*Original Research*

# Influence of the Treatment Process on Nitrogen Content in Humic Acids Extracted from Sewage Sludge

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**Abstract**

Humic-like substances (HA) were extracted from sludge from three sewage treatment plants with different treatment technologies. Investigations of the extracted humic-like substances (HA) were carried out by means of elementary analysis and spectroscopic methods.

Results of elementary analysis show that the percentage content of nitrogen is different for HA extracted from sludge derived from the subsequent treatment stages. The influence of the treatment process on nitrogen content also was observed. The percentage content of nitrogen was of the range from 5.05% to 8.99%. The highest value of nitrogen for HA extracted from sludge was obtained from the nitrification and denitrification chamber.

The spectroscopic methods confirmed the presence of nitrogen functional groups.

**Keywords:** humification process; humic-like substance; nitrogen; C/N ratio; sludge; sewage treatment plants

## Introduction

Elemental analysis is one of the most commonly used tools for the characterization of humic acids and provides information on the distribution of major elements, mainly: C, H, N, O and S. However, the atomic ratio: C/N, H/C, O/C can also be useful in identifying types of humic acids and monitoring their structural changes [1].

The C/N atomic ratio is used as an index of organic material maturity (compost, soil, sewage sludge), the H/C atomic ratio is a measure of aromatization and condensation of humic-like substances (HA) during the humification process and the O/C atomic ratio may reflect the increase or decrease of oxygen functional groups [1, 2].

The percentage content of nitrogen bound by HA in sewage sludge and in compost is one of the main criterion of usefulness of sewage sludge compost for agricultural purposes [3]. For humic acids extracted from soil C/N atomic ratio, corresponding to the degree of the humification process and the maturity of the natural organic material, ranges from 10.1 to 30.0 while for HA extracted from sewage sludge it is much lower and amounts to 7.6-11.4 [3-7]. The C/N atomic ratio is one of many parameters that allow estimating humic-like substance maturity. The evaluate HA maturity a lot of spectroscopic (EPR, NMR, IR and UV/VIS) and analytical method is also used.

The aim of this work was to observe the influence of the individual processes of the sewage treatment process on nitrogen content in humic-like substances extracted from sewage sludge collected from three treatment plants with different technological processes.

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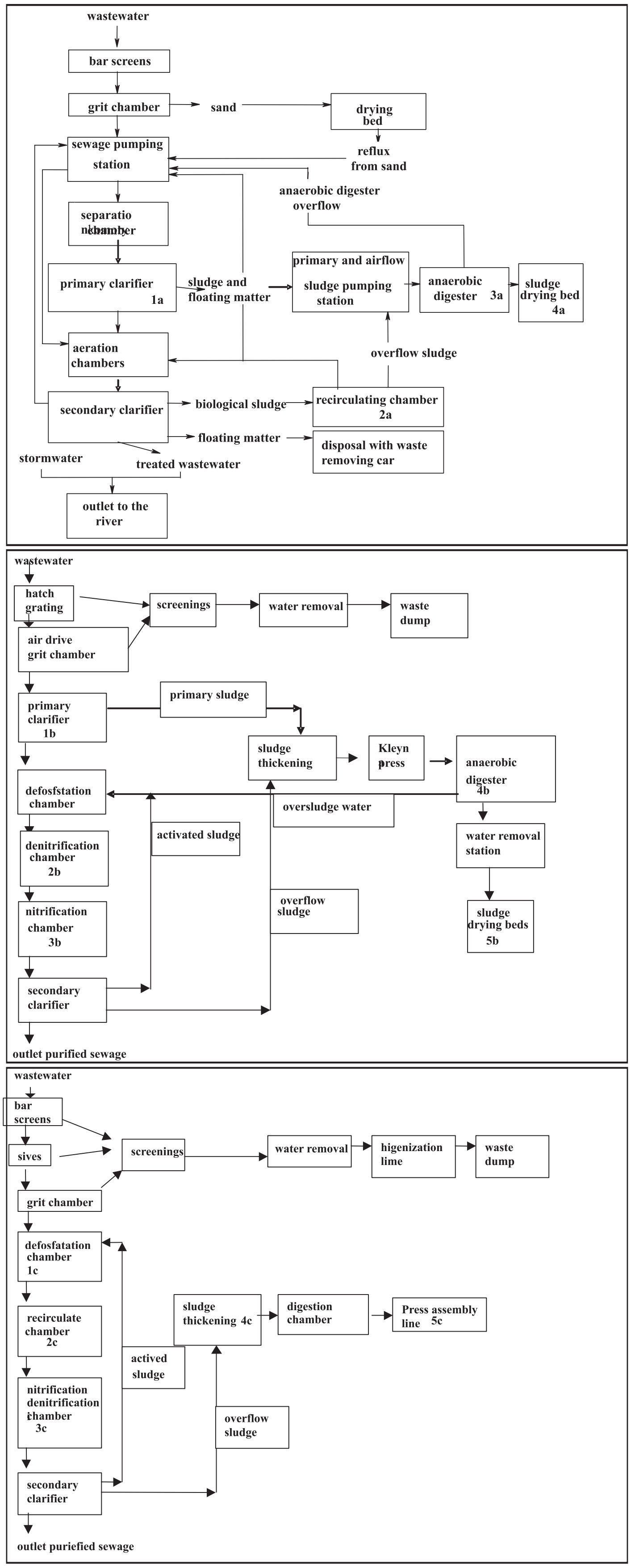


