

Treatment of Wool Scouring Waste Using Anaerobic Digestion with and without Chemicals Addition

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Abstract—The aim of this study was to investigate the effectiveness of anaerobic digestion for the treatment of wool scouring wastes. The experiments design comprised three ratios of waste (W) to seed(S) (W:S) of 25:75, 50:50 and 75:25, corresponding to 1.9, 1.7 and 1.5g tCOD/g TS, respectively, with or without chemicals addition. NH_4Cl was added to the reactors as a source for nitrogen to achieve C:N:P of 420:14:3. A cationic flocculent was added at 0.5 and 0.75% to enhance flocculation of sludge. The results showed that the reactors that received W:S at a ratio of 25:75 produced the largest volume of biogas. The final soluble COD (sCOD) was below the limits for discharge to the sewer system.

Keywords—Anaerobic digestion, wool processing waste, organic loading, biogas.

I. INTRODUCTION

A number of physico-chemical and biological pre-treatment processes have been investigated for the treatment of wool scouring wastes. Well-known pre-treatment processes include acid-cracking, chemical flocculation, solvent extraction, aerobic and anaerobic biological processes [1] - [4]. Chemical processes have usually been associated with high operating costs due to the large amount of chemicals required. Economic factors have therefore limited application of chemical processes [5]. Aerobic biological processes can be economically acceptable if a large land area is available but can also be expensive when extensive mechanical aeration is required (Robinson and Gibson, 1985). Aerobic treatment was in found in many cases to be inefficient achieving only partial oxidation of organics and partial flocculation of wool grease [6]. Other problems with aerobic treatment of wool scouring waste are foaming and high sludge production.

Anaerobic digestion is has been widely used to treat wool scouring effluents mainly because of its relatively low energy requirement and economic operating costs. However the main challenges have been the high oxygen demand of these effluents and their slow biodegradability, especially the wool wax. In addition, the presence of a variety of organic and inorganic constituents in both dissolved and insoluble form and the poor phase separation characteristics have also been found to affect the performance of anaerobic digesters for

wool scouring effluents.

The aim of this study was to assess the effectiveness of anaerobic digestion for biogas production and removal of COD from the wastewater generated during wool scouring with and without chemicals addition. The effectiveness of anaerobic digestion for the treatment of the Vic wool waste samples and the potential for biogas production were assessed using batch anaerobic reactors. The scope comprised (i) effect of organic loading (ii) potential enhancement using chemical addition to ensure balanced carbon to nutrients ratio and (iii) addition of flocculent to enhance settling of sludge.

II. MATERIALS AND METHODS

A. Materials

Wool scouring effluents were collected from a wool processing industry in Australia. It was stored at 4°C prior to use. Two wool scouring waste samples, namely sample 1 and 2 were used in this study. Sample 1 was collected from centrifuge and sample 2 was a concentrated form of sample 1 obtained using a decanter

The characteristics of the two samples are given in Table I. The mixed anaerobic culture used as seed was obtained from anaerobic sludge digester located at a large domestic wastewater treatment plant in Melbourne, Australia. It was stored at 4°C prior to use. The characteristics of the seed are also given in Table I.

B. Methodology

Batch anaerobic reactors of 250 mL volume each were operated at mesophilic conditions (35°C) for 35 days. The effective volume of each reactor was 100 mL. The experiments design comprised three different W:S ratios of 25:75, 50:50 and 75:25 (Table II). The chemicals used were NH_4Cl and a flocculent. According to the characterization of the wool waste, it was found that nitrogen is the limiting reactant. Thus, NH_4Cl was added to the reactors as a source for nitrogen for the anaerobic microorganisms to achieve a ratio of COD:N:P of 420:14:3. Whereas, a polyacrylamide cationic flocculent (Zetag 7635) was added at 0.5 and 0.75% to enhance flocculation of sludge and grease removal in wool (results not discussed in this paper). After the addition of all components, the reactors were flushed with 100% N_2 gas,

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sealed with natural rubber sleeve stopper and kept in the shaker for 35 days at 35°C and 100 rpm. The performance of the reactors was monitored by measuring the daily biogas production, biogas methane composition and final tCOD, sCOD, tP, sP, tN, sN and, tNH₄, sNH₄.

