

The Reaction Front Hypothesis in Solid-State Digestion

Estimation of Minimum Size of Viable Seed Body

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Abstract

An alternative mechanism for the anaerobic digestion of a bed of solids was recently proposed. A multizoned reaction front might form around a suitable body of seed material, then advance through the bed, within the solid phase. Such a solid-phase mechanism might coexist with liquid-phase digestion but one or the other of these two parallel mechanisms might generally be dominant. It is envisaged that solid-phase digestion would be favored by the presence of viable seed bodies: single particles of a suitable seed material above a minimum size or equivalent aggregates. A key determinant of the feasibility of this mechanism is expected to be the minimum viable size for a seed body (d_{\min}). This would depend on the thickness of the reaction zones, some of which must initially be accommodated within the seed body. In this article, we present some theoretical estimates of d_{\min} , which indicate a magnitude of 7–700 mm. Such values suggest that solid-phase digestion might be the norm in semi-dry waste digesters. Such digestion might be rare in unseeded landfills but it would appear likely that it could easily be initiated by suitable seeding.

Index Entries: Anaerobic digestion; biomethanation; landfill; reaction front; rapidly solubilized organics; slowly solubilized organics; solid-phase digestion; seed body; digester.

Introduction

Most conventional models of biomethanation or anaerobic digestion place the reaction zone in the liquid phase, even for solid substrates. This is correct for small particles in a slurry or suspension. However, a solid-phase mechanism is plausible for a bed of larger solids, such as organic wastes (1), and might provide a better habitat for the complex of syntrophic species involved. Growth in a solid matrix might enable each species to find

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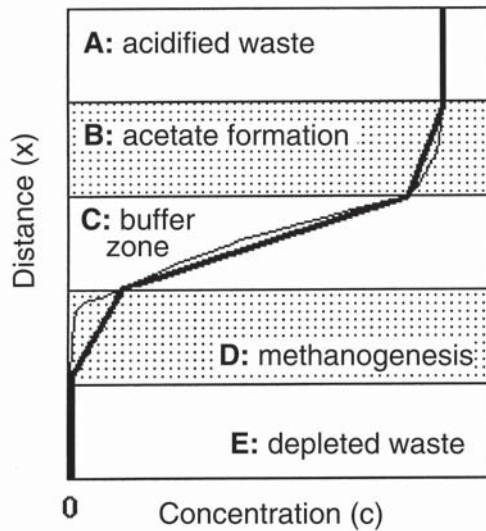


Fig. 1. VFA concentrations across reaction front. Actual profile: faint line; model basis: bold lines; main reaction zones: shaded. The front, comprising zones B–D, advances slowly into zone A.

an optimal microenvironment, with diffusion effecting metabolite exchange with other microenvironments nearby. Similar mechanisms apply in conventional, mixed, batch anaerobic digestion, but the disruption of spatial associations by mixing may interfere with syntrophic relationships, especially at startup (2). Thus, models predict that minimal mixing might be preferable in the early stages (3). However, mixing can also help to disperse acid-inhibitory intermediates, such as acetate.

No mixing is possible in a solid medium but spatial separation of the successive reaction steps, into distinct acetogenic and methanogenic zones, could be as effective (see Fig. 1). The zones in Fig. 1 are defined by the planes at which certain reaction steps start or stop and are marked by changes in the acetate concentration (conventionally measured as volatile fatty acids [VFA]). The faint curve shows the general form of the true concentration profile; the bold lines show the profile assumed for modeling purposes.

The “reaction front” model of solid-state digestion proposes that these reaction zones, with an intervening buffer zone, form a reaction front that gradually advances through the solids (4). The front cannot cross voids but spreads from particle to particle through solid-solid contact, which may be why compaction and moderate shredding of the waste are generally beneficial (5). (Both phases, liquid and solid, are, of course, continuous in a packed bed of soft, flexible, particles.) The depths of zones B–D vary according to the local composition of the waste but they are relatively thin. Most of the waste mass lies in zone A (initially) or E (finally).

The reaction front model applies only to a bed of solids with high nutrient availability and little or no moisture movement. Thus, it does not

apply to conventional anaerobic digestion, to “flushing bioreactors,” or to the digestion of composted wastes. However, it probably does apply to many semi-dry municipal waste digesters and, at least in part, to many landfills receiving unsorted municipal solid wastes.

