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Stoichiometry of the aerobic biodegradation of the organic fraction of municipal solid waste (MSW)

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Abstract

An elemental analysis was applied to describe the composition of the organic fraction of municipal solid waste (MSW). The initial elemental composition was constant at $C_5H_{8.5}O_4N_{0.2}$. The changes of the composition during the biodegradation process and the final waste composition were strictly dependent on the process conditions. The decrease in carbon content due to biodegradation increased with temperature at which the experiments were conducted, from 20% at 20 °C to about 40% at 37–42 °C after 96 hours. It was correlated with the amount of oxygen that was utilised in the investigated processes of aerobic biodegradation of the waste suspension. The amount of oxygen required for biodegradation of organic fraction of MSW was estimated on the basis of stoichiometric equations and increased from 0.92 moles per 1 mole of waste at 20 °C to 1.6 moles at 42 °C within 96 hours of the experiments.

Introduction

The organic fraction of municipal solid waste (MSW) should be excluded from wastes that are delivered to landfills and degraded by means of biological methods, either aerobic and anaerobic. Biodegradation of solid waste contributes to a meaningful reduction of its volume, deactivation of toxic components, energy recovery in the form of biogas and compost production (humus).

Aerobic conversion of biowaste in laboratory scale batch experiments was presented in this work in order to establish an elemental formula of MSW and stoichiometry of its aerobic biodegradation. The segregated organic fraction of household waste was ground, suspended in tap water and aerated in the bioreactors, as described by Kahle (1995). By grinding the substrate, by implementing the process in the liquid phase and by applying intensive aeration one can shorten the biodegradation time, as compared to the traditional composting methods (Miksch 1995).

Municipal solid waste contains thousands of organic compounds. It is impossible to determine each of them individually. Therefore various collective analyses are performed to comprise a greater or minor part of the organic matter. One of them is elemental analysis. Knowledge of the elemental composition of organic waste enables the evaluation of its biodegradability on the basis of carbon to nitrogen ratio (C/N), the composition of the biogas produced in the anaerobic processes or the amount of oxygen required for the aerobic stabilisation of waste.

The objective of this investigation is to determine the elemental composition of the organic fraction of MSW and to describe the process by means of the stoichiometric equations (elemental balance). Also the influence of temperature on changes of the elemental composition is investigated.

Stoichiometry of aerobic biodegradation

The organic matter of waste or wastewater can be characterised by the following approximate chemical composition: $C_{18}H_{19}O_9N$ (Pöppel 1988; Henze et al. 1995). This average elemental composition was calculated on the basis of formulae for carbohydrates, fats and proteins.

The general aerobic biological transformation of solid waste can be described by means of the following equation:

$$\begin{aligned}&\text{Organic matter}\\&\quad +O_2 + \text{nutrients} \xrightarrow{\text{Bacteria}} \text{new cells}\\&\quad +\text{resistant organic matter}\\&\quad +CO_2 + H_2O + NH_3 + SO_4^{2-} + PO_4^{3-} + \cdots +\\&\quad +\text{heat}\end{aligned}$$

If the solid waste organic matter is represented as $C_aH_bO_cN_d$, biosynthesis of new cells and production of sulphate and phosphate is not taken into account and the composition of the resistant organic matter is represented as $C_wH_xO_yN_z$, then the amount of oxygen required (on molar basis) for the aerobic stabilisation of the organic fraction of MSW can be estimated by the following equation (Tchobanoglous et al. 1993):

$$\begin{aligned}C_aH_bO_cN_d \;&+\; 0.5(n \cdot y + 2s + r - c)O_2\\&\rightarrow nC_wH_xO_yN_z\\&+\; sCO_2 + rH_2O + (d - nz)NH_3 \quad (1)\end{aligned}$$

where $r = 0.5\cdot[b-n\cdot z-3\cdot(d-n\cdot z)]$, $s = a-n\cdot w$, $n =$ moles of organic matter in the output/moles of organic matter in the input.

