Journal of Environmental Protection and Ecology 12, *No* 3A, 1525–1532 (2011)

Environmental legislation

DETERGENTS LEGISLATIVE FRAMEWORK AND ECOTOXICOLOGICAL TESTING METHODOLOGY

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Abstract. Detergents industry is a competitive industry, with a large opening to innovation and economical development. Although very useful for sanitation, the big domestic and industrial detergents consumption has a significant contribution to surfactants concentrations increase in towns sewage and implicit to surface water contamination. At European level, detergents and cleaning products have a special place in legislative framework of the European Community because are manufactured in big quantity and they may affect the environment both during manufacture and using processes. In the last years surfactants biodegradability was the most significant problem. For this reason, at European level through Regulation (EC) No 2004/648 (and its next amendments), strict regulations were introduced in order to assure the environment and human health safety. After Romania adhesion to the EU, the European Regulation of detergents becomes also an applicable law at national level through Governmental Decision No 658 /2007. The present paper wants to give a special attention for the following aspects: (1) the national and international legislative framework concerning the commercial surfactants – products for human use, in order to assure their free circulation on the market; (2) the requirements of Detergents European Regulation concerning the final biodegradability of surfactants and complementary risk assessment for their potential recalcitrant metabolites on aquatic organisms; (3) the most practical and sensible methods for surfactants ecotoxicological testing.

Keywords: detergents, ecotoxicity, risk, environment.

AIMS AND BACKGROUND

Surfactants industry is a competitive industry, with a large opening to innovation and economical development. Although very good for sanitation, the big domestic and industrial detergents consumption has a significant contribution to surfactants concentrations increase in towns sewage and implicit to surface water contamination. The negative effects manifested through presence of surfactants in surface water are mostly due to superficial – active proprieties – detergents surfactants characteristic, indifferently of class type. Industrial surfactants are grouped in 4 categories in accordance with molecule charge in solutions: anionic with a negative ion in polar group; cationic with a positive ion; nonionic without

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charge; amphoteric with negative or positive charge in accordance with solution pH (Fig. 1) (Ref. 1):

anionic surfactant:

$$CH_3–(CH_2)_n–CH_2–\underbrace{C_6H_4}–SO_3^-Na^+$$

n = 6–10

nonionic surfactant:

$$R–CH_2–O–\underbrace{(CH_2–CH_2–O)_n}–CH_2–CH_2–OH$$

n = 10–12

cationic surfactant:

$$\left[CH_3–(CH_2)_n–CH_2–\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{N}}–CH_3\right]^+ Cl^-$$

n = 10–16

amphoteric surfactant:

alkyl betaine

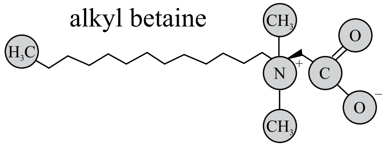

Fig. 1. Surfactants classes

Unfortunately, a lot of sintetic surfactants, which are manufactured in big amount and are used in commercial detergents composition are biodegradability resistant, they persist and foam in treatment plants of waste water and even in surface water (lakes and rivers).

In the present the ecological evaluation of surfactants, the biodegradability and ecological toxicity are very important. The biodegradability is even more important than use efficiency or manufacture cost. The surfactants biodegradability means their biochemical decomposition in the presence of some microorganisms capable to destroy, in natural conditions, the surfactants unwanted properties (foam and toxicity) for aquatic wildlife[2].

The paper will confer a special attention to cationic surfactants, frequent use in laundry and dishes detergent and balsam manufacture, as well as amphoteric surfactants used in personal caring products manufacture (which are hair shampoo and balsam, liquid soap and cleaning lotion) and for industrial cleaning agents, because the control of this type of surfactants (cationic and amphoteric) was not legislated until the apparition of European Regulation, due to the absence of standard method – EN European or ISO international norm or European directive method associated for chemical quantitative assessment for this type of active substances. Also, until 2004, any European or national program for a standard method or directive associated for cationic and amphoteric surfactants biodegradability test, did not exist, although regulations concerning the accepted minimum biodegradability rate for this active substances used in commercial detergents composition have already existed[3,4].