The substrate is considered here as falling into two fractions: rapidly solubilized organic matter (RSO) and slowly solubilized organic matter (SSO). These fractions correspond roughly to the conventional division into readily and slowly digestible organics. The distinction is drawn because RSO is *less* digestible than SSO in a bed of solids, in which substrate concentrations cannot be controlled. The high nutrient availability in RSO generates acetate faster than it can be utilized, causing severe acid inhibition of the process. Thus, the classifications used in conventional anaerobic digestion are misleading.

The key features of the model are as follows:

1. After the initial acidification of the waste, no further reaction occurs at any point until the front arrives.
2. The front can only form at the surface of a “viable seed body”.
3. The front comprises three distinct zones.
4. The zones may be thin and marked by steep concentration gradients.
5. The reaction front gradually advances into the waste as the waste adjacent to it is depleted of RSO.
6. RSO is fully utilized within the reaction front, in a localized process.
7. SSO is utilized in a dispersed process after the front has passed.

A viable seed body must be composed of a lean material well populated with methanogens and large enough to accommodate zones C and D while the front is forming (6). Previously digested waste is therefore a good source, provided that its particle size range is adequate.

The reaction mechanism envisaged is as follows. The conversion of RSO to acetate is completed in zone B. The acetate then diffuses through zone C, which provides enough mass transfer resistance to protect zone D from excess acetate. Methanogenesis occurs in zone D, completing the conversion of RSO to biogas. The depths of the zones are self-regulating and vary with local conditions. The reaction steps for SSO are the same, but spatial separation of the steps is less significant. Its conversion is mostly completed in zone E, where the whole process is hydrolysis limited, so it can proceed without spatial separation. However, hydrolysis, acidogenesis, and acetogenesis do begin in zone B. They continue in zone C, as shown by the slight curvature of the true VFA profile (Fig. 1). The acetate yielded is converted into methane in zone D. However, because the conversion of SSO is hydrolysis-limited, the total conversion of SSO achieved in the thin, acid-inhibited zones of the reaction front is small.

The overall rate of the process is determined by the area of the reaction front, which leads to a simple mathematical model (7). The rate-limiting reaction is probably acetogenesis, in zone B. The digestion of SSO is not rate limiting, because it mainly occurs in the inhibition-free and relatively deep

zone E. The hydrolysis of RSO is relatively fast, by definition. Acidogenesis is also fast. Methanogenesis could be rate limiting—but, if it were, zone D would expand until it was not. (The local acetate concentration would rise and the diffusing acetate would reach the substrate-limited biomass in zone E, pushing back the D:E boundary.) Acetogenesis is the only step not ruled out by this argument.

All the reaction in zone A is totally acid inhibited, so inhibition must be severe in zone B. Thus, the overall rate-limiting reaction is the acid-inhibited, acetogenic step in the breakdown of RSO. This is why readily solubilized organic matter is *not* always readily digestible. In a fixed bed, it can be biodegraded only when the profound acid inhibition it causes is locally relieved by the arrival of the reaction front.

Such heterogeneous mechanisms can be more effective than their homogeneous equivalents (8). In conventional anaerobic digestion processes, protection from inhibitory acetate concentrations is effected by limiting the substrate concentration but with spatial separation of the steps this limitation can be lifted. Moreover, the reaction front would provide an ideal environment for syntrophic partnerships, with contrasting micro-environments in close proximity. This would greatly facilitate electron transfer and the two-way exchange of metabolites. Interestingly, some recent modeling studies of conventional anaerobic digestion have predicted that an unmixed initial period, with the inoculum concentrated in a small part of the digester, would be beneficial (3). While this might be difficult to achieve in practice in a fluid, in a solid it would arise naturally. Such studies thus support the suggestion that a heterogeneous mechanism could be more effective.

Seeding techniques would be a critical determinant of the dominant mechanism. The proposed heterogeneous mechanism probably dominates in waste digesters seeded with previously digested waste; the conventional homogeneous mechanism probably dominates in unseeded 'flushing bioreactor' landfills. However, in the early stages, it is likely that the process is metastable, at best, and readily 'flipped' into the alternative mode. Moreover, these two parallel mechanisms are not incompatible and might co-exist, especially in 'unflushed' landfills. This paper estimates the key dimensional parameters that determine whether viable seed bodies are common and thus whether natural occurrences of solid-phase digestion are probable.