The terms $C_aH_bO_cN_d$ and $C_wH_xO_yN_z$ represent the empirical elemental composition of the organic material at the beginning and at the end of the process, respectively.

If complete conversion is accomplished, the corresponding expression is applied:

$$\begin{aligned}C_aH_bO_cN_d \;+\; \left(\frac{4a+b-2c+3d}{4}\right)O_2 &\rightarrow aCO_2\\+\left(\frac{b-3d}{2}\right)H_2O + dNH_3.& \qquad (2)\end{aligned}$$

Table 1. Process conditions in the performed experiments

Experiment No.	Temperature (°C)	pH	Total solids (g l^{-1})	Volatile suspended solids (g l^{-1})
1	20	6.42	60.9	57.9
2	30	6.22	75.9	72.0
3	37	6.22	67.2	64.5
4	42	6.42	60.9	57.9

Materials and methods

Substrate

The substrate contained a fresh organic fraction of MSW. Its composition was defined so as to correspond with typical Polish household waste (Steglinski 1999). The solid wastes were ground to obtain particles with a size of 3–5 mm. Subsequently, the waste pulp was suspended in tap water and aerated in a bioreactor. The initial content of total solids (TS) was in the range from 60.9 to 75.9 g l^{-1} and an initial pH of the suspension was 6.22 or 6.42 (Table 1).

Bioreactors and process parameters

The batch experiments were conducted in 6-litre working volume bioreactors FL-10. They were equipped with standard control and measurement devices. Temperature, pH, pO_2, carbon dioxide concentration in the off-gases, aeration flow rate, foam level and rotary speed of the stirrer were measured in the processes. Experiments were conducted at 20, 30, 37 and 42 °C (Table 1). To keep the pO_2 level above 10% and eliminate oxygen limitation, pure oxygen had to be used to aerate the suspension. The oxygen electrode was calibrated in relation to pure oxygen. The aeration intensity was changed in the range from 0.08 to 2 vvm, depending on the oxygen uptake rate.

Analytical methods

The elemental composition of waste expressed as carbon, hydrogen, nitrogen and sulphur (CHNS) dry weight content was determined by means of an elemental analyser NA 2500 (CE Instruments, Italy).

Additionally total solids (TS) and volatile suspended solids (VSS) were determined by the gravimetric method (Liwarska-Bizukojc et al. 2001). The oxygen content in the waste was calculated from the formula:

$$X_O = TS - X_C - X_H - X_N - X_{ash} \quad (3)$$

where X_C, X_H, X_N, X_{ash} are the contents (g kg^{-1}) of carbon, hydrogen, nitrogen and ash, respectively, and TS is the total solids (g kg^{-1}).

Total organic carbon (TOC) was determined by a carbon analyser (Coulomat 702, Ströhlein, Germany).

Results and discussion

Stoichiometric balance

Three suspensions, whose total solids content varied from 60.9 to 75.9 g l^{-1}, were subjected to the elemental analysis. It should be stressed that the composition expresses both viable matter (bacteria) and non-viable matter (organic particles). The contribution of biomass in the stoichiometric balance was not distinguished due to the small concentration of viable microorganisms in comparison to the total organic matter (from 0.16 to 1.8% of VSS), as it was estimated on the basis of RNA content (Liwarska-Bizukojc & Ledakowicz 2001; Liwarska-Bizukojc et al. 2001), and the difficulties in the separation of biomass from waste suspension.

The ratio of hydrogen, oxygen, and nitrogen to carbon was approximately on the same level in each suspension (Table 2). Therefore, the average elemental composition of the organic waste suspension was established at $C_5H_{8.5}O_4N_{0.2}$. Sulphur was not taken into account in the elemental composition because its content was negligibly small, below 0.1%. The obtained elemental composition of the waste was compared with the average composition of three basic components of the organic matter: carbohydrates, fats and proteins, given in literature (Pöppel 1988; Henze et al. 1995). It occurred that carbohydrates were the main component in the investigated substrate. Its elemental composition, especially expressed in C-mole formulae ($CH_{1.8}O_{0.9}$), was in good agreement with the experimental results ($CH_{1.68}O_{0.73}N_{0.034}$). At the same time the elemental composition of fats ($CH_{0.75}O_{0.25}$) and proteins ($CH_{0.86}O_{0.5}N_{0.14}$) was significantly different from the composition of the investigated wastes.