Other reason for this study is that in scientifical literature the references concerning ecotoxicological characterisation of cationic and amphoteric surfactants are relatively reduced.

In the aerobic biodegradation process of organic substances, therefore in case of surfactants, the following concepts are available: *primary biodegradability* – means the loss of structural identity (in case of surfactants the loss of superficial tension which cause the foam); *inherent biodegradability* – the potential biodegradability or probability to be biodegradable, which is means more than 20% and below the maxim level of biodegradability (90% for anionic surfactants and 80% for nonionic surfactants); and *ultimate biodegradability* – regard the biodegradation to the water, carbon dioxide, mineral salts and biomass, which means mineralisation[1].

Concerning the legislative framework, at European level, detergents and cleaning products have a special place, because they are produced in big amounts and may affect the environment by their manufacture (through discharges in environment: water, air, soil) and especially by their use, through wastewater discharges with and without treatment in specific installations, reaching to surface waters.

In the last 10 years, the surfactants biodegradability has been a problem of interest, reason for which the European frameworks were focused on the heavy biodegradable surfactants use restriction and their long-term environment compatibility assessment, consider the surfactants aquatic toxicity high rate and especially of active compounds from formulated products[5].

The last UE Regulations concerning surfactants area (European Regulation No 648/2004/EC and its next amendments), show the orientation for easy and total biodegradable surfactants use (mineralised). Since October 8, 2005, the publication data of New European Regulation, all surfactants class used as raw materials in commercial detergents, must accomplish the 'ultimate biodegradability' conditions, practical to show their degradation at CO_2 and H_2O (mineralisation)[6–9].

In related annex of Regulations are specified the test methods for detergents surfactants and cleaning products assessment, as follows:

• *Annex I* specifies that only EN ISO /IEC 17025 or GLP (Good Laboratories Practice) certified laboratories are competent and authorised for surfactants conformity assessment services;

• *Annex II* specifies that is obligatory to assess the surfactants primary biodegradability. The reference method is *OECD confirmatory test*, applied as well in the disputes resolve, which impose at lest 80% biodegradability assessment. Are indicated as well, analytical methods for surfactants chemical determination (anionic, nonionic, cationic and amphoteric) – active compounds in detergents composition;

• *Annex III* specifies the laboratory testing methods for ultimate biodegradability of surfactants (*mineralisation assessment – accepted minimum percentage is 60%*) – OECD methods indicated in 67/548/CEE Directive and/or international norms EN/ISO for ultimate biodegradability assessment. The reference method specified for surfactants mineralisation laboratory testing – EN ISO 14593:1999 standard – *Ultimate aerobic biodegradability assessment of organic compounds* *in aqueous medium*; *Inorganic carbon analysis from closed bottle* (*CO_2 headspace test*);

• *Annex IV* refers to the environment risk assessment (aquatic environment component) in case of recalcitrant metabolites which may arise after biodegradability tests, in context of Directive No 93/67/CEE, Regulation No 793/93 (CEE) and Regulation No 1488/94;

• *Annex VIII* indicates the analytical and testing methods which must be applied for commercial detergents control, namely: reference method (*confirmatory test*) for primary biodegradability assessment of surfactants in continuous flow biological installations with active sludge and analytic methods for chemical quantitative determinations of surfactants concentrations in biodegradability test period[6].

At national level remarkable efforts are made to establish the administrative and legislative frameworks for implementation of the European legislation concerning the effective control and efficient supervision of surfactants system for human health and environment protection, reason for which we consider that is necessary to confer a special attention to a new methodology development which allows the assessment of surfactants adverse effects on a environment component. In this context the Romanian Parliament approved the Governmental Decision No 658/2007 concerning the establishment of some measures for application of Regulation No 648/2004 of the European Parliament and Counsil regarding the surfactants[10].