1a

2b

3c

Fig. 1. Block diagrams of the treatment plants in Sosnowiec-Zagórze P-I (Fig 1a), Jastrzębie Zdrój P-II (Fig 1b) and Dąbrowa Górnicza P-III (Fig 1c) with marked points of sampling.

## Experimental Procedures

Sludge samples for studies were collected according to Polish standards (in broad range according to ISO/5667/3 standard), from three bio-mechanical sewage treatment plants in Sosnowiec-Zagórze (P-I), Jastrzębie Zdrój (P-II) and Dąbrowa Górnicza (P-III) [8]. From the sewage sludge treatment in Sosnowiec-Zagórze samples were taken from: the primary clarifier (1a), the recirculation chamber (2a), the anaerobic digester (3a) and the drying bed (4a) (Fig.1a). From the sewage sludge treatment in Jastrzębie Zdrój samples were taken from: the primary clarifier (1b), the nitrification chamber (2b), the denitrification chamber (3b), the anaerobic digester (4b) and the drying beds (5b) (Fig.1b). From the sewage sludge treatment in Dąbrowa Górnicza samples were taken from the dephosphatation chamber (1c), the recirculation chamber (2c), the nitrification and denitrification chamber (3c), after sludge the densifier (4c) and after the press (5c) (Fig.1c).

HA were also extracted from the sampled sludge. For this purpose 40 g of air-dried sludge was first shaken for 24 h with 200 $cm^3$ of 0.5 M NaOH and then centrifuged. Residual sludge after centrifugation was again flooded with base solution (200 $cm^3$) and again shaken. Solutions from these two extractions were then combined. Raw HA was precipitated from the solution of humic and fulvic acids by acidifying with a (10%) solution of hydrochloric acid to pH=1. Residual solution after centrifugation contained fulvic acids. To obtain pure HA, the raw humic-like substance was dissolved in 200 $cm^3$ of 0.5 M NaOH solution, centrifuged, and filtered to remove impurities. Humic-like substances were then reprecipitated with hydrochloric acid and washed several times with water. Pure HA in the form of powder was obtained by lyophilization [2].

To determine the elementary composition changes in the extracted HA at each stage of purification, the percentage content of carbon and nitrogen was determined by means of Series II CHNO/S 2400 Perkin Elmer elementary analyzer. According to the results of elemental analysis the C/N atomic ratio of HA extracted at each stage of purification was calculated to monitor the ripening of sewage sludge.

