

# Efficiency of Non-Ionic Surfactant Removal in Biological Sewage Treatment Plants

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## Abstract

The removal of non-ionic surfactants (NS), as well as a long-chained ethoxylates, short-chained NS and poly(ethylene glycols)(PEG), was investigated in two sewage treatment plants (STP) of the activated sludge type and one trickling filter type. The indirect tensammetric method (ITM), and the ITM combined with the Bismuth Active Substances (BiAS) separation scheme (BiAS-ITT) were used for the determination of NS and their metabolites. On average, 85% reduction of total NS was determined in the activated sludge type STP and 53% reduction in the case of the trickling filter type STP. Significant concentrations of NS metabolites (short-chained NS and PEG) were determined in raw sewage, which indicate that NS biodegradation had already started in the sewer system. Both tensammetric methods prove to be a useful tool in monitoring NS and their metabolites in STP.

**Keywords:** sewage treatment plant, non-ionic surfactants, ethoxylates, poly(ethylene glycols)

## Introduction

Non-ionic surfactants (NS) are a major source of synthetic organic carbon directed into the aquatic environment. NS are commonly used in detergent formulations and are finally directed in their entirety into the sewer. Efficiency of NS removal in sewage treatment plants (STP) is the major factor in the elimination of these substances from sewage. Unfortunately, data concerning NS removal in STP are fragmentary and scanty. However, a relatively large number of papers are devoted to the fate and determination of alkylphenol ethoxylates (APE) and their derivatives in effluents of STP and in surface water [1-6]. This is due to the fact that APE are not completely biodegraded, and alkylphenol and short chain APE have been recognized as endocrine disrupters. Generally, the determination of APE and their metabolites was limited to the effluents of STP. The APE concentration varied widely.

The highest APE concentrations reported in several papers were of the order of 0.35 mg l<sup>-1</sup> [4]. Only several papers are devoted to the fate of alcohol ethoxylates (AE) in STP, despite the fact that currently AE are the major group of NS [7]. A significant contribution to this question is the programme of monitoring seven Dutch STPs [8]. Sixty-eight individual AEs having alkyl chains from 12 to 15 carbon atoms were monitored. AE concentrations in the influents varied from 1.6 to 4.7 ppm, while in the effluents the results were within the range of between 2.2 and 13 ppb. The efficiency of AE removal varied between 99.6 and 99.9%. It is worth mentioning that such high removal efficiency is higher than that reported in the model biodegradation testing, where only 96.8 ± 0.5% primary biodegradation was determined [9]. However, the data for monitoring Dutch STP shows good agreement with the mathematical model [10, 11]. The efficiency of removal of other significant NS groups, such as amine ethoxylates, polyol ethoxylates, and oxyethylene-oxypropylene block copolymers, was not investigated due to the lack of ana-

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lytical methods. Thus, the available data are incomplete to build a coherent picture of NS biodegradation in STP.

The state-of-art of NS analysis is the main reason for the lack of a general picture of NS biodegradation in STP. A recent tendency in this area is the development of methods oriented to the determination of a large number of individual substances. A good example is the determination of AE having alkyl chains from 12 to 15 carbon atoms. Sixty eight individual AE were determined using the LC-MS technique with thermospray ionization, after suitable isolation of AE from the water matrix on a C8 spe cartridge [12]. The HPLC determination of AE after their derivatization with phenyl isocyanate and UV detection represents a similar approach [10]. However, the NS mixture in surface water may contain approximately 1,500 individual substances [2]. Therefore, methods oriented to the determination of total NS concentration are still useful.

