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# EFFECT OF ALKALIZATION PROCESS ON CHANGES IN THE CHEMICAL COMPOSITION OF SECONDARY SLUDGE

The paper addresses the problem of how the alkalization of partly dewatered (98.2% and 98.8% $H_2O$) secondary sludge with a calcium hydroxide suspension influences the chemical composition of the organic fraction (which undergoes changes induced by hydrolysis processes). The process of sludge stabilization was assessed in terms of the COD/TOC ratio and the atomic O/C ratio. As a consequence of the hydrolysis processes, the content of proteins and fats as well as other organic substances (primarily simple acids) decreased, which manifested itself as a decrease of the oxygen and nitrogen content in the sludge being alkalized, and an increase in the value of the COD/TOC ratio, which was concomitant with a decrease in the atomic O/C ratio. It was found that treatment with low calcium hydroxide doses sufficed to stabilize the sludge. The products obtained are of no environmental nuisance and can be used for agricultural applications.

## 1. INTRODUCTION

The primary objective of sludge stabilization is to eliminate the emission of objectionable odours and to reduce the number of pathogenic organisms. Sludge is commonly stabilized with biochemical, physical and chemical methods, where use is made of strong oxidizers or pH adjustment. Among the cheapest alkalizers is lime, which provides both stabilization and decontamination of sludge [1]–[4]. $OH^-$ ions are powerful toxicants to microorganisms, as can be inferred, for example, from the changes in the ionization of the protein components in amine and carboxyl groups [5]. And these changes account for the loss of enzymatic and biological activity. The chemical reactions that occur in the course of stabilization with various lime forms produce changes in the chemical composition of the sludge [6]–[8]. As yet, the problem of how the application of lime influences the chemical composition of the organic fraction in the sludge from biological treatment of municipal sewage has not been sufficiently con-

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sidered in the literature. It seemed therefore advisable and worthwhile to elucidate this problem by undertaking research onto the changes in the chemical composition of such sludge. One of the methods for assessing the changes in the chemical composition of secondary sludge upon lime alkalization is elemental analysis. The aim of this study was to demonstrate that the irreversible changes in the organic substance of the sludge can be substantiated by assessing quantitatively the content of carbon, hydrogen, nitrogen, sulphur and oxygen before and after the process of $Ca(OH)_2$ alkalization.

## 2. EXPERIMENTAL

### 2.1. SCOPE OF THE STUDY AND MATERIALS USED

The scope of the study includes experiments on partly dewatered (98.8% and 98.2% $H_2O$) raw secondary sludge from municipal sewage treatment plants of choice, situated in the south-west and the west of Poland. The size of the samples (volume and mass) was chosen so as to conform with the requirements of pilot-scale tests.

#### 2.1.1. SEWAGE SLUDGE

The physicochemical parameters of the sludge used in the experiments are specified in table 1. Sludge samples were collected at two medium-sized municipal sewage treatment plants (STP 1 and STP 2).

Table 1

Physicochemical composition of the sludge

| Parameter/unit | Source of origin | |
|---|---|---|
| | STP 1 | STP 2 |
| pH | 7.13 | 6.93 |
| Water content, % | 98.8 | 98.2 |
| Ash, % | 26.5 | 23.5 |
| Organic substance, % | 73.5 | 76.5 |
| Fats in organic substance, % | 1.96 | 5.15 |
| Proteins in organic substance, % | 35.31 | 36.44 |
| Total phosphorus, % | 0.13 | 0.28 |
| Total nitrogen, % | 6.1 | 5.99 |

#### 2.1.2. CALCIUM HYDROXIDE SUSPENSION

Use was made of analytically pure, powdered $Ca(OH)_2$, which served for the preparation of a $Ca(OH)_2$ suspension in the $Ca(OH)_2$ solution. The $Ca(OH)_2$ suspension in the saturated solution was prepared in the following way: an appropriate portion of $Ca(OH)_2$ triturated in a mortar and a defined volume of decanted supernatant from the thickened sludge used for the purpose of the study were placed in a closed vessel and shaken mechanically for approximately 3 minutes.