TABLE I
CHARACTERISTICS OF THE WOOL WASTE SAMPLES AND THE SEED USED IN THIS STUDY

Parameter	Sample 1	Sample 2	Seed
pH	5.00	8.62	7.51
Total Solid (TS), mg/L	22,800	27,600	19,600
Volatile Solid (VS), mg/L	9,600	10,000	6,800
Total COD, mg/L	30,200	34,300	41,000
Soluble COD, mg/L	13,400	17,800	3,300
Total Phosphorus, mg/L PO ₄₃ -	244	320	1,940
Soluble Total Phosphorus, mg/L PO ₄₃ -	51	225	714
Total Nitrogen (TN), mg/L N	600	610	1,900
Soluble Total Nitrogen, mg/L N	430	420	880
NH ₃ -N, mg/L	124.5	152	115
grease, mg/L	15200	12800	18200

C. Analytical Methods

Total solids (TS) and volatile solids (VS) were measured gravimetrically according to the Standard Method [7]. The measurements of total COD (tCOD) and soluble COD (sCOD), total phosphorus (tP), soluble phosphorus (sP), total nitrogen (tN), soluble nitrogen (sN) and NH₄-N, were made by colorimetric techniques using HACH Spectrophotometer (DR/4000). The biogas produced in each reactor was measured using a water displacement device [8]. The content of methane in the biogas was determined as follows. A known volume of the headspace gas (v₁) produced in a serum bottle used in the biochemical methane production (BMP) experiments was syringed out and injected into another serum bottle which contained 20 g/L KOH solution. This serum bottle was shaken manually for 3-4 min so that all the CO₂ and H₂S were absorbed in the concentrated KOH solution. The volume of the remaining gas (V₂), which was 99.9% CH₄, in the serum bottle was determined by means of a syringe. The ratio of V₂/V₁ provided the content of CH₄ in the headspace [9].

TABLE II
EXPERIMENTS DESIGN FOR ANAEROBIC DIGESTION REACTORS FOR WASTE SAMPLE 1 AND 2

Reactor	Wool waste mL	Seed mL	NH ₄ Cl	Flocculent %
Control*	50	50	-	-
Blank-1*	50	0	-	-
R11-1a*	25	75	-	-
R11-1b*	25	75	+	-
R11-1c#	25	75	+	0.50%
R11-1d#				0.75%
R12-1a*	50	50	-	-
R12-1b*	50	50	+	-
R12-1c#	50	50	+	0.50%
R12-1d#	50	50	+	0.75%
R13-1a*	75	25	-	-
R13-1b*	75	25	+	-
R13-1c#	75	25	+	0.50%
R13-1d#	75	25	+	0.75%
Blank-21#	50	0	-	-
R21-1a#	25	75	-	-
R21-1b#	25	75	+	-
R21-1c#	25	75	+	0.50%
R22-1a#	50	50	-	-
R22-1b#	50	50	+	-
R22-1c#	50	50	+	0.50%
R22-1d#	50	50	+	0.75%
R23-1a#	75	25	-	-
R23-1d#	75	25	+	0.75%

R11-R13 received sample 1 (total of 35 reactors).

R21-R23 received sample 2 (total 18 reactors)

