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ALKALINE STABILISATION OF PRIMARY SLUDGE
PART 2. ANALYSES OF THERMALLY RELEASED PRODUCTS

Physicochemical and molecular changes in polymeric matrix of alkaline-stabilised primary sludge cake from Municipal Wastewater Treatment Plant of Krotoszyn in Poland (about 35,000 habitants) are described. The primary sludge was stabilised for 1 day and 35 days by calcium hydroxide doses up to 24%^{d}. The alkaline treatment led to preferential hydrolysis of proteins and fats contained in organic polymeric material of the raw sludge. Changes in the sludge macromolecular composition caused by calcium hydroxide suspension were analysed by gas chromatography–mass spectrometry (GC–MS) analyses of the products of both pyrolysis and pyrolysis–in situ methylation (using tetramethylammonium hydroxide (TMAH)) obtained from the Soxhlet pre-extracted sludge cakes stabilised for 35 days. Thermally released compounds from sludge polymeric matrix are mainly fatty acids, predominantly unsaturated stanols and sterols, as well as *n*-alk-1-ene/*n*-alkane pairs. *n*-Alkylbenzenes are found to be minor components in the pyrolysis products.

1. INTRODUCTION

An organic fraction of the sewage sludge comes predominantly from household wastes and faeces [1] and therefore is a complex mixture of fats, proteins, amino acids, sugars, cellulose, humic substances and microorganisms as well as the products of their biotransformation. The sludge has been generated in the Municipal Wastewater Treatment Plant (MWTP). A rational utilisation of sewage sludge in the form of a soil fertiliser presents an important problem [2]. Lime stabilisation of the sludge is regarded as an attractive alternative to aerobic or anaerobic digestion, since it leads to a high-quality fertiliser for acidic soils [3]. Besides, lime is a common alkaline stabiliser used in WWTPs for preparation of sludge which could be easier dewatered, as well as to prevent odour problems and to destroy pathogenic microorganisms [4]–[6]. This is particularly important because in Poland, where acidic soils account for approximately 80% of arable land [7], the application of

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a high-quality lime-organic fertiliser with no anthropogenic organic and inorganic pollutants is particularly recommended.

Laboratory tests were carried out in order to show the changes in the composition of the sludge polymeric organic matter originating from the Krotoszyn MWTP and caused by calcium hydroxide used as alkaline stabilisation agent. The physicochemical characteristics of the sludge–calcium hydroxide composites were determined. The changes in the molecular composition of the products released by pyrolysis and pyrolysis in situ methylation of the pre-extracted sludge cake were analysed using GC–MS.

2. MATERIALS AND METHODS

The experiments were carried out on filter cake obtained from primary sludge collected at the Krotoszyn Wastewater Treatment Plant (Midland Poland). The sludge was treated with suspension of calcium hydroxide (3, 6, 9, 12 and 24%^{d} doses) as a stabilising agent. The resultant sludge-calcium hydroxide composites were seasoned for 1 day and 35 days. The dewatered filter cakes were air-dried, powdered to particle size below 0.2 mm, and exhaustively pre-extracted with organic solvent [8]. Standard methods were used to analyse the content of total organic matter, proteins, fats and elemental composition of carbon, hydrogen, nitrogen and sulfur in the sludge cake. Prior to these analyses, inorganic carbon was removed from the sludge cake by 24 hours treatment with 6 N hydrochloric acid which was followed by washing away the chlorine ions.

The Soxhlet pre-extracted sludge composites were subjected to pyrolysis in an electrically heated quartz tube furnace at a temperature of 600 °C under flow of argon. Evolving pyrolysis products were trapped in the dichloromethane at the outlet. Pyrolysis–methylation products were obtained in the same way, where in situ methylation was achieved with a twofold tetramethylammonium hydroxide (TMAH) homogenised with the sample prior to its pyrolysis. The trapped hydrocarbons were solvent-fractionated using *n*-hexane, and *n*-hexane fractions of the pyrolysis and pyrolysis–methylation products were analysed by GC–MS for molecular composition of thermally released compounds.