The identification of functional groups was done by means of infrared (IR) and $^1$H NMR spectroscopy. Infrared spectra of HA samples were recorded with a Perkin Elmer FTIR Spectrum One spectrometer, from KBr pellets (1 mg sample and 100g KBr).

The $^1$H NMR spectra were collected on 5 mg of humic acid dissolved in 0.3 M NaOD in $D_2O$. All measurements were conducted on Bruker Avance 400 Ultra Shield spectrometer at room temperature. The parameters of the $^1$H NMR measurements were as follows: relaxation delay D1 = 5 s; acquisition time AQ = 1.4 s; line broadening LB = 10 Hz; receiver gain RG = 1000; time domain TD = 64 K.

## Discussion of Results

The obtained results of the percentage content of nitrogen in HA extracted from sewage sludge sampled from subsequent treatment stages from three plants are high and they range from 5.01% to 8.99% (Table 1) while the percentage content of nitrogen in HA extracted from soil or peat usually do not exceed 4% [2, 5, 9]. One can conclude that the HA extracted from sewage sludge are rich in nitrogen. However, the percentage content of nitrogen in humic-like substances extracted from compost and sewage sludge were higher and ranged from 5.10% to 7.90% [3, 4, 10].

The obtained results of the percentage content of nitrogen in HA extracted from sewage sludge after the nitrification and denitrification chamber from P-III (3b-8.99%) is significantly higher than the percentage content of nitrogen in humic acids extracted from soil, peat, compost and sewage sludge determined previously [2-5, 9, 10].

The character of changes of the percentage nitrogen content in humic-like substances extracted from sewage

Table 1. Elementary composition and H/C, O/C and C/N atomic ratio values of humic-like substances (HA) extracted from sludge collected from treatment plants in Sosnowiec Zagórze (PI), Jastrzębie Zdrój (PII) and Dąbrowa Górnicza (PIII). The samples are numbered according to the diagram in Fig.1.

| Sample | %C | %N | C/N | Sample | %C | %N | C/N | Sample | %C | %N | C/N |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1a | 57.40 ±0.07 | 5.26 ±0.16 | 12.7 ±0.64 | 1b | 50.45 ±0.72 | 5.21 ±0.12 | 11.35 ±0.57 | 1c | 40.80 ±0.96 | 7.72 ±0.54 | 6.18 ±0.31 |
| 2a | 54.56 ±0.72 | 5.05 ±0.02 | 7.47 ±0.37 | 2b | 42.81 ±0.38 | 6.39 ±0.02 | 7.76 ±0.39 | 2c | 41.27 ±0.71 | 6.54 ±0.15 | 7.30 ±0.37 |
| 3a | 49.30 ±0.33 | 6.57 ±0.32 | 8.69 ±0.43 | 3b | 41.10 ±0.05 | 6.21 ±0.025 | 7.80 ±0.39 | 3c | 39.09 ±0.9 | 8.99 ±0.14 | 4.30 ±0.21 |
| 4a | 47.65 ±0.15 | 5.32 ±0.02 | 10.2 ±0.51 | 4b | 40.10 ±0.87 | 5.69 ±0.33 | 8.14 ±0.41 | 4c | 41.08 ±0.89 | 7.08 ±0.32 | 6.60 ±0.33 |
| | | | | 5b | 39.54 ±0.16 | 5.01 ±0.02 | 9.14 ±0.46 | 5c | 41.01 ±0.65 | 6.62 ±0.37 | 7.20 ±0.36 |

± SD

sludge collected from subsequent stages of treatment from P-I, P-II and P-III varies for each plant. It is probably caused by different unit processes and differences in the technological treatment process used in these plants. However, the influence of the nitrification and denitrification processes seem to be crucial for nitrogen content (Table 1).

