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Calorimetric studies of solid wastes, sewage sludge, wastewaters and their effects on soil biodegradation processes

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Abstract Calorimetric studies of solid wastes, sewage sludge, wastewaters and their environmental effects focus on three main research areas. The first research area involves determination of selected thermal and physical parameters characterizing the above substances, such as specific heat, thermal conductivity and others. The second area covers processes of total or gradual destruction of the examined substances at a fixed composition of the gaseous phase. The methods applied in this case enable to determine the heat of combustion or the calorific value of the analyzed material, as well as changes in the rate of heat production, measured by differential scanning calorimetry (DSC). The third area of calorimetric studies covers microbial calorimetry as a method for non-destructive monitoring of organic matter biodegradation in order to measure the kinetic and thermodynamic parameters of the investigated processes, i.e., wastewater treatment, composting and decomposition of organic soil matter, as well as to determine the stability of wastes. This paper describes, based on available literature data, the major directions of investigations, using different calorimetric methods, of solid wastes, sewage sludge and wastewaters and additionally their effects on soil microbial processes. The paper also presents the selected calorimetric studies and analyses the biodegradation kinetics of organic wastewaters and glucose decomposition in the presence of phosphogypsum in different soils.

Keywords Calorimetry · Solid wastes · Sewage sludge · Wastewaters · Soil

Introduction

Significant amounts of urban and industrial wastes, sludge of various origins and byproducts of the food and farming industry produced every year require a choice of such methods including their development and processing, so that their final product does not pose any danger to humans and their environment. The main directions in processing and disabling organic waste and sludge include: environmental usage, storing in landfills, thermal utilization and composting. The choice of the most proper method must be supported by an accurate technical, ecological and economic analysis, which includes the conditions resulting from the national law and the EU's regulations [1, 2]. Calorimetric methods may be widely applied to examination of solid waste and sludge and their influence on the soil. When compared to the situation 20 years ago [3], an enormous methodological progress and a significant extension of the research scope may be noticed. The discussed methods are used in: identifying thermal properties of materials, examining their physicochemical changes during processes when they are transformed, as well as calorimetric description of metabolic activity in microbiological systems.

The following article aims at presenting the main directions of the studies on the analyzed substances with the use of calorimetric methods. The combination of these

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methods and different analytical techniques significantly broadens their application in examination of waste materials and environmental studies. The descriptions of the experimental equipment and the measuring procedures are included in the quoted literature. This work also presents selected results of the author's own research in connection with the composting urban waste and biodegradation of organic substances in soils.

Thermophysical properties of organic wastes

Values calculated by the use of calorimetric methods and thermal analysis are applied to development of technologies for processing, treating and developing of sewage and solid waste. They are also used for modelling the processes of mass and energy transportation in the examined systems. The quantities that express thermal properties of solid or liquid substances are: specific heat, thermal conductivity, thermal diffusivity and others [4, 5]. The first two parameters are determined by the calorimetric methods.

The mass-specific heat (c) indicates how much of energy must be provided to 1 kg of a substance to increase its temperature by 1 K and is expressed in J kg^{-1} K^{-1}. The specific heat is most often calculated on the basis of cooling curves of the examined substance in calorimeters of various kinds, e.g. the differential reaction calorimeter [6], heat flow or isothermal calorimeters [7–9]. The method of differential scanning calorimetry (DSC) is also applied for determination of the specific heat [10]. Limitations to the application of DSC method result mostly from difficulties in preparing representative, several milligram-sized samples of the examined materials, e.g.: urban waste, sludge or soil. The specific heat in the case of heterogeneous mixtures, such as solid waste, sludge and sewage, depends on their physicochemical composition, content of water and temperature.

