Alkali pretreatment and high solids anaerobic digestion of lignocellulosic agricultural residues with coal fly ash and fermented food waste neutralisation

M. Dewiandratika, S.M. Grimes, S.R Smith

Department of Civil and Environmental Engineering, Imperial College London,
London SW7 2AZ, United Kingdom
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Presenting author email: maryam.dewiandratika15@imperial.ac.uk

Lignocellulosic agricultural residues (LAR) are abundant and represent a major potential renewable energy source. Anaerobic digestion (AD) is one of the main opportunities available for recovering energy from LAR as biogas and is particularly suited to the treatment of and value recovery from biodegradable waste materials. However, LAR is relatively resistant to AD and requires pretreatment to remove lignin and increase microbial access to the degradable cellulose and hemicellulose fractions. One of the most widely used methods is alkaline pretreatment and conventionally, inorganic alkaline chemicals, such as sodium or calcium hydroxide, are used. However, the high alkalinity as a result of alkaline pretreatment is inhibitory to the AD process and inorganic acid addition is often used to neutralise the pH (Abudi et al., 2016; Elsayed et al., 2018). This represents a significant demand for chemical reactants and cost, affecting the overall economic viability of the process. Another common method to decrease the pH after alkali pretreatment is by washing with deionised water and filtering the pretreated material (Dai et al., 2018; Sabeeh et al., 2020). However, this leads to the loss of solubilised hemicellulose that would otherwise contribute to methane (CH_4) production during AD. To address these challenges, this study evaluated the suitability of coal fly ash (CFA), a major alkaline industrial waste, as an alternative alkaline pretreatment of LAR. The ability of food waste (FW), which rapidly ferments and acidifies due to the production of volatile fatty acids (VFAs), to neutralise the pH value was also investigated. Adopting an integrated approach to the management of CFA and FW in the AD of LAR, may provide a route to beneficial utilisation of CFA and FW whilst also reduce their potentially severe environmental disposal impacts.

Coal fly ash was supplied from a coal-fired power station in North Yorkshire, UK and barley straw (BS) was used as a representative type of LAR. Barley straw was prepared by milling to a particle size of 1 mm. The minimum alkalinity requirement to maximise the effect of pretreatment on the digestibility of BS was determined by incubating BS in calcium oxide (CaO) solutions at three alkalinity concentrations equivalent to:2,000, 5,000, and 11,000 mg $CaCO_3$/L, and deionised water was used as a control treatment. Calcium oxide was used as it is the primary alkaline component in CFA which contributes to the alkalinity of the material through its reaction with water to form calcium hydroxide ($Ca(OH)_2$) (Achternbosch et al., 2015). A solid to liquid ratio (S/L) of 1:7 was used to adjust the final dry solids content to an approximately 18% with deionised water, to saturate the BS for dry AD treatment and to minimise water use. The data from the experiment with pure chemicals was used to inform the dose of CFA required, based on the typical alkalinity value of the material.

A BS to CFA ratio of 2:1 on a dry weight basis was selected for alkali pretreatment to anticipate the alkalinity values of CFA. Coal fly ash was mixed with deionised water at a solid loading of 6.25% and shaken for 12 hours. Barley straw was then added to the mixture and incubated for seven days. Alkalinity concentration of CFA solution used for pretreating BS was measured before BS addition by acid titration according to standard methods (APHA, 1999). The effect of pretreatment on the contents of cellulose, hemicellulose, and lignin (total fibre) in the BS was determined following standard methods (ISO, 2006; 2008). The effect of BS biodegradability after pretreatment on biogas and methane (CH_4) production was evaluated using a biochemical methane potential (BMP) test. Pretreated BS was neutralised by adding synthetic food waste (FW) (Saputri et al., 2018), which was fermented for seven days at 30°C and had a pH value equivalent to 3.7. The fermented FW was supplied at rates of 10, 25 and 50% of the total mass (on a volatile solids (VS) basis) and was thoroughly incorporated with the pretreated BS by manual mixing. The preliminary BMP tests were performed under batch, solid-state and mesophilic conditions in air-tight glass reactors. The inoculum used was digested sewage sludge and supplied at substrate to inoculum ratio of 1:1 on a VS basis. The capacity of the reactors was 1 L and the working volume was equivalent to 0.6 L. The reactors were fitted with a substrate feeding port, a gas sampling port, and a gas collection port connected to a water displacement system to determine the volume of biogas produced.

