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Role of Leaching and Hydrolysis in a Two-Phase Grass Digestion System

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Grassland is ubiquitous in Ireland, covering over 91% of agricultural land. Grass biomethane has shown to be a sustainable biofuel with a very strong energy balance. Anaerobic digestion is a mature technology, particularly wet continuous digestion. However, the retention periods for grass digestion are relatively long, typically over 60 days. Recently, dry batch digestion has become quiet prevalent; retention times are lower, at about 30 days, but because half of the feedstock is left in the digester for a second cycle as an innoculum, the actual retention time is of the order of 45 days. A methodology that is at the development stage is a two-stage system. The first stage is a dry batch leaching stage (hydrolysis and acidogenesis). The leachate produced is treated in an upflow anaerobic sludge blanket (UASB), where methanogenisis occurs. This should allow for the shorter retention times of the dry batch process because there is no need to leave half of the feedstock in the digester as an innoculum for a second cycle. This paper concerns itself with the leaching process. How should it be carried out? What recirculation rate should be used? Should the grass silage be from a pit (ca. 20% dry solids) or from a bale (ca. 30% dry solids)? Should the grass silage be flooded or sprinkled? An experimental process was set up that allowed for four scenarios. These scenarios included sprinkling and flooding of pit silage and bale silage. The results of the analysis were used to generate a model that predicted the application of the leach beds with a UASB. The results suggested that sprinkling of bale silage was the preferable option. It suggested that, with a 40 day retention time, gas production of 0.4 m^3 of CH_4/kg of volatile solids added could be achieved. This would be a similar value to a wet continuous system operating at a 60 day retention time and more efficient than a one-stage dry batch process.

1. Introduction

1.1. Benefits of Grass Biomethane. In the Irish context, grass is a high-yielding crop producing 11−15 tons of dry solids (DS) ha^{-1} $annum^{-1}$; this may be compared to 8−10 tons of DS ha^{-1} $annum^{-1}$ in central Europe.[1,2] Grassland does not require annual ploughing of soil and is a carbon sink. It covers about 91% of total agricultural land in the country. Farmers in Ireland are well-versed in all aspects of grass husbandry. Grass biomethane (renewable natural gas) has been suggested as the optimal non-residue biofuel in Ireland.[3] Singh and co-workers[4] suggested that biomethane could substitute between 7 and 33% (practical scenario to technical scenario) of natural gas in Ireland using indigenous feedstocks. The practical scenario (7% substitution) would involve the construction of 4 slaughter digesters, 4 municipal digesters, and 183 rural/centralized anaerobic digesters based on slurry and grass all at a scale of about 50 kilotons $annum^{-1}$ of feedstock.[4] Grass biomethane has a minimum impact on sensitive environments in Ireland. The size of the cattle herd in Ireland is in decline, leading to an estimated present excess of 100 kha of grassland; this excess may not be converted to arable land because of cross-compliance.[4] As a result, grass biomethane will not result in reduced food production.[3]

Smyth et al.[1] reported that the energy balance of grass biomethane based on a two-stage continuously stirred tank reactor (CSTR) facility is far superior to indigenous European biofuel systems, such as rapeseed biodiesel and wheat ethanol. The gross energy of grass biomethane (122 GJ ha^{-1} $annum^{-1}$) is comparable to tropical biofuels, such as palm oil biodiesel from southeast Asia (120 GJ ha^{-1} $annum^{-1}$) and sugar cane ethanol from Latin America (135 GJ ha^{-1} $annum^{-1}$).[1,5,6] The greenhouse gas savings of grass biomethane including carbon sequestration benefit is well above the 60% reduction level required to satisfy the European Union (EU) sustainability criteria for biofuels for facilities built after 2017.[7]

1.2. Technologies for Grass Monodigestion. In Ireland, the technologies proposed for grass monodigestion are either dry batch digesters or CSTR digesters. In the dry batch digester, grass silage is introduced into the batch digester and initially water is sprinkled over the feedstock, generating leachate, which is recirculated and resprinkled over the feedstock. Gas production starts, increases, peaks, decreases, and ceases. The digester is

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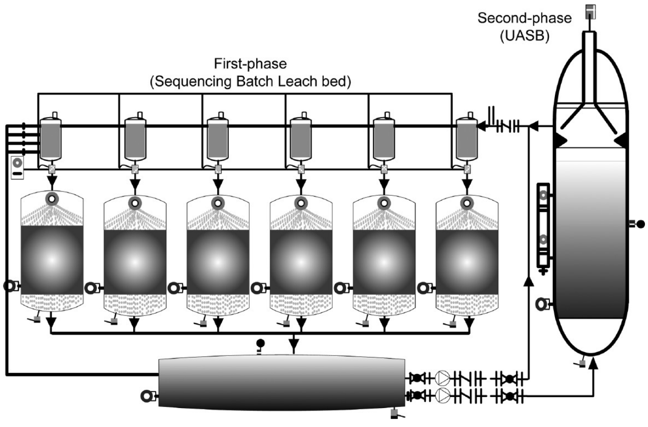

Figure 1. SLBR−UASB.

reopened; half of the feedstock is unloaded; and half is left as an inoculum for the next batch.[8] The length of each cycle (time between loading and unloading) is about 30 days, but because half of the substrate is left as an inoculum, the actual retention time is of the order of 45 days.[9] CSTR digesters may be of a single or multi-stage type. The two-stage system involves the recycle of liquid digestate back to the first digester. The hydraulic retention time (HRT) of these systems is normally beyond 60 days, with an organic loading rate (OLR) of less than 3 kg of VS m^{-3} day^{-1}. A full-scale grass digester facility (two-stage CSTR) in Austria operated at a HRT of 70−80 days, with an OLR of 1.4 kg of VS m^{-3} day^{-1}.[10]

A suggested improvement on both of these systems is the combination of a dry batch digester (leaching) system with a high rate reactor, such as an upflow anaerobic sludge blanket (UASB) reactor. The benefit of the UASB is that it can be loaded to 20 kg of chemical oxygen demand (COD) m^{-3} day^{-1} (equivalent to 14 kg of VS m^{-3} day^{-1} in the case of grass silage feedstock) while effecting a 90% destruction of COD.[9,11] This is an OLR of potentially 10 times higher than for the CSTR system. The leach beds will not require half of the feedstock to be left in the batch as inoculum as required in the dry batch system. Therefore, the actual retention time can be reduced below 45 days. Using a number of batch digesters fed in sequence, a consistent level of COD can be produced and supplied to the UASB, allowing for a consistent level of biogas production. The suggested scheme for grass digestion is known as sequencing leach bed reactor complete with UASB (SLBR−UASB; Figure 1).

1.3. Relevance and Objective of Research. Because the efficiency of the UASB has been proven through many applications in full-scale anaerobic digestion facilities, the focus of this paper is on the performance of the leaching process. The result from the study is used to model the performance, including the time-related volatile solids (VS) destruction, the level and consistency of COD produced, and prediction of the achievable methane through the SLBR−UASB process. It is an objective of this work to assess the potential methane production and the retention time of the SLBR−UASB.