3. RESULTS AND DISCUSSION

3.1. CHEMICAL COMPOSITION OF FILTER CAKE

The changes in a chemical composition of the filter cake caused by calcium hydroxide suspension after 1 day and 35 days of its stabilisation (water content, loss of total organic substance, elemental composition, the content of fats and proteins) are given in table 1. Independently of the time of sludge stabilisation, with an increase in calcium hydroxide dose up to 24%^{d}, its susceptibility to dewatering gradually improved. This is probably a result of physicochemical modification of sludge particulate due to alkaline hydrolysis, in which a remaining polymeric organic material becomes more hydrophobic. Indeed, an addition of calcium hydroxide to the sludge has a pronounced effect on the hydrolysis of organic matter. As is shown in table 1 and in figure 1 (1-day stabilisation), the per cent of organic matter being hydrolysed is almost linearly correlated with the dose of calcium oxide in the sludge. In respect to the time of stabilisation, this process proceeded very quickly at the beginning of alkaline stabilisation. One-day stabilisation of the composite containing 24%^{d} of calcium hydroxide resulted in nearly 46% hydrolysis of organic matter. In this process, fats and proteins were hydrolysed preferentially in ca. 55% and 57%, respectively (figure 1). Longer stabilisation (up to 35 days) did not improve significantly the hydrolysis efficiency, whose values raised by about 20%.

Table 1

Physicochemical characteristic of sludge cake obtained from the raw sludge stabilised for 1 day and 35 days using various calcium hydroxide doses

Dose of calcium hydroxide introduced to sludge						
$Ca(OH)_2$ dose in raw sewage sludge [g/dm^3]	0.00	2.09	4.18	6.27	8.36	16.72
$Ca(OH)_2$ dose in dry sewage sludge cake [%^{d}]	0.00	3.00	6.00	9.00	12.00	24.00
Sludge cake stabilised for 1 day						
Water content in filter cake [%]	90.05	90.72	90.04	89.56	89.02	85.58
Organic substance in sludge cake ($Ca(OH)_2$ free) [%^{d}]	73.51	72.13	71.18	70.00	68.20	59.74
Composition of mineral free organic substance:						
– carbon [%^{d}]	51.75	53.51	55.74	56.03	56.94	61.66
– hydrogen [%^{d}]	7.75	7.93	8.23	8.31	8.24	9.22
– organic nitrogen [%^{d}]	6.79	6.65	5.94	5.50	5.18	5.01
– fats [%^{d}]	27.91	27.16	25.82	24.78	24.15	23.50
– proteins [%^{d}]	42.43	41.59	37.13	34.38	32.39	31,31
Sludge cake stabilised for 35 days						
Water content in filter cake [%]	90.65	90.55	89.50	89.01	88.30	84.56
Organic substance in sludge cake ($Ca(OH)_2$ free) [%^{d}]	67.46	65.19	63.79	62.47	61.30	52.18
Composition of mineral free organic substance:						
– carbon [%^{d}]	53.44	53.19	54.59	56.00	56.19	66.34
– hydrogen [%^{d}]	7.81	8.30	8.39	8.23	7.46	8.68
– organic nitrogen [%^{d}]	6.09	5.94	4.97	5.00	4.82	4.78
– fats [%^{d}]	26.59	26.09	25.66	24.33	23.26	21.12
– proteins [%^{d}]	37.82	37.11	34.15	31.27	30.12	29.14

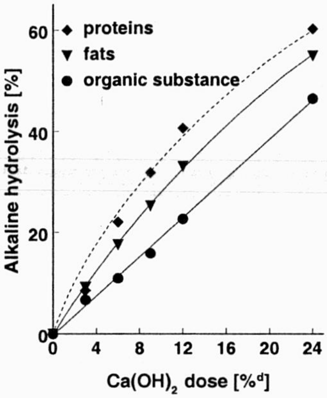

Fig. 1. Enhanced alkaline hydrolysis of proteins and fats versus calcium oxide content in sludge composites after their stabilisation for 1 day

The course of alkalisation is not only reflected by the hydrolysis efficiency, but also by the changes in an elemental composition of the filter cake. Within the range of calcium hydroxide doses used the content of carbon in an organic matter of the sludge cake increased by about 14%, while that of nitrogen fell down from 6.7 to 4.7%. Hence, the atomic C/N ratio continuously increased with an increase in the dose of alkaline agent and duration of stabilisation process (figure 2). Prolonging the stabilisation time from 1 day to 35 days caused an increase in the of C/N ratio by about unity within the whole investigated range of alkaline agent dose. The dependence presented suggests that structural units bearing nitrogen functional groups (amines, amino acids, amides and other nitrogen containing heterocompounds) are preferentially released due to hydrolysis of polymeric organic matter.