The BiAS and CTAS procedures are commonly recommended for the determination of total NS concentration. However, both are time- and labour-consuming and, most significantly, are hardly suitable for NS determination in treated sewage due to high detection limits [13]. Tensammetric methods provide a much better opportunity for determining total NS concentration both in raw as well as in treated sewage. Three tensammetric methods addressed to NS determination have been developed: the indirect tensammetric method (ITM) [14], adsorptive stripping indirect tensammetry (AdSIT) [15] and the ITM combined with the BiAS separation scheme (BiAS-ITM) [16]. The lowering of the tensammetric peak of ethyl acetate, due to competitive adsorption of NS-to-be-determined, is the analytical signal in all three methods. Anionic surfactants do not hinder the determination. The detection limit of the ITM is 2 µg in the sample. This corresponds to 10 ppb in the water sample, which is sufficient for the determination of NS in river water and in raw and treated sewage. Adsorptive preconcentration of NS is applied in the AdSIT. The AdSIT detection limit depends on the applied time of preconcentration and may be improved by half an order of magnitude in comparison to the ITM. The BiAS-ITM is more selective than the ITM. Only NS having more than 4 oxyethylene subunits are determined. The detection limit of the BiAS-ITM is the same as the ITM (2 µg in the sample). Residual ethoxylates (i.e. long-chained ethoxylates) and their major metabolites: poly(ethylene glycols) and short-chained ethoxylates can be determined with these methods. The methods were checked during investigation of the biodegradation testing of fatty alcohol ethoxylates [9], oxoalcohol ethoxylates [17], alkyl phenol ethoxylates [18] as well as during nearly fifteen years of monitoring of NS in the River Warta in Poznań (Poland) [19].

Three STPs of different treatment levels and capacities were selected for the investigation of the efficiency of NS removal: a conventional very small trickling filter-type STP in Nekla, a typical relatively small activated sludge type STP in Kostrzyn Wielkopolski and a large modern activated sludge STP in Kozięglowy, which treats sewage

from Poznań and removes nitrogen and phosphorus during treatment.

## Experimental

### Sewage Treatment Plants

Three STP were investigated in terms of NS removal: i) a conventional, very small trickling filter-type STP with auxiliary rush constructed wetland in Nekla, with a productivity of 400 m<sup>3</sup> per day, ii) a typical, relatively small activated sludge-type STP in Kostrzyn Wielkopolski with a productivity of 1,400 m<sup>3</sup> per day, and iii) a large modern activated sludge STP in Kozięglowy with a productivity of 200,000 m<sup>3</sup> per day, which treats sewage from Poznań and removes nitrogen and phosphorus during treatment.

Grab samples were taken on several random days. The samples were immediately preserved with formalin: 5% in the case of raw sewage and 1% in the case of effluent.

### Apparatus and Reagents

A General Purpose Electroanalytical System µAUTOLAB was used for alternating current voltammetric measurements (called tensammetric measurements). The system was manufactured by ECO Chemie (Utrecht, The Netherlands). The measurements were performed at a standard mode (without application of phase sensitivity), as well as at frequency of 60 Hz, a superimposed alternating voltage amplitude of 2 mV and a scan voltage rate of 400 mV min<sup>-1</sup>. Controlled-temperature hanging mercury drop electrode equipment (Radiometer, Denmark) was used. An additional platinum wire auxiliary electrode was applied and a glass beaker was replaced by a quartz beaker.

Triton X-100, (Rohm and Haas), surfactant C12E1 (Fluka), PEG 200 and PEG 1500 (both Carl Roth) were used without additional purification.

Purified sodium sulphate and sodium chloride of Analar grade were used for the preparation of the aqueous base electrolytes.

Freshly distilled ethyl acetate was used. Other reagents used were also of Analar grade.

All solutions used in the analysis were prepared in water triply distilled from a quartz apparatus. Only freshly distilled water was used.

The modified Dragendorff reagent [20] was prepared by mixing solutions A and B before use. Solution A: 1.7g of basic bismuth (III) nitrate, 65 g of potassium iodide and 220 ml of glacial acetic acid ( 1000 ml. Solution B was an aqueous solution containing 290g of barium chloride dihydrate in 1000 ml.

The solution for dissolving the precipitate (solution C) was prepared from 12.4g of tartaric acid and 18 ml of ammonia solution (25%) made up with water to 1000 ml. A silica gel cartridge (Bakerbond SPE silica gel 7086-03)

was used for the purification of this solution.

#### Separation of Long- and Short-Chained Ethoxylates and Poly(ethylene glycols) from a Raw or Treated Sewage Sample

This separation was performed as described in a previous paper [21]. Briefly, sodium chloride (60g) and sodium hydrogencarbonate (0.2g) were dissolved in 200 ml of filtered sample. The solution was sequentially extracted with two portions of ethyl acetate (total volume, 50 ml) and three portions of chloroform (total volume, 50 ml). The ethyl acetate fraction contains the long- and short-chained ethoxylates while the chloroform fraction contains PEG.