2. Hydrolysis and Leaching

2.1. Soluble and Insoluble Substrates. When we consider hydrolysis, the substrate may be divided into two types: soluble and insoluble. Soluble substrate includes monomers (monosaccharides, amino acids, and long-chain fatty acids) that are readily solubilized, absorbed into the cells of microorganisms, and metabolized. Insoluble substrate includes macromolecules (disaccharides, oligosaccharides, proteins, and lipids) that require enzymatic hydrolysis to break down to their constituent monomers.[12] The major substrate in lignocellulosic material is insoluble substrate in the form of celluloses and hemicelluloses. During the leaching process, soluble substrates that are hydrolyzed from insoluble substrate accumulate in the liquor. The concentration of this hydrolyzed substrate is represented by the mass of COD in the liquid. As soluble substrate increases, insoluble substrate decreases.

2.2. Leaching: Sprinkling versus Flooding. Leaching involves passing of liquid (initially water) through the feedstock. This may be achieved by either sprinkling onto the feedstock or flooding. When the flooding methodology is used, the feedstock is submersed at all time and a liquid is recirculated through the submersed feedstock. In the sprinkling system, the feedstock is soaked by the liquid falling from a height onto the feedstock in a closed loop. The benefit of the flooding method is that all of the feedstock is submersed, in theory allowing for the soluble substrate to be solubilized more rapidly. It also allows the bacterial biomass and enzymes to have constant access to the feedstock and, thus, should result in a high hydrolysis rate of insoluble substrate. On the other hand, according to the first-order kinetic reaction, the hydrolysis rate depends upon neither the bacterial biomass concentration nor the enzyme concentration and only depends upon a parameter called the hydrolysis rate constant.[13] If the first-order kinetic equation is true, the hydrolysis rate constant could be dependent upon physical conditions, such as the sprinkling rate, bulk density of feedstock, distribution of liquid over feedstock, and force of liquid, which is dependent upon the vertical distance between the sprinkling head and feedstock. Potentially, the sprinkling method could be more beneficial because the liquid is sprinkled from a height, increasing the hydrolysis rate constant and, consequently, the hydrolysis rate of insoluble substrate.

2.3. Hydrolysis of Grass. As a lignocellulosic material, grass is composed of three main components: cellulose, hemicellulose, and lignin (Figure 2). Lignin represents the most recalcitrant part of the plant structure because of its non-water-soluble nature.[14] Cellulose is resistant to hydrolysis because of its crystallinity and the strong protection offered by hemicellulose and the lignin seal. Hemicellulose shows less resistance against hydrolysis and can be easily solubilized because of its random amorphous structure.

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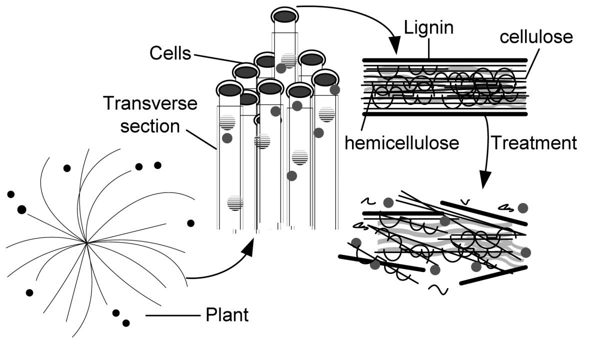

Figure 2. Lignocelluloses before and after pretreatment.

The elements of grass that are difficult to solubilize include the fibrous components of the structural carbohydrates.[11,15] Hydrolysis is considered a rate-limiting step. A fraction of the VS in grass is not amenable to hydrolysis. According to Nizami et al.,[9] for the grass silage used in this experiment, 1 kg of VS when destroyed produces 1.4 kg of COD. However, also, a fraction of the COD converted from the hydrolyzed substrate may not be amenable to degradation. Typically, an UASB can generate 90% destruction of COD and produce 0.35 m^3 of CH_4 for each kg of COD destroyed.[11]

2.4. Increased Hydrolysis Rate by Pretreatments. To reduce the effect of the rate-limiting hydrolytic stage associated with inefficient solubilization of various components because of the lignin seal, cellulose crystallinity, and degree of polymerization, different pretreatment methods may be used.[16,17] The desirable effect of pretreatment on grass is indicated in Figure 2. Promising pretreatments for agricultural residues and herbaceous crops include steam pretreatment, lime pretreatment, liquid hot water, and ammonia-based pretreatment.[15,16] Alkali, ammonia fiber/freeze explosion (AFEX), and liquid hot water are also reported as promising pretreatments.[18−21] Among these, the use of liquid hot water is simple. It enhances the accessibility of cellulosic surfaces to various enzymes and microbes and the solubilization of the hemicellulose. Additionally, the solubilization of soluble carbohydrates, such as xylan, is significantly increased, resulting in a high COD strength in the liquid leachate. It was observed that the use of liquid hot water could increase the hydrolysis rate of lignocellulosic material by a factor of 6.[11] Moreover, the higher water input in the digester can reduce the risk of condensation and precipitation of lignin and hemicelluloses over the cellulosic surfaces.[15]

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Table 1. Characteristics of Pit and Bale Silages

	pit silage	bale silage
pH	4.4	4.3
ammonia (% of total N)	12	9
protein (% DS)	12.3	9.5
ME (MJ kg^{-1} of DS)	8.8	10
DMD or *D* value (% DS or *D* value)	60	64
silage intake or palatability (g kg^{-1} W0.75)	63	89
lactic acid (% DS)	2.1	4.3
lactic acid (% total acids)	65	7.3
VFA (% DS)	1.1	1.6
PAL (mequiv kg^{-1} of DS)	757	821
NDF (% DS)	66	59
soluble sugars (% DS)	0.1	5
FME (MJ kg^{-1} of DS)	5.8	8.2
FME/ME ratio	0.71	0.81
oil (% DS)	2.9	3.3
C (% DS)	46.225	43.035
H (% DS)	5.85	5.82
N (% DS)	1.93	1.61
DS (% total)	19	30.66
VS (% total)	90	92.46

2.5. Focus of Paper. This paper focuses on the hydrolysis of grass in a batch leach bed reactor under aerobic conditions. Sprinkling and flooding conditions are assessed for bale and pit silages. Hot water (ca. 40 °C) is the leaching medium and may also be considered as a simple pretreatment. A kinetic model proposed by Pelillo et al.[22] is used to assess the optimal hydrolysis parameters (sprinkling or flooding and bale or pit silage). The model will also allow for the prediction of the methane production and retention time of the SLBR−UASB digester system.

3. Materials and Methods

3.1. Feedstock. Bale and pit silages were used in the analysis (Table 1). Bale silage is differentiated from pit silage predominately by the solids concentration; bale silage is of the order of 30% solids, while pit silage is of the order of 20% solids content.