EXPERIMENTAL

The primary biodegradability assessment of cationic and amphoteric surfactants was performed according to *OECD confirmatory test* specified in the European Regulation No 648/2004/EC Annex VIII.1. The method describes a small activated sludge plant in continued flow (Fig. 2), designed to simulate the classical treatment of urban wastewaters[11,12]. The surfactants removing was daily monitored based on surfactants content (in mg/l) from input synthetic sewage and from effluent water (collected after 24 h of experiment). Effective biodegradability testing phase was about minimum 21 days (the next stage of initiation phase and acclimatisation – biological acclimatisation of installation) and no more than 6 weeks.

The optimum work conditions were: constant input flow of 1 l/h; constant aeration of test solutions – about 2 mgO_2/l; retention time (TRH) in aeration tank about 3 h and constant recirculation flow; the input with new synthetic sewage containing about 10 mg/l surfactants (cationic and amphoteric) and collection of effluent (treated water) each day; the synthetic sewage from aeration tank was inoculated with 3 ml of fresh biologic effluent (freshly collected from a treatment plant dealing with a predominantly domestic sewage); and the running of activated sludge plant was continuous at 19–24^{o} C temperature, for about 60 days.

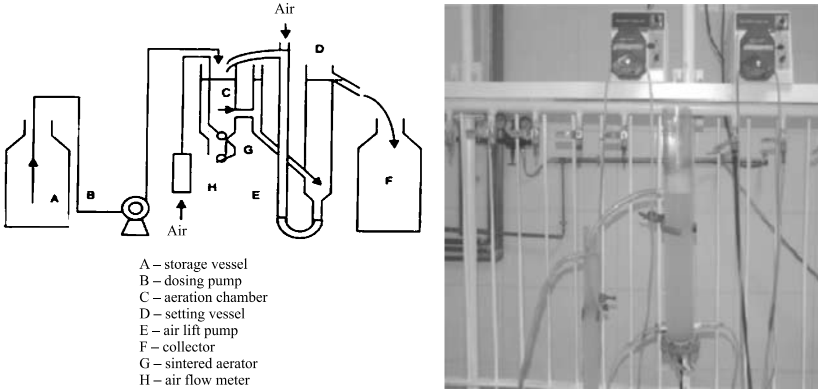

Fig. 2. Activated sludge laboratory plant

Test solutions were: synthetic sewage of 10 mg/l cationic surfactant (Fluke standard – Hyamine 1622) and 10 mg/l amphoteric surfactant (standard based on cocamidopropyl betaine (CAPB)); and mixture solution with cationic (10 mg/l) and amphoteric (10 mg/l) surfactants.

Experimental phase duration was 36 days for the biodegradability tests led on nutritive solutions with cationic and amphoteric surfactants and 30 days for the biodegradability test of mixture nutritive solution with cationic and amphoteric surfactants.

Removing efficiency of organic mater*:* η, in percents, was every day calculated with the following mathematical relation:

$$\eta\% = \frac{Sa_{\mathrm{i}} - Sa_{\mathrm{e}}}{Sa_{\mathrm{i}}} \times 100,$$

where Sa_{i} is surfactant concentration from synthetic sewage, in mg/l; Sa_{e} – surfactant concentration from treated water (effluent), collected over 24 h, in mg/l.

Quantitative dosage of cationic and amphoteric surfactants was performed according to the methods indicated in Regulation No 648/2004 concerning the surfactants (Annex II) – DIN/EN 38409/1989-07 and Orange II method – Boiteux 1984 (Table 1). In order to check the efficiency of the process the chemical oxygen demand (COD) – SR ISO 6060/1996 and dissolved organic carbon (DOC) – SR ISO 8245/1995 were measured at least twice per week. The content of dry matter from aeration tank – SR EN 872/2005 was determined twice per week; oxygen concentration from aeration tank was assessed according to SR EN 25814/1999; the pH of nutritive solutions was assessed according to SR ISO 10523/1997 and the room temperature was kept between 19–24°C.

