Pretreatment of Lignocellulosic Biomass with Tannery Wastewater for Solid-State Anaerobic Digestion

A.B. Yazid, S. Grimes and S.R. Smith

Department of Civil and Environmental Engineering, Imperial College, London, SW5 2AZ, United Kingdom
Keywords: lignocellulose, tannery, anaerobic digestion, pretreatment, biogas.
Presenting author email: aby108@ic.ac.uk

In 2017, rice, corn, groundnut, sugar cane and wheat production in Nigeria generated approximately 28 x 10^6 t of waste, lignocellulosic crop residues. Globally, approximately 181.5 x 10^9 t of lignocellulosic biomass (LB) is generated annually. In economically developing countries like Nigeria, LB waste is commonly disposed by uncontrolled burning *in situ* or at open dumpsites, which represents a significant environmental crisis, and alternative, effective management practices need to be sought. The consequences of this include the reduction in local air quality, deterioration of public health, specifically relating to respiratory disease, and negative effects on global air quality due to discharge of significant quantities of climate impacting pollutants.

Anaerobic digestion (AD) is a process where a consortium of microorganisms in the absence of oxygen converts a variety of biodegradable feedstocks into biogas rich in methane (CH_4), that is a valuable, renewable energy source, and nutrient-rich biomass called digestate, which can be recycled to farmland as a fertilizer source, thus contributing to a circular economy for nutrients (Momayez et al., 2019). This process could therefore offer many advantages and benefits for the treatment and recovery of value from lignocellulosic agricultural residues in developing countries to treat this major problematic waste stream and also assist in meeting local community energy needs. However, in their raw state these materials are relatively resistant to microbial degradation in the AD process and so they are a comparatively poor feedstock for direct biogas production. Lignocellulosic biodegradation can be increased by applying alkaline pretreatment to enable the microbial hydrolysis of cellulose and hemicellulose (Momayez et al., 2019). Conventional approaches to alkaline pretreatment generally involve the addition of industrial alkalis such as sodium hydroxide (NaOH), lime (CaO), hydrated lime ($Ca(OH)_2$) and ammonia (NH_3). However, there are also opportunities to use alternative, industrial alkaline waste by-product streams as more cost-effective pretreatment materials to improve the digestibility of lignocellulosic feedstocks for AD. For example, wastewater from tanneries has high alkalinity (>12,000 mg/l) (Thorstensen, 1992), and may be potentially suitable as an alkaline pretreatment for AD of lignocellulosic waste. This strategy can also provide a sustainable solution to the management of these waste streams, which also often cause serious environmental disposal problems.

The leather industry in Nigeria is mainly based in the State of Kano, which is amongst the largest leather tanning and processing centres globally and is also one of the most polluting industries in the country. The Kano State Ministry of Environment reported that approximately 3 x 10^6 L d^{-1} of untreated tannery wastewater (TWW) is discharged into river Challawa. Therefore, identifying alternative beneficial uses for TWW, to reduce uncontrolled effluent discharges to the land and river system, is an urgent priority to improve the quality of the environment and public health in Kano, Nigeria. Current developments in treatment technologies for TWW focus on segregating the wastewater streams from soaking, beamhouse and tanning operations, to reduce the production of toxic hydrogen sulphide (H_2S) gas, which has caused a significant number of fatalities in Nigeria (UNIDO, 2011), but there has been little progress towards the treatment or identifying possible uses of TWW. In particular, the alkaline properties of tannery beamhouse wastewater (TBWW) could be suitable as a possible pretreatment for lignocellulosic agricultural wastes generated in Nigeria for dry AD processes with high solids feedstocks. For example, Vazifehkhoran et al. (2018) examined the effects of unsegregated TWW on wheat straw (WS) AD and showed that the pretreatment conditions increased CH_4 yield by 123%. To our knowledge, TBWW has not been investigated for AD pretreatment. Furthermore, using separated TBWW for AD of LB has the advantage of producing chromium (Cr) - free digestate suitable for use in agriculture as a fertilizer.