### 2.2. EXPERIMENTAL METHODS

The study was performed in three simultaneously conducted experimental series, involving five sludge portions each, i.e. 15 portions altogether. An approximately 60 $dm^3$ volume of sludge was prepared and thereafter poured in equal portions (3 $dm^3$) into vessels which acted as reactors. Each of the reactors was then left over a period of 1.5 to 2 hours to allow the sludge to thicken. Next, the supernatant was poured into small vessels, which contained weighed portions of powdered $Ca(OH)_2$, and shaken mechanically for about 3 minutes to enable the $Ca(OH)_2$ suspension to be formed. The suspensions prepared via the above route with different $Ca(OH)_2$ doses were placed in appropriate reactors, which contained 3 $dm^3$ sludge portions. In order to homogenize the components of the sludge, the content of the reactor was stirred mechanically for 5 minutes (30 rev $min^{-1}$). Each sample was then matured for the duration of the chemical reaction, which was set at 24 h, 35 days and 88 days. After the defined time of maturation had passed, the sludge samples were analysed. The extended time of the chemical reaction (35 days and 88 days) was applied in order to determine how the time of the $Ca(OH)_2$ contact with the sludge influences the efficiency of stabilization.

The physicochemical composition of the sludge was also determined for the samples with no $Ca(OH)_2$ added (blank determination). Such samples are treated as reference that enables comparisons of the sludge compositions obtained with particular doses of $Ca(OH)_2$ suspension. Each sludge sample was analyzed immediately after the time of its stabilization had passed. For the purpose of analysis, the sludge samples were filtered by gravitation through an ash-free filter paper. Upon filtration, separate physicochemical analysis was performed for the sludge cake and for the filtrate. The sludge cake was analyzed for water content, calcium, mineral and organic matter, as well as oils and fats in ether extract; elemental analysis included nitrogen, carbon, hydrogen and sulphur.

### 2.3. METHODS OF ANALYSES

Analyses were performed using conventional measuring methods. The physicochemical properties of the sludge samples, i.e. water content, volatile substances, pH, fats, oils and calcium, were determined according to relevant Polish standards [9].

Water content was established from the difference in mass between non-dewatered samples and samples dried at 105 °C until a constant weight was achieved. The sludge pH was measured three times, and the last of the readouts was assumed as the valid one. Organic substances were determined (upon water content analysis) by calcining the sludge samples at 600 °C (dark heat) and defining the difference between dry residue (at 105 °C) and ash (at 600 °C). Oils and fats were determined quantitatively by extraction in the Soxhlet apparatus with petroleum benzine for 4 hours. The elemental composition of the sludge samples (C, H, N and S) was established according to the requirements for the quantitative analysis of organic compounds, as specified by BOBRAŃSKI [10]. The elemental analysis of organic carbon, hydrogen and nitrogen was conducted with dried samples (105 °C) and ground samples (in a mortar for analytical powder) using a 2400 CHN Perkin-Elmer analyzer. Elemental sulphur was determined by combustion of the sludge sample in a flask filled with oxygen, according to the Schöniger method [10]; the quantity of the sulphur oxides formed was determined spectrophotometrically. Oxygen content was computed from the difference to 100%, using the formula: 100–(C + H + N + S) = $O_2$ (%).

## 3. ASSESSING THE PHYSICOCHEMICAL COMPOSITION OF THE SLUDGE FROM THE VALUES OF THE COD/TOC RATIO AND THE ATOMIC O/C RATIO

The chemical changes that occur in the secondary sludge examined are reflected in the values of the COD/TOC ratio and the O/C atomic ratio. The progress of the stabilization process induced by the hydrolysis of proteins, fats and carbohydrates is described by the changes in the value of the COD/TOC ratio, which occur in response to the increase in the $Ca(OH)_2$ dose and to the extended duration of the alkalization process. Of the latter two, the $Ca(OH)_2$ dose has a decisive contribution to the change in the COD/TOC ratio (tables 2 and 3).