The percentage content of nitrogen in humic-like substances extracted from sewage sludge after leaving the primary clarifier (1a and 1b) from P-I and P-II are comparable. However, the percentage content of nitrogen is much higher in HA extracted from the sewage sludge after the dephosphatation chamber (1c) in treatment plant P-III. Hence it can be assumed that the dephosphatation process is responsible for the increase of percentage content of nitrogen. Yet the essential changes of nitrogen content in humic acid extracted from sewage sludge take place after the nitrification and denitrification processes. Both these processes are carried out in P-II and P-III. However, they are realized in a different way. The nitrification and denitrification processes in P-II are carried out in two separate chambers, while in P-III these processes are realized in one chamber whereas the sewage sludge is treated alternately i.e. nitrification is followed by denitrification. Probably this technological difference results in the varied percentage content of nitrogen in humic acid extracted from sewage sludge from plants P-II and P-III after these processes (2a,3a,3b).

The humic-like substances extracted from sewage sludge after the nitrification and denitrification processes are enriched in nitrogen both in treatment plant P-II and in P-III. However, in plant P-III, where nitrification and denitrification processes are carried out separately, nitrogen concentration is lower.

In the humic-like substances extracted from sewage sludge from P-II the nitrogen content increases after the denitrification process but after nitrification a slight decrease of nitrogen content is observed. The nitrification and denitrification processes carried out in one chamber (P-III) enrichment the HA in nitrogen much more effectively.

It can be assumed that if these processes are carried out separately nitrogen escapes into the atmosphere, which makes nitrogen concentration enrichment of HA in sewage sludge difficult.

After the subsequent stages of the treatment process the nitrogen content in humic-like substances extracted from sewage sludge decreases to 27% and 22% in P-III and P-II, respectively. However, humic-like substances extracted from sewage sludge from P-III after treatment process still contain the highest nitrogen concentration.

Due to the absence of the nitrification and denitrification process in the sewage sludge treatment in P-I the change of the percentage of nitrogen content differs significantly in comparison with plants P-II and P-III. In humic-like substances extracted from sewage sludge from treatment plant P-I the increase of nitrogen content is observed after leaving the digestion chamber where in the case of P-II and P-III after the fermentation processes a decrease of nitrogen content takes place.

This may be due to the fact that in the case of P-I the fermentation process is also accompanied by the process of nitrification and denitrification of the sludge not conducted before. Since the fermentation is carried out in anaerobic conditions denitrification may dominate. Whereas the decrease of the nitrogen content after the anaerobic digester process in the case of treatment plants P-II and P-III may be associated with the ripening of the sludge and particularly with its aromatization.

On the other hand it is interesting to compare C/N atomic ratio values determined on the basis of elementary analysis for humic-like substances extracted from sewage sludge collected from the studied plants P-I, P-II and P-III. The stabilization of C/N atomic ratio was not observed in each plant. However, the lowest value of C/N atomic ratio was obtained for humic acid extracted from the sewage sludge from plant P-III, both at the beginning and at the end of the treatment process. This is the result of the highest nitrogen content in the humic-like substances.

The presence of nitrogen functional groups in the humic-like substances structure was confirmed by IR and NMR spectroscopic methods [11, 12]. The IR example spectra revealed an absorption band characteristic for amine functional groups ($\nu_d$=1540 cm$^{-1}$) (Fig.2). Moreover, on $^1$H NMR example spectra the signals in the range 3.6-6.5 ppm originating from protons bounded to N or O atoms are observed (Fig.3, Table 2) [11, 12]. The intensity of signals in the chemical shift range from 4.3-3.2 ppm increases during the treatment process. The C/N atomic ratio, the intensity increase of signals originate from protons bounded to N or O atoms during the treatment process and the presence of absorption band characteristics for amine functional groups ($\nu_d$=1540 cm$^{-1}$) to markedly confirm enrich of humic-like substances in nitrogen functional groups and point to the