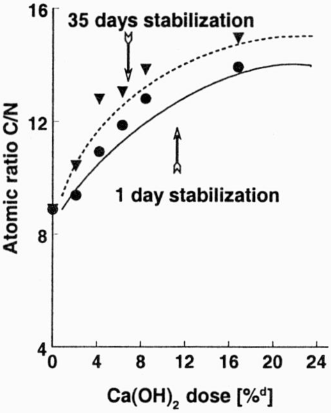

Fig. 2. Atomic C/N ratio versus calcium hydroxide dose in the sludge stabilised for 1 day and 35 days

3.2. THERMALLY RELEASED VOLATILE CONSTITUENTS OF SLUDGE CAKE

In *n*-hexane fractions of the pyrolysis and pyrolysis–methylation products obtained from the Soxhlet pre-extracted filter cake, a molecular composition of the following groups of compounds was analysed: fatty acids (in pyrolysis products) or fatty acids methyl esters (in pyrolysis–methylation products), stanols and sterols, *n*-alkenes + *n*-alkanes, and *n*-alkylbenzenes as well as linear alkylbenzenes of anthropogenic origin.

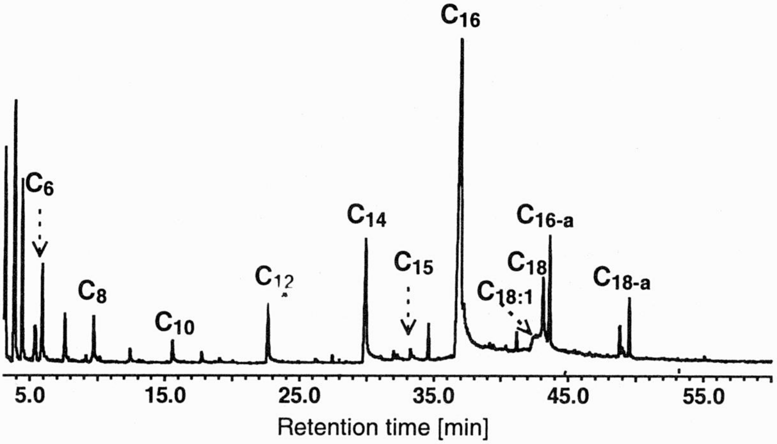

Fig. 3. Mass chromatogram of thermally released fatty acids from sludge cake being stabilised for 35 days with $9\%^{d}$ calcium oxide dose. Number of carbon atoms in the fatty acid homologue is indicated by C_n

Monocarboxylic fatty acids were the most abundant compounds present in the thermally released products. Homological composition of these compounds in pyrolysis products (figure 3, fatty acids thermally released from the sludge cake stabilised for 35 days with $9\%^{d}$ calcium hydroxide dose) appeared to be very similar to that of lipids [8]. Also composition of fatty acids methyl esters released by in situ pyrolysis–methylation highly resembles this of fatty acids released by conventional pyrolysis. The sludge cake composites with various content of calcium hydroxide gave nearly the same composition of the compounds discussed; however, their overall quantities in the samples analysed (assessed by applied methods) were gradually smaller as bigger dose of calcium hydroxide was added to the raw sludge. We suggest that in the laboratory experiment carried out, fatty acids released from sludge matrix by alkaline hydrolysis form insoluble calcium alkanoates remaining in the solid sludge fraction. Upon pyrolysis the salts underwent rather thermal decarboxylation giving *n*-alkanes, while upon pyrolysis–methylation the above alkanoates partly yielded fatty acids methyl esters and only partly underwent thermal decarboxylation. In fatty acids released from the polymeric sludge substance, the straight-chained homologues prevailed. They are represented by homologues within the C_{12}–C_{18} range, where palmitic acid (C_{16}) is the most prominent (figure 3). Their chromatographic profiles showing a high predominance of even carbon-numbered homologues suggest only minor biodegradation of the sludge. Besides, thermally released fatty acids or fatty acids methyl esters contain small amount of unsaturated $C_{18:1}$ fatty acid and also low-molecular weight *n*-alkanoic acids. The latter were not found in lipids [8]. Their presence in the thermally released compounds is explained by thermal degradation of the high-molecular weight homologues. In mass chromatogram of fatty acids from pyrolysis products (figure 3), amides of palmitic ($C_{16\text{-a}}$) and stearic ($C_{18\text{-a}}$) acids can be found as well.