Bale silage was obtained from the Irish Agricultural Institute (Teagasc). The herbage was harvested on June 2 (first cut, early mature) from a homogeneous perennial ryegrass (*Lolium perenne*) dominant plot. The herbage was field-wilted for 24 h before being baled. According to Nizami et al.,[11] ensiling the grass silage through wilting results in higher conservation of water-soluble carbohydrates (WSCs) and reduced volatile fatty acids (VFA) in the silage. Higher contents of WSCs result in higher COD in the reactor; this accelerates the hydrolysis process and increases the biomethane production. The bales of herbage were wrapped in 6 layers of polythene stretch film and stored for around 5 weeks to allow for ensilage to take place. They were then repackaged as small square bales stored at the normal room temperature ready for experimental use.

Pit silage in this work was taken from the pit of a farm in Cork, Ireland. It originated from a pasture dominated by ryegrass (*L. perenne*), which was conserved unwilted and without any additive. It had been left covered with polyethylene plastic for 3 months to ferment. The pit silage collected for the experiment was stored in a freezer at a temperature below 0 °C. It was allowed to defrost naturally before use.

Silage was chopped in a mobile macerator (approximated capacity of 10 kg of silage h^{-1}) to a particle size in the range of 50−70 mm.

3.2. Experimental Setup. The experiment was carried out in a 50 L stainless-steel leach bed reactor (Figure 3). The silage was supported on a fine stainless-steel mesh screen to prevent feedstock throughput. A sprinkle head is installed on the bottom of

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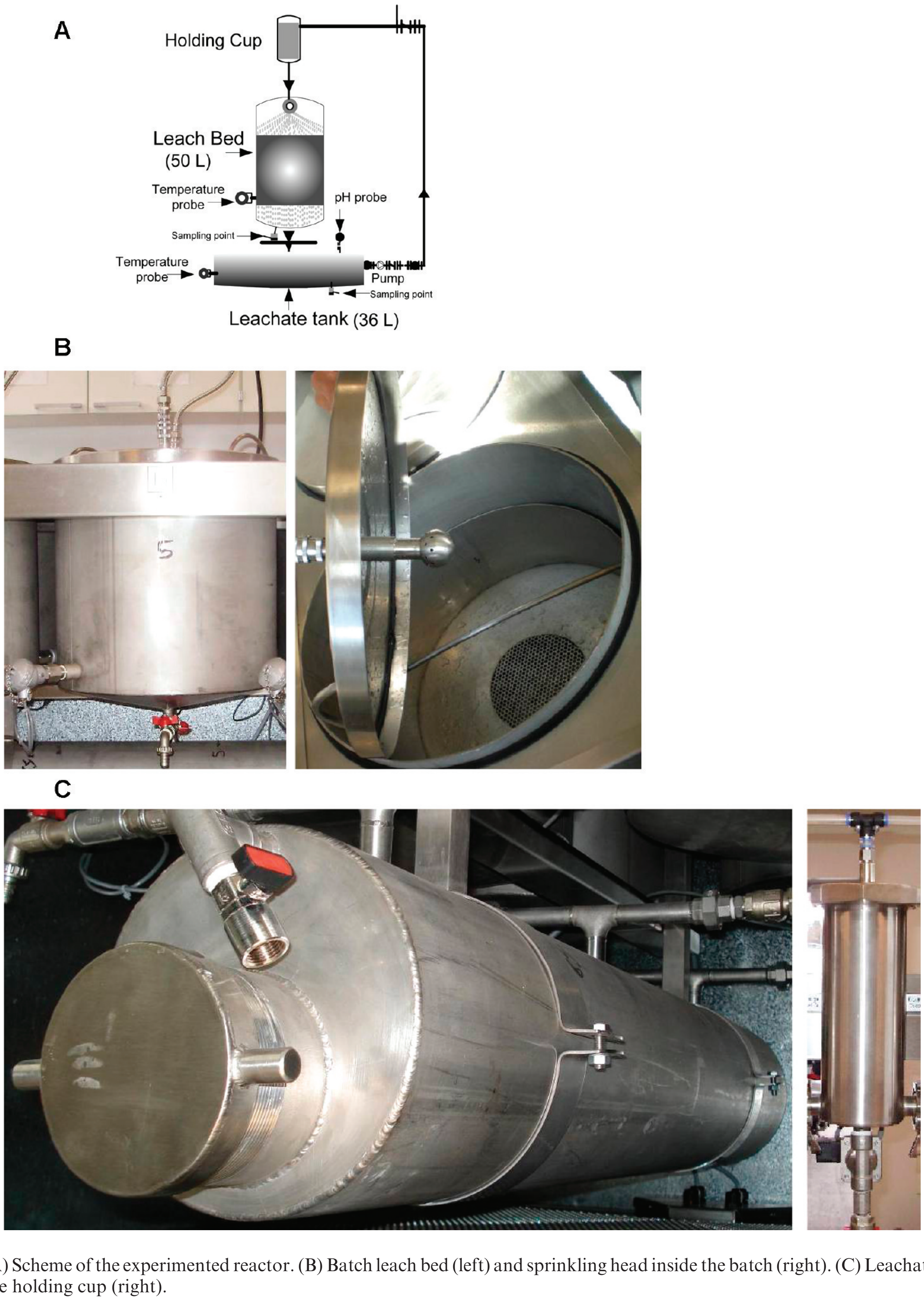

Figure 3. (A) Scheme of the experimented reactor. (B) Batch leach bed (left) and sprinkling head inside the batch (right). (C) Leachate tank (left) and leachate holding cup (right).

the lid to distribute liquid leachate across the grass feedstock. A holding cup holds the leachate until a certain level is reached, and an automatic valve opens when the cup is full, allowing the leachate to flow to the sprinkle head. After passing through the leach bed, the leachate is collected in a 36 L stainless-steel leachate tank (Figure 3C). The leachate may be sampled from this tank, in particular, for COD assessment. A variable-speed pump connects the leachate tank to the holding cup. A heating panel is installed below the leachate tank and is used to control the temperature of both the leachate bed and leachate tank.

