COMPARISON OF PHYSICAL AND CHEMICAL TREATMENT METHODS FOR RICE MILL WASTEWATER AND SUBSEQUENT BIOMETHANE AND AMMONIA GENERATION

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Abstract— A small scale rice industry produces about 7000 Liter effluent per day having a Chemical Oxygen Demand ranging from 4000 to 7000 ppm. The effluent contains mainly long chain carbohydrates which is ideal source of biogas production. In this research work, physical and chemical methods for treatment of rice mill waste were investigated and compared. Filtration, centrifugation and adsorption were used in physical method where as chemical methods included lime treatment and hydrogen peroxide treatment. Filtration and centrifugation did not reduce COD values because impurities were mainly in form of dissolved solids. Adsorption using bottom ash obtained from boiler located at rice mill reduced COD of effluent by ca. 28%. Lime treatment ranging from 0.1 gm lime per 100 ml effluent to 2 gm per 100 ml effluent reduced COD from ca. 23% to 43%, respectively. Hydrogen peroxide treatment gave best results of all treatments with ca. 98% reduction in COD values. Sludge production was ca. 60% less in peroxide treated effluent as compared to lime treated effluent. The sludge obtained from lime and peroxide treatment methods was further added to a batch anaerobic digester for biogas production. Lime treated sludge reduced biogas production of a stable biogas producing digester due to increase in pH from ca. 7.2 to 11.5. Biogas production was enhanced markedly when hydrogen peroxide treated sludge was added to anaerobic digester as compared to lime treated sludge.

Keywords— Rice Mill Waste; Adsorption; Lime: Hydrogen Peroxide; Biogas.

I. INTRODUCTION

Variety of wastes generated by industrial and domestic activities has increased tremendously worldwide. Estimated waste generation in the world was about 12 Billion tons in year 2002 which is expected to increase to 19 billion tones per year by 2025 [1]. India alone generates about 350 Million tons of solid waste comprising of agricultural and organic waste [2]. This waste is generated mainly by agricultural activities, municipal solid waste, waste from food processing industries and industries handling agriculture products. A recent report of central pollution control board of India estimated that about 38.254 Million liter per day of sewage was generated by class 1 cities and class 2 towns. This sewage comprises of municipal and industrial waste out of which only 35% is treated and there is a yawning gap of 65% of untreated sewage [3].

Rice is the prime cereal crop in India which occupies an area of ca. 42 million hacter with an annual production of 76 million tons. This amounts to nearly 42% of the country's food grain production. One of the dominant rice processing technique is parboiling which requires large quantities of ground water. A typical small scale parboiled rice manufacturing industry requires groundwater in the range of 900 to 1200 L per ton of rice paddy. During the process the water becomes unusable with high COD, BOD, TSS and TDS loads [4]. This effluent is discharged directly to paddy fields or drained to river just after primary treatment. This rice mill effluent has a typical Chemical Oxygen Demand (COD) ranging from ca. 2000 mg/L to ca. 7000 mg/L. It contains mainly dissolved carbohydrates, minerals and is acidic in nature with pH ranging from 4.5 to 5.5. The research in the field of rice mill wastewater treatment is nascent. Malik et al used biodegradation technique for rice mill effluent treatment. Authors reduced COD level to 75% of the initial COD value using biodegradation. However, the technique needs about 15 days for this reduction. A small scale industry has to have a 15 days of effluent storage to use biodegradation technique which is not feasible. Aother research group utilized microbial fuel cells for treatment of rice mill waste. Authors reduced COD levels to almost 97% using microbial fuel cells [5]. However, microbial fuel cell technology demands high capital investment when scaled up and again it is time consuming which requires larger storage capacity of effluent. There is a need of fast and economical method for rice mill waste treatment. Moreover, the rice mill effluent has a huge potential of energy generation owing to its high organic loading. Rao et al investigated anaerobic co-digestion of various agricultural wastes. Their research revealed that co-digestion of various food wastes enhances biogas production [6].

