 'smoke chambers' are also causing air pollution. If the RLPE is subjected to anaerobic treatment, the pollution due to effluent discharge can be significantly controlled and the biogas generated can be utilized to dry rubber sheets so as to replace the biomass which is burned in inefficient smoke chambers. Hence an investigation was taken up for studying the possibilities of anaerobic treatment of RLPE with the intension of energy production in the form of a methane rich biogas.

Materials and Methods

To understand the basic characteristics of RLPE relevant for anaerobic digestion the pH value, Total Solid content (TS), Volatile Solid content (VS), Biochemical oxygen demand (BOD) and Chemical oxygen demand (COD) were observed as per the procedure detailed by (APHA, 2017).The pH of RLPE samples were measured using a digital pH meter MK-VI with pH range of 0-14 pH and a resolution of 0.01. Oven drying method was adopted for determining TS and was expressed in mg L^{-1} dry basis. To obtain VS of the sample the residue from TS was ignited in a muffle furnace at 550 ˚C for 15 to 20 minutes. The difference between TS and ash obtained was taken as VS (mg L^{-1}). Similarly, five-day BOD and COD was determined using standard procedure outlined by APHA (2017).

In order to understand the biomethanation characteristics and possibilities for anaerobic digestion of RLPE a batch anaerobic digestion study with 4 treatments replicated thrice was conducted (Fig. 1and 2). Water displacement method was adopted to measure the daily gas production from experimental digesters. Five litre capacity plastic digesters connected with 3 litre capacity graduated cylinders used as water displacement meters were set up for the experiment as shown in Fig 1. Cow dung was used as inoculum for the 3 treatments whereas effluent collected from a conventional biogas plant was used for the 4^{th} treatment. Daily biogas production was measured for 75 days. The pH values and TS were noted before and after digestion. The four treatments for the experiment were as below:

T0 – Fresh Cow dung : water (1:1)
T1 –Cow dung mixed with RLPE in the ratio (1:1)
T2 – Cow dung mixed with water and RLPE (1:1:2)
T3 – Effluent from conventional biogas plant: RLPE (1:1)

Results and Discussion

The results of the investigations on the characteristics of rubber latex processing effluent (RLPE) and the batch anaerobic digestion of RLPE are presented and discussed in the sub sections below.

Characteristics of RLPE

The results of the analyses done for various Physico-chemical characteristics of RLPE samples are given in Table 1. RLPE was very dilute waste water with TS and BOD, in the ranges of 9281-12892 mg/L and 2040 - 3106 mg/L, respectively. The pH was in the acidic range and was observed to vary in the range between 5.1 and 6.1 during the period of investigation. These results are comparable with the values obtained by Ramanan and Vijayan (2015) and Brooks (2017). Ramanan and Vijayan (2015) reported TS of 9700 mg/L, BOD of 4300 mg/L and a pH of 5.7 ± 0.30 for RLPE. In a survey conducted by Chaiprapat and Sdoodee (2007) on 20 rubber processing factories in Pathalung and Songkhla provinces of Thailand, it was found that the BOD of RLPE ranged between 680–7384 mg/L and TS between 715–13,813 mg/L where as RLPE tested by Promnuan *et al.,* (2019) had a pH of 5 and TS of 4619 mg/L. The RLPE used for the present study also had characteristics in the range of values in these reports.

The Volatile Solid content was found to be 2356 mg/L and this value was also similar to the reported value of 1845 mg/L by Jacob (1994) and 2260 mg/L by Promnuan *et al.,* (2019) for rubber sheet processing effluent. Bovas and James (2010) reported a BOD of 3599 mg/L and TS of 3090 mg/L for rice mill effluent, which could be successfully subjected to anaerobic treatment. The COD of RLPE were observed to be 5856 mg/L and was higher than rice mill effluent. BOD: COD ratio of 0.44 obtained in this study showed good biodegradability and possibility for anaerobic digestion. Bovas and James (2010) observed a BOD: COD ratio of 0.88 for rice mill effluent, whereas James and Kamaraj

(2009) reported a ratio of 0.57 for sago factory effluent. In both these cases good biodegradability was achieved by them. Promnuan *et al.,* (2019) reported a COD of 6667mg/L and Chaiprapat and Sdoodee (2007) reported a COD range between 1118 and 11,105 mg/L for RLPE, which were supportive of the values obtained in the present study. This wide range variation of values reported by Chaiprapat and Sdoodee (2007) can be explained by the result of Brooks (2017), that the characteristics of RLPE depends on the quality of the raw material used and processing process adopted by the industry.