Buffer Zone Model

Basis of Model

The model is based on steady-state conditions in an advancing reaction front. The preceding acceleration phase is not modeled but the underlying mechanisms are described here, to place the model in context. This phase can be considered in two stages: front maturation (which can be very slow) and front expansion (which can be absent).

Initially, the buffer zone might be much thicker than it is in the mature reaction front. If the population of methanogens in the seed material is low, a thick buffer zone is needed, to limit the flux of acetate into the methanogenic zone. The same mechanism of spatial separation of reaction steps applies but the extra mass transfer resistance limits the reaction rate. The size of the seed body then determines what follows. If it is large enough, the methanogenic zone expands into the buffer zone and the local process accelerates; if it is too small, the buffer zone expands into the methanogenic zone and the local process slows down and stops. Thus, front maturation minimizes the thickness of the buffer zone and maximizes the local reaction rate.

The length of the maturation phase varies widely. In a poor seed material, it might take years, since the few methanogens present have to grow into the acid-inhibited environment of the buffer zone to minimize its thickness. However, in a seed material rich in methanogens, front maturation might only take a few hours.

In either case, the true lag phase must be negligible. If methanogenesis did not begin very soon after substrate began to diffuse into the seed body, irreversible inhibition would result. However, the early stages of a prolonged maturation phase might be difficult to distinguish from a true lag.

The front begins to advance when the substrate becomes locally depleted. (In the case of a prolonged maturation phase, this might occur before front maturation is complete. However, the essential concepts of the present model would remain valid.) System geometry then determines whether front expansion occurs. Planar seeding would generate planar fronts, of constant area, and thus a constant-rate overall process. Dispersed seed bodies would generate spherical fronts, of expanding area, and thus an (initially) accelerating overall process.

The model is centered on the reaction front. Conditions within and near the advancing front are locally constant (assuming a homogeneous mass of waste). The area of the front may change in nonplanar geometries but only slowly, because the front advances slowly (7). Thus, once the front has begun to advance, quasi-steady-state conditions can be assumed and a simple diffusion model can be applied.

The application of a steady-state model after a seed maturation phase that might have taken years inevitably raises questions about the validity of the initial conditions. However, the main changes occurring during seed maturation are minor and largely confined to the seed body: some methanogen growth into the buffer zone and a consequent increase in the acetate concentration gradient. This growth must be fueled by acetate diffusion from the waste but at the low rate needed could be met by diffusion from the acetate pool in the bulk of the waste mass. Hydrolysis of the waste in contact with the seed body might contribute later, towards the end of the maturation phase, but no gross changes in the waste composition or particle size are expected.

Table 1
Estimated Concentration Differences Across Zones

Symbol	Location	VFA concentration (mg/L)
C_A	A:B interface	47,725
C_B	B:C interface	~47,725
C_C	C:D interface	~800
C_D	D:E interface	~0
$C_B - C_C$		~47,000
$C_C - C_D$		~800

Mass-Transfer Model

The reaction front is marked by a sharp drop in VFA concentration, with the greater part of the drop likely to occur across the buffer layer. This allows use of the physical model shown in Fig. 1, in which the concentration profile is simplified to the series of straight lines shown in bold. The major inhibitor is assumed here to be acetate. There is an ongoing debate about the relative contributions of higher homologs and of low pH, but this does not materially affect the present argument.

Assuming planar geometry and a continuous, homogeneous substrate mass, the application of Fick’s Law across zone C gives

$$M' = D \cdot (C_B - C_C)/x_C \tag{1}$$

in which M' is the mass flux of acetate, D is the diffusivity of acetate, and x_C is the thickness of zone C. The concentration terms C_A to C_D are defined in Table 1. Since the other variables can be estimated to an order of magnitude or better, a value for the mass flux would thus give an estimate of the thickness of the buffer layer.

The mass flux can be estimated from the rate of methanogenesis, because the mass flux through zone C must equal the rate of utilization in zone D at steady state.