The value of the COD/TOC ratio for raw sludge ranges from 2.7 to approximately 2.9, and approaches 3.1 upon alkalization and seasoning for 35 days. Those changes are associated with the decrease of the oxygen content in the chemical structure of the sludge components, which is described by the molecular formulae (tables 2 and 3). For instance, in the raw secondary sludge (water content $w$ = 98.8%) of the molecular formula $C_{10}H_{17}O_{5.4}N_{1.7}S_{0.04}$, oxygen content accounted for 35% of the organic substance mass; in the sludge which was obtained after 35-day stabilization with a $Ca(OH)_2$ dose of 8.36 kg per one cubic meter and had the molecular formula $C_{10}H_{18}O_{4.0}N_{1.1}S_{0.02}$, oxygen content accounted for 29% of the organic substance mass (table 2). Those changes are reflected in the value of the atomic O/C ratio, which amounted to 0.54 for raw sludge and totalled 0.40 after alkalization with a 8.36-kg dose of $Ca(OH)_2$ per one cubic meter for 35 days (table 2). The changes were parallelled by a decrease of more than 25% in the proportion of nitrogen, a 40% decrease of sulphur in the organic substance mass and a 14% increase in the proportion of

Table 2

Molecular formulae, COD/TOC ratios, atomic O/C ratios and weight % of chemical elements in the organic substance for partly dewatered secondary sludge (98.8% $H_2O$) related to calcium hydroxide dose and time of alkaline stabilization

| Reaction time, d | Dose of $Ca(OH)_2$ | | pH | Molecular formulae | $\frac{COD}{TOC}$ | $\frac{O}{C}$ | Weight percent of elements in organic substance | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | kg/m³ of sludge | kg/kg d.m. of sludge | | | | | C | H | O | N | S |
| 0 | 0 | 0 | 7.13 | $C_{10}H_{17}O_{5.4}N_{1.7}S_{0.04}$ | 2.70 | 0.54 | 48 | 7 | 35 | 9.7 | 0.5 |
| 1 | 1.39 | 0.11 | 8.48 | $C_{10}H_{17}O_{5.8}N_{1.7}S_{0.03}$ | 2.72 | 0.58 | 47 | 7 | 36 | 9.3 | 0.3 |
| 1 | 2.78 | 0.23 | 9.23 | $C_{10}H_{17}O_{5.5}N_{1.6}S_{0.02}$ | 2.77 | 0.55 | 48 | 7 | 35 | 9.1 | 0.3 |
| 1 | 4.18 | 0.34 | 10.30 | $C_{10}H_{18}O_{5.4}N_{1.5}S_{0.02}$ | 2.91 | 0.54 | 49 | 7 | 35 | 8.6 | 0.2 |
| 1 | 6.27 | 0.51 | 11.96 | $C_{10}H_{19}O_{4.9}N_{1.4}S_{0.02}$ | 3.03 | 0.49 | 50 | 8 | 33 | 8.1 | 0.2 |
| 1 | 8.36 | 0.68 | 12.53 | $C_{10}H_{19}O_{4.7}N_{1.3}S_{0.02}$ | 3.08 | 0.47 | 52 | 8 | 32 | 7.7 | 0.2 |
| 35 | 1.39 | 0.11 | 8.12 | $C_{10}H_{17}O_{4.4}N_{1.5}S_{0.04}$ | 2.95 | 0.44 | 52 | 7 | 31 | 9.1 | 0.5 |
| 35 | 2.78 | 0.23 | 8.94 | $C_{10}H_{16}O_{4.3}N_{1.3}S_{0.03}$ | 2.93 | 0.43 | 53 | 7 | 30 | 8.3 | 0.5 |
| 35 | 4.18 | 0.34 | 10.08 | $C_{10}H_{17}O_{4.3}N_{1.3}S_{0.02}$ | 2.97 | 0.43 | 54 | 7 | 30 | 8.1 | 0.3 |
| 35 | 6.27 | 0.51 | 11.64 | $C_{10}H_{17}O_{4.1}N_{1.2}S_{0.02}$ | 3.01 | 0.41 | 54 | 8 | 30 | 7.9 | 0.3 |
| 35 | 8.36 | 0.68 | 12.29 | $C_{10}H_{18}O_{4.0}N_{1.1}S_{0.02}$ | 3.08 | 0.40 | 55 | 8 | 29 | 7.1 | 0.3 |
| 88 | 1.39 | 0.11 | 8.11 | $C_{10}H_{17}O_{3.8}N_{1.3}S_{0.05}$ | 3.11 | 0.38 | 55 | 8 | 28 | 8.6 | 0.7 |
| 88 | 2.78 | 0.23 | 8.59 | $C_{10}H_{17}O_{3.6}N_{1.2}S_{0.04}$ | 3.12 | 0.36 | 56 | 8 | 27 | 8.1 | 0.6 |
| 88 | 4.18 | 0.34 | 9.73 | $C_{10}H_{17}O_{3.3}N_{1.1}S_{0.03}$ | 3.14 | 0.33 | 58 | 8 | 26 | 7.5 | 0.5 |
| 88 | 6.27 | 0.51 | 11.42 | $C_{10}H_{17}O_{3.2}N_{1.1}S_{0.02}$ | 3.16 | 0.32 | 59 | 9 | 25 | 7.2 | 0.4 |
| 88 | 8.36 | 0.68 | 12.03 | $C_{10}H_{17}O_{3.1}N_{1}S_{0.02}$ | 3.22 | 0.31 | 59 | 9 | 25 | 6.9 | 0.3 |

