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ALKALINE STABILISATION OF PRIMARY SLUDGE PART 1. ANALYSES OF LIPIDS

Calcium hydroxide (up to 24%^d) in a form of suspension added to primary sludge from Municipal Wastewater Treatment Plant (MWTP) modified its physicochemical properties in the alkaline stabilisation process that lasted for 1 day and 35 days. Qualitative and quantitative (in relative terms) changes in molecular composition of non-polar fraction of extractable lipids, caused by the alkaline agent, were determined using gas chromatography–mass spectrometry (GC–MS). Fatty acids as well as stanols and sterols are the two major groups of compounds in the fraction. Calcium hydroxide treatment selectively removes fatty acids from the sludge lipids, but it does not remove stanol and sterol compounds during sludge stabilisation. The alkaline agent does not affect molecular assemblage of the two groups of compounds. *n*-Alkanes resembling domination of odd-carbon numbered homologues are the minor components of the sludge lipids.

1. INTRODUCTION

An important problem of a sludge disposal is its use as a fertiliser that can be spread on arable land [1]. This can solve some of the problems related to the sludge storage. Sludge stabilisation by lime suspension is regarded as an attractive alternative to aerobic or anaerobic digestion, particularly in a small or seasonal MWTP. Lime, a common alkaline agent, easily dewateres the sludge, reduces its odour and eliminates pathogens [2], [3]. The stabilisation product is a high-quality lime-rich organic material with no anthropogenic contaminants. When used as a fertiliser, it not only provides the crops with organic nutrients, but it also minimises the uptake of metals by plants grown on acidic soil [4]. However, there is no literature on the molecular changes of sludge organic matter produced by domestic users in the course of its alkaline stabilisation by calcium hydroxide suspension.

In our study, the changes in physicochemical properties of the products of sludge being stabilised by calcium hydroxide are presented. Additionally, transformations in

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the molecular composition of the sludge lipids occurring during the process were determined using GC-MS.

2. MATERIALS AND METHODS

Dewatered raw primary sludge from Municipal Wastewater Treatment Plant in Krotoszyn (Midlands of Poland) was treated with suspension of calcium hydroxide in various doses (3, 6, 9, 12 and 24%^d; index 'd' refers to sludge dry mass) used as a stabilising agent. The sludge-calcium hydroxide composites were matured for 1 day and 35 days. Standard methods were used to analyse filtrate and filter cake. In the filtrate, pH value was measured and the contents of mineral constituents, proteins and fats were determined. In the sludge cake, the contents of total organic matter, proteins and fats were determined and elemental analyses of carbon, hydrogen, nitrogen and sulphur were carried out. Lipids were obtained by exhaustive Soxhlet extraction of the stabilised cake using dichloromethane-methanol 93:7 (v/v) as a solvent. Analyses of molecular composition were performed for the *n*-hexane fractions of the lipids by gas chromatography interfaced with mass spectrometry.

3. RESULTS AND DISCUSSION

3.1. PHYSICOCHEMICAL CHARACTERISTIC OF THE FILTRATE AND SLUDGE CAKE

Some general trends in the changes of physicochemical properties of the sludge cake and filtrate upon increasing the calcium hydroxide dose up to 24%^d of the sludge solids are as follows: (i) dewatering of the composite became more effective – water content in the sludge cake decreased from 90 to 84%, (ii) yellow colour of the filtrate solution gradually deepened, (iii) carbon content in organic fraction of the sludge cake increased from about 52 to 66%, (iv) the pH of the filtrate being stabilised for 1 day increased from neutral to the value of 11.5 and it paralleled the reduction of microbial activity and odour release; respective pH value of the filtrate from composite being stabilised for 35 days was about half a unit lower compared to the corresponding filtrate stabilised for 1 day, (v) dose of alkaline agent and duration of the sludge stabilisation caused preferential hydrolytic release of fats and proteins (partly moved into filtrate), and resulted in an increase of mixed liquid volatile suspended solids and chemical oxygen demand in the filtrate as well as an enhancement of ammonia release into filtrate (figure 1). An abrupt increase of ammonia concentration upon calcium hydroxide addition up to 6%^d is due to the enhancement of protein hydrolysis at higher pH. There is a characteristic peak of ammonia concentration in the filtrate at

about 6%^d dose of calcium hydroxide (pH ~9, figure 1). An increase of the calcium hydroxide dose above 6%^d of sludge dry mass further raised the pH value, which made the evolution of ammonia from the filtrate to the gaseous phase more effective, and in consequence reduced its concentration in a liquid phase.