This research work focuses on development of fast, sustainable and feasible treatment method of rice mill effluent which can be easily scaled-up in existing small scale industry. The second part of this research focuses on energy generation through anaerobic co-digestion using the sludge obtained from the treatment process.

II. DETAILS EXPERIMENTAL

All the chemicals used in this research work were bought from Merck India unless otherwise specified. All experiments were performed in duplicates and error encountered was in the range of ±15%.

2.1 Characterisation of wastewater

The rice mill wastewater was obtained from a nearby small scale industry. The wastewater was characterized in terms of pH, turbidity and Chemical Oxygen Demand (COD) within one hour of sample collection. COD was measured as per BIS 3025 part 58: 2006.

2.2 Physical methods

2.2.1 Adsorption

Rice mill wastewater was treated with different quantities of bottom ash obtained from the boiler of rice mill plant. Bottom ash amount in the range of 0.1 to 1 gm was added in 100 ml of rice mill waste and the suspension was allowed to mix at room temperature for time intervals ranging from 1 hour to 3 hour. After the specific time interval the solution was filtered with Whattman filter paper of size 40 micron and filtrate was characterised in terms of turbidity and COD.

2.3 Chemical Methods

2.3.1 Lime treatment

Commercial grade lime was used for treatment of rice mill wastewater. Rice mill wastewater of 50 ml volume was pipetted out in 5 different flasks. Lime was added in the quantities of 0.5, 1, 1.5 and 2 gm to these five flasks and mixed thoroughly for one hour using magnetic stirrer. The suspension was filtered using vacuum filter and filtrate was analyzed for pH and COD. Wet weight and dry weight of filter cake was measured. The procedure was repeated for 2,3,4,5 and 12 hours of time intervals.

2.3.2 Hydrogen Peroxide treatment

Different quantities of commercial grade 30% hydrogen peroxide solution ranging from 5 ml to 50 ml was added to 50 ml rice mill wastewater. To this solution, about 0.1 gm ferrous sulphate was added as a catalyst and stirred gently overnight. The solution was vacuum filtered and filtrate was analyzed in terms of pH and COD. Wet weight and dry weight of filter cake was measured.

2.4 Anaerobic digestion of rice mill waste

Experiments were carried out with a working volume of 200 ml in an air tight filter flask (BOROSIL) of volume 500 ml. The flask opening was closed by rubber stoppers. 100 ml of sludge obtained after rice mill wastewater treatment was mixed with 100 ml cow dung slurry and poured into air tight flasks. As a control experiment, another anaerobic digester was kept in parallel with 200 ml of cow dung slurry in it. The flasks were static throughout, except manual mixing thrice a day. Biogas was collected through a gas outlet pipe located in rubber stopper. The volume of biogas generated in the batch reactor was measured using downward displacement technique.

2.5 Gas chromatography

Gas sample was analyzed by Gas Chromatography (CHEMITO) with following operating conditions, Injection temperature -100°C, Column - Porapak Q, Flow rate -10ml/min, Oven temperature - 40°C to 100°C, Detector temperature - 250°C.

III. RESULTS AND DISCUSSION

Rice mill wastewater was collected every week for a period of 16 weeks. The samples had a pH in the range of 4.2 to 5.2 and COD in the range of 3200 to 5500 mg/L. Rice mill wastewater sample was free of suspended solids and hence, vacuum filtration did not reduce COD of rice mill waste to large extent. All rice mill industries have a boiler to generate steam or hot water which generates bottom ash. Total of 10 bottom ash samples were analyzed for BET specific surface area and results indicated the BET specific surface area in the range of 3.2 to 4.8 m2/gm. This bottom ash obtained from boiler was used as an adsorbent.