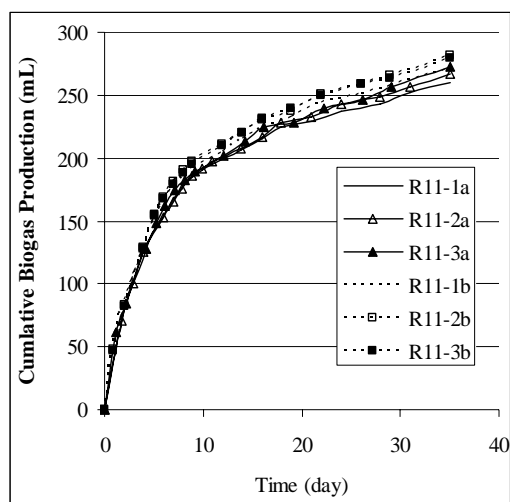
* run in triplicate,

run in duplicate

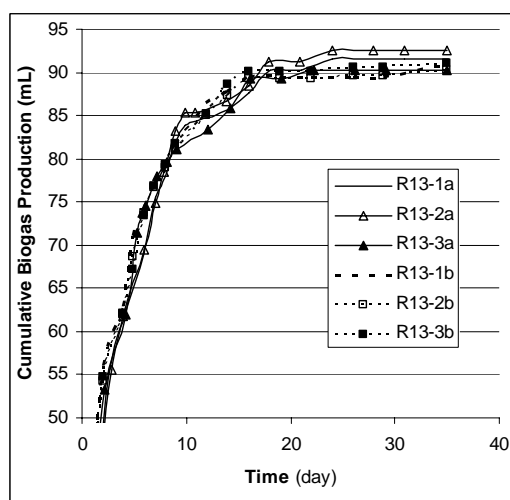
III. RESULTS AND DISCUSSION

Biogas production in each reactor was measured on a daily basis. The cumulative biogas production (CBP) measured for the triplicate and duplicate runs showed a high level of reproducibility. For example, the CBP from R11-1a, R11-1b, and R11-1c were 259.9, 266.9 and 272.4 mL, respectively. The results obtained for the reactors that received W:S ratio of 25:75 with or without NH₄Cl (i.e. all R11-1 and R11-2 reactors) are shown in Fig. 1. Similar reproducibility was observed for R13 reactors (Fig. 1).

The organic loading corresponding to the different waste (W) to seed (S) (W:S) ratios added into the reactors are summarised in Table III.



(a)



(b)

Fig. 1 Cumulative biogas production (CBP) for reactors with (A) W:S at 25:75 and (B) reactors with W:S at 75:25

TABLE III
THE ORGANIC LOADINGS CORRESPONDING TO EACH W:S RATIO USED IN THIS STUDY

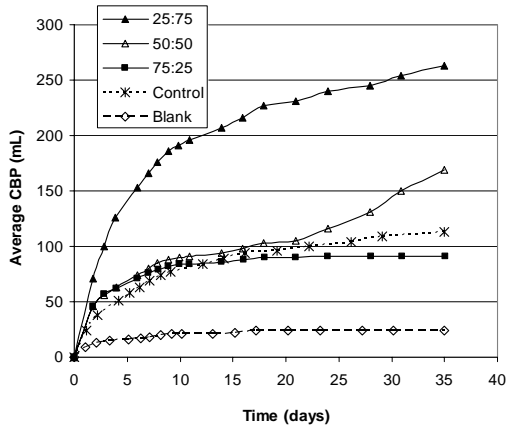
Reactors	Wool waste mL	Seed mL	gCOD/gVS	gCOD/gTS	gtCOD waste /gtCO D seed
R11	25	75	5.11	1.9	0.2
R12	50	50	4.34	1.7	0.7
R13	75	25	3.70	1.50	2.2
R21	25	75	5.17	1.82	0.3

Figs. 2a, 2b, 2c and 2d) show that the average total CBP collected from the reactors that received W:S at 25:75, with or without chemical addition, was much higher than that produced at W:S of 50:50 and W:S of 75:25. The average total CBP at W:S of 25:75, 50:50 and 75:25, were 266.4, 169.5 and 91.4 mL, respectively. The same trend of decreased CBP with increased organic loading was observed for the reactors that received NH_4Cl (Fig. 2b), the reactors that received NH_4Cl + 0.5% flocculent (Fig. 2c) and those that received NH_4Cl + 0.75% flocculent (Fig. 2d). This trend indicates an inverse relationship between the organic loading and the CBP. The COD for the seed used in this study was higher than that for the waste samples giving rise to this apparent inverse relationship. The CBP correlated with the loading in terms of g tCOD waste/ g tCOD seed.