The carbon to nitrogen ratio (C/N) is one of the most critical environmental factors for aerobic biodegradation. The C/N value depends on the composition of waste. In the conducted experiments the initial C/N was about 25 and remained in the optimum range of 20 to 30 for aerobic composting (Tchobanoglous et al. 1993).

The stoichiometry describing the biodegradation process was evaluated on the basis of the initial elemental composition of the waste and the final elemental composition of the organic matter. The stoichiometric coefficients were calculated according to Tchobanoglous et al. (1993). These coefficients enabled the estimation of the molar amount of oxygen required for the aerobic biodegradation of the organic waste suspension. The theoretical background of the applied stoichiometric description of aerobic biodegradation is shown above (Equations (1)–(3)). The established equations are listed in Table 3. It should also be mentioned that the calculations were performed for the first 96 hours of each experiment.

The amount of the oxygen consumed was mainly dependent on temperature and varied in the range from 0.92 to 1.65 moles per 1 mole of waste. The highest amount of oxygen was obviously desired at the highest temperatures 37 and 42 °C. Additionally, the amount of the oxygen required for the total oxidation of the biodegraded matter was estimated. The stoichiometric equations are presented in Table 4. Assuming the total oxidation of the substrate, the theoretical amount of oxygen was only dependent on the initial elemental composition of the waste. Comparing these virtual coefficients with the experimental ones, it occurred that total oxidation demands at least 4–5 times more oxygen than was utilised within 96 hours of the experiment.

Changes of elemental composition and carbon balance

The content of carbon, hydrogen and oxygen decreased significantly during the biodegradation process. At the same time the content of nitrogen decreased slightly (Table 5). The changes of carbon, hydrogen and oxygen content are shown in Figures 1 to 3. The highest rates of carbon, hydrogen and oxygen conversion were observed during the first 72 hours of experiment, especially in the processes conducted at lower temperatures 20 and 30 °C. Subsequently, only slight decrease of carbon, hydrogen and oxygen content was noted.

Temperature had the strongest influence on the decrement of these element contents. At 20 °C only 20% of carbon was transformed into CO_2, whereas at 37 and 42 °C it doubled to 40% (Table 5). Con-

Table 2. Initial elemental composition of the waste suspensions in four experiments

Experiment No.	TS (g l^{-1})	Elemental composition in relation to 1 g of TS	Elemental composition expressed in C-moles
1 and 4	60.9	$C_{4.6}H_{7.6}O_{3.2}N_{0.14}$	$CH_{1.6}O_{0.69}N_{0.03}$
3	67.2	$C_{4.9}H_{8.4}O_{3.7}N_{0.17}$	$CH_{1.71}O_{0.75}N_{0.035}$
2	75.9	$C_{5.5}H_{9.2}O_{4.1}N_{0.21}$	$CH_{1.67}O_{0.75}N_{0.038}$
Average		$C_5H_{8.5}O_4N_{0.2}$	$CH_{1.68}O_{0.73}N_{0.034}$

Table 3. Stoichiometric equations for the aerobic biodegradation processes

(–)	(–)
1	$C_{4.6}H_{7.6}O_{3.2}N_{0.14} + 0.92O_2 \rightarrow C_{3.6}H_{6.3}O_{2.6}N_{0.12}\ 0.935CO_2 + 0.57H_2O + 0.02NH_3$
2	$C_{5.5}H_{9.2}O_{4.1}N_{0.21} + 1.04O_2 \rightarrow C_{4.1}H_{7.1}O_{2.9}N_{0.17} + 1.27CO_2 + 0.744H_2O + 0.04NH_3$
3	$C_{4.9}H_{8.4}O_{3.7}N_{0.17} + 1.65O_2 \rightarrow C_3H_{5.3}O_2N_{0.13} + 1.8CO_2 + 1.41H_2O + 0.04NH_3$
4	$C_{4.6}H_{7.7}O_{3.2}N_{0.14} + 1.55O_2 \rightarrow C_{2.8}H_{4.8}O_{1.8}N_{0.12} + 1.63CO_2 + 1.24H_2O + 0.02NH_3$