Batch anaerobic digestion of RLPE

Most organic effluents are easily biodegraded. Possibilities for biodegradation of RLPE were important to evolve a proper anaerobic treatment protocol for anaerobic digestion in a high rate bioreactor. Atagana *et al.,* (1999) reported RLPE had the ability to support microbial population.

Table.1 Characteristics of RPLE

Sl. No.	Parameters	Mean value
1	Total solids, mg/L	11086.7
2	Volatile solids, mg/L	2356
3	Biochemical Oxygen Demand, mg/L	2572.9
4	Chemical Oxygen Demand, mg/L	5856
5	pH	5.6
6	BOD : COD ratio	0.44

Table.2 Parameters of batch digestion study

Sl. No.	Treatments	Total solids (TS), mg/L		TS Reduction (%)	pH	
		Initial	Final		Initial	Final
1	T0	27382	11920	56.46	7	8.1
2	T1	15520	6600	57.47	6.7	7.8
3	T2	19524	9550	51.08	6.9	7.8
4	T3	6527	4527	30.63	7	8.2

Fig.1 Experimental set up for batch anaerobic digestion

Fig.2 Arrangement of experimental digesters for batch anaerobic digestion

Fig.3 Daily biogas production in batch anaerobic digestion study

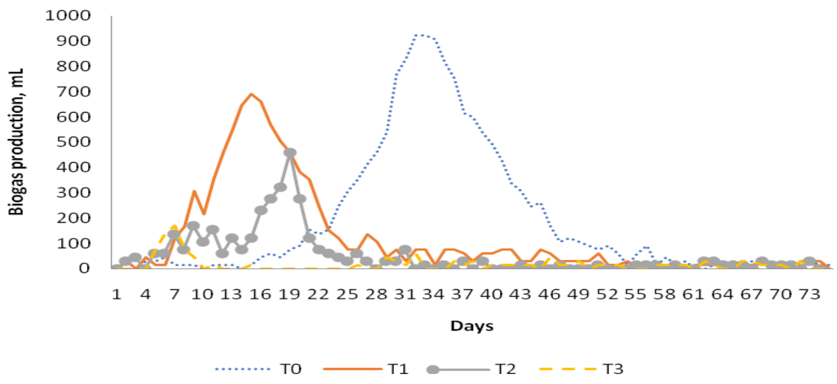
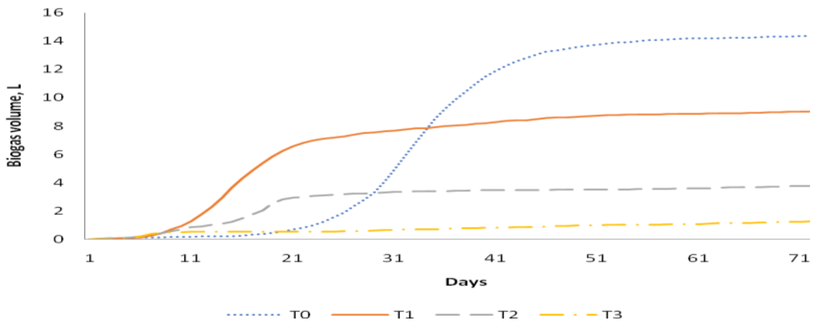


Fig.4 Cumulative biogas production in batch study



From Table 2 it can be seen that T0, the control treatment exhibited a TS reduction of 56.46%. Similar TS reductions of 57.47 and 51.08 per cent were obtained for T1 and T2 respectively. Bovas and James (2010) observed 60.2% TS reduction for a batch digestion study of rice mill effluent which was conducted for duration of 135 days. TS reduction in T3 was 30.63 % which was lower than other treatments. The result from T3 showed that the inoculum used in T3 was inferior to ordinary cow dung slurry to be used as inoculum.

The pH in all treatments was observed to be raised at the end of digestion. The final pH of all the treatments reached the values in the range 7.8-8.2. A similar trend was observed by Ramanan and Vijayan (2015) also. From Fig 3 it can be seen that T0 had slow gas production in the beginning and picked up gas production after two weeks. The peak gas production of 923 mL occurred on 32nd day and started declining after 34th day. Up to 49th day gas production was good, later biogas production reduced to below 100 mL. This indicated that a Hydraulic Retention Time (HRT) of 50 days will be suitable for conventional anaerobic systems for energy production from cow dung in similar climatic conditions.