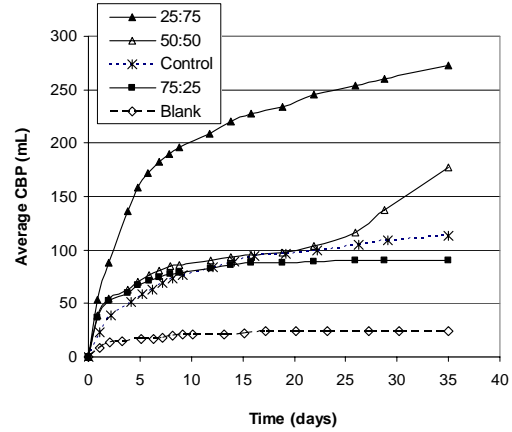
The average total CBP at W:S of 75:25 was almost 64% less than that produced at W:S of 25:75 and less than that produced in the control (i.e. seed only). This suggests that at W:S of 75:25 (2.2 g tCOD waste /g tCOD seed) some feed constituents were present at a concentration level that was inhibitory to the anaerobic micro-organisms population in the reactors.

The carbon: phosphorus: nitrogen ratio for both waste samples indicated that nitrogen was the limiting constituent; therefore NH_4Cl was used to balance deficiency in nitrogen. The CBP at high ratios of W:S, i.e. 50:50 and 75:50, indicated inhibitory effects and showed that NH_4Cl , under these conditions, had no significant effect on CBP (Figs. 3-5). The use of NH_4Cl at W:S of 25:75 had a slight positive effect on CBP.

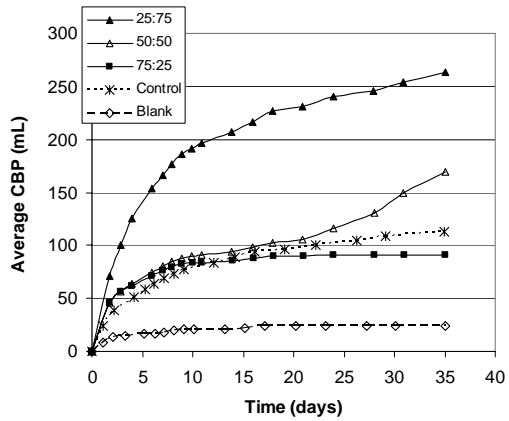
The results shown in Figs. 3-5, indicate that the rate of biogas production in the reactors, under these conditions, correlate with the volume of waste added. The reactors that received W:S at a ratio of 25:75 produced gas at an exponential rate during the first 10 days whereas the rate was slower at W:S of 50:50 and 75:25. This decrease in rate of gas production suggests potential inhibition to the activity of anaerobic micro-organisms at the concentrations of waste substrates present in the reactors at these ratios. The amount of CBP in the reactors that received W:S of 50:50 increased sharply after 20 days, suggesting that the anaerobic culture adapted to the waste and was able to resume their degradation activity. The anaerobic culture in the reactors with a W:S of 75:25 were almost inactive after 10 days and showed no adaptation or recovery signs during the last 25 days of the run. Furthermore, it was observed that the CBP in all reactors that received W:S of 75:25 was less than that produced in the control. For example, around 85 mL of biogas was produced in R13 (no chemical addition), compared with 113 mL produced in the control, conforming potential inhibition to the anaerobic micro-organisms at these conditions



(a)

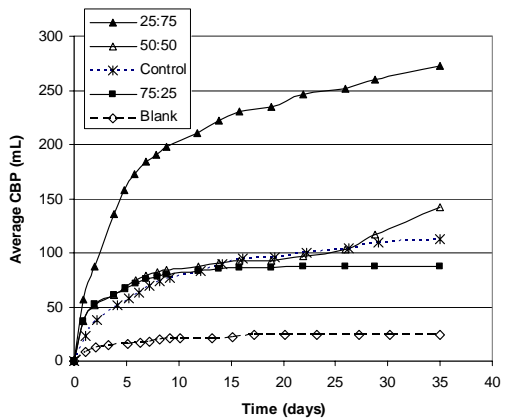


(d)