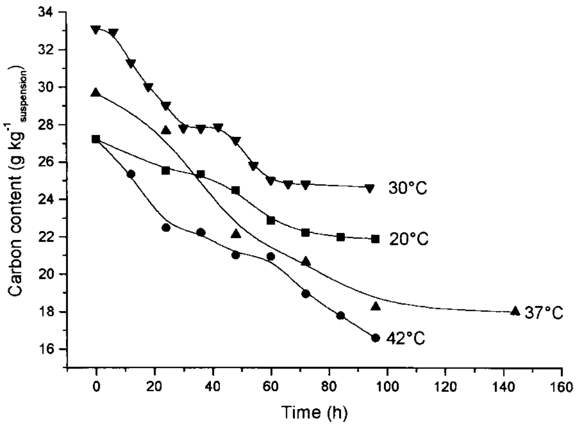

Figure 1. The influence of temperature on changes of carbon content.

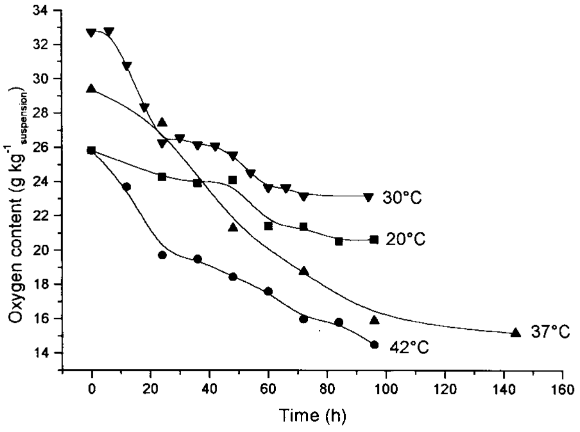

Figure 3. The influence of temperature on changes of oxygen content.

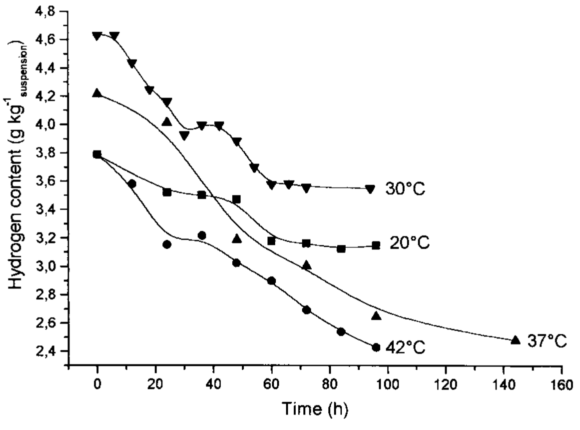

Figure 2. The influence of temperature on changes of hydrogen content.

sequently, the carbon conversion rate at 20 °C was approximately twice lower (0.0556 g C l^{-1} h^{-1}) than at 37 and 42 °C (0.119 g C l^{-1} h^{-1}). The decrease of carbon content reflects best the total efficiency of the biodegradation process. The decrement and changes of elements suggests that the optimum temperature of the biodegradation process is about 37 °C. This confirms the previously obtained experimental data on temperature impact of such processes (Liwarska-Bizukojc et al. 2001). A further increase of temperature seems to be of no use. This might be explained by the fact that the autochthonous aerobic microorganisms, which take part in this process, are mainly mesophilic.