#### Determination of the Total Concentration of Non-Ionic Surfactants Using ITM

The determination was generally performed according to the procedure described in a previous paper [14]. The procedure, originally developed for river water, was adapted for raw and treated sewage.

An aliquot of ethyl acetate fraction containing approximately 2.5-25  $\mu\text{g}$  was evaporated with gentle heating in a small quartz beaker. The residue was dissolved in an accurately measured solution of 1.50 ml of ethyl acetate. The solution was then transferred into a 25 ml calibrated flask along with water used for rinsing. 12.5 ml of 1 mole  $\text{l}^{-1}$  sodium sulphate solution was added and the mixture diluted to volume with water. The mixture containing an excess of ethyl acetate was vigorously shaken and the emulsion transferred into a voltammetric cell. The emulsion was then stirred for 10 min. to achieve clarity of the solution due to evaporation of excess of ethyl acetate. This excess of ethyl acetate needed to be removed, as evidenced by the disappearance of turbidity.

After a period of rest (30 sec.), the tensammetric curve of ethyl acetate was recorded in the cathodic direction using a new mercury drop and starting from (-1.20) V (vs. SCE). The difference between the height of the peak of ethyl acetate (recorded in a separate measurement) and that of ethyl acetate in the presence of substances-to-be-determined is the analytical signal. The results were quantified using a calibration curve of Triton X-100. Precision of determination was 12.2%.

#### Determination of Concentration of Long-Chained Ethoxylates by the BiAS-ITM

Determination was performed according to the procedure described in the previous paper. The procedure, which was originally developed for river water [22], was adapted for raw and treated sewage.

An ethyl acetate fraction was evaporated by gentle heating in a small quartz beaker. The residue was dissolved in a mixture of 2 ml of methanol and 16 ml of

water. Solution A (8 ml) and solution B (4 ml) of the modified Dragendorff reagent were mixed and added to the sample. The reacting mixture was stirred for 20 min. and left for 10 min. Orange-coloured precipitate was filtered through a G5 glass filter. No washing of the precipitate was done.

The precipitate was dissolved in 20 ml of hot solution C. The filter and the beaker were then washed with 3-4 ml of water, which was subsequently added to the solution containing the dissolved precipitate. After cooling the solution, the volume was made up to 25 ml with water.

An aliquot of the solution was transferred to a 25 ml volumetric flask. 2.5 ml of 5 M aqueous sodium chloride and 1.80 ml of ethyl acetate were added and the flask filled to the mark with water. The rest of the procedure was performed as described above. Precision of determination was 4.3%.

#### Determination of the Concentration of Short-Chained Ethoxylates by the ITM

The filtrate, after precipitation of long-chained ethoxylates (as described above), was diluted to 50 ml with water and 10 g sodium chloride was added and dissolved. A short-chained ethoxylates fraction was extracted with three portions of ethyl acetate having a total volume of 25 ml. Extracts were collected in a 25 ml volumetric flask and filled to the mark with ethyl acetate. An aliquot of ethyl acetate solution was evaporated by gentle heating in a small quartz beaker. The residue was then dissolved in an accurately measured 1.50 ml of ethyl acetate and the solution transferred into a 25 ml calibrated flask along with water used for rinsing. 12.5 ml of 1 mole  $\text{l}^{-1}$  sodium sulphate solution was added and the mixture diluted to a volume with water. The ITT determination was performed as described above using the calibration curve of surfactant C12E1. Precision of determination was 17%.

#### Determination of the Total Concentration of Poly(ethylene glycols) by the ITM

Determination was generally performed according to the procedure described in a previous paper [21]. Briefly, an aliquot of chloroform fraction containing PEG was evaporated. The residue was dissolved in an accurately measured 1.50 ml portion of ethyl acetate. This solution was transferred to a 25 ml calibrated flask, a supporting electrolyte (sodium sulphate) added, and the mixture diluted to volume with water. The rest of the procedure was performed as described above using the calibration curve of the 1:1 mixture of PEG 200 and PEG 1500.