(b)

Fig. 2 Average CBP in the reactors that received varying W:S ratios (A) with no chemical addition, (B) with NH_4Cl , (C) with NH_4Cl + 0.5% flocculent and (D) with NH_4Cl + 0.75% flocculent



(c)

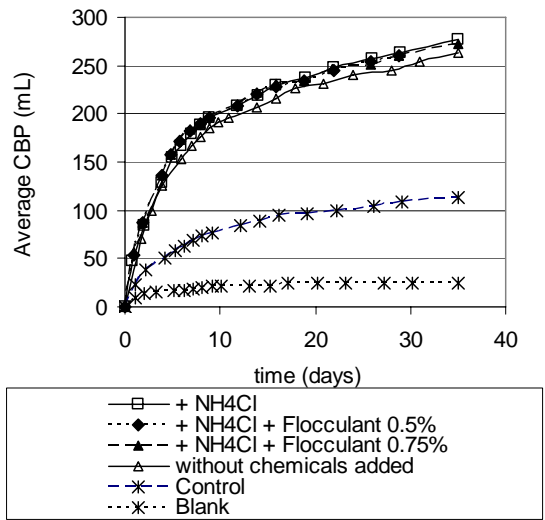


Fig. 3 Average CBP from the reactors that received waste sample 1 at W:S of 25:75

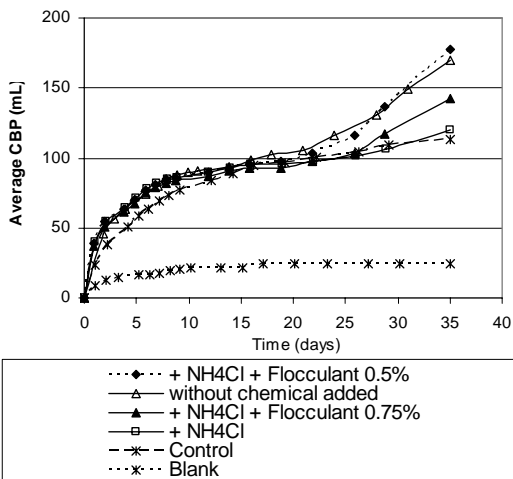


Fig 4 Average CBP from the reactors that received waste sample 1 at W:S of 50:50

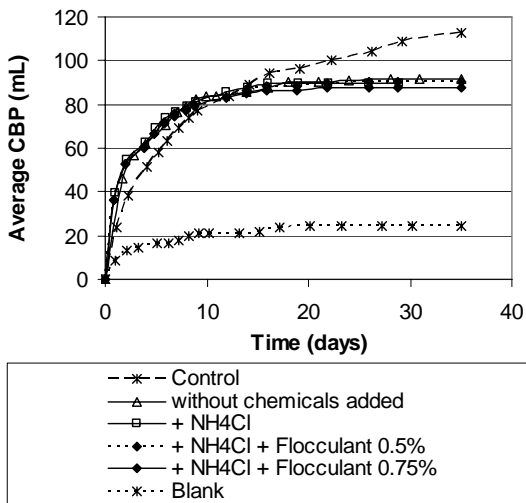


Fig. 5 Average CBP from the reactors that received waste sample 1 at W:S of 75:25