The presence of stanol and sterol compounds and their unsaturated derivatives in thermally released products (figure 4, sludge stabilised for 35 days with $3\%^{d}$ $Ca(OH)_2$, compound assignments to respective peaks are listed in table 2) implies that these compounds are also bound within the sludge macromolecular matrix. Namely, apart from stanol and sterol compounds found in lipids (coprostanol, cholesterol, cholestanol as well as their 24-ethyl and 24-methyl [8]), thermally released steroidal compounds are abundant in unsaturated C_{27}–C_{29} cholestenes (peaks 1–11 in figure 4). This suggests that chemically bound steroidal compounds are non-saponifiable under the alkaline stabilisation conditions. Namely, calcium hydroxide action retained stanols and sterols in the sludge particulate, independently of the amount of calcium hydroxide applied. Also their homological composition is independent of alkaline stabiliser content. We suggest that these compounds are unavailable for straight extraction with organic solvents and are the products of the thermal decomposition of oxysterols bound with sludge matrix [9] and thermally released in the pyrolysis and pyrolysis–methylation processes.

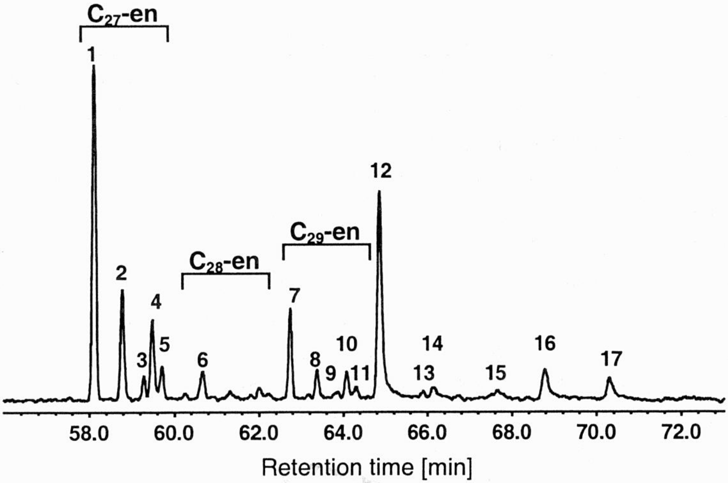

Fig. 4. Mass chromatogram of the stanol and sterol compounds released thermally by pyrolysis of sludge cake after stabilisation for 35 days with $3\%^{d}$ $Ca(OH)_2$. Assignment of stanol and sterol compounds to peak numbers on mass chromatogram is presented in table 2

Table 2

Assignment of stanol and sterol compounds to peak numbers on mass chromatogram in figure 4

Peak number	Molar mass	Stanol/sterol
1	370	C_{27} cholesten
2	370	C_{27} cholesten
3	370	C_{27} cholesten
4	370	C_{27} cholesten
5	370	C_{27} cholesten
6	384	C_{28} cholesten
7	398	C_{29} cholesten
8	398	C_{29} cholesten
9	398	C_{29} cholesten
10	398	C_{29} cholesten
11	398	C_{29} cholesten
12	388	5β(H)-cholestan-3β-ol (coprostanol)
13	386	cholest-5-en-3β-ol (cholesterol)
14	388	5α(H)-cholestan-3β-ol (cholestanol)
15	386	5β(H)-cholestan-3-one (coprostanone)
16	402	24-methyl-5β(H)-cholestan-3β-ol (24-methylcoprostanol)
17	416	24-ethyl-5β(H)-cholestan-3β-ol (24-ethylcoprostanol)