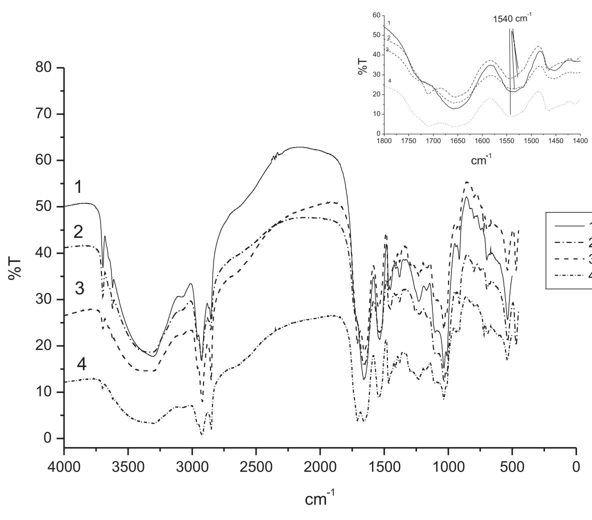


Fig. 2. Intensities of $\nu_d$=1540 cm$^{-1}$ frequency on IR spectra for humic-like substances extracted at each stage of sewage treatment plant in Sosnowiec- Zagórze P-I.

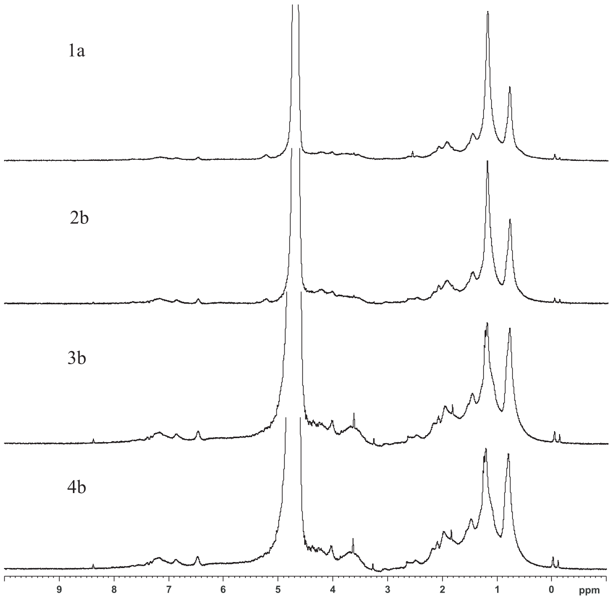


Fig. 3. [1]H NMR spectra of humic-like substances extracted from sludge sampled from respective places of the treatment plant in Sosnowiec-Zagórze P-I.

Table 2. Percentage participation of hydrogen aromatic, aliphatic and functional group atoms calculated from [1]H NMR spectra of humic-like substances extracted from sewage sludge samples taken at various stages of sewage treatment at a plant in Sosnowiec-Zagórze P-I.

| Sample | $H_{Ar}$ [%] | $H_{R\text{-}O}$ [%] | $H_{Ali}$ [%] |
|---|---|---|---|
| 1a | 1.90 ± 0.26 | 13.63 ± 0.53 | 84.50± 0.02 |
| 2a | 2.91±0.14 | 14.40 ± 0.08 | 82.82 ± 0.07 |
| 3a | 5.67± 0.19 | 16.51 ± 0.60 | 77.71 ± 0.53 |
| 4a | 5.84 ± 0.07 | 16.92 ± 0.12 | 77.35±0.46 |

±SD

influence of treatment process on nitrogen content changes in HA extracted from sewage sludge.

## Conclusions

The obtained results show that percentage content of nitrogen in humic-like substances extracted from sewage sludge is relatively high and depends on the treatment technology applied in the studied plants. It was observed that unit processes, e.g. nitrification, denitrification, fermentation and dephosphatation, influence nitrogen concentration. It was found that nitrification and denitrification processes carried out in one chamber in nitrogen enrich the humic-like substances more effectively than in the case of conducting these processes in two separate chambers. The presence of nitrogen groups in humic acid has been confirmed by spectroscopic method. The changes of nitrogen content during sewage sludge treatment were observed.

The C/N atomic ratio, the intensity increase of signals originate from protons bounded to N or O atoms during the treatment process and the presence of absorption band characteristics for amine functional grups (($\nu_d$=1540 cm$^{-1}$) confirm transformation of nitrogen in humic acid extracted from sewage sludge.

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