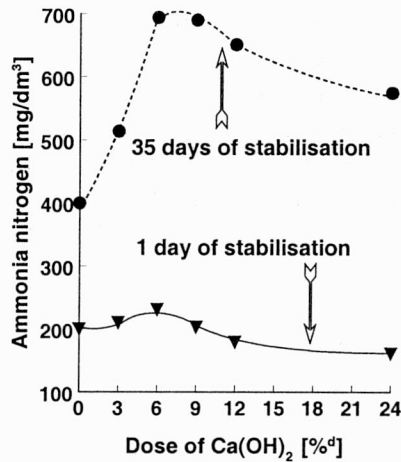


Fig. 1. Changes of ammonia nitrogen concentration in the filtrates from the sludge–calcium hydroxide composites as a function of calcium hydroxide dose

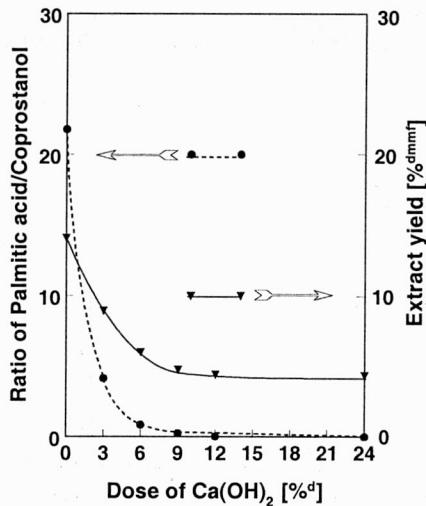


Fig. 2. Changes in the ratio of relative concentration of palmitic acid (C₁₆) to coprostanol in the lipids (broken line) and extract yield (solid line) from the sewage-sludge composites stabilised for 35 days as a function of calcium hydroxide dose

A calcium hydroxide dose up to 9%^d also considerably reduced the amount of extracted material (to one-third of the initial value), while Ca(OH)₂ dose above 9%^d caused no further decrease of the extract yield (figure 2, solid line).

3.2. MOLECULAR COMPOSITION OF NON-POLAR FRACTION OF LIPIDS

A non-polar fraction constitutes about 30% of the lipid mass, irrespective of the calcium hydroxide dose used for stabilisation. In figure 3, the total mass chromatograms of the selected non-polar fractions are shown. The non-polar fraction from the raw sludge (no calcium hydroxide added) being stabilised for 35 days (trace A in figure 3) revealed presence of the two major groups of compounds: free fatty acids as well as stanols and sterols, with domination of the former. A homological composition of the fatty acids (figure 3) was found to be similar to that reported earlier for

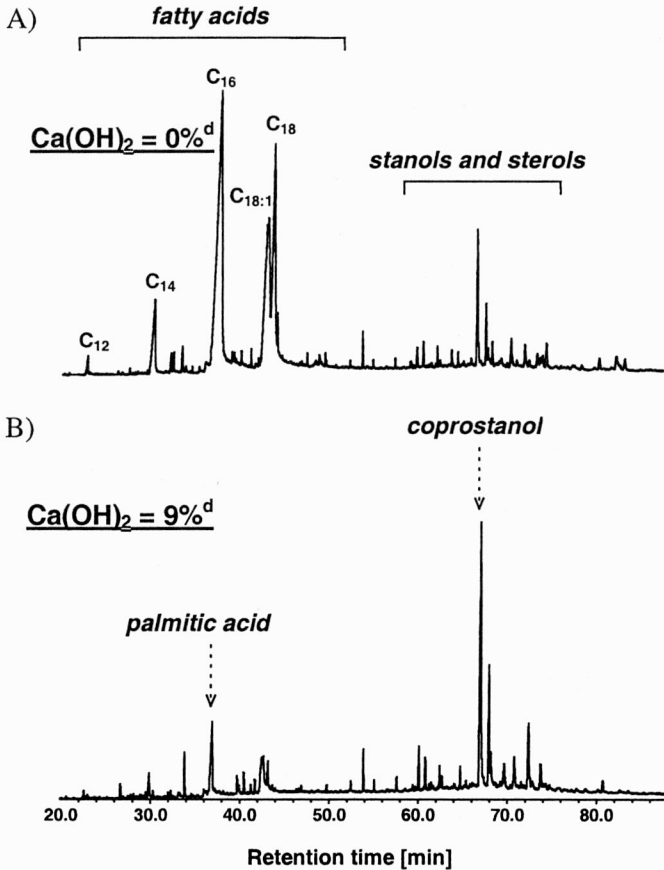


Fig. 3. The composition of lipids from the primary sludge stabilised for 35 days without calcium hydroxide (mass chromatogram – trace A) and with 9%^d of calcium hydroxide dose (mass chromatogram – trace B)

municipal sludge and solid wastes [5]. Also a total content of free fatty acids in the samples analysed decreased gradually as the $\text{Ca}(\text{OH})_2$ dose increased; however, their homological composition remained unaffected. In contrary to fatty acids, calcium hydroxide dose did not affect the content and composition of stanols and sterols present in the non-polar lipid fraction, which remained practically intact. This is illustrated by mass chromatograms A and B in figure 3, where in the former fatty acids are dominant and stanols and sterols are minor, while in the latter a relative proportion of these groups of compounds (characteristic of municipal sewage) is reverse. From the composite containing 24%^d of calcium hydroxide, fatty acids were completely removed, and stanols and sterols became the major group of compounds. The rate of removal of fatty acids from unbound lipids was faster at lower $\text{Ca}(\text{OH})_2$ dose and continued to slow down with each subsequent $\text{Ca}(\text{OH})_2$ dose added to the composite. This is exemplified by the ratio of the most prominent compounds in fatty acids and stanols, i.e. hexadecanoic acid (palmitic acid) vs. coprostanol (peaks of these compounds are shown in figure 3). Their integrated ratio falls sharply from 22 in raw sludge to the value lower than unity in composite with 9%^d of calcium hydroxide dose (broken line in figure 2). For the composites with a higher calcium hydroxide dose further decrease in this ratio is rather insignificant. The most likely explanation for the change in the palmitic acid to coprostanol ratio is exhaustion of easily removable organic acids contained in the unbound lipids upon sludge treatment with calcium hydroxide at the dose of about 9%^d. In the alkaline suspension applied, free fatty acids as well as those released hydrolytically from the polymeric matrix are converted to insoluble in water calcium alkanoates, and therefore become inaccessible to extraction with organic solvents.