## Results and Discussion

Two activated sludge type STP of different sizes and one very small old-fashioned trickling filter type STP

were investigated in order to determine NS reduction during treatment. The investigation was performed with grab samples taken on several random days. The most thorough investigation was performed with the STP in Kozięglowy which treats sewage for Poznań, and its efficiency has an influence on the condition of the River Warta below the city. This is a modern, newly built STP with removal of nitrogen and phosphorus. The results are shown in Table 1. Raw sewage which fed the STP within the period of the research contained 4.6-5.9 mg l<sup>-1</sup> of NS, including 2.7-3.3 mg l<sup>-1</sup> of long-chained ethoxylates which are precipitated with the modified Dragendorff reagent. During treatment in the STP, these concentrations were reduced to 0.7-1.0 mg l<sup>-1</sup> of total NS and 0.35-0.45 mg l<sup>-1</sup> of long-chained ethoxylates *i.e.* 85-87%. Apart from long-chained ethoxylates, the total NS concentration includes 'short-chained ethoxylates', *i.e.* NS, which do not undergo precipitation with the modified Dragendorff's reagent but are determined by the ITM. The concentration of this fraction in raw sewage of the STP in Kozięglowy varied between 2.0-2.8 mg·l<sup>-1</sup> and was reduced to 0.35-0.55 mg l<sup>-1</sup> during treatment *i.e.* on average by 81%. The presence of PEG was also found both in raw sewage (0.2-1.1 mg l<sup>-1</sup>), as well as in the effluent (0.05-0.45 mg l<sup>-1</sup>). The PEG concentration was reduced on average by 85%. The presence of PEG, which

is an intermediate product of ethoxylate biotransformation in raw sewage, indicates that partial biodegradation already occurred in the sewer. The high concentration of short-chained NS in raw sewage indirectly supports this conclusion.

The results concerning the much smaller activated sludge-type STP in Kostrzyn Wielkopolski are shown in Table 2. The STP does not remove nitrogen and phosphorus. Raw sewage which fed the STP within the period of the research contained 4.6-10.9 mg l<sup>-1</sup> of NS, including 1.0-2.6 mg l<sup>-1</sup> of long-chained ethoxylates. During treatment in the STP, these concentrations were reduced to 0.75-1.3 mg l<sup>-1</sup> of total NS and 0.55-0.65 mg l<sup>-1</sup> of long-chained ethoxylates. The reduction of total NS during treatment was 85-86% on average, while concentration of long-chained ethoxylates was, on average, 60%. The concentration of short-chained NS was reduced from 2.0-7.2 mg l<sup>-1</sup> in raw sewage to 0.2-0.3 in the effluent of STP, *i.e.* it was reduced on average by 92%. PEG concentration varied from 1.1 to 2.0 in raw sewage and was reduced to the range between 0.05-0.25 mg l<sup>-1</sup>, *i.e.* on average by 90%.

The trickling filter-type STP in Nekla with auxiliary rush wetland was investigated only in terms of the reduction of long-chained ethoxylates and PGE. The results are given in Table 3. The concentration of long-chained eth-

Table 1. Total concentration of ethoxylates (TEex) and concentrations of long- (LCh) and short-chained (SCh) ethoxylates as well as poly(ethylene glycols) (PEG) in influent and effluent of STP in Kozięglowy (Poland).

Day	Raw sewage [mg l <sup>-1</sup> ]					Treated sewage [mg l <sup>-1</sup> ]					Reduction [%]				
	TEex	TEcalc	LCh	SCh	PEG	TEex	TEcalc	LCh	SCh	PEG	TEex	TEcalc	LCh	SCh	PEG
A	5.3	5.7	3.3	2.4	1.1	0.7	0.85	0.45	0.4	0.1	87	85	86	83	91
B	8.2	5.9	3.1	2.8	1.0	0.7	0.95	0.4	0.55	0.2	91	84	87	80	80
C	4.65	5.0	2.7	2.3	0.9	0.7	0.85	0.4	0.45	0.05	84	83	85	80	94
D	4.75	5.4	3.1	2.3	0.2	0.7	0.7	0.35	0.35	0.45	85	87	89	80	78
E	4.6	4.8	2.8	2.0	0.85	1.0	0.7	0.35	0.35	0.15	78	85	88	83	82
Av.	5.5	5.4	3.0	2.4	0.8	0.7	0.8	0.4	0.4	0.2	85	85	87	81	85

Table 2. Total concentration of ethoxylates (TEex) and concentrations of long- (LCh) and short-chained (SCh) ethoxylates as well as poly(ethylene glycols) (PEG) in influent and effluent of STP in Kostrzyn Wielkopolski (Poland).

