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Modelling the effects of environmental conditions on the biodegradation of organic material in municipal landfills

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Abstract

The rate of methane production in municipal landfills is influenced by a large number of processes. The relevance of these various interacting processes can be evaluated on the basis of a mechanistic model. The aim of this research is to evaluate the relevance of environmental conditions (pH, temperature, moist content) on the methane production rate in municipal landfills. This evaluation is based on model simulations with the mathematical model described below, and model parameters taken from literature resources or laboratory experiments. The hydrolysis of solid organic matter is regarded as the rate-limiting process. However, reported specific hydrolysis rate constants vary over several orders of magnitude. The question of which hydrolysis rate constant is representative for a landfill section, could be answered more accurately if the rate of hydrolysis is regarded as a function of the type of environmental condition (pH, temperature, moist content), the type of organic material, and the bio availability of the organic material.

Introduction

One of the main challenges in municipal landfill research is to predict the rate and total production of methane from landfills, as well as to predict the long-term stability of the waste. Methane is produced during the anaerobic decomposition of the organic fraction of the waste. Production of biogas (CO_2, CH_4) determines the long-term stability of the waste.

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The rate of methane production in municipal landfills is influenced by a large number of processes. In order to evaluate the relevance of these various interacting processes, a mechanistic model is required. The literature gives examples of the implementation of fundamental knowledge of physical and (bio) chemical processes in mathematical models [e.g. 1-3]. Mechanistic models require input in terms of rate constants, and effects of environmental conditions on these rate constants. What limits the application of mechanistic models is that the kinetics of the various processes inside the landfill are not well known yet.

The aim of this research is to evaluate the relevance of environmental conditions (pH, temperature, moist content) on the methane production rate in municipal landfills. The role of hydrolysis as the rate-limiting step in the degradation process is also discussed. The evaluations are based on model simulations with the mathematical model described below, and model parameters taken from literature resources or laboratory experiments.

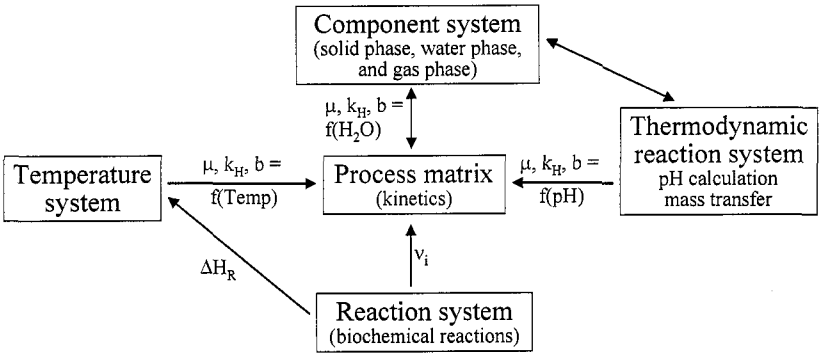

Figure 1: General model structure (μ = specific growth rate, k_H = specific hydrolysis rate, b = rate of decay, ν = stoichiometric coefficients, ΔH_R = reaction enthalpy).

Model description

This section gives a general overview of the structure of the applied model. For a more detailed description is referred to Haarstrick [3].

The general structure of the applied model is depicted in Figure 1. The different structural elements of Figure 1 refer to the individual components of the differential equation system, which is given in eqn (1) and is explained below.

$$dS/dt = S * R_{(S)} * \nu * f_{Temp} * f_{pH} * f_{moist} \quad (1)$$

S Component concentrations (in g/kg dried waste). The component system contains the concentrations of the organic and inorganic components in the solid, liquid, and gas phase. Linked to the component system is the thermodynamic system, which allows the following thermodynamic

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equilibrium calculations: calculation of the speciation of each of the components, calculation of the equilibrium concentrations in the gas phase (via Henry coefficients), calculation of mineral precipitation and dissolution reactions (e.g. $CaCO_3$), calculation of the pH.

t Time step (in days)

$R_{(s)}$ Reaction rates for biodegradation reactions based on Monod-kinetics (in d^{-1}). The process matrix contains the kinetic parameters of the biodegradation reactions (e.g. maximum specific degradation rates, half-velocity constants, inhibition constants).