Writing the volumetric rate of acetate utilization in the methanogenic zone as R , it follows that

$$M' = R \cdot x_D \tag{2}$$

An estimate of the volume of zone D and hence of its relative thickness, x_D , can be obtained by assuming a constant value of dc/dx through zones C and D. Thus:

$$\begin{aligned} dc/dx &= (C_B - C_C)/x_C \\ &= (C_C - C_D)/x_D \\ x_D &= (C_C - C_D) \cdot x_C/(C_B - C_C) \end{aligned} \tag{3}$$

Inspection of Fig. 1 and Table 1 shows that a constant value of dc/dx is an acceptable approximation. In fact, dc/dx steadily increases in magnitude

from the C:D interface, as methanogenesis begins and the effects of acid inhibition diminish, before peaking, then gradually decreasing to zero toward the D:E interface, as substrate concentration becomes rate limiting. The mean gradient in zone D is thus unknown but might exceed that in zone C, in contrast to the representation in Fig. 1. Moreover, the value of x_D as derived in Eq. 4 (below) is not critical.

Estimation of Parameters

Table 1 shows the estimated VFA concentrations at the zone boundaries. The basis for these estimates is as follows. First, the VFA concentration in acidified waste may be taken as equal to the highest value commonly observed in leachates. In 20 lysimeters that failed to proceed beyond the acidogenic stage (9), the mean VFA level was 28.014 kg/m³, with an SD of 19.710. The mean plus 1 SD has been taken as the value of C_A . Second, acetate is formed in zone B, by the breakdown of more complex substrates, and also diffuses in from zone A. This is balanced by outward diffusion into zone C. Now, C_B must be lower than C_A to relieve the acid inhibition of acetate formation in zone B but it may not be much lower. These calculations take C_B as equal to C_A , to give a "worst-case" prediction of buffer layer thickness. Third, the maximum permissible VFA concentration in conventional anaerobic digestion, commonly taken as about 0.8 kg/m³, is used for C_C . Finally, acid intermediates do not accumulate in the hydrolysis-limited breakdown of SSO, so C_D is taken as zero.

The relative thicknesses of zones C and D can be obtained by applying these data to Eq. 3.

$$\begin{aligned} x_D &= 800x_C/47,000 \\ &= \sim 0.02x_C \end{aligned} \quad (4)$$

The key conclusion is that zone C is much thicker than zone D. Any error in assuming dc/dx to be constant is unlikely to be large enough to change this conclusion.

The reaction front forms at the interface between a seed body and the waste in contact with it. Zones C and D form within the seed body before advancing into the waste. Since the seed body must initially accommodate both these zones, zone D would occupy 2% of its volume at most, in planar geometry, with zone C occupying at most 98%. (These values are maxima, because an oversized seed body would also have an inert core, starved of substrate, which might occupy much of its volume.)

No data on the diffusivity of acetate in wastes seem to have been published but in the absence of moisture movement, maximum values would be obtained in a mass of fresh foodstuff saturated with leachate. Cell membranes are highly permeable to acetate, so the diffusivity (D) of acetate in such systems approaches the rates observed in water (F. A. Oliveira, personal communication). Thus, a value of about 1.5×10^{-9} m²/s was reported for the diffusion of acetate in a block of turnip at 35°C (10).

This may be taken as a reliable, if approximate, estimate of the maximum value of D . However, even slight drying would reduce D greatly, especially in plant matter, as the cell membranes retreat from the cell walls, leaving internal air spaces. In a heterogeneous bed of moist, uncompacted mixed solids, with high tortuosity and often poor interparticle contact, a value of $1.5 \times 10^{-11} \text{ m}^2/\text{s}$ or below would not be surprising. D might vary widely in different parts of the same bed, so a range of volumes is applied in Table 2. Mesophilic conditions are assumed.

A rough estimate of the volumetric rate of methanogenesis can be obtained from performance data for high-solids waste digesters, provided that the reaction front mechanism is indeed dominant in a moist bed of wastes, which seems likely. These digesters are typically seeded with 50% by volume of previously digested waste, so a methanogenic zone occupying 2% of the seed would initially account for about 1% of the digester volume. The depth of this zone remains constant (on average) as the front advances, so its volume increases in proportion to its area. The geometry of the reaction front is unknown in current digesters, but with 50% seeding the advancing fronts quickly meet, so the methanogenic zone might roughly double in volume, from 1 to 2% of the digester volume.