hydrogen in the stabilized sludge. The extension of stabilization time to another 8 weeks further improved the parameters of the sludge being stabilized; the value of the COD/TOC ratio increased further by 5% and 2%, for raw sludge and alkalized sludge, respectively. There was also observed a further decrease in oxygen, by 14%, and nitrogen, by 3%, as well as a simultaneous increase in hydrogen, by 12%, and carbon, by 7% (table 2). Similar changes were found to occur in the secondary sludge with a 98.2% $H_2O$ (table 3).

The decrease in the proportion of oxygen in the chemical structure of the sludge is associated with the decrease in the content of organic acids and amino acids in response to the hydrolysis of fats and proteins, with the decrease in the content of glycerol due to the hydrolysis of fats, as well as with the hydrolysis and solubilization of carbohydrates [7]. These changes can be described by the changes in the values of the atomic O/C ratio, which depends on the values of the COD/TOC ratio [11]. That is

Table 3

Molecular formulae, COD/TOC ratios, atomic O/C ratios and weight % of chemical elements in the organic substance for partly dewatered secondary sludge (98.2% $H_2O$) related to calcium hydroxide dose and time of alkaline stabilization

| Reaction time, d | Dose of $Ca(OH)_2$ kg/m$^3$ of sludge | Dose of $Ca(OH)_2$ kg/kg d.m. of sludge | pH | Molecular formulae | $\frac{COD}{TOC}$ | $\frac{O}{C}$ | C | H | O | N | S |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Weight percent of elements in organic substance | | | | |
| 0 | 0 | 0 | 6.31 | $C_{10}H_{17}O_{4.8}N_{1.4}S_{0.07}$ | 2.87 | 0.48 | 51 | 7 | 33 | 8.4 | 1 |
| 1 | 1.39 | 0.08 | 7.56 | $C_{10}H_{16}O_{4.8}N_{1.4}S_{0.06}$ | 2.85 | 0.48 | 51 | 7 | 33 | 8.3 | 0.8 |
| 1 | 2.78 | 0.16 | 8.90 | $C_{10}H_{16}O_{4.8}N_{1.3}S_{0.04}$ | 2.86 | 0.48 | 51 | 7 | 33 | 7.7 | 0.8 |
| 1 | 4.18 | 0.23 | 11.26 | $C_{10}H_{16}O_{4.7}N_{1.2}S_{0.05}$ | 2.88 | 0.47 | 52 | 7 | 33 | 7.4 | 0.7 |