v Stoichiometric coefficients, which are taken from the (biochemical) reaction system. Figure 2 gives an overview of the anaerobic biodegradation reactions that were considered in the simulations. Organic matter is converted into glucose via an hydrolysis reaction. Glucose is anaerobically converted into acetic acid via acetogenesis or acidogenesis. Finally, the acetic acid is converted into methane via methanogenesis. A second mechanism of methane production is by reaction of H_2 with CO_2.

f_{Temp}, f_{pH}, f_{moist} Temperature factor (-), pH factor (-), and moist factor (-), which describe the effects of temperature, pH, and water content on the reaction rates. The factors are figures between 0 and 1 as illustrated in Figure 3. The mathematical formulations are given in eqns (2) - (4), the required parameters in Table 1. The parameters of the temperature function were calibrated on the basis of laboratory measurements [4]. The pH factor and moist factor were calculated on the basis of literature data and are assumed to be similar for the main degradation pathways.

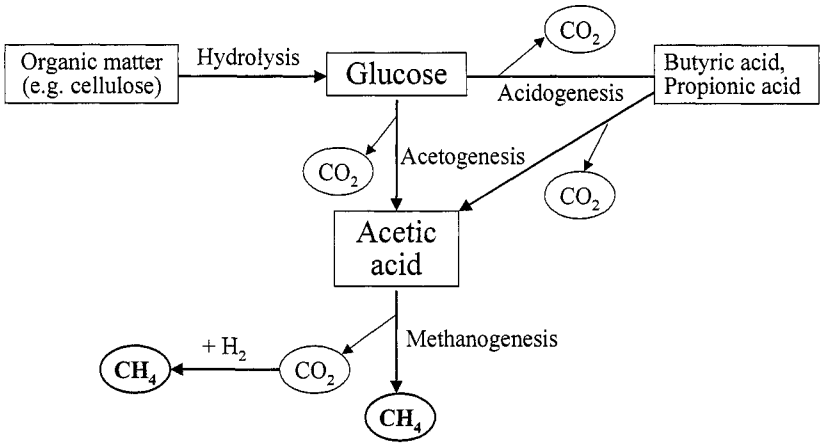

Figure 2: Anaerobic reaction scheme as used in the model simulations.

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$$f_{Temp} = \exp - (\kappa (T_{act} - T_{opt}))^2 \quad (2)$$

$$f_{pH} = K_{pH} / [(K_{pH} + (10^{pHact}/10^{pHopt1} + 10^{pHopt2}/10^{pHact} - 2)] \quad (3)$$

$$f_{moist} = 0.5 + 1/\pi * \arctan[(fr_{H2O,act} - fr_{H2O,opt}) * A] \quad (4)$$

In eqns (2) – (4), subscript 'act' refers to actual values, subscript 'opt' to optimal values. T is the temperature (in °C), fr_{H2O} the water content (in m/m %). κ, K_{pH} , and A are constants, which values are given in Table 1.

The model contains a large number of model parameters, as illustrated in Table 1. On the one hand, model formulation is based on measured key parameter data under well-defined conditions in the laboratory, and on the other hand on published parameter data (see Table 1 and 2). Following this approach, we have been able to simulate the results of batch reactor experiments with municipal solid waste reasonably well [4].

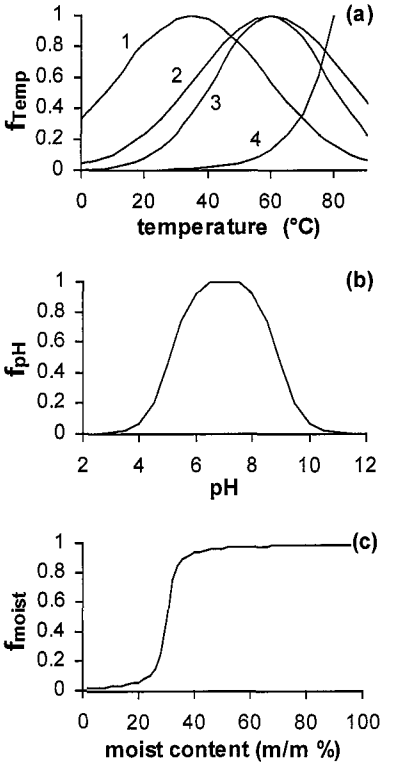

Figure 3: Graphical presentation of the effect of (a) temperature, (b) pH, and (c) moist content on the rate of biodegradation. Different f_{Temp} were calculated for acetogenesis/acidogenesis (line 1), methanogenesis (line 2), hydrolysis (line 3), and the rate of decay (line 4).