The thermal conductivity (k) defines the ability of a substance to conduct heat through a unit of the surface of materials having the same thickness and elementary difference of temperature (1 K) between conducting surfaces. At the conditions of a fixed heat flow, the thermal conductivity is expressed by the coefficient k (W m^{-1} K^{-1}) in Eq. 1.

$$q = -kA\,\mathrm{d}T/\mathrm{d}x \qquad (1)$$

The rate of heat flow is expressed by q (W); k (W m^{-1} K^{-1}) is a thermal conductivity coefficient; A (m^2) is a field of the cross-section towards the heat conduction; $\mathrm{d}T/\mathrm{d}x$ (K m^{-1}) is a temperature gradient between the two surfaces.

The thermal diffusivity—α (m^2 s^{-1})—is calculated on the basis of Eq. 2, as a relation of the thermal conductivity (k) to the product of material density (p) and its specific heat (c).

$$\alpha = k/(\rho \cdot c) \qquad (2)$$

Thermal properties of plant-originated materials, foods and agricultural materials and methods of their calculation have been widely discussed in scientific literature [11, 12].

Heat of combustion and calorific value of organic wastes and sewage sludge

Limitations connected with possibilities of storing or environmental usage of organic waste and sludge have triggered the development of various methods to be used for their thermal conversion [13–15]. A recovery of thermal energy, a significant reduction of mass and volume of the studied substances, partial or total elimination of harmful substances make the thermal methods very useful in disabling of organic materials. The limitations of these methods result from physicochemical properties of wastes and amounts of solid, liquid and gas products formed during the processes. The usage of the waste and the profitability of thermal methods are mostly determined by the content of organic matter and water. The application of the combustion calorimetry [16, 17] provides a possibility of determining the heat of combustion (HC) and the calorific value (CV) of organic substances. By the use of calorimeters equipped with the so-called calorimetric bomb, the process of total oxidation of the substance takes place under the high-pressure O_2 conditions.

The (gross) HC is defined as the amount of heat produced during a total combustion of one mass unit of the examined substance in the calorimetric bomb at conditions specified as: initial oxygen pressure of 2.0–4.0 MPa, final temperature range of 293–308 K, products in the form of ash, liquefied water, CO_2 and N_2 in the form of gas, as well as HCl and H_2SO_4 in water solution. The CV (net HC) expresses the amount of heat produced during the combustion of one mass unit of the examined substance assuming that water in the combustion products remains in form of steam. The CV may be calculated by subtraction of the heat equivalent of water contained in a sample and the water formed during the combustion from the HC in the temperature of 293 K.

Data on the HC and the CV of biomass or sludge and the products derived during their processing are available in numerous case studies and in the subject literature [17–19]. The HC values for solid urban waste (a mean for 210 samples after magnetic separation of metal, humidity of 9.3–50% H_2O) were equivalent to 11 kJ g^{-1}; for a dry mass of typical urban waste ranged between 13 and 17 kJ g^{-1} and for a dry mass of pig faeces were

17.9 kJ g^{-1} [17]. Konno [20] provides the following HC values: for cattle faeces 16.85 kJ g^{-1}, poultry faeces 11.01 kJ g^{-1}, urban sludge 4.66–15.84 kJ g^{-1}, sludge from a brewery 17.77 kJ g^{-1}, rice straw 15.73 kJ g^{-1} and compost 9.46 kJ g^{-1}. The author has used a percentage coefficient expressing the ratio of microbiologically released heat to their HC for assessment of the content of easily decomposable substances in soil. CVs of different kinds of forest residues have also been reported [21].