3.3. Experimental Procedure. In the study, four sub-experiments were performed as per Table 2: sprinkling−pit silage (S−P), sprinkling−bale silage (S−B), flooding−pit silage (F−P), and flooding−bale silage (F−B). The experiment was started by adding water to fill up the leachate tank in the case of sprinkling experiments. For the flooding experiments, additional water was added to flood the leach beds. A total of 40 L of water is added to the system for the sprinkling experiments, and a total of 75 L of water is added to the system for the flooding experiments. The added water was heated to 40 °C before experiments began. This water was entirely

Table 2. Summary of Experimental Cases

run	leaching method	silage type	grass loaded (kg)	DS loaded (kg)	VS loaded (kg)	water added (L)	theoretical COD loaded[a] (kg)	maximum theoretical COD concentration[b] (g L^{-1})	recirculation rate (L day^{-1})
S−P	sprinkling	pit	5.0	0.99	0.88	40	1.23	28.0	100.0
S−B	sprinkling	bale	5.0	1.5	1.38	40	1.93	44.41	100.0
F−P	flooding	pit	5.0	1.15	1.06	75	1.48	18.79	50.0
F−B	flooding	bale	5.0	1.5	1.38	75	1.93	24.61	50.0

[a] On the basis of 1 kg of VS = 1.4 kg of COD; e.g., for run S−P, 0.88 kg of VS × 1.4 = 1.23 kg of COD. [b] On the basis of full destruction of volatiles. Takes into account water added and moisture in silage; e.g., for run S−P, moisture = 4.01 kg (4.01 L). COD concentration = 1.23 kg of COD × 1000/(4.01 + 40) = 28.0 g L^{-1}.

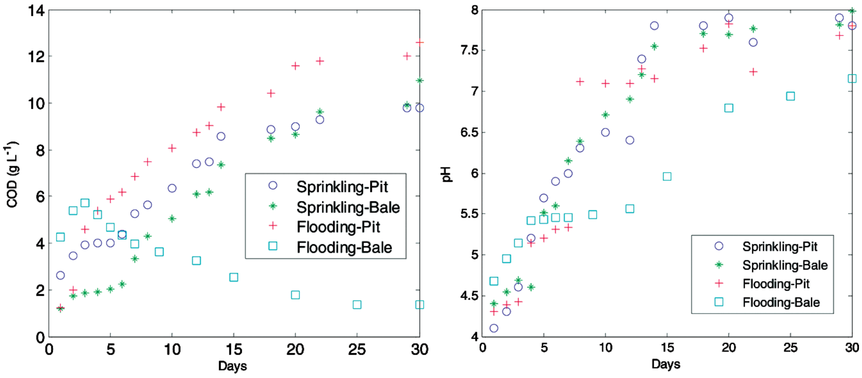

Figure 4. Measured COD and pH for different experimental runs.

removed from the system upon completion of a sub-experiment, and new water was then added for the next sub-experiment. In all cases, 5 kg of macerated grass silage was placed in the leach bed. For flooding experiments, grass in the leach bed was entirely submersed in water, while in the case of sprinkling, the water level was set under the mesh screen and, therefore, well below the grass feedstock. The pump started to circulate the water and distribute through the grass feedstock at a rate of 100 L day^{-1} in the case of sprinkling and 50 L day^{-1} in the case of flooding. Liquid leachate was sampled from the leachate tank to measure the COD concentration. Each sub-experiment was continued for a 30 day period. At the end of each sub-experiment, post-leaching grass was weighted and tested for DS and VS contents. Because it is not possible to take a VS sample midway through a hydrolysis test, each sub-experiment was repeated over a shorter time frame to generate VS on intermediate days (for example, day 10 or 15). This is required for curve fitting in the kinetic modeling process discussed later (refer to Figure 6).

3.4. Analytical Methods. DS and VS contents were measured using methods detailed by the American Public Health Association (APHA).[23] The COD concentration was measured by a COD analyzer set, model HACH DRB200 and DR/2800. A complete grass silage analysis report based on their feeding value for dairy cattle was conducted by the Agri-Food and Biosciences Institute (AFBI), Belfast, U.K. C, H, and N contents in grass silage were analyzed by the Department of Chemistry, University College Cork, Cork, Ireland, using the ultimate analysis method. Scanning electron microscopy (SEM) was carried out on a FEI Inspect F system operating at 10 kV to examine the changes within the grass silage structure under flooding conditions after a 30 day leaching period. Samples were placed on a conductive carbon tape prior to imaging.

4. Results

4.1. Variation in VS and COD. Figure 4 indicates the variation of COD and pH over time for the four experimental runs. In most cases, COD increases up to day 30, except the run F−B, where the COD peaks at day 3 and subsequently declines. Because experiment runs were not performed under anaerobic conditions, COD would be partially degraded by the bacterial biomass naturally occurring in the grass feedstock. The decrease of COD indicates the higher rate of COD degradation than the hydrolysis rate. The VS removal after 30 days for each run is shown in Table 3. The highest VS removal is shown in the run S−B (70.6%). It may be concluded that the sprinkling of bale silage use is the best condition for hydrolysis. The hydrolysis rate for the runs S−P and F−P are similar (60.6% VS removed as compared to 63.8%). Therefore, the sprinkling method may be more favorable than the flooding method, which requires more liquid and, hence, extra thermal energy to heat. The low percentage of VS destruction in the run F−B may be caused by the pH inhibition. It is suggested by Veeken et al.[24] that, in the pH range of 5.0−7.0, decreased pH inhibits the hydrolysis rate as a linear function. The run F−B shows an obvious difference in pH to the other runs; the pH remains below 6.0 to day 15.

4.2. Changes of the Grass Structure Because of Leaching. Patterns of the grass structure before and after leaching, as observed through the eye of SEM, are shown in Figure 5. The structure of grass feedstock preleaching (Figure 5A) shows the covering of hemicellulose and lignin seal over the crystalline structure of cellulose. This covering prevents the cellulose from exposure to external environments. The purpose of the leaching process (as per Figure 2) is to break through the structure by disordering the lignin and hemicellulose covering, allowing for hydrolysis to take place within the internal cellulose core. Figure 5B shows the surface of grass silage after leaching under flooding conditions. The hemicellulose, which ties up cellulose strands, is loosened and ruptured. The lignin and cellulose structures, which originally stretch in straight lines, are now significantly distorted.

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Table 3. Percent of DS and VS Destruction after 30 Days of Leaching

experimental run	percentage of DS destroyed (%)	percentage of VS destroyed (%)	measured COD at day 30 (g L^{-1})	COD as a percentage of the maximum theoretical (%)
S−P	61.4	60.6	9.8	35.0
S−B	70.6	70.6	10.98	24.7
F−P	64.2	63.8	12.6	67.1
F−B	35.3	31.9	1.37	5.6