Day	Raw sewage [mg l <sup>-1</sup> ]					Treated sewage [mg l <sup>-1</sup> ]					Reduction [%]				
	TEex	TEcalc	LCh	SCh	PEG	TEex	TEcalc	LCh	SCh	PEG	TEex	TEcalc	LCh	SCh	PEG
A	9.4	8.4	1.2	7.2	1.2	1.2	0.85	0.65	0.2	0.05	87	90	46	97	96
B	10.9	5.5	2.0	3.5	2.0	0.75	0.9	0.6	0.3	0.25	94	84	70	91	88
C	6.6	4.6	2.6	2.0	1.5	1.0	0.9	0.6	0.3	0.2	85	80	77	85	87
D	5.6	6.5	1.0	5.5	1.1	1.3	0.8	0.55	0.25	0.1	77	88	45	95	91
Av.	8.1	6.2	1.7	4.6	1.4	1.0	0.85	0.6	0.25	0.15	86	85	60	92	90

Table 3. Concentrations of long- (LCh) and poly(ethylene glycols) (PEG) in influent and effluent of STP in Nekla (Poland)

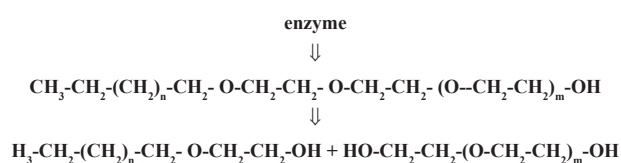
Day	Raw sewage [mg l <sup>-1</sup> ]		Treated sewage [mg l <sup>-1</sup> ]		Reduction [%]	
	LCh	PEG	LCh	PEG	LCh	PEG
A	2.9	0.75	1.2	0.55	58	27
B	2.0	0.45	1.0	0.15	50	67
C	2.2	0.65	1.1	0.25	50	62
Av.	2.4	0.62	1.1	0.32	53	52

oxylates was reduced from 2.0-2.4 mg l<sup>-1</sup> in raw sewage to 1.0-1.2 in the effluent of STP, *i.e.* it was reduced on average by only 53%. PEG concentration varied from 0.45 to 0.75 in raw sewage and was reduced to the range between 0.15-0.55 mg l<sup>-1</sup> *i.e.* on average by 52%.

A relatively low degree of NS biodegradation in the investigated STP is a surprising conclusion of the measurements performed: in both STP of the activated sludge type, average total NS removal is approximately 85%. This concerns both total NS concentration measured directly (TE<sub>ex</sub>), as well as the NS total concentration calculated as the sum of long- and short-chained NS (TE<sub>calc</sub>). The degree of reduction of long-chained ethoxylates (LCh) in the considered STP is the same or lower than the reduction of the total NS concentration. Only 60% of the long-chained ethoxylates was biodegraded in the STP in Kostrzyn Wielkopolski. This fact supports the conclusion concerning the low degree of NS biodegradation. However, the efficiency of the removal of AE, which are the major NS, varied between 99.6 and 99.9% [8]. The removal of anionic surfactants in the STP in Kostrzyn Wielkopolski in the same samples was found to be 97.5%. Thus, the relatively low percentage of NS removal is barely explainable. In considering the possible reasons for this effect, the presence of NS persistent to biodegradation may be taken into account.

The degree of NS removal seems to be dependent on the technical level of the STP. The trickling filter type STP in Nekla exhibited a significantly lower percentage of NS removal than both STP of the activated sludge type. Surprisingly, the removal of anionic surfactants (AS) in this STP and the same samples was on average 97%. Thus, the NS removal seems to be more vulnerable to the technical level of the treatment process than AS removal.