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Table 1: Overview of model parameters. The list of crucial parameters is based on [5].

Parameter group	Parameter type	Nr of para-meters	Applied values for crucial parameters	Sources
Characteristics biomass & organics	Structural formulas	4		
	Enthalpies of formation	4		
Biodegradation reactions (26)	Maximum specific degradation and hydrolysis rates, rates of decay	10	k_H = 0.2 d^{-1} μ_{max_me} = 0.21 d^{-1} b_{me} = 0.001 d^{-1} b_{an} = 0.001 d^{-1}	[4] Estimated from [4] Estimated Estimated
	Half-velocity constants	9		
	Inhibition constants	8		
	Yield (fraction substrate into biomass)	6	Y_{me} = 0.05 Y_{ac} = 0.2	[2,4] [2]
Thermodynamic reactions (15)	Equilibrium constants	11		
	Reaction enthalpies	11		
Physical parameters	Densities	4		
	Heat capacities	2		
Environmental parameters	Parameters pH function f_{pH}	3	$pH_{opt,1}$ = 6.8 $pH_{opt,2}$ = 7.2 K_{pH} = 50	Estimated from [1,6]
	Parameters moist function f_{moist}	2	$H2O_{opt}$ = 30 m/m% A = 50	Estimated Estimated
	Parameters temperature function f_{temp}	10	K_{me} = 0.03 $T_{opt,me}$ = 60 °C K_{hydro} = 0.04 $T_{opt,hydro}$ = 60 °C	[4] [6] [4] Estimated from [4]

Table 2: Overview of maximum specific degradation rates.

Process	Reported range in k_H and μ_{max} (d^{-1})	Source	k_H and μ_{max} (d^{-1}) applied in simulations
Hydrolysis (1^e order) of cellulosic materials	~ 0.00005 - 0.2	[1,4,7,8]	0.2
Aceto/acidogenesis	1 - 3	[6]	2
Methanogenesis	0,1 - 0,5	[1,4]	0.21

Results and discussion

In Table 2 an overview is given of the reported range in maximum specific rate constants for the main degradation pathways. From a comparison of maximum specific rate constants, it becomes clear that the process of hydrolysis is generally the rate-limiting process in the digestion of organic material into methane. This general conclusion is consistent with the results of sensitivity analyses performed with mechanistic models that were developed to simulate biodegradation

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processes in landfills [5,9]. With hydrolysis being the rate-limiting process, we will demonstrate the effect of environmental conditions on the rate of hydrolysis as well as on the rate of methane production.

Since the reported range in maximum specific hydroloysis rate constants (k_H) is extremely large (Table 2), we first investigated the effect of the magnitude of k_H on the rate of methane production. In Figure 4 the results are shown of simulations with k_H-constants ranging from 0.2 d^{-1} to 0.00002 d^{-1}. The simulations were performed at an optimal pH (pH 7), temperature (60 °C), and moist content (50%). The initial conditions of the simulations are given in Table 3 (best-case scenario), the most crucial model parameters in Table 1. With k_H-constants of 0.2 d^{-1} and 0.02 d^{-1}, the initial amount of 60 g/kg organic matter is completely biodegraded within 0.5 – 2 years. With a k_H-constant of 0.002 d^{-1}, it takes 10 years to biodegrade ~10% of the initial 60 g/kg organic matter. With k_H-constants of 0.0002 d^{-1} or 0.00002 d^{-1}, the rate of biodegradation is predicted to be extremely low. In the latter simulations, the supply of small organic compounds (glucose, acetate) by hydrolysis is so low, that the biomass population is actually decreasing (results not shown).