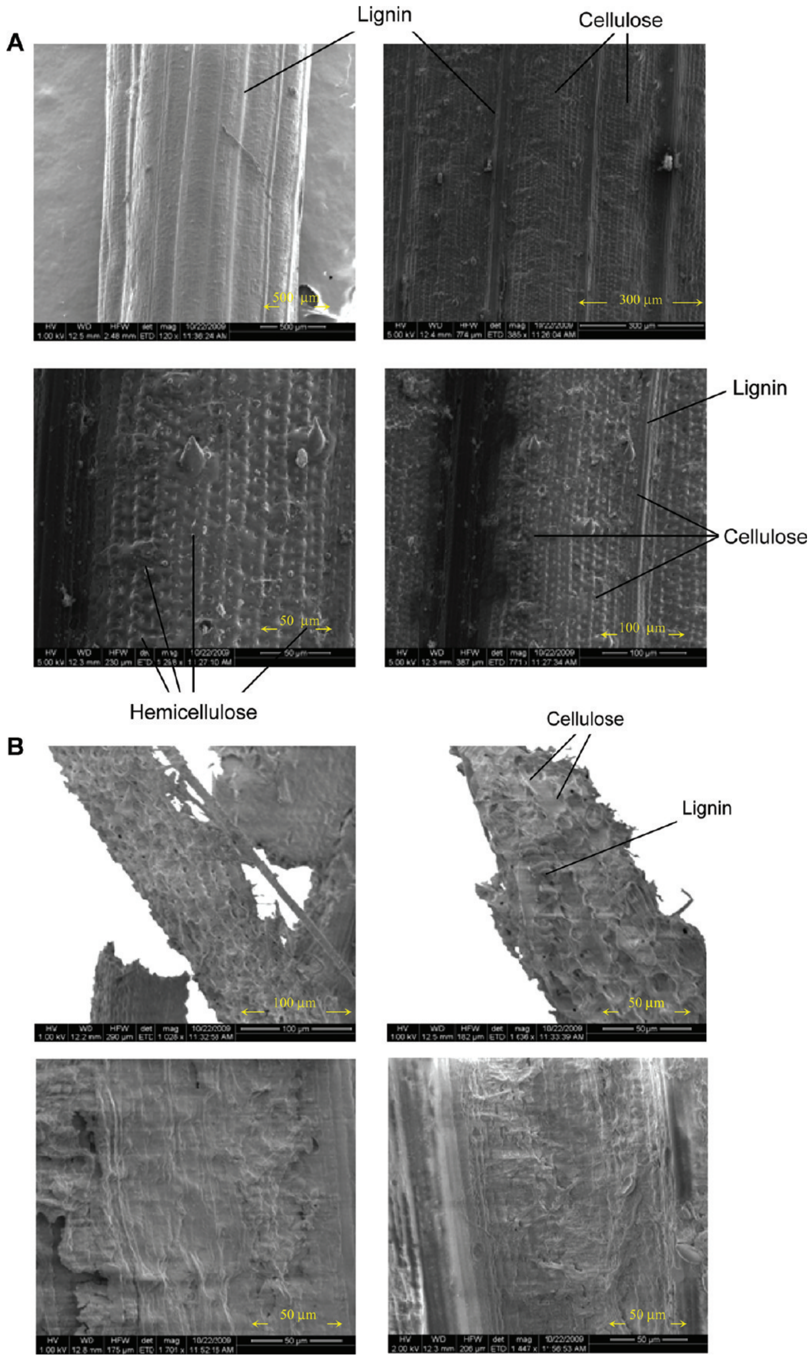

Figure 5. (A) Grass silage structure before leaching. (B) Grass silage structure after hydrolysis under flooding conditions.

5. Kinetic Modeling

5.1. Characteristics of the Model. To generate a relationship between VS removal and observed COD, a simple kinetic model is built. The model was proposed by Pelillo et al.,[22] who studied the aerobic degradation of olive mill effluents. The model comprises three differential equations, which describe the rate of change of three state variables, including insoluble substrate (S_I), soluble substrate (S_S), and bacterial biomass (X). Insoluble substrate requires hydrolysis to convert to soluble substrate. The soluble substrate thus increases as the insoluble substrate decreases during the hydrolysis process. Hydrolysis takes place in the enzymatic reaction. Enzymes are produced by bacterial biomass, which metabolizes soluble products. Equation 1 describes the reduction of insoluble substrate during the hydrolysis

Table 4. Parameters Used in the Leaching Model[22]

	State Variables
S_I	insoluble substrate concentration (g of CODS L^{-1})
S_S	soluble substrate concentration (g of CODS L^{-1})
X	bacterial biomass concentration (g of CODX L^{-1}).
	Fitting Parameters
k_h	hydrolysis rate constant (L g^{-1} of CODX day^{-1})
k_c	consumption rate of soluble substrate by bacterial biomass (L g^{-1} of CODX day^{-1})
k_d	bacterial biomass death rate (day^{-1})
Y	bacterial biomass yield on soluble substrate (g of CODX g^{-1} of CODS)
S_{Io}	non-biodegradable fraction in the insoluble substrate (g of CODS L^{-1})
S_{So}	non-biodegradable fraction in the soluble substrate (g of CODS L^{-1}).
	Initial Conditions
S_{Iini}	initial insoluble substrate concentration before the leaching (g of CODS L^{-1})
S_{Sini}	initial soluble substrate concentration before the leaching (g of CODS L^{-1})
X_{ini}	initial bacterial biomass concentration before the leaching (g of CODX L^{-1})
	Note
CODX	COD contributed by bacterial biomass
CODS	substrate COD (COD equivalent in the case of insoluble substrate)

Table 5. Parameters in the Kinetic Model

	S−P	S−B	F−P	F−B
S_{Iini} (g of CODS L^{-1})	28.0	44.41	18.79	21.11
S_{Sini} (g of CODS L^{-1})	0.0	0.0	0.0	3.5
X_{ini} (g of CODX L^{-1})	0.50	0.33	0.20	0.55
k_h (L g^{-1} of CODX day^{-1})	0.085	0.045	0.36	0.44
k_c (L g^{-1} of CODX day^{-1})	0.09	0.09	0.01	0.17
k_d (day^{-1})	0.05	0.02	0.045	0.08
Y (g of CODX g^{-1} of CODS)	0.10	0.14	0.06	0.12
S_{Io} (g of CODS L^{-1})	2.0	0.0	1.10	14.5
S_{So} (g of CODS L^{-1})	1.20	0.0	0.60	0.20

process. Equation 2 describes the increase of soluble substrate from hydrolysis of insoluble substrate minus the total consumption of soluble substrate by the bacterial biomass. Equation 3 describes the bacterial biomass growth; this equates to the yield of new bacterial biomass minus the death of existing biomass.[22] All parameters in these equations are defined in Table 4.

$$dS_I/dt = -k_h(S_I - S_{Io})X \tag{1}$$

$$dS_S/dt = k_h(S_I - S_{Io})X - k_c(S_S - S_{So})X \tag{2}$$

$$dX/dt = Yk_c(S_S - S_{So})X - k_dX \tag{3}$$

5.2. Fitting Parameters to the Model. The differential equation set of this model was solved using the ODE45 solver, a built-in function of MATLAB. Runge−Kutta integration techniques are applied in the solver. Parameters to fit the observed data are shown in Table 5, and the fitting curves for each run are shown in Figure 6.

5.2.1. Initial Conditions. The initial condition in the model was input to parameters S_{Iini}, S_{Sini}, and X_{ini}, which represent initial insoluble substrate, soluble substrate, and bacterial biomass, respectively. S_{Sini} and X_{ini} are based on a curve fitting.

S_{Iini} was estimated from the VS content in grass feedstock input, taking into account the COD equivalent of VS at 1.4 g of COD g^{-1} of VS (previously calculated in Table 2).