Treatment T3, inoculated with effluent from biogas plant did not exhibit gas production after the first week and the daily gas production remained very low throughout the remaining period of the experiment which lasted for 75 days. It can be inferred that effluent from existing anaerobic systems should be used as inoculum only after ascertaining its methanogenic capacity. Treatment T1, mixture of cow dung and RLPE (1:1), showed maximum gas production of 690 mL on 15th day and declined to below 100 ml after 24th day. T2, mixture of cow dung, water and RLPE (1:1:2), obtained peak gas production of 460 mL on 19th day and rapidly declined to very low levels. This indicated that 25-day HRT can be recommended for conventional anaerobic systems for the treatment and energy production of RLPE. During the study both T1 and T2 showed maximum gas production within 3 weeks and thereafter decreased. The treatment T3, obtained 160 mL of daily gas production on 8th day which was the maximum daily gas production in T3. The difference of biogas production between T1 and T2 was due to the change in solid contents. T0 and T1 were different not only by the TS content but also on the ratio of partially soluble and insoluble compounds in cow dung compared to more soluble organics in RLPE.

The cumulative biogas production from different treatments is shown in Fig. 4. The control treatment had more cumulative biogas production of 14.43 L. Total gas production in T1, T2 and T3 are 9.07 L, 3.80 L and 1.26 L, respectively. Biogas productivity of 3.60, 2.26, 0.95 and 0.315 L/L was achieved for the treatments T0, T1, T2 and T3, respectively. These differences in cumulative biogas production are due to the difference of total solids in the treatments.

This study concluded that RLPE could be subjected to biomethanation and cow dung can be used as inoculum. Even at a lower inoculum ratio the system could be started up yielding substantial amount of biogas coupled with good TS reduction. Treatment T3 proved that if effluent from an existing biogas plant is used as inoculum, it should be ascertained that the system is functional with active microbial population.

Chen *et al.,* (2008) was of the view that ammonia concentrations in the range between 1.7–14 g/L can partly inhibit methanogenesis. Nguyen and Luong (2012) was of the view that ammonia present in RLPE affects its biodegradation, while Jariyaboon *et al.,* (2015) found that RLPE had 9 g/L of ammonia nitrogen and it did not seriously affect the fermentation activity but H_2SO_4 used for coagulating the skim latex increased the sulfate concentration in the RLPE and that inhibited the methanogenic activity. Rahman *et al.,* (2019) also had a similar opinion with regard to sulfate concentration as the result of using H_2SO_4 and found that it resulted in increased levels of H_2S in the biogas produced. Promnuan and O-Thong (2017) suggested the use of sulphate reducing bacteria to remove sulfate before anaerobic treatment. Jariyaboon *et al.,* (2015) proposed a two-stage system with acidogenic phase in the first stage and methanogenic phase in the second stage. They were of the view that RLPE cannot be properly digested using a single stage digester. But the present study was taken up in a latex processing plant where only formic acid was used for coagulation of latex. Hence it can be inferred that the use of inorganic acids like sulphuric acid for rubber latex processing may be discouraged.

Xu *et al.,* (2013) studied the effect of inoculum obtained from anaerobic digesters using municipal sewage, food waste and dairy waste in digesting corn stover using a batch digester. It was found that corn stover inoculated with dairy waste in the ratio 1:2 gave the best results. Neves *et al.,* (2004) found that inoculums with higher specific methanogenic activity can give better methane yields and lesser variation on increasing the feed inoculum ratio. The results from the present study shows that RLPE from latex coagulated with formic acid can be subjected to biomethanation in a better way if inoculated with cow dung slurry. This indicated that cow dung as inoculum had good specific methanogenic activity. Sulphate reducing bacterial consortium may be required only if the latex is coagulated with inorganic acids like H_2SO_4. It was also observed that small amounts of ammonia will not affect anaerobic digestion considerably. This result obtained in the study is also supported by the findings of Jariyaboon *et al.,* (2015). James and Kamaraj (2002) has described various anaerobic high rate systems for organic effluent treatment. Many previous studies confirm the possibility of anaerobic high rate bioreactors for the treatment and energy conversion of organic effluents (Najafpour *et al.,* (2006), Elangovan and Philip (2009), Bovas and James (2010),Young *et al.,* (2012), Kim *et al.,* (2017), Ittisupornrat *et al.,* (2019) and Rahman *et al.,* (2019)). Hence studies on the use of high rate anaerobic systems for RLPE may be taken up so as to reduce the HRT further and make the system cost effective.

From the present study it could be concluded that RLPE could be subjected to biomethanation and cow dung slurry can be used as inoculum. Even at a lower inoculums: RLPE ratio, system could be started up yielding substantial amount of biogas coupled with good TS reduction. Further investigations are required to test the possibilities for high rate anaerobic treatment of RLPE. The use of formic acid for latex coagulation is a better option as the effluent treatment process is trouble free and facilitates anaerobic digestion to produce methane rich biogas to be used to dry rubber sheets.

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