Chain compounds released thermally upon pyrolysis are represented by *n*-alk-1-enes/*n*-alkanes pairs within the range of the low-molecular weight homologues extending to C_{18} (a profile is not shown). The prevalence of relative concentration of odd carbon-numbered homologues in *n*-alkanes above C_{10} is characteristic of these hydrocarbons, while the reverse predominance of even carbon-numbered homologues is observed for respective *n*-alke-1-nes. We suggest that the features of *n*-alkanes result from decarboxsylation of fatty acids esters and calcium alkanoates, while these of *n*-alk-1-enes are due to partial chain cracking of thermally released alkyl ethers linked with macromolecular sludge polymeric matrix. In the pyrolysis–methylation, the profile of these compounds is characterised by a higher abundance of *n*-alk-1-enes whose homologous feature is very similar to that of the respective compounds in pyrolysis products. Much lower concentration of *n*-alkanes in the pyrolysis–methylation products can be interpreted as a result of the methylation of chemolytically released fatty acids to respective methyl esters rather than their thermal decarboxylation. Further support of thermal decomposition of fatty acids upon pyrolysis and their preservation upon pyrolysis–methylation comes from the presence of *n*-alkylbenzenes in pyrolysis products, and their lacking in the pyrolysis–methylation products. It is most probable that they are formed *via* aromatisation of unsatureted fatty acids upon pyrolysis [10]. They extend up to C_{24} with a gradual decrease in homologue relative concentration with its chain length.

Among the markers were also characterised linear alkylbenzenes (LABs) of anthropogenic origin. They are recognised as urban waste-specific markers [11]–[14]. They were detected only in thermally released products of the pre-extracted sludge cake and characterised by the same homologous pattern with homologues of alkyl chains ranging from C_9 to C_{13}, where C_{11} and C_{12} prevail. The source of the compounds discussed is related to the use of detergents in households, i.e. to linear alkylbenzene sulphonates (LASs). The above compounds could result in a partial thermal decomposition of some LASs incorporated into polymeric structure of the sludge.

4. CONCLUSION

A laboratory-scale approach allows evaluation of the effect of calcium hydroxide on the changes in molecular composition of the sludge during alkaline stabilisation. The degree of enhancement of hydrolytic decomposition of sludge organic matter is directly related to the dose of calcium hydroxide, increase in pH and time of stabilisation. In the sludge organic matter, fats and proteins are the most susceptible to the hydrolysis. The main groups of the chemical markers associated with polymeric sludge particulate are fatty acids, bound or entrapped stanols and sterols as well as surfactant derivatives of anthropogenic origin. Composition of fatty acids, stanols and sterols as well as other steroidal unsaturated derivatives thermally released from sludge polymeric matrix remains intact after sewage treatment with calcium hydroxide.

Pyrolysis and pyrolysis in situ methylation techniques combined with GC–MS analyses of thermally released liquid products are the complementary techniques for the determination of the composition of the sludge organic matter.

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ALKALICZNA STABILIZACJA WSTĘPNYCH OSADÓW CZĘŚĆ II. ANALIZA PRODUKTÓW UWOLNIONYCH TERMALNIE

Opisano kształtowanie się właściwości fizykochemicznych komunalnego osadu wstępnego po jego alkalicznej stabilizacji zawiesiną wodorotlenku wapnia w zależności od dawki czynnika alkalizującego oraz czasu stabilizacji. Stwierdzono preferencyjny przebieg hydrolizy układów polimerowych zawartych w materii organicznej osadu najbardziej podatnych na ten proces, tj. tłuszczów i białek. Stopień rozkładu hydrolitycznego polimerowej matrycy organicznej osadu jest wprost proporcjonalny do dawki zawiesiny czynnika alkalizującego, a także do czasu stabilizacji. Skład molekularny produktów uwolnionych termicznie wykazał, że polimerowe jednostki substancji organicznej osadu zawierają kwasy tłuszczowe związane w postaci estrów oraz struktury steroidowe związane mostkami tlenowymi z matrycą polimerową. Termiczny rozkład matrycy polimerowej osadu prowadzi do tworzenia się *n*-alk-1-enów/*n*-alkanów oraz alkilobenzenów, które są produktami termicznego przekształcenia pochodnych kwasów tłuszczowych (estrów w glicerolowych jednostkach strukturalnych, soli wapniowych kwasów tłuszczowych itp.).