Table 4. Stoichiometric equations with the assumption of total oxidation of organic matter

Process No. (–)	Initial TS (g l^{-1})	Stoichiometric equations (–)
1 and 4	60.9	$C_{4.6}H_{7.6}O_{3.2}N_{0.14} + 5O_2 \rightarrow 4.6CO_2 + 3.59H_2O + 0.14NH_3$
3	67.2	$C_{4.9}H_{8.4}O_{3.7}N_{0.17} + 5.28O_2 \rightarrow 4.9CO_2 + 3.94H_2O + 0.17NH_3$
2	75.9	$C_{5.5}H_{9.2}O_{4.1}N_{0.21} + 5.91O_2 \rightarrow 5.5CO_2 + 4.28H_2O + 0.21NH_3$

Table 5. The decrement of carbon, hydrogen, oxygen and nitrogen in the process of aerobic biodegradation

Experiment No.	Temperature (°C)	Initial TS (g l^{-1})	Time (h)	Decrement of element content (%)			
				C	H	O	N
1	20	60.9	72	18.4	16.6	17.3	6.3
			96	19.5	17.1	20.1	17.1
2	30	75.9	72	25.1	23.1	29.28	20.1
			96	25.6	23.3	29.34	14.6
3	37	67.2	72	30.6	28.7	36.2	–
			96	38.5	37.3	46	20.5
			114	39.4	41.1	48.4	10.3
4	42	60.9	72	30.4	29	38.2	1.4
			96	39	35.9	43.9	13.2

It should also be noted that the carbon decrement in process 3 after 96 and 144 h was almost the same (Table 5). The prolongation of the process by an additional 48 hours did not bring a significant difference in the decrement of carbon content (1% change). This indicates that almost all biodegradable substrate was consumed in the first 96–120 hours of the process.

Additionally, on the basis of TOC determination (total and in the liquid phase) and carbon dioxide measurement in the off-gas, the carbon balance was established. In Figure 4 the carbon balance for the biodegradation process at temperature 42 °C is shown as an example. Moreover, the amount of carbon dioxide calculated on the basis of elemental balance (Table 3) is equivalent to the amount determined experimentally (Figure 4). The carbon balances established for the aerobic biodegradation processes were fulfilled and the correctness of the performed analysis and measurements were confirmed.

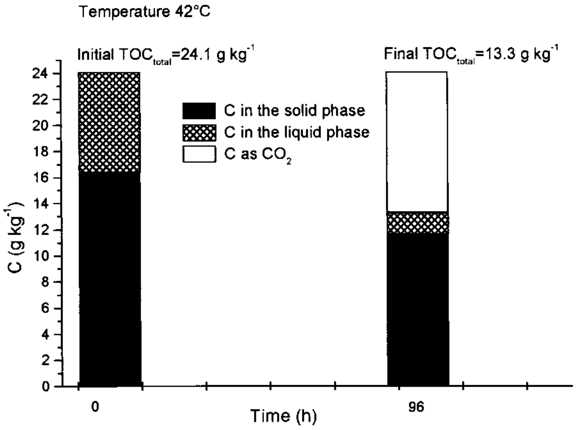

Figure 4. Carbon balance for the aerobic biodegradation process No. 4.

Conclusions

On the basis of the conducted experiments the following conclusion can be drawn.

- The average elemental composition of the organic fraction of the municipal solid waste is presented as $C_5H_{8.5}O_4N_{0.2}$
- The decrement of carbon content increases significantly with temperature from 20% at 20 °C to 40% at 37 and 42 °C after 96 hours of the biodegradation process. At the same time the amount of oxygen utilised for aerobic biodegradation of the suspension estimated on the basis of the stoichiometric equations also increases with temperat-

ure from 0.92 moles at 20 °C to about 1.6 moles at 37 and 42 °C.

- The amount of oxygen required for the total oxidation of such wastes is about 5 times higher than it was calculated on the basis of experimental data, taking 96 hours run into account.
- Comparing the changes and the decrement of carbon, hydrogen, oxygen and nitrogen content, one may suggest that the optimum temperature for such biodegradation processes is 37 °C (mesophilic range).

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