The results showed that the minimum alkalinity required to solubilise hemicellulose and lignin in BS was 5,000 mg $CaCO_3$/L, which reduced the hemicellulose and lignin content by 20% and 12%, respectively, compared to untreated BS. Raising the alkalinity concentration to 11,000 mg $CaCO_3$/L further increased the solubilisation of hemicellulose and lignin to 34% and 25%, respectively. In contrast, the fibre fractions at the smaller alkalinity concentration equivalent to 2,000 mg $CaCO_3$/L were not significantly ($P>0.05$) different from the control. Assuming a ratio of 2:1 (BS:CFA) and S/L of 1:7 are used for the pretreatment of BS with CFA, an active/free CaO content of 7 wt% and 15 wt% would be required to provide alkalinity concentrations of 5,000 and 11,000 mg $CaCO_3$/L, respectively, which the CaO requirement are within the range of values reported for CFA(Achternbosch et al., 2015). However, the alkalinity of CFA samples used for the experiments was smaller than obtained values (5000 mg $CaCO_3$/L) and the free CaO content was equivalent to 0.4 wt%, which could be related to the age and carbonation of the material. Therefore, the alkalinity of the CFA sample was supplemented with pure CaO to achieve free CaO values of 7 wt% and 15 wt%.

The final pH of BS pretreated with pure CaO was 8.5 and 12 for 5,000 mg $CaCO_3$/L and 11,000 mg/L pretreatments, respectively, which is suboptimal for AD. The proportion of fermented FW required to reduce the pH from 8.5 to 6.7 was equivalent to 25% of the total mass. Increasing the rate of FW addition to 50%, which may be a practicable maximum for amendment of pretreated LAR, reduced the pH from 12 to 9.5. Therefore, further acidification was required to lower the pH close to a neutral value suitable for AD and this was achieved by acetic acid addition, which is also a potentially available as a secondary resource.

A preliminary BMP experiment was carried out for BS pretreated with CFA supplemented with CaO to provide alkalinities of 5,000 and 11,000 mg $CaCO_3$/L. In this case no neutralisation step was performed, which will be adopted in later experiments. The total fibre of the digested residue was determined and compared to that of pretreated materials (Figure 1). The results showed that pretreatment increased the solubilisation of the total fibre, compared to the control, but higher fractions of the fibres were solubilised in AD rather than in the pretreatment step. Alkali pretreatments of 5,000 and 11,000 mg $CaCO_3$/L significantly improved the biodegradability of BS based on total fibre reduction by 2 and 2.5 times, respectively, compared to the untreated BS. The specific biogas yield was also directly proportional to fibres biodegradation and increased from 94 mL/g VS for the control, to 118 and 187 mL/g VS, for the 5,000 and 11,000 mg $CaCO_3$/L alkali pretreatments, respectively. The increase in fibres biodegradability and specific biogas yield have demonstrated that CFA can be used as an inexpensive alternative material to provide alkalinity and decrease or eliminate chemical demands in LAR pretreatment and AD, that could lead to significant economic benefits at an industrial level.

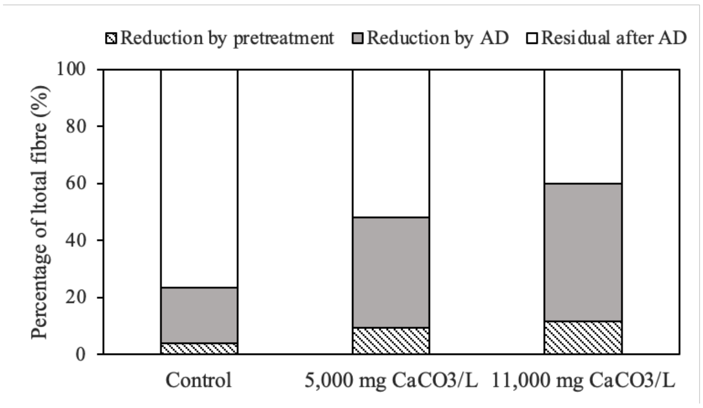

Figure 1. Reduction of total fibre after pretreatment and AD, and the residual total fibre after AD

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