Application of DSC for thermal examination of organic wastes, sewage sludge and soil organic matter

The DSC method enables the measurement of the changes in the heat power of a sample in the conditions of increasing temperature and reaction time, at a defined composition of the gaseous phase of the reaction environment. The DSC examinations are often supplemented with thermogravimetric measurements (TG) that provide information on mass changes in a substance occurring during the increase of temperature, as well as on the time of these changes. Differential thermogravimetric (DTG) graphs are the first derivative of TG measurements, which responds to rate changes in mass loss. The last decade marks the time of a particular interest in methods of thermal analysis when used for thermal characterization of municipal waste [22] and sewage sludge [23], quality of compost [24], maturity degree of composts [25] and its biological stability [26], combustion and pyrolysis of sewage sludge [19], stabilization of stored sludge [27], characteristics of stored compost, solid municipal wastes and other types of waste [28, 29]. The thermal analysis methods combined with other tests were used in examination of anaerobic decomposition of cattle and poultry faeces [30]. The DSC method may also be applied for assessment of soil organic matter quality [31–33], to the study of humic substances [34, 35], characterization of grass during its decomposition [36], as well as for measurement of combustion enthalpy of soil organic matter [37].

Calorimetric examinations of biodegradation processes in wastewaters, sewage sludge and solid wastes

Cities and industry are the main source of wastewaters, sewage sludge and solid wastes which require the treatment with mechanical, chemical or biological methods. Kinetics and effectiveness the biological methods depend on metabolic activity of the system during processes of aerobic or anaerobic biodegradation. The methods of isothermal calorimetry make it possible to monitor changes of the rate of metabolically generated heat and to calculate total heat effects in the examined processes. A combination of calorimetric method with respirometric measurements is known as calorespirometry.

Redl and Tiefenbrunner [38] have examined with the microcalorimetric method the changes in hydrolytic activity of wastewater and sludge collected from a municipal waste treatment plant. Fortier et al. [39] have used a constant-flow microcalorimeter combined with an external bioreactor for examining biodegradation processes in the presence of phenol and the following ions CN^-, $Cr_2O_7{}^{2-}$, Cd^{2+} and Cu^{2+}. A similar measurement technique has been applied to study the course of biological treatment of industrial wastewaters [40, 41]. An isothermal microcalorimeter was used for monitoring anaerobic digestion of wastewaters from cheese industry, distilleries and yeast plant [42]. Using a 2 dm^3 bioreactor, Aulenta et al. [43] have examined activity changes of active sludge using calorimetric and respirometric methods, and they have also characterized bioenergetics of nitrification and denitrification processes in aerobic and anaerobic conditions in the presence of Hg^{2+} ions. Daverio et al. [44] have applied the calorimetric method to biokinetic characteristics of the nitrification process in the presence of active sludge collected directly from a waste treatment plant. The authors have estimated the value of the thermal coefficient of $N\text{-}NH_4$ changes during the nitrification to be 18.24 ± 0.2 J mg^{-1} of $N\text{-}NH_4$, and that of the calorespirometric coefficient to be 189 ± 13 kJ mol^{-1} of O_2.

Composting is a thermophilic process of aerobic biodegradation of a heterogeneous organic substrate that leads to formation of a partially humificated and microbiologically stable organic mass. It is used for processing solid organic waste and sewage sludge into a product that can be used in environment. Composting occurs spontaneously in natural conditions a household composting plant. Maintaining optimal composting temperature depends on the rate of heat production (RHP) during biodegradation [45]. Industrial-scale composting is conducted in bioreactors of various constructions with a possibility of optimizing the conditions of the process, which include: loading with a substrate, speed of mixing and aeration, chemical composition, humidity, thermal conditions and other factors [46]. The heat of biodegradation may be used in the so-called sludge biodrying [47]. The Dano biostabilizer is a type of bioreactor used in Poland. It is a cylindrical, steel device, 3.6 m in diameter, 32 m in length, inside of which processes of urban waste mixing, aeration, mashing and biodegradation take place. The obtained intermediate product is subjected to following mechanical processing and final so-called maturing. The changes in thermal conditions of the composting process in the Dano biostabilizer have been identified during a 1-year-long cycle of operation. The authors have taken measurements of compost samples collected from a production line and stored in piles [48]. A characteristic course of rate changes in metabolic heat production for the composting reaction during a 24-h operation cycle of the Dano biostabilizer is shown in Fig. 1 [49]. In this case, samples of the composted mass were collected directly from the biostabilizer and immediately analyzed using the isothermal microcalorimetric method. A calorimetric output was determined at 298.15 K from a steady state part of thermograms. The changes of metabolic activity of composts subjected to drying and moisturizing have been examined with the microcalorimetric method [50]. In another paper, the methodological problems concerning microcalorimetric measurements of microbial activity compost samples have been presented [51].