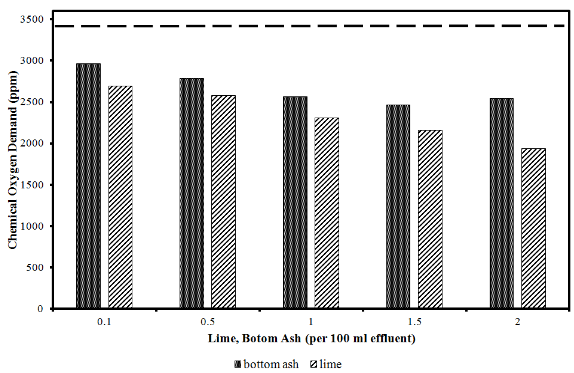

Figure 1: Effect of adsorption on bottom ash and lime treatment on COD values of effluent after three hours of treatment. Dotted line indicates COD value of original effluent

No chemical treatment was given to enhance adsorption capacity of bottom ash.

Figure 1 shows COD values obtained after adsorption for three hours. As bottom ash amount increased from 0.5 gm per 100 ml to 2 gm per 100 ml, the COD reduction was marginal. Maximum COD reduction of ca. 28% after three hours was achieved using bottom ash as adsorbent. No further COD reduction was achieved when adsorption was carried out for more than three hours (results not shown). The BET specific surface area of bottom ash was very less compared to standard adsorbents available. It is known that bottom ash requires activation by chemical method or steam to increase its adsorption capacity [7-8]. Since small scale rice mill industries do not have facility to activate bottom ash, the adsorbent used in this experiment was also not given any activation treatment and hence there was marginal decrease in COD values even after increasing adsorbent content and time. Since bottom ash was not available in large quantities, the maximum amount of bottom ash used was 2 gm per 100 ml effluent.

As physical treatment methods were not giving desired reduction in COD values of effluent, chemical methods were employed. Alum and Lime are widely used as precipitants and flocculants in effluent treatment in many chemical process industries [9]. Hence experiments were carried out with alum and lime. Surprisingly, no sludge formation was observed when alum was used in the same amount as lime and solution remained turbid. Therefore, lime was used for waste treatment. Figure 2 shows results of lime treatment on COD value of effluent after three hours of treatment. The decrease in COD was about 43% when 2 gm lime was added in 100 ml effluent whereas addition of 0.1 gm lime in effluent reduced COD to ca. 23%. About 7000 Liter of effluent per batch is generated in a rice mill from where effluent sample was collected. Therefore, as per the experimental results obtained based on 2gm lime per 100 ml effluent, the industry would require about 140 kg of lime for one batch of effluent which would not be feasible and that would increase hardness of treated effluent due to presence of calcium ions. Moreover, effluent pH increased to about 11.5 after addition of lime. Increased amount of lime addition would also increase acid requirements to neutralize the effluent. Hence, quantity of lime addition was restricted to 2 gm of lime per 100 ml effluent. Moreover, further reduction in COD was not observed when extra 2 gm of lime was added in already treated effluent with 2 gm of lime. The sludge production was more when lime was used because of its limited solubility in water.

As per the central pollution control board of India, the desirable COD limit for effluent to be discharged in river is ca. 125 mg/L [3]. This limit was not achieved by any of the methods mentioned above. Therefore, a novel treatment method based on oxidation using hydrogen peroxide was investigated. Hydrogen peroxide is used in effluent treatment, for disinfection as well as for reduction of organic loading of effluent [10-13]. However, it has not been used for organic loading removal for food processing effluent treatment so far. Figure 2 indicates COD of the effluent after addition of commercial grade 30% hydrogen peroxide solution. There was a marked decrease in COD when hydrogen peroxide volume increased. A minimum of 31% and maximum of 98% COD removal was achieved using 5 ml and 90 ml hydrogen peroxide.