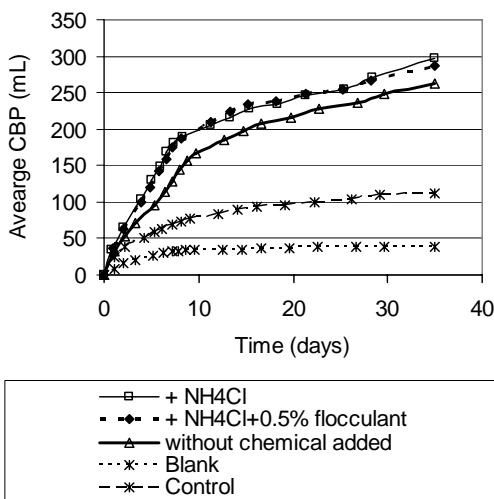


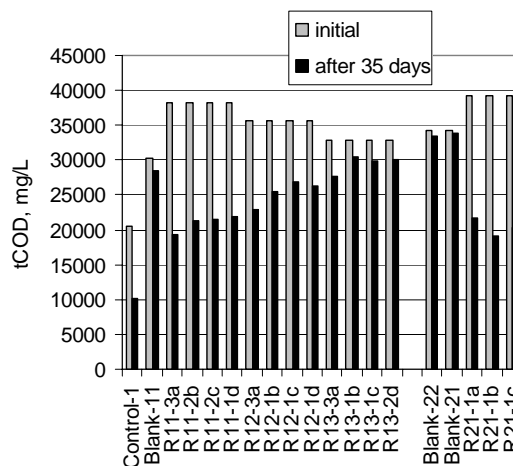
Fig. 6 Average CBP from the reactors that received waste sample 2 at W:S of 25:75

The CBP from the reactors that received waste sample 2 demonstrated similar trends compared with that for the reactors that received sample 1. It was observed that only the reactors with W:S of 25:75 produced biogas amounts considerably higher than that collected from the control (Fig. 6). In addition it was also noted that CBP at W:S at 25:75 was higher than that produced at other W:S ratios (results not shown because the runs were terminated after a5 days).

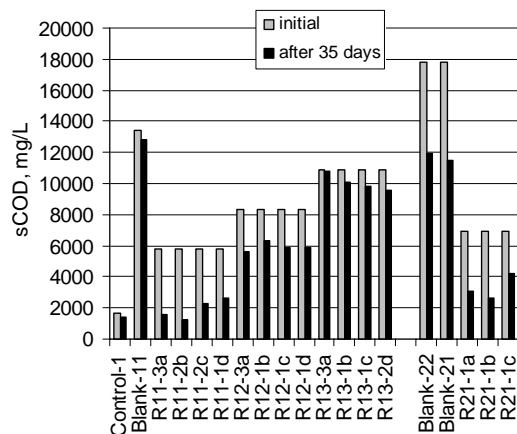
The total volume of biogas produced using sample 2 at W:S of 25:75 was 300 mL, which is slightly higher than the 266 mL of biogas produced using waste sample 1 at the same W:S ratio. These results are in agreement with the COD values for sample 1 and 2 being 30,200 and 34,300 mg/L respectively.

Analysis of the biogas produced from the reactors at different time intervals showed that methane constituted around 50 – 90% of the gas produced. The reactors that received W:S of 25:75 produced biogas of around 70-80% methane for waste sample 1 and 80-90% for waste sample 2.

For both waste sample 1 and 2, the percentages of tCOD and sCOD removal in reactors with W:S ratio of 25:75 were higher than other ratios, at around 40-50% and 50-80%, respectively. All R11 reactors had a final sCOD around 2000 mg/L and all R21 reactors had a final sCOD less than 4000 mg/L, ie supernatant meet permissible discharge limits to sewer system at no surcharge.



(a)



(b)

Fig. 7 Initial and final COD for waste sample 1 (A) total COD and (B) Soluble COD

IV. CONCLUSION

The results obtained in this study showed that treatment of wool waste sample 1 and 2 using anaerobic digestion at a W:S ratio of 25:75 can reduce the concentration of sCOD to the levels acceptable for sewer discharge. In addition the CBP from the reactors that received waste samples at a W:S of 25:75 was comparable with that the anaerobic digesters treating domestic wastewater treatment plants waste activated sludge. The addition of NH_4Cl , with or without flocculent, showed no significant effect on the volume of CBP and COD removed, compared with that from reactors that received no chemicals at all.

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