A pursuit for an efficiency increase and optimization of composting process gives a reason for its mathematical modelling. It refers both to composting in natural conditions and in bioreactors of various constructions [51]. It may be assumed that bioreactors are calorimeters, in which intensive production of metabolic heat takes place [52–54]. A part of the produced heat warms the composted mass up to the temperature equivalent to the scope of thermophilic biodegradation, and the remaining part is lost. Changes of the thermal power during composting are directly connected with the kinetics of microbiological growth. These changes may be identified using mathematical dependencies [55]. The thermal power of a biomass can be determined directly by the calorimetric method or indirectly by means of respirometric measurements and experimentally identified calorimetric coefficients, e.g.: 452 kJ mol^{-1} of O_2 for organic waste [54] or 20.6 J cm^{-3} of O_2 and CO_2 for decomposition of glucose and other organic compounds in bacterial monocultures [56], as well as for processes of aerobic fermentation [57]. Calculation of heat losses from the examined systems requires thorough knowledge of the thermal properties (described earlier in this article) and other values that characterize elements of solid, liquid and gaseous phases during composting in a physically defined system of the bioreactor. Modelling attempts of composting processes in bioreactors of a device similar to the Dano biostabilizer have been undertaken by Kishimoto et al. [58].

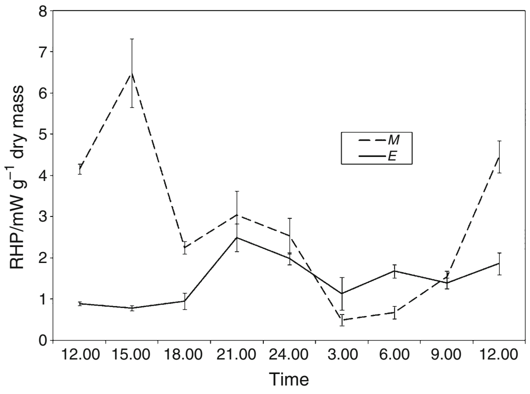

Fig. 1 Changes of metabolic heat production rate (mW/1 g of dry mass) from the composted mass during a 24-h cycle of solid urban waste composting inside the middle (*M*) and the end part (*E*) of the Dano biostabilizer [49]

Calorimetric and kinetic characteristics of biodegradation of organic substances in soils

The RHP in isothermic conditions is an indicator of soil metabolic activity during organic matter decomposition. Most of the microcalorimetric examinations of soils have focused on decomposition of easily biodegradable sugars [32, 59–62]. The fundamental works Wadsö and co-workers [63–65], Sparling [66–68] and Takahashi’s group [59, 69] have initiated the development of modern soil microbial calorimetry. The content of a soil biomass is identified using the microcalorimetric method [66, 70, 71]. Based on the determined thermograms (RHP changes), the intensity changes of the biodegradation process and their total thermal effect are recognized, and kinetic and thermodynamic parameters are estimated [72, 73]. The basic criteria have been established for determination of soil health using microcalorimetry as the main technique complemented by the study of physical, chemical and biological features of soil [74]. Relatively little attention has been devoted to microcalorimetric study on the effects of organic amendments on soil microbial activity and biomass content [75]. Composted municipal waste and organic manure [76], cattle manure, municipal refuse compost, earthworm casts [77], organic fertilizer made from the residue of grain whiskey distilling and yeast extract have been used as soil amendments [78]. Research on biodegradation of organic waste-like substances, such as organic manure and those including: sludge, straw, grass, compost, cattle faeces, etc., is rather scarce [20]. Dziejowski [79] has examined decomposition of animal wastewaters in soil. Wastewaters were collected directly from a sewer at a pig farm. The effect of solid–liquid effluents from anaerobic digesters on soil microbial activity was analyzed by isothermal calorimetry and DSC method [33].