The presence of PEG and short-chained NS in raw sewage seems to be surprising at first sight, as these substances are not commonly used in detergent formulations. However, these substances are typical biotransformation by-products of ethoxylates due to the reaction [23]:



This biotransformation occurred in the sewer. Basically, the concentration of PEG and short-chained NS may serve as a measure of the degree of biodegradation in a sewer.

Our paper demonstrates the potential of tensammetric methods in NS determination in real matrices, including such difficult ones as raw and treated sewage. Total NS concentration measured by ITM represents NS having 1-30 oxyethylene subunits, *i.e.* both long- and short-chained ethoxylates, as well as NS of non-ethoxylate structure such as alkylpolyglucosides. The long-chained ethoxylates, which are determined by the BiAS-ITT procedure, represent the same NS which are determined by the classical BiAS procedure. The only difference between classical BiAS and the BiAS-ITT is that bismuth (III) is determined in the BiAS while ethoxylates are determined in the BiAS-ITT. However, in both cases, highly selective precipitation with modified Dragendorff reagent is used for isolation of ethoxylates from the water matrix. It is worth stressing that only ethoxylates having 5-30 oxyethylene subunits are determined in both procedures (*i.e.* long-chained ethoxylates). The short-chained ethoxylates concentration, *i.e.* concentration of ethoxylates having 1-4 oxyethylene subunits can be calculated from the difference between the ITM result (total NS) and the BiAS-ITT result (long-chained ethoxylates) as well as determined separately. Thus the tensammetric techniques provide the opportunity for double-checking the results. This double-checking is shown in Tables 1 and 2, where total NS concentration is shown both as the experimental result of the ITT method (T<sub>ex</sub>), as well as the calculated value (T<sub>calc</sub>), *i.e.* the sum of the long- and short-chained ethoxylates. The results of this comparison are far from ideal. Five from eighteen completely investigated samples show a significant difference between the experimental and calculated results of total NS concentration. In one case this difference is almost 100%. On the other hand, the majority of the investigated samples exhibits good agreement of the experimental and calculated NS total concentration which is confirmation of reliability of experimental methods.

The question arises what the reasons are for the difference between the experimental and calculated NS total concentration. The determination or calculation of the short-chained NS concentration is the most probable source of error. The error of choice of standard [24] may be a sig-

nificant source of error due to the fact that the composition of the mixture of short-chained NS is unknown and may be different for different samples. The mixture of short-chained NS may contain short-chained ethoxylates having different hydrophobic parts, *e.g.* alkyl phenol, fatty alcohol or oxo-alcohol of different alkyl chain length. Each component of this mixture creates the analytical answer according to its own calibration curve, which may differ significantly from the calibration curve of the chosen standard. This error is unavoidable at the present stage of knowledge of the composition of the mixture of the short-chained NS. Interference by an unknown substance may also be the source of experimental error. In this term, the determination of the short-chained NS is much more vulnerable than the determination of the long-chained ethoxylates (*i.e.* long-chained NS) which are separated by a very selective stage of precipitation with modified Dragendorff reagent.

Apart from the information concerning NS concentration, tensammetric methods provide information concerning the PEG concentration. This information can be useful in the calculation of the total balance of NS and their metabolites in sewage treatment. PEG concentration can also be useful in the evaluation of the degree of biodegradation of ethoxylates during sewage transportation in the sewer system.

The determination of NS and their metabolites by tensammetric methods: ITM and BiAS-ITT is less expensive and considerably faster than by HPLC or LC-MS and provides general information concerning NS biodegradation in STP. On the other hand, HPLC and especially LC-MS, provides more precise information concerning a particular compound. Thus, LC-MS and HPLC, as well as tensammetric methods supplemented each other rather than competed.

### Conclusions

1. In two STP of the activated sludge type, the total non-ionic surfactant concentration was reduced by on average 85%, while in one STP of the trickling filter type, non-ionic surfactant concentration was reduced by only 53% on average.
2. Raw sewage of the investigated STP contained a significant concentration of poly(ethylene glycols) and short-chained non-ionic surfactants, which are the products of the of biotransformation ethoxylates in the sewer system. These metabolites were removed in the investigated STP of the activated sludge type by 81-92%.
3. Total concentrations of NS, and long-chained ethoxylates in raw and treated sewage can be determined by tensammetric methods, as well as their metabolites: short-chained NS and poly(ethylene glycols).

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