The aim of this research, therefore, is to apply TBWW, characteristic of Kano, Nigeria, in the alkaline pretreatment of LB to improve digestibility and biogas production by dry mesophilic anaerobic digestion (MAD). The research will identify opportunities for using TWW effluents as valuable resources by stimulating new approaches to TWW management including for LB pretreatment.

A batch, chemostat apparatus (1000 mL) was designed and constructed for the AD experiments and fitted with a volume displacement system to measure and collect biogas through a hypodermic needle (Thangamani and

Rangasamy (2011)) (Figure 1). The main source of alkali present in TBWW is $Ca(OH)_2$. Therefore, the effects of TBWW as an AD pretreatment were examined by increasing the dose of $Ca(OH)_2$ mixed with wheat straw (WS) (5 g) at rates of 5, 10, 15 and 20% (w/w), with a water loading of 10 ml / g WS, and incubating the mixtures at 35ºC (reflecting the typical ambient temperature in Kano, Nigeria) for a period of 7 days. The WS was prepared by grinding with a cross-beater mill to pass a 1 mm sieve. The effect of pretreatment time was quantified using the 10% $Ca(OH)_2$ dose rate condition and pretreating ground WS for 1, 3, 7 and 14 days in an incubator at 35ºC. Alkali pretreated and control samples (incubated with deionized (DO) water for the same time durations) were washed 10 times with DO water to remove $Ca(OH)_2$ and the acid and neutral detergent fibre contents (cellulose, hemicellulose and lignin) were determined following Van Soest (1967). The effect of $Ca(OH)_2$ pretreatment on the AD of WS was examined by pretreating 10 g of ground WS with 1 g of $Ca(OH)_2$ at 35ºC for 7 days. The pretreated WS was inoculated with digested sewage sludge obtained from a mesophilic AD plant at a ratio of 2:1 (inoculum:WS; VS:VS) and was transferred to the chemostats maintained at 35ºC in an incubator. The monitored parameters included: total solids (TS), volatile solids (VS), fibre content, biogas production rate and composition.

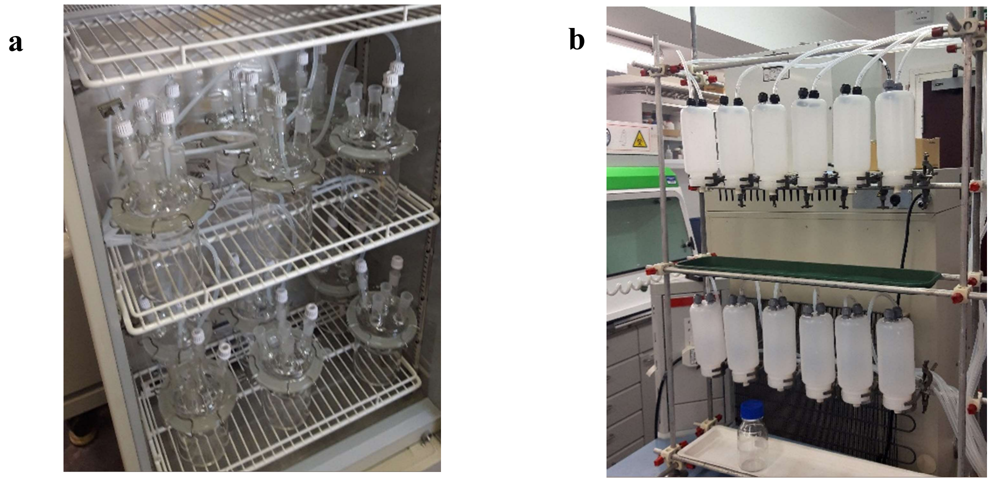

Figure 1: A batch chemostat construction for the anaerobic digestion experiments with (**a**) 1000 mL reactors for wheat straw digestion and (**b**) 500 mL HDPE bottles fitted with hypodermic needles for gas measurement.