Such digesters have been reported as capable of treating $16 \text{ kg (volatile solids [VS])}/(\text{m}^3 \cdot \text{d})$ under thermophilic conditions (11), so at least $4 \text{ kg}/(\text{m}^3 \cdot \text{d})$ would be expected in a mesophilic digester. Assuming 50% conversion of VS to acetate (some does not biodegrade; some forms carbon dioxide or follows parallel pathways), this equates to conversion of acetate to biogas at $2 \text{ kg}/(\text{m}^3 \cdot \text{d})$. A rate of $1.5 \text{ kg}/(\text{m}^3 \cdot \text{d})$ in zone E and $0.5 \text{ kg}/(\text{m}^3 \cdot \text{d})$ in zone D can be estimated by assuming that zones B–D contribute little to the biodegradation of SSO and guessing an RSO:SSO ratio of 1:3. Zone D is estimated in the preceding paragraph to occupy 2% of the digester volume, so R is of the order of $25 \text{ kg}/(\text{m}^3 \cdot \text{d})$ or $0.0003 \text{ kg}/(\text{m}^3 \cdot \text{s})$. A range of volumes around this is applied in Table 2.

Model Results

Combining Eqs. 1, 2, and 4 gives:

$$D \cdot (C_B - C_C)/x_C = R \cdot (0.02)x_C$$

Hence

$$x_C^2 = D \cdot (C_B - C_C)/0.02R$$

Thus, for mid-range data

$$\begin{aligned} x_C^2 &= (1.5 \times 10^{-10}) \cdot (47)/(0.02) \cdot (0.0003) \\ x_C &= 0.0343 \text{ m} \end{aligned}$$

This implies a buffer zone 34.3 mm thick (with wide local variations, according to the composition and state of the waste). This, in turn, gives a thickness of 0.7 mm for the methanogenic zone, provided it is well popu-

Table 2
Model Results for Range of Input Data^a

Value of D (m ² /s)	Value of R (kg/[m ³ ·s])	Estimate of x_c (mm)	Estimate of d_{min} (mm)
1.5×10^{-9}	3.0×10^{-3}	34	70
1.5×10^{-9}	3.0×10^{-4}	108	221
1.5×10^{-9}	3.0×10^{-5}	343	699
1.5×10^{-10}	3.0×10^{-3}	11	22
1.5×10^{-10}	3.0×10^{-4}	34	70
1.5×10^{-10}	3.0×10^{-5}	108	221
1.5×10^{-11}	3.0×10^{-3}	3	7
1.5×10^{-11}	3.0×10^{-4}	11	22
1.5×10^{-11}	3.0×10^{-5}	34	70

^aThe midrange values quoted in line 5 are derived in the text.

lated with methanogens. Thus, the minimum total thickness of a slab-shaped seed body is 70 mm. This can be taken as roughly approximating to the minimum diameter of a spherical seed body (d_{min}). Thus

$$\begin{aligned}d_{min} &= 2(x_c + x_D) \\ &= 2.04x_c\end{aligned}$$

In practice, these figures represent minima, for ideal seed materials. Seed material with a low population of methanogens would require thicker layers or larger seed bodies.

Discussion

The broad methodology of the preceding derivation is believed to be reliable. However, there are circularities of argument. The derivation assumes that a reaction front does form, in order to estimate the space it would require. In addition, the estimation of reaction rate in the methanogenic zone assumes that a reaction front mechanism is acting. Thus, this derivation does not prove the existence of such a mechanism but it may serve as a pointer to further work.

The numerical results must clearly be regarded as tentative. Many of the numerical values are estimates and one is guessed. Therefore, the values of x_c shown in Table 2 cover a wide range of values of the most uncertain variables. The highest value tabulated for D is unlikely to be exceeded in practice, as already noted. However, values outside the range shown for R are not inconceivable, since there are several major uncertainties in its estimation, including those regarding x_D and the RSO:SSO ratio.

Nevertheless, this derivation suggests that the reaction front model is plausible. The formation of the front depends on the presence of viable seed bodies but the sizes needed are not excessive. The spatial variability of D and R and hence of d_{min} increases the probability that viable seed bodies will

exist in some areas. The reaction front seems likely to be robust and capable of advancing into unfavorable materials, once established, so the process would proceed, even with sparsely effective seeding. However, closely spaced seeding is needed for a high-rate process.

The lower values of d_{\min} are compatible with the range of particle sizes found in many wastes, so viable seed bodies might be quite common. However, the higher values exceed the largest waste particle sizes, in which case formation of the front might be a rare event, perhaps requiring aggregates to reach an effective d_{\min} . The implications of this for different environments will be considered separately.