| 1 | 6.27 | 0.35 | 12.03 | $C_{10}H_{16}O_{4.5}N_{1.2}S_{0.04}$ | 2.88 | 0.45 | 54 | 7 | 31 | 7.5 | 0.6 |
| 1 | 8.36 | 0.47 | 12.41 | $C_{10}H_{15}O_{3.7}N_{1.1}S_{0.04}$ | 2.96 | 0.37 | 57 | 7 | 28 | 7.3 | 0.6 |
| 35 | 1.39 | 0.08 | 7.39 | $C_{10}H_{17}O_{4.6}N_{1.3}S_{0.08}$ | 2.91 | 0.46 | 52 | 7 | 32 | 7.8 | 1.1 |
| 35 | 2.78 | 0.16 | 8.19 | $C_{10}H_{16}O_{4.7}N_{1.2}S_{0.07}$ | 2.90 | 0.47 | 52 | 7 | 33 | 7.1 | 1 |
| 35 | 4.18 | 0.23 | 10.96 | $C_{10}H_{16}O_{4.5}N_{1.1}S_{0.07}$ | 2.95 | 0.45 | 53 | 7 | 32 | 6.7 | 1 |
| 35 | 6.27 | 0.35 | 11.62 | $C_{10}H_{16}O_{4.0}N_{1.0}S_{0.06}$ | 3.10 | 0.40 | 55 | 7 | 30 | 6.5 | 0.9 |
| 35 | 8.36 | 0.47 | 11.87 | $C_{10}H_{16}O_{3.2}N_{0.9}S_{0.05}$ | 3.09 | 0.32 | 58 | 8 | 27 | 6.3 | 0.8 |
| 88 | 1.39 | 0.08 | 7.25 | $C_{10}H_{17}O_{4.8}N_{1.2}S_{0.10}$ | 2.92 | 0.48 | 52 | 7 | 33 | 7 | 1.4 |
| 88 | 2.78 | 0.16 | 7.98 | $C_{10}H_{16}O_{4.7}N_{1.1}S_{0.09}$ | 2.93 | 0.47 | 52 | 7 | 33 | 6.7 | 1.3 |
| 88 | 4.18 | 0.23 | 10.56 | $C_{10}H_{16}O_{4.4}N_{1.0}S_{0.09}$ | 2.97 | 0.44 | 53 | 7 | 31 | 6.5 | 1.3 |
| 88 | 6.27 | 0.35 | 11.07 | $C_{10}H_{16}O_{3.9}N_{0.9}S_{0.09}$ | 3.04 | 0.39 | 56 | 7 | 29 | 6.2 | 1.3 |
| 88 | 8.36 | 0.47 | 11.38 | $C_{10}H_{16}O_{3.2}N_{0.8}S_{0.07}$ | 3.14 | 0.32 | 60 | 8 | 25 | 5.9 | 1.2 |

Table 4

Molecular formulae, atomic O/C ratios and COD/TOC ratios of anaerobically digested sludge [7]

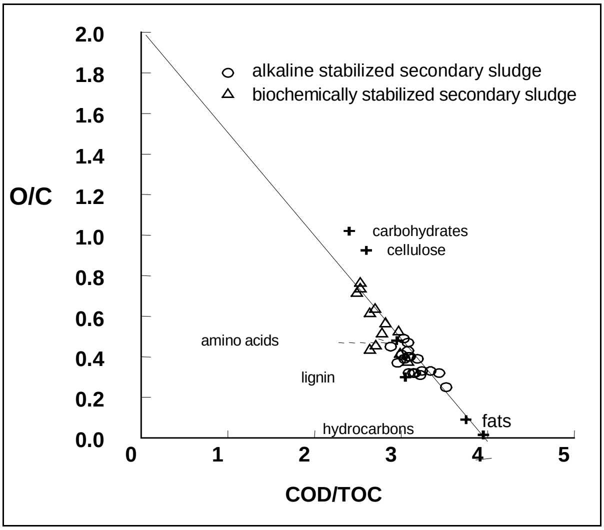
| Type of anaerobically digested sludge | Molecular formulae | $\frac{COD}{TOC}$ | $\frac{O}{C}$ |
|---|---|---|---|
| Secondary sludge | $C_{10}H_{15}O_{5.2}N_{1.1}$ | 2.78 | 0.52 |
| Secondary sludge | $C_{10}H_{16}O_{6.4}N_{1.1}$ | 2.70 | 0.64 |
| Secondary sludge | $C_{10}H_{18}O_{5.3}N_{0.9}$ | 2.97 | 0.53 |
| Secondary sludge | $C_{10}H_{15}O_{4.2}N_{0.7}$ | 2.99 | 0.42 |
| Secondary sludge | $C_{10}H_{15}O_{4.6}N_{1.6}$ | 2.71 | 0.46 |
| Secondary sludge | $C_{10}H_{18}O_{4.4}N_{0.3}$ | 2.64 | 0.44 |