The further part of this work presents the results of the author’s own research on decomposition of organic substances in soils. The calorimetric method has been used to examine the biodegradation process of liquid cattle manure in the soil. Liquid cattle manure represents a large group of organic waste produced in agriculture. Those substances are mostly used for fertilization purposes. Another point of the research referred to the influence of non-organic industrial waste on biodegradation of glucose in the soil.

Table 1 Characteristics of soils

No.	Soil	Texture	pH (KCl)	N/%	C_{org}/%	P_2O_5/mg/100 g	MgO/mg/100 g	K_2O/mg/100 g
1	Cambisol	Loamy sand	6.30	0.057	0.42	24.05	5.97	15.78
2	Luvisol	Sandy loam	5.40	0.086	0.97	8.93	5.47	10.12

Phosphogypsum (PG), obtained when producing phosphoric acid from phosphorites, is an example of waste with a potential use in agriculture [80]. Gypsum constitutes the main ingredient of PG. Phosphates, fluorides and heavy metals are present in it in small quantities. Also, trace amounts of radioactive elements were identified in it [81–83]. Significant amounts of PG are stored as waste in piles, which poses a threat to the natural environment. Some attempts to utilize PG as a fertilizer providing calcium and sulphur have been undertaken. PG has also been used to improve properties of soils and for their desalination [80].

Two soils characterized in Table 1 have been used for the purpose of this work. The soils were collected in the agricultural experimental stations of the University of Warmia and Mazury in Olsztyn in Bałcyny and Tomaszkowo regions.

The liquid manure was collected at a cattle farm after 4–5 months of storage. The manure contained 3430 mg dm^{-3} of nitrogen, 2.1% of a dry mass and its pH was 6.1. The cattle liquid manure was used in a dose of 40 mg of N per 100 g of the soil no. 2.

Graphs in Fig. 2 describe the course of changes of the RHP and the total heat produced during the decomposition of liquid cattle manure in 50 g of soil no. 2. The highest RHP (maxRHP) of 86 μW g^{-1} of soil was noticed after the time (PT) of 38 h. After 50 and 100 h, the total heat effects were 8.9 and 14.8 J g^{-1}, respectively. The calorespirometric coefficient, calculated on the basis of additional measurements, was 18.2–19.8 J cm^{-3} O_2.

The PG was collected from the production line of phosphoric acid at the Phosphoric Fertilizers Plant in Gdańsk. PG contained: 49.19% of SO_4^{2-}, 1.2% of P_2O_5 and 20.5% of H_2O, as well as 0.66% SO_4^{2-}, 0.6% of P_2O_5 in a water-soluble form (1:1 w/w) and 130 mg of F kg^{-1} PG. Decomposition of glucose in soils with no PG and with 25% of PG was studied. The examined samples of soil had a mass of 50 g and contained 50 mg of glucose. Additionally, water was introduced in such amounts so that its final content was equal to 60% of the maximum water holding capacity (MWHC) calculated for the examined soils with no PG. The calorimetric measurements were carried out in a KRM differential calorimeter, at the temperature of 298.15 K, using measuring vessels with the capacity of 0.5 dm^3. The calculations were performed according to the procedure described in the author's previous article [79].