S_{Sini} is dependent upon not only the type of silage but also the leaching condition. The soluble substrate COD curve of the run F−B indicates a S_{Sini} value of 3.5 g of CODS L^{-1}, while for the runs S−P, S−B, and F−P, the value is 0. This indicates the better initially solubilizing capability of bale silage under flooding than sprinkling conditions. With reference to silage properties in Table 1, it may be noted that bale silage has a higher percentage of soluble sugar (5%), as compared to only 0.1% in pit silage. This soluble sugar can be quickly solubilized in the flooding liquid, producing an initial COD concentration at an early stage of the leaching process.

X_{ini} is unlikely to be determined by measurement unless a known amount of bacterial biomass is initially added to the leach bed. However, this experiment aims to examine the system without additive, which can be considered as a base case for an actual application.

5.2.2. Fitting Parameters. Parameters k_h, k_c, k_d, Y, S_{Io}, and S_{So} are estimated by the curve fitting. They show some variations in the value among different runs. Flooding cases have a greater k_h than sprinkling cases. This indicates a rapid hydrolysis response under flooding conditions. Parameters k_c, k_d, and Y are more related to conditions of bacterial biomass during the leaching process; thus, they vary. The parameter S_{Io} is significantly high in the run F−B. In effect, this indicates a limited conversion from insoluble to soluble substrate for bale silage under flooding conditions, although the conversion through hydrolysis occurs at a high rate. In contrast, bale silage under sprinkling conditions (run S−B) shows a value for S_{Io} of 0. This indicates that all of the VS content can be hydrolyzed if a sufficient retention time of silage is allowed in the reactor. In the case of pit silage (runs S−P and F−P), the parameter S_{Io} is relatively close to 0, indicating that more than 90% of the insoluble substrate can be degraded. For parameter S_{So}, the value is low in all cases, indicating that most of the insoluble substrate converted to soluble substrate can be degraded and, therefore, may be digested in an anaerobic reactor.

6. Application of Experimental Output and Model

6.1. One- and Two-Stage Digestions. Hydrolysis and acidification of substrate take place in the leaching process in the first phase of a two-phase digester system. Methanogenesis occurs in the second-phase reactor. Hofenk et al.[25] studied two-phase anaerobic digestion of organic fraction of municipal solid waste (OFMSW) and concluded that one- and two-phase digesters could produce a similar biogas yield unless the hydrogen produced in the acidification process (in the first-phase reactor) can be captured and converted to methane. However, Gunaseelan[26] suggested that the two-phase digester allows for optimal growth conditions in separate chambers for hydrolytic and methanogenic bacteria, and thus, a high digester performance resulting in a high methane yield can be expected. Lin and Ouyang[27] compared a single-phase UASB and a CSTR acid-phase digester connected with an upflow methane-phase digester in sludge digestion. They reported higher VS destruction in the two-phase system than in the single-phase system.

6.2. Application of SLBR−UASB to Grass Digestion. Lehtomäki et al.[28] investigated the performance of the

(25) Hofenk, G.; Lips, S.; Rijkens, B. A.; Voetberg, J. W. Two-phase anaerobic digestion of solid organic wastes yielding biogas and compost. *EC Contract Final Report ESE-E-R-040-NL*, 1984; p 57.

(26) Gunaseelan, N. V. Anaerobic digestion of biomass for methane production: A review. *Biomass Bioenergy* **1997**, *13* (1−2), 83–114.

(27) Lin, H. Y.; Ouyang, C. F. Upflow anaerobic sludge digestion in a phase separation system. *Water Sci. Technol.* **1993**, *28* (7), 133–138.

(28) Lehtomäki, A.; Huttunen, S.; Lehtinen, T. M.; Rintala, J. A. Anaerobic digestion of grass silage in batch leach bed processes for methane production. *Bioresour. Technol.* **2008**, *99* (8), 3267–3278.