why it was possible to take into account (and include into the diagram illustrating the relationship between O/C and COD/TOC) the values calculated for secondary sludge stabilized in anaerobic and aerobic conditions (tables 4 and 5) and for secondary sludge stabilized in alkaline environment (tables 2 and 3). The relationship between O/C and COD/TOC is depicted in the figure. As a result of those transformations, the sludge tested is below the sludge stabilized in aerobic or anaerobic processes. This is an indication that the chemical changes induced by carbon hydroxide alkalization are more profound than those induced, for example, by methane fermentation or aerobic stabilization processes. This finding is substantiated by the considerably greater reduction in the proportion of oxygen groups in the chemical structure of the sludge stabilized via alkalization as compared to the sludge stabilized using biochemical methods (aerobic or anaerobic).

Table 5

Molecular formulae, atomic O/C ratios and COD/TOC ratios of aerobically digested sludge [7]

| Type of aerobically digested sludge | Molecular formulae | $\frac{COD}{TOC}$ | $\frac{O}{C}$ |
|---|---|---|---|
| Secondary sludge | $C_{10}H_{17}O_{7.2}N_{1.9}$ | 2.49 | 0.72 |
| Secondary sludge | $C_{10}H_{18}O_{5.7}N_{1.3}$ | 2.82 | 0.57 |
| Secondary sludge | $C_{10}H_{18}O_{7.8}N_{1.4}$ | 2.53 | 0.77 |
| Secondary sludge | $C_{10}H_{22}O_{6.2}N_{3.2}$ | 2.64 | 0.62 |
| Secondary sludge | $C_{10}H_{17}O_{7.4}N_{1.3}$ | 2.53 | 0.74 |




Relationship between the atomic O/C ratio and the COD/TOC ratio
for digested secondary sludge and secondary sludge stabilized by alkalization

## 4. CONCLUSIONS

1. The chemical changes that occur in secondary sludge during alkaline stabilization are shown by the change in the values of the atomic O/C ratio and the COD/TOC ratio. The extent of those changes increases with the $Ca(OH)_2$ dose applied and with the extension of the stabilization process.

2. The change in the value of the atomic O/C ratio is concomitant with a decrease in the proportions of nitrogen and sulphur in the organic substance mass of the stabilized secondary sludge.

3. The decrease in the proportion of oxygen in the chemical structure of the sludge is attributable to the decrease in the content of organic acids and amino acids in response to the hydrolysis of fats and proteins.

4. Alkalization of secondary sludge with carbon hydroxide produces more extensive chemical changes than those produced by methane fermentation or aerobic stabilization.

5. The chemical composition of secondary sludge stabilized via an alkaline method is similar to those of fatty acids or carbohydrates. When secondary sludge is stabilized by aerobic or anaerobic method, its chemical composition resembles that of a mixture of cellulose, carbohydrates and proteins.

6. Sludge stabilization by an alkaline method is recommendable for small- and medium-sized municipal wastewater treatment plants, where the application of biochemical processes (aerobic or anaerobic stabilization) is not cost-effective.

7. Low calcium hydroxide doses suffice to stabilize the sludge.

8. The product obtained is of no environmental nuisance and can be used for agricultural applications.

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