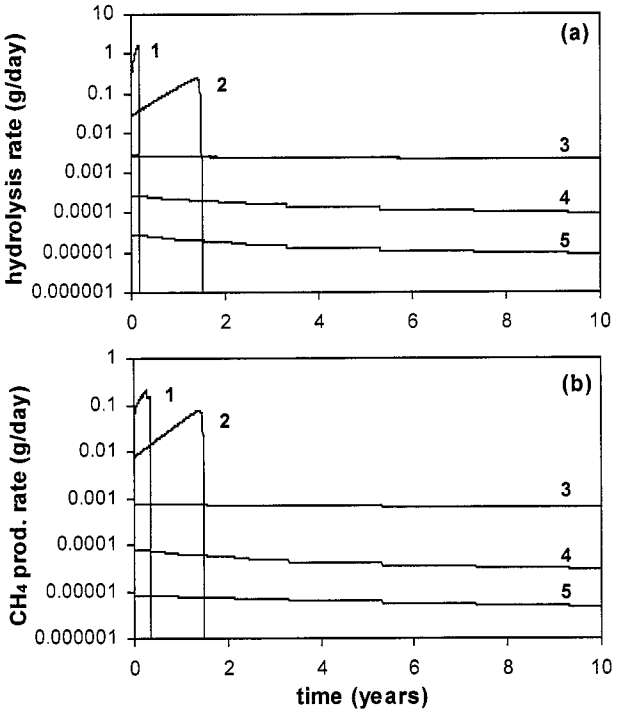

Figure 4: Simulation of the effect of k_H on (a) the rate of hydrolysis and (b) the rate of methane production in municipal landfills. Numbers refer to the k_H-constant used: 1= 0.2 d^{-1}, 2 = 0.02 d^{-1}, 3 = 0.002 d^{-1}, 4 = 0.0002 d^{-1}, and 5= 0.00002 d^{-1}.

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Table 3: Summary of the initial conditions of the simulations shown in Figure 4 and 5.

Variable	Best-case	Worst-case
[Organic material] (g/kg)	60[a]	60[a]
[Anaerobic biomass] (g/kg)	0.7[a]	0.7[a]
[Methanogenic biomass] (g/kg)	0.7[a]	0.7[a]
Temperature (°C)	60	30
pH	7.0	4.0
Moist content (m/m%)	50	20
Duration (years)	10	10

[a] The initial concentrations of organic material and biomass are based on concentrations measured in a municipal landfill near Braunschweig [3].

Referring to the results shown in Figure 4, it clearly turns out that knowledge of the rate of hydrolysis is very important for the prediction of the rate of methane production in a landfill. Therefore, the question of why the reported range in k_H-constants is so wide, must carefully be investigated and answered. There are several possible explanations: the environmental conditions (pH, temperature, moist content) may differ, the type of cellulosic material may differ, its bio availability (specific surface area) may differ, and in case the k_H-constant was obtained by fitting, the mathematical formulation of the mechanistic model may differ.

A k_H-constant of 0.2 d^{-1} was measured for the hydrolysis of cellulose in municipal waste under ideal environmental conditions (pH 7, 60°C, water saturated) [4]. k_H-constants of 0.025 – 0.2 d^{-1} were measured for the hydrolysis of carbohydrates under ideal environmental conditions as well [8]. k_H-constants of 0.00004 – 0.0001 d^{-1} were obtained by fitting experimental biodegradation data to a mechanistic model [7]. The researchers cited in Table 2 used a first-order kinetic to describe hydrolysis (eqn 5). In our model, we applied a Monod-type formulation as proposed by Henze [6] (eqn 6).

$$R_{hydro} = - k_H * X * S \quad (5)$$

$$R_{hydro} = - k_H * X * S / (S + X*K_{S,H}) \quad (6)$$

In eqns (5) and (6), R_{hydro} is the rate of hydrolysis (d^{-1}), X the concentration of biomass (g/l), S the concentration of solid organic matter (g/l), and $K_{S,H}$ the half-velocity constant for hydrolysis. The Monod-type formulation has the advantage that in case of large concentrations of organic matter, the rate of hydrolysis is only dependent on the biomass concentration and becomes independent of the concentration of organic matter. This difference in model formulation explains why k_H-constants of $\leq$0.0002 d^{-1} were not applicable in our model (Figure 4). The k_H-constant of 0.2 d^{-1} was used for subsequent simulations, while this value was measured under ideal and well-defined environmental conditions (pH 7, 60°C, water saturated), and while no fitting procedure was applied [4].

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The effect of environmental conditions on the rate of methane production was investigated on the basis of two simulations: a worst-case scenario and a best-case scenario (Figure 5). The worst-case scenario represents a section of the landfill that is acidified (pH 4), that contains little moisture (20%), and with a relatively low temperature (30 °C). In the best-case scenario, the landfill has a neutral pH (pH 7), there is sufficient moisture available (50%), and the temperature has reached optimal values (60 °C). The initial conditions of both simulations are summarized in Table 3, the most crucial model parameters in Table 1.