Landfills

Solid-phase digestion probably occurs in many landfills, possibly coexisting with liquid-phase digestion in different areas or even in the same area. The dominant mechanism is likely to be determined by the initial conditions, notably waste shredding, seeding and irrigation. Where viable seed bodies are rare, irrigation with neutralized leachate readily induces liquid-phase digestion.

In an unlined, unseeded landfill, the surrounding soil and subsoil might act as a single, huge, seed body. Solid-phase digestion would be dominant. Thus, in this model, the slowness of biodegradation in modern "dry tomb" landfills might be owing to inadequate seeding and not to lack of moisture, as is generally assumed.

In a lined, unseeded landfill, good seed material is likely to be scarce, so d_{\min} might be much greater than the values shown in Table 2 and viable seed bodies equally rare. Soil could, in principle, provide an adequate seed material but might rarely form sufficiently coherent aggregates in practice. Irrigation, especially with leachate, is likely to interfere with the formation of the front in such an aggregate, by adding to the acetate flux into the nascent buffer zone. Thus, the recirculation of leachate might trip the process into liquid-phase digestion. This might be beneficial for old waste in which solid-phase digestion has failed to start but it might prevent the onset of solid-phase digestion in fresh waste.

Seeding a landfill with digested sewage sludge alone would contribute no seed bodies of viable size. However, thick layers of paper waste impregnated *in situ* with digested sewage sludge might be effective. Solid-phase digestion would be dominant and the overall rate of stabilization could be regulated by adjusting the spacing of the seed layers. Because both the seed materials are wastes, there is no necessary loss of void volume. Moreover, whatever their thickness, the seed layers can be well spaced, so they need not occupy a large fraction of the void.

Digesters

Liquid-phase digestion is dominant in wet digestion processes, including irrigated beds and slurry digesters (high solids or low solids). However, solid-phase digestion might dominate in "semi-dry" systems, where the waste forms a bed of moist solids.

In such a digester seeded with previously digested waste, good seed material is plentiful. If d_{\min} is below the mean particle size of the seed material (d_{sp}), viable seed bodies are common. However, if d_{\min} is much above d_{sp} , the process may depend on aggregates to form viable seed bodies. The observed benefits of high seeding rates might be due to the need for aggregates to occur frequently. If $d_{\min} \gg d_{sp}$, aggregates are essential, so isolated seed bodies are ineffective. (However, a small volume of seed, placed in layers d_{\min} thick, in an unmixed digester, might be effective.) If $d_{\min} \ll d_{sp}$, many of the seed bodies are oversized, with the core of each simply wasting space. A smaller volume of screened seed material might be equally good. With typical seeding rates of 50% by volume, even a modest reduction would liberate significantly more digester capacity.

Laboratory Studies

Solid-phase digestion of fresh wastes is achievable at 0.5- to 10-L scale without leachate recycle (6,12) but most bench-scale studies have favored liquid-phase digestion. (High-rate irrigation is easier to achieve in a bed of solids than in a landfill, so liquid-phase digestion is readily induced at bench scale. Conventional anaerobic digestion also scales down well, for a soluble feedstock.) The reason for the paucity of reports of simple, batch digestion of solid wastes might be that only the lowest values of d_{\min} shown in Table 2 could be accommodated at bench scale. Moreover, unless a separate seed material was added, the common experimental technique of pulverizing the feedstock would disrupt any viable seed bodies present.

Conclusion

Anaerobic digestion processes might follow either of two alternative, parallel pathways in a bed of rich solids: (1) liquid-phase digestion, in which the main reactions occur in the interstitial liquid; or (2) solid-phase digestion, in which the main reactions occur within the solids. If so, the initial conditions would play important roles in determining which, if either, is the dominant process. These conditions would include the presence or absence of viable seed bodies.

Tentative calculations suggest that the initiation of solid-phase digestion would require a minimum seed body diameter of the order of 7–700 μm . The lower values here are comparable with typical particle sizes in wastes. Further work is needed to refine these estimates, in order to determine whether natural seed bodies of viable size are common; if they are, the established landfill models will require modification; if they are not, supplementary seeding of landfills receiving organic wastes could prove highly effective. There may also be scope for increasing the throughput of digesters by redesigning the seeding methods.

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