The results from the fibre analysis in relation to varying $Ca(OH)_2$ loading rates and pretreatment times showed that $Ca(OH)_2$ selectively targeted the degradation of hemicellulose. This behavior was consistent with Chang et al. (1998) and may be explained by the breakdown of acetyl bonds present in hemicellulose, however, cellulose and lignin fibres are unchanged. With a pretreatment time of 7 days, the results showed that 50% of hemicellulose fibres in WS were solubilised at the 5% dose rate of $Ca(OH)_2$, compared to the untreated control, however, there was no significant effect of increasing the dose rate above 5% (Figure 2). Hemicellulose solubilisation increased to approximately 40% after a 1-day pretreatment period, compared to the untreated control, and increased to approximately 50% after 7 days. Extending the pretreatment period further to 14 days increased hemicellulose degradation to 56%, albeit not significantly ($P>0.05$) (Figure 2).

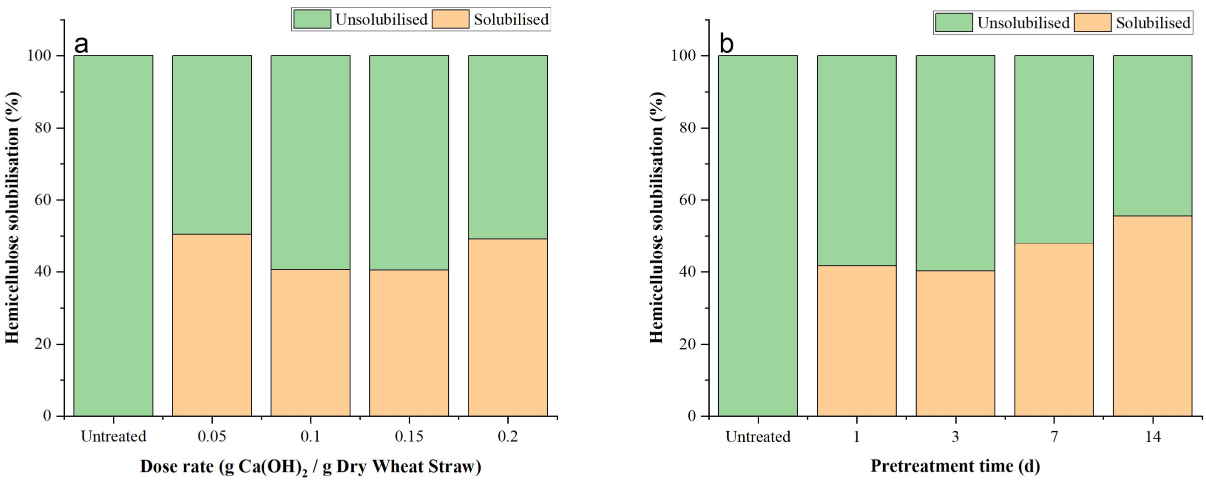

Figure 2: Wheat straw hemicellulose solubilisation from varying (**a**) $Ca(OH)_2$ dose rate at constant pretreatment time of 7 days and (**b**) pretreatment time for 10% $Ca(OH)_2$ constant dose rate.

Cumulative specific biogas yield of $Ca(OH)_2$ pretreated WS was approximately 100 mL biogas / g VS added, demonstrating the effect of the $Ca(OH)_2$ pretreatment on the digestibility of WS compared to untreated control of which was approximately 69 mL biogas / g VS added (Figure 3). Cumulative biogas production of $Ca(OH)_2$ pretreated WS was approximately 1200 ml biogas / g VS destroyed in 5 days, demonstrating the high rate of bioconversion, compared to the untreated control, which was approximately 600 ml biogas / g VS destroyed in 17 days (Figure 3). Thus, a 200% increase in biogas production with 33% reduction in hydraulic retention time was achieved by WS pretreatment. The specific biogas yield of pretreated WS, based on hemicellulose VS only, was equivalent to 61% of the theoretical value derived using the Buswell equation.