The stanol-sterol profiles in the lipids (not shown) are characterised by a high predomination of coprostanol ($5\beta(\text{H})$ -cholestan-3- β -ol) as well as cholesterol (cholest-5-en-3 β -ol), cholestanol ($5\alpha(\text{H})$ -cholestan-3- β -ol), and their 24-methyl and 24-ethyl counterparts. This group of compounds is classified as sewage-specific molecular markers of anthropogenic origin [6]. The coprostanol is the product of cholesterol hydrogenation by the intestinal microflora in higher mammals and therefore was adopted as the diagnostic marker of municipal wastes and domestic effluents [7]. These compounds are known to be highly hydrophobic and are found to display a strong tendency to absorption on the sludge particulates [8]. On this basis we presume that during alkaline stabilisation of the sludge they remain associated within organic polymer. This explains their high concentration in the sludge cake obtained using also a high dose of $\text{Ca}(\text{OH})_2$ for stabilisation. The stanol and sterol stability upon alkaline treatment of sludge complements the earlier findings that these compounds are stable after sludge treatment with various other agents [9].

Apart from fatty acids, stanols and sterols, the extracted lipids contain low concentration of *n*-alkanes extending a homological range from C_{23} to C_{33} . Their homological composition is practically the same, regardless of the amount of $\text{Ca}(\text{OH})_2$

used for stabilising the sludge. The chromatographic profiles of *n*-alkanes show a strong predominance of the odd carbon-numbered homologues with the carbon preference index of 1.8 [10]. This fingerprint strongly suggests the input of *n*-alkanes from the cuticular waxes of contemporary plants [11]. However their partial input from anthropogenic petro-origin contaminants cannot be excluded [12].

4. CONCLUSIONS

Alkaline stabilisation was found to enhance the decomposition of the sludge organic fraction and thus superior to standard anaerobic and aerobic digestion. The extent of hydrolytic decomposition of sludge organic matter depends on the dose of calcium hydroxide (pH) and duration of stabilisation process. Chemical markers of the sewage sludge originate from human wastes. Fatty acids are removed from sewage free lipids as a result of their transformation to calcium alkanoates being insoluble in water and organic solvents. In contrast, hydrophobic faecal coprostanol, cholesterol and their derivatives, which were detected in all the samples examined, remained intact upon treating the sewage sludge with calcium hydroxide. A small portion of lipids is represented by *n*-alkanes, the constituents of cuticular waxes.

Also the relative abundances of the two major group of compounds, i.e. fatty acids and stanols and sterols, vary greatly upon raising of the sludge pH (the dose of alkaline stabiliser); however, their molecular composition remains practically unchanged. The product of the sludge stabilisation by calcium hydroxide has the form of particulate material characterised by ease of dewatering. During stabilisation process calcium hydroxide effectively decomposed putrescible sludge organic matter into more stable forms. The sludge-lime composite could be used as an environmentally friendly fertiliser for arable land.

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ALKALICZNA STABILIZACJA WSTĘPNYCH OSADÓW CZĘŚĆ I. ANALIZA LIPIDÓW

Przedstawiono wyniki badań stabilizacji alkalicznej osadów wstępnych pochodzących z oczyszczalni ścieków komunalnych. Stosowano zawiesinę wodorotlenku wapnia w dawkach od 0 do 0,24 kg/kg suchej masy osadu. Oceniono zmiany właściwości fizykochemicznych osadów po ich stabilizacji przez 1 dobę i przez 35 dób. Alkalizacja osadu wodorotlenkiem wapnia powoduje wydzielanie się gazowego amoniaku, który jest uwalniany wskutek hydrolizy substancji organicznej osadu. Znaczna jej część przechodzi następnie do roztworu w postaci związków małocząsteczkowych, zwiększając chemiczne zapotrzebowanie tlenu. Oceniono jakościowo-ilościowe zmiany zachodzące pod wpływem czynnika alkalizującego w składzie molekularnym frakcji niepolarnych lipidów, tj. wolnych kwasów tłuszczowych oraz stanoli i steroli. Alkalizacja osadu wodorotlenkiem wapnia prowadzi do powstawania trudno rozpuszczalnych soli wapniowych kwasów tłuszczowych, nie wpływa natomiast na zawartość stanoli i steroli.