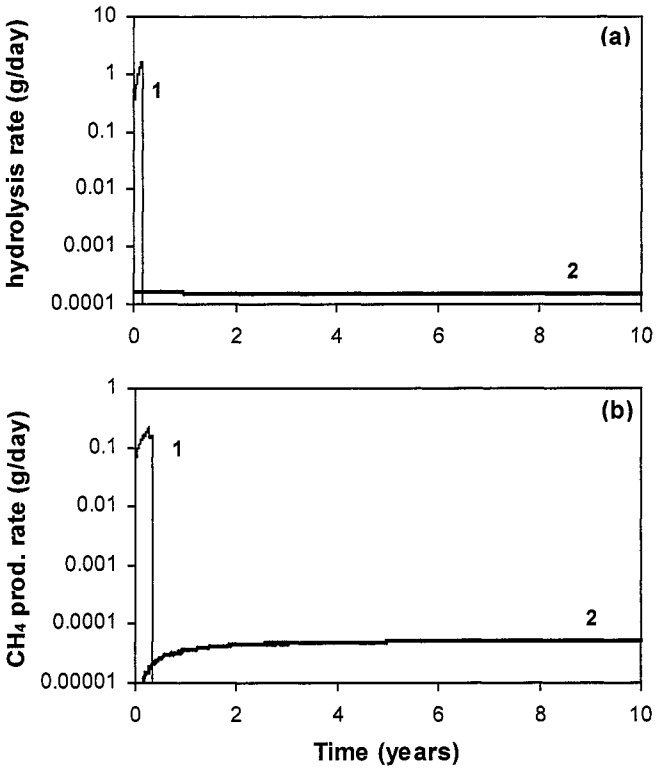

Figure 5: Simulated results for the effect of environmental conditions on (a) the rate of hydrolysis, and (b) the methane production rate. Numbers refer to the chosen scenario: 1= best-case scenario, 2= worst-case scenario. The initial conditions of the simulations are given in Table 3.

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Table 4: Net effect of environmental conditions on the rate of hydrolysis.

Scenario	f_{Temp}	f_{pH}	f_{moist}	$f_{Temp} * f_{pH} * f_{moist}$
Worst-case	0.24	0.07	0.06	0.001
Best-case	1.00	1.00	0.97	0.97

Figure 5 illustrates that in the best-case scenario, the initial amount of 60 g/kg organic material is completely biodegraded within 100 days. In the worst-case scenario, the rate of biodegradation is predicted to be very low: only 1% of the initial 60 g/kg organic material is biodegraded in 10 years. We can calculate the net effect of environmental conditions on the rate of hydrolysis on the basis of the values of f_{Temp}, f_{pH}, and f_{moist} calculated from eqns (2) - (4). The results of this calculation are presented in Table 4. For the best-case scenario, it clearly turns out that the chosen environmental conditions hardly affect the rate of hydrolysis. However, for the worst-case scenario the rate of hydrolysis is decreased by a factor of 1000 compared to the best-case scenario.

Although the moist-function and pH-function have not been calibrated yet, it is clear from these theoretical calculations, that environmental conditions may significantly affect the rate of hydrolysis, and therefore the rate of methane production in landfills. The next research steps and model refinements are (a) to calibrate the pH-function and moist-function on the basis of laboratory data or field data, (b) to make the k_H-constant dependent on the type of organic material, and (c) to make the rate of hydrolysis dependent on the availability of the organic material.

Conclusions

The effect of environmental conditions (pH, temperature, moist content) on the rate of methane production from municipal solid waste has been illustrated on the basis of a mechanistic model. The environmental factors determining the rate of hydrolysis have been investigated as well, as hydrolysis is regarded as the rate-limiting step in the degradation of organic matter into biogas (CH_4, CO_2) and reported hydrolysis rate constants vary over several orders of magnitude.

It is clear from the theoretical calculations, that environmental conditions may significantly affect the rate of hydrolysis, and therefore, the rate of methane production in landfills. The question of which hydrolysis rate constant is representative for a landfill section, could be answered more accurately if the rate of hydrolysis is regarded as a function of the type of environmental condition (pH, temperature, moist content), the type of organic material, and the availability of the organic material.

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