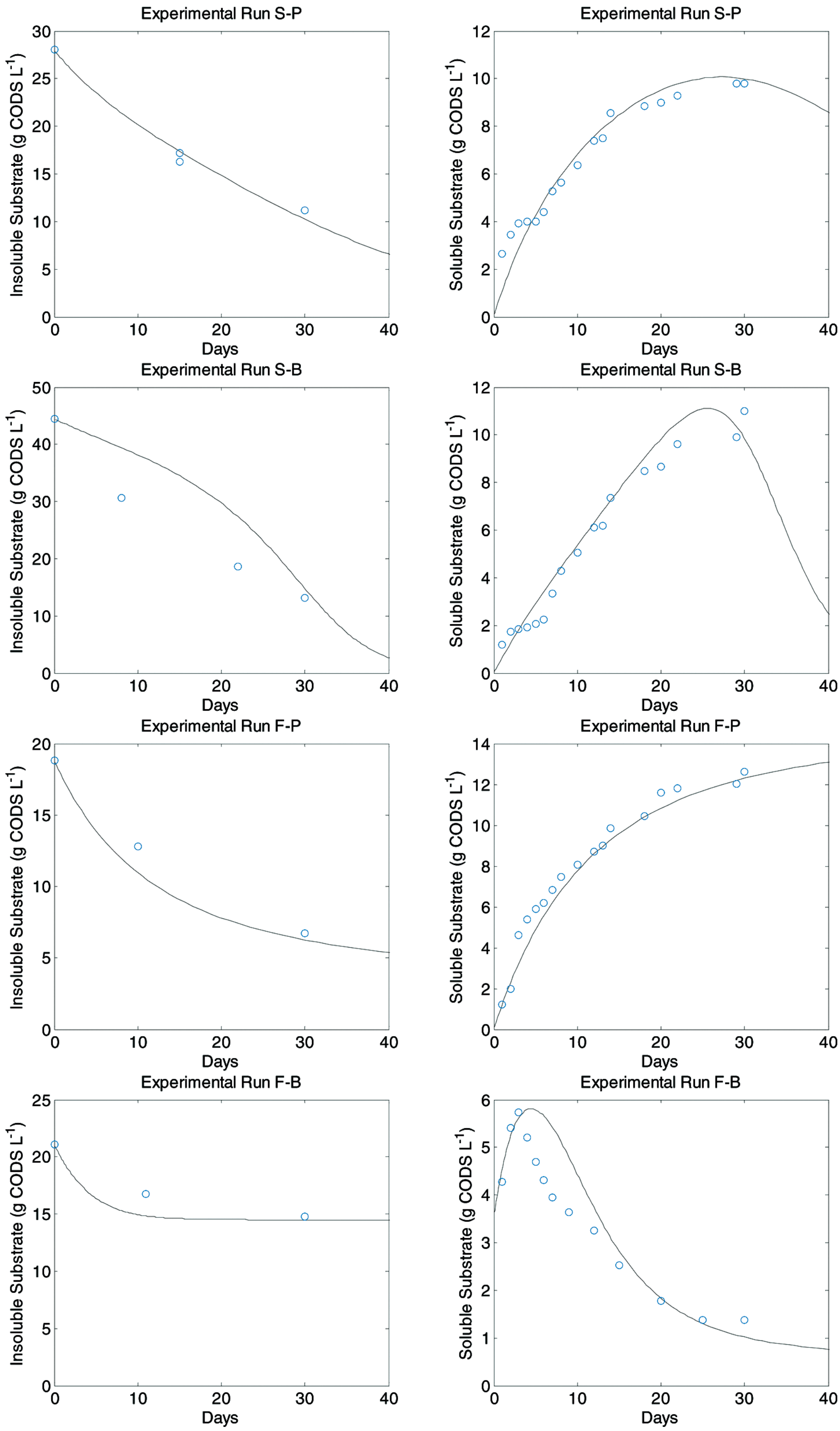

Figure 6. Variation of insoluble and soluble substrates: (○) experimental data and (—) simulating model. The data for insoluble substrate (VS) is by necessity taken from more than one run of the experiment. We cannot take a VS sample midway through a hydrolysis test. The data from days 0 and 30 is from one run, but the intermediate data is, by necessity, from other runs. The soluble substrate (COD) is from only one run of the experiment and is associated with the run from which the first and last (days 0 and 30) insoluble substrate is taken.

single-stage dry batch leach bed anaerobic digester in comparison to the same leach bed followed by an UASB, using grass silage as a feedstock. They found 83% of the extracted COD converted to methane in the single-stage leach bed, as opposed to 92−95% in the leach bed−UASB system. Moreover, they reported a high UASB efficiency (above 90%) corresponding to a high influent COD strength; this efficiency decreased to 45−55% when the influent COD

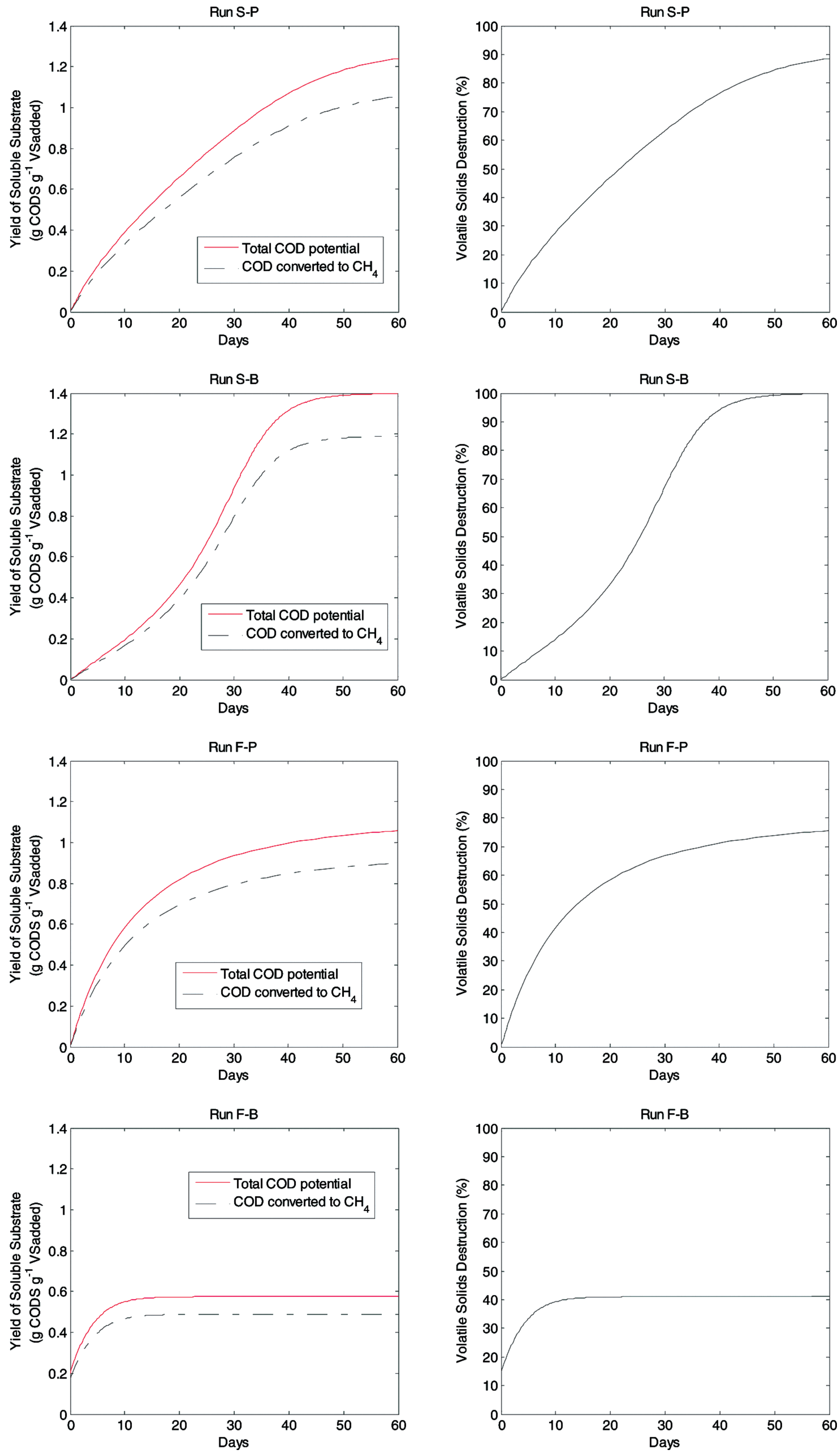

Figure 7. Cumulative yield of soluble substrate and corresponding percentage of VS destruction.

dropped to ca. 1 g L^{-1}.[28] A similarity is found in the study by Shin et al.[29] in a SLBR−UASB system for food waste digestion. They reported COD removal efficiency over 96% at a high influent COD (between 6.6 and 8.6 g L^{-1}). The influent COD in their experiment was maintained consistently high using a series of batch leach beds with a time lag of 2 days between feeding.[29]

(29) Shin, H. S.; Han, S. K.; Song, Y. C.; Lee, C. Y. Performance of UASB reactor treating leachate from acidogenic fermeter in the two-phase anaerobic digestion of food waste. *Water Res.* **2001**, *35* (14), 3441–3447.

There is significant potential for this system (SLBR–UASB) applied to grass digestion in Ireland. A study by Smyth et al.[1] suggested a size of about 140 ha under grass to be amenable for a farm-based grass–biomethane facility.[1] Thamsiriroj and Murphy[30] using a two-stage CSTR grass digestion facility at small pilot scale found a methane yield from bale silage in Ireland of 455 m^3 kg^{-1} of VS_{added}. This is equivalent to over 90% destruction of VS. However, the experiment was performed under a long HRT and low OLR (HRT, 221 days; OLR, 0.5 kg of VS m^{-3} day^{-1}). The results of this study suggest 70.6% destruction of VS from bale silage under sprinkling conditions (S–B) within 30 days. There is significant potential for the batch leach bed to achieve a higher percent destruction of volatiles with additional retention time and, thus, to compete with the CSTR system.