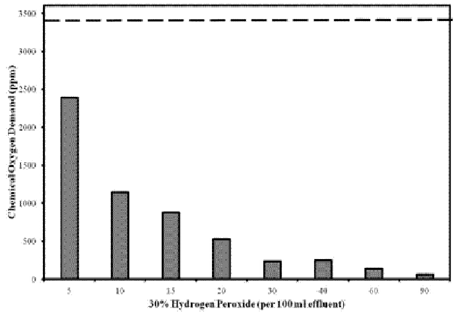

Figure 2: Effect of addition of 30% hydrogen peroxide solution on COD of effluent after 3 hours. 0.4 mM Anhydrous Ferrous sulphate was used as a catalyst. Dotted line indicated COD value of original effluent.

Though, desirable COD limit of effluent was already achieved while adding 60 ml hydrogen peroxide solution. Sludge production was ca. 80% less than that obtained during lime treatment. The effluent pH remained in the range of 5.5 to 6.5 after addition of hydrogen peroxide. Turbidity of hydrogen peroxide treated effluent (98% removal of COD) was ca. 5 which is very close to turbidity of tap water. Following table compares the effluent characteristics treated with lime and 30% commercial grade hydrogen peroxide solution.

Table 1:

	Lime treatment	**Hydrogen Peroxide treatment**
Color	Dark Yellow	Pale yellow to colorless
Odour	Foul	Odorless
pH	More than 11	5 to 6
Sludge obtained per 100 ml effluent	Ca. 2 gm to 4 gm depending upon addition of lime	Ca. 0.6 gm to 1.6 gm
Maximum COD reduction*	Ca. 43%	Ca. 98%
Amount required to achieve maximum COD reduction	20 kg per 1000L effluent	600 L per 1000L effluent

As above table indicates, hydrogen peroxide proved to be a very important chemical for treatment of rice mill wastewater. However, it should be noted that rice mill effluent has high amount of carbohydrates which is a rich source of bio-methane production through anaerobic digestion process. In fact, Kotharia et al suggested use of rice mill wastewater to produce hydrogen through fermentative/anaerobic route [14]. Hence, the sludge obtained after treatment with lime and hydrogen peroxide was investigated for bio-methane production using anaerobic digester.

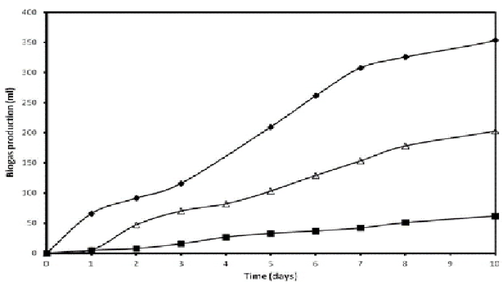

Figure 2: Biogas production in anaerobic digester using (◆) cow dung + hydrogen peroxide treated sludge,(△)cow dung, (■)cow dung + lime treated sludge.

Figure 3 shows the profile of biogas produced over the time using the sludge obtained by lime treatment as well as hydrogen peroxide treatment. Biogas production using hydrogen peroxide treated sludge was almost five times more than that treated by lime. Biogas production using lime treated sludge was even lesser than that obtained by only cow dung. The pH of lime treated sludge was higher than 11 due to strong basic nature of lime. It is known that anaerobic digester functions with maximum efficiency in ph range of 6 to 7 [15]. Biogas production reduces markedly in basic pH range (pH more than 8) due to ammonia toxicity [15].

CONCLUSIONS

Rice mill wastewater was treated successfully with commercial grade 30% hydrogen peroxide solution. Chemical oxygen demand of effluent was reduced to 98% after treatment with hydrogen peroxide solution and sludge production was minimum of all treatments which reduce the load of solid waste management. Lime treated effluent was giving foul odour and a maximum COD reduction of ca. 43% was achieved which was not sufficient for discharge of effluent to river or municipal drainage system. Biogas production increased two folds when sludge obtained after hydrogen peroxide treatment was fed to anaerobic digester whereas ammonia toxicity was observed during anaerobic digestion of lime treated sludge due to alkaline nature of the sludge. Though a very clear and odorless effluent was obtained after hydrogen peroxide treatment, more research efforts are required to make the hydrogen peroxide treatment economical for small scale industries.

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