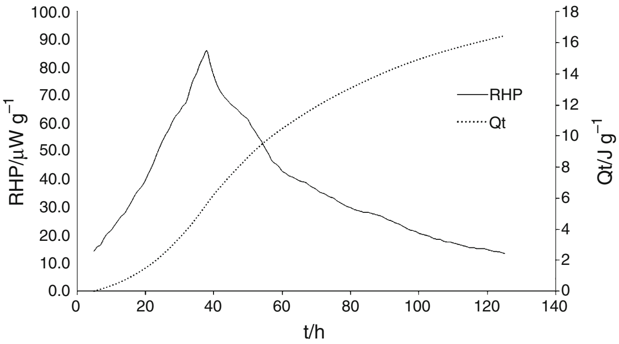

Fig. 2 The changes of the rate of heat production during the cattle liquid manure decomposition in the soil no. 2

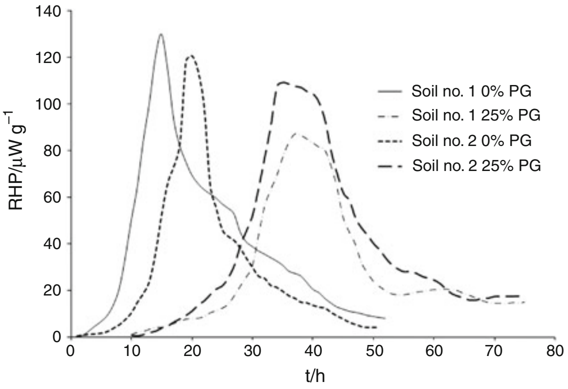

Fig. 3 The rate of heat production (RHP) during glucose decomposition in various soils containing 0 and 25% of phosphogypsum (PG)

Figure 3 represents the changes of the RHP during decomposition of glucose in soil no. 1 and 2 containing PG (25% PG), compared to soils without that ingredient (0% PG). Table 2 includes findings of the calorimetric measurements describing the courses of the thermograms in Fig. 3, where: PT—peak time, maxRHP—maximum RHP, Qt(*t*)—total heat produced after the time *t*, *k*—apparent rate constant calculated using the Guggenheim method in the time span of *t*1–*t*2. %MHP—a percentage coefficient expressing the ratio of metabolically produced heat to the heat (enthalpy) of glucose combustion.

The results show that introduction of PG to soils no. 1 and 2 has increased the time of glucose biodegradation and visibly decreased the rate of the examined process. This is confirmed by the increasing PT time, lowering the

Table 2 Characteristics of glucose biodegradation in soils containing 0 and 25% of phosphogypsum

Soil no.	PG content/%	PT/h	maxRHP/μW g^{-1}	Qt(50)		Qt(70)		*k*/h^{-1}	*t*1–*t*2/h
				J g^{-1}	%MHP	J g^{-1}	%MHP		
1	0	14.5	131	7.46	47.9	n.d.	n.d.	0.227	6–12
1	25	37	87	5.4	34.7	7.01	45.1	0.162	21–34
2	0	19.5	122	5.37	34.5	n.d.	n.d.	0.219	8–18
2	25	35.5	109	6.98	44.9	8.27	53.1	0.164	25–35

maxRHP value and lowered values of the apparent rate constant. Changes of the %MHP indicator suggest a stronger accumulation of chemical energy (of biomass and metabolites) in soil no. 1. PG, when introduced to soils, causes an increase of soil acidification to pH < 4. That effect may result in the changes of soil microorganisms when compared to the soils with no PG. The fungi-assisted metabolism of glucose is most likely to be a preferred direction of biodegradation [84].

Conclusions

The review of literature on the application of calorimetric methods for examination of solid waste, sewage sludge and wastewaters, as well as selected results of own research make it possible to draw the following conclusions:

- thermophysical properties determined by means of calorimetric methods and the results of measurements taken with thermal analysis methods are used in developing methods of storing, thermal processing and modelling of technological processes, as well as in defining stability and physiochemical characteristics of solid and liquid waste;
- microbiological calorimetry, used both individually and in connection with other methods of microbiological analysis, is widely applied for examination of biodegradation processes during composting, wastewater treatment and examination of organic sludge stability;
- calorimetric measurements of microbiologic activity of soils are applied to estimation of microbial biomass and to determine kinetic and thermodynamic characteristics of decomposition processes of organic amendments and to examine the influence of xenobiotic substance on their course.

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