6.3. Achievable Methane Yields from SLBR–UASB. The kinetic model (on the basis of fitting parameters from Table 5) can be further applied to examine extended retention times. Figure 7 shows cumulative COD in the leachate simulated in the kinetic model over a 60 day leaching period without aerobic degradation. The percentage of VS destruction is also indicated. The COD extracted would be used to produce biogas in the UASB reactor (retention time of 1 day).

It is assumed that 85% of the COD obtained from the leaching step is converted to biogas in the UASB reactor. The 15% remaining includes consumption by aerobic (in leach bed) and anaerobic (in UASB) bacterial biomass and the non-biodegradable fraction of COD. It is also assumed that the hydrolysis characteristics of the leach bed in connection to UASB do not change as compared to the single leach bed as in our experiment. This assumption is on the conservative side, because normally, the effluent from the UASB reactor, which is recirculated to the leach bed, will contain a significantly lower level of COD content; this would facilitate a high leaching performance (increase in the k_h value), as compared to the liquid leachate, which carries a high COD strength. From Figure 7, the percentage of VS destruction for sprinkling cases is higher than flooding cases. It may therefore be concluded that the sprinkling method is more efficient for grass silage hydrolysis than flooding. Sprinkling would result in a shorter retention time and a relatively higher methane yield than flooding.

6.4. Suggested Operation of the SLBR–UASB. A proposed operation of a SLBR–UASB system would involve insertion of feedstock to the leach beds on a weekly basis. For example, if a system is composed of 6 batch leach beds, the retention time of grass feedstock in each batch will be 42 days. From Figure 7, the COD removed (converted to CH_4) at day 42, is 0.934, 1.143, 0.855, and 0.489 g of COD g^{-1} of VS_{added} for the runs S–P, S–B, F–P, and F–B, respectively. Theoretically, 1 kg of COD produces 0.35 m^3 of CH_4.[11,31] Methane yields estimated from this basis are equal to 0.33, 0.40, 0.30, and 0.17 m^3 kg^{-1} of VS_{added} for the runs S–P, S–B, F–P, and F–B, respectively. Bale silage under the sprinkling conditions could produce the highest methane yield, followed by pit silage under the sprinkling conditions. This is comparable to the 0.455 m^3 of CH_4 kg^{-1} of VS_{added} in a two-stage CSTR, with a HRT of 221 days.[30]

(30) Thamsiriroj, T.; Murphy, J. D. Difficulties associated with monodigestion of grass as exemplified by commissioning a pilot-scale digester. *Energy Fuels* **2010** (doi: 10.1021/ef1003039).

(31) Von Sperling, M.; de Lemos Chernicharo, C. A. *Biological Wastewater Treatment in Warm Climate Regions*; IWA Publishing: London, U.K., 2005.

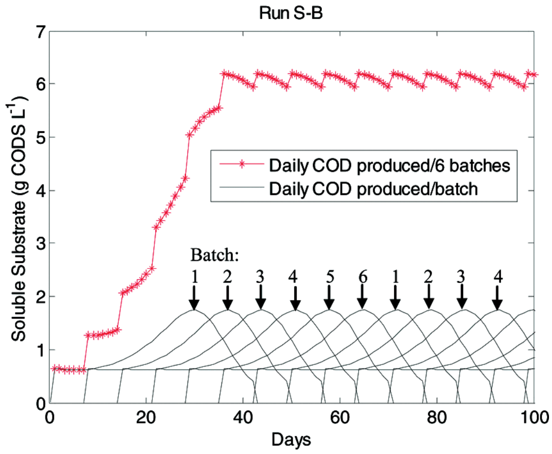

Figure 8. Influent COD to UASB reactor simulated for sprinkling bale silage (S–B) in a sequentially fed 6 leach bed reactor system with feeding every 7 days.

Figure 8 shows the influent COD input to the UASB reactor simulated for the run S–B with 6 leach beds, 7 days between sequential feeding, and a retention time of 42 days. For example, the first batch is filled on day 1, batch 2 on day 8, etc. On day 42, digestate from the first batch is removed and batch 1 is refilled with new grass feedstock. The top curve in Figure 8 shows the cumulative COD as a sum of the daily COD produced from the 6 batches. Thus, when the leach beds are operated in series, a consistent COD influent can be achieved. For this particular run (S–B), the average COD can be maintained at about 6 g of COD L^{-1} to feed the UASB reactor. Shin et al.[29] reported COD removal efficiency over 96% at a COD between 6.6 and 8.6 g L^{-1}. The result in Figure 8 is slightly below this range. If a higher COD level is required to feed the UASB and achieve higher COD efficiency, either the initial quantity of water should be reduced (increasing concentration) or the retention time should be reduced somewhat (reducing overall reduction in VS). Alternatively, the sprinkling rate could be increased to increase the hydrolysis rate. Caution must be exercised in combining the two systems. The UASB is typically designed on two aspects: OLR and upflow velocity. The upflow velocity should be less than 0.1 m/h. This may clash with the sprinkling rate required for the leaching process. Two pumps may be added, but this may add to the complexity and cost of an up-scaled system. Alternatively, once a new batch of grass is filled, a high sprinkling rate may be performed for a short period (e.g., 24 h), while the UASB is disconnected to obtain an initial high COD strength. Subsequently, the UASB is connected, and the leachate is fed at a lower rate to the UASB. This will thus reduce the electrical energy demand of the pump, and a consistently high COD level can be achieved.

7. Conclusions

In a two-phase anaerobic digestion system, the first stage must concern itself with conversion of VS to COD. The second phase is concerned with the conversion of the COD to CH_4. This process examined the hydrolysis of grass silage in two forms: bale silage (at 30% DS content) and pit silage (at 19% DS content). It also compared sprinkling as a method of conversion of solids to COD to flooding. The results of an experimental process suggest the best case is sprinkling of bale silage. A kinetic model of the process was generated that allowed for simulation of a SLBR−UASB reactor. The model suggested that, if 6 leach beds are fed sequentially every 7 days (cycle time of 42 days) and a sprinkling hydrolysis is effected on bale silage, then there is potential to achieve a consistent leachate with a COD of 6 g L^{-1} and generate 0.4 m^3 of CH_4/kg of VS added. This offers great advantages over existing anaerobic digestion systems proposed for grass silage in terms of both retention time and methane production. The methane production potential is in the high range suggested for grass digestion, which is typically of the order of 0.3−0.4 m^3 of CH_4 kg^{-1} of VS added.[11] Dropping the retention time from over 60 days for a wet process digesting grass to 42 days for the two-stage process described here is very significant. The 30% reduction in size must lead to a marked decrease in capital costs, leading to lower production costs and more profitable renewable energy production.

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