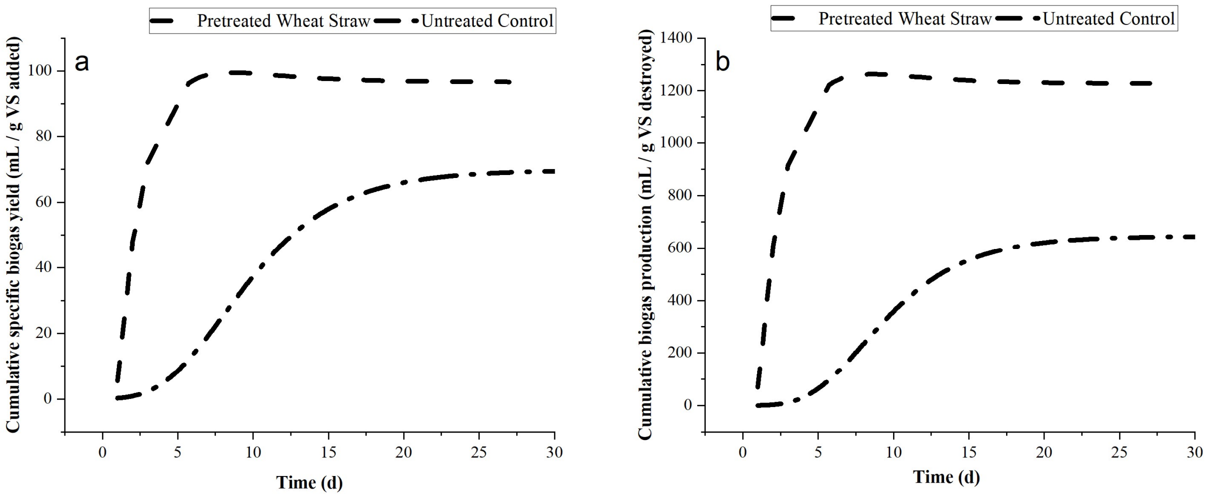

Figure 3: Effect of $Ca(OH)_2$ pretreatment on (**a**) specific biogas yield (**b**) biogas production on wheat straw compared to an untreated control.

Therefore, the preliminary results presented here demonstrate the significant potential of $Ca(OH)_2$ present in TBWW for pretreating WS to increase the degradation and biogas yield from mesophilic AD of lignocellulosic agricultural wastes. Further investigations will be conducted on other substrates and on using organic acids for neutralizing $Ca(OH)_2$ to adjust the pH of the pretreated feedstock into a suitable range for AD. The research outcomes will provide a framework for the design and implementation of TWW treatment technologies for pretreating lignocellulosic agricultural waste to facilitate the management of, and maximise beneficial resource recovery from, this major waste stream in Nigeria by AD. This will significantly reduce: (1) negative effects of both agricultural and leather industries on the local environment, (2) global pollutant emissions, and (3) local energy deficits; it will also benefit the local agriculture industry by providing a high quality, sustainable digestate fertiliser for crop production.

Acknowledgements
Anas Balarabe Yazid is supported by a PhD scholarship from the Islamic Development Bank.

References

Chang, V. S., Nagwani, M. & Holtzappl, M. T. (1998). Lime pretreatment of crop residues. *Applied Biochemistry and Biotechnology,* 74**,** 135-159.

Momayez, F., Karimi, K. & Taherzadeh, M. J. (2019). Energy recovery from industrial crop wastes by dry anaerobic digestion: A review. *Industrial Crops and Products,* 129**,** 673-687.

Thangamani, A. & Rangasamy, P. (2011). *Management of industrial tannery solid waste for biogas production: Anaerobic digestion, structuring, feasibility studies, laboratory scale demonstration,* Mauritius LAP LAMBERT Academic Publishing.

Thorstensen, T. C. (1992). *Fundamentals of pollution control for the leather industry*, Shoe Trades Publication.

UNIDO. United Nations Industrial Development Organization (2011). *Introduction to treatment of tannery effluents* [Online]. Vienna, Austria. Available: https://www.unido.org/sites/default/files/2011-11/Introduction_to_treatment_of_tannery_effluents_0.pdf [Accessed 20/08/2019].

Van Soest, P. J. W., R. H. (1967). Use of detergents in the analysis of fibrous feeds. IV: Determination of plant cell-wall constituents. *Journal of Official Analytical Chemists,* 50**,** 50-55.

Vazifehkhoran, A. H., Shin, S. G. & Triolo, J. M. (2018). Use of tannery wastewater as an alternative substrate and a pre-treatment medium for biogas production. *Bioresource Technology,* 258**,** 64-69.