Table 1. Performance parameters and the interferences for quantitative cationic and amphoteric surfactants determinations from standard solutions (control solutions)

Performance parameters and interferences	DIN/EN 38409/1989-07 (cationic surfactants dosage) – Fluke standard – Hyamine 1622	Orange II method– Boiteux 1984 (amphoteric surfactants dosage) – standard based on cocoamidopropyl betaine (CAPB)
Wavelength	628 nm	485 nm
The Lambert–Beer rule	concentration domain 0.4–4 mg/l	concentration domain 0.4–4 mg/l
Calibration curve equation	$y = 0.0029+0.1669x$	$y=0.0054+0.1507x$
Residual standard deviation (Sy)	0.0083	0.0258
Method standard deviation (Sx_0)	0.0499 mg/l	0.117 mg/l
Variation coefficient (Vx_0)	2.41%	5.66%
Interferences	small concentration of anionic surfactants	small concentration of cationic surfactants; this interference could be removed by sample pH adjustment at alkaline values

RESULTS AND DISCUSSION

We obtained an acclimatisation period of experimental laboratory plant about 10–12 days and an effective degradation phase about 20–26 days:

- COD: 70–89% remove efficiency obtained for the biodegradability tests of nutritive solutions with only surfactant content and respective 70–78% remove efficiency for biodegradability tests of cationic and amphoteric surfactant mixture;
- DOC: 80–83% remove efficiency for all the 3 biodegradability tests.

The daily biodegradation percentages were graphically represented (removed surfactant %) depending on the duration of the test (in days), to obtain the biodegradability curve (Fig. 3), from which were determined: the acclimatisation period of installation (in days), the effective degradation phase (in days), and the maximum degradation level (in percents).

Biodegradation capacity was calculated as an arithmetic average of daily remove efficiency values of test surfactant, obtained in effective biodegradation period, during which degradation has been regular and the operation of the plant trouble-free (Fig. 3).

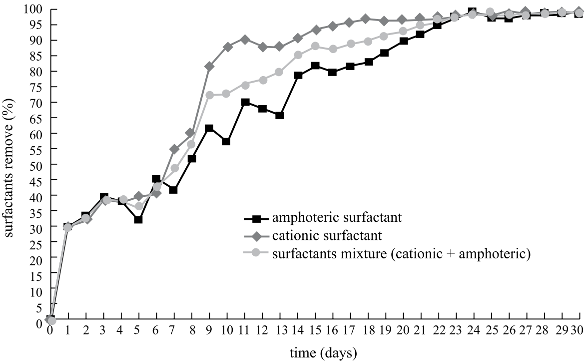

Fig. 3. Biodegradation curve of cationic and amphoteric standard solutions and for mixture solutions

We obtained a cationic surfactant remove about 30–60% in acclimatisation period and a biodegradability percentage about 94% in effective biodegradation phase. Concerning the amphoteric surfactant remove we obtained about 28–77% in acclimatisation period and a biodegradability percentage about 96% in effective biodegradation phase.

The efficiency of cationic and amphoteric surfactants remove from nutritive mixture solution was 30–70% in acclimatisation period and biodegradability percentage was 92.8% for the total of active substance (cationic and amphoteric).

The biodegradation percentages obtained for each type of surfactants were: 95% for cationic surfactant, and 90% for the amphoteric surfactant.

CONCLUSIONS

The OECD confirmation test for primary biodegradability has led to conclusion that both standard surfactants (Hyamine 1622 and cocoamidopropyl betaine) meet the standard criteria, the biodegradability percentages being more than 90% for the cationic surfactant and at limit for the amphoteric surfactant. Concerning the biodegradability of mixture solution (cationic and amphoteric surfactants) we have obtained biodegradability percentage about 92% for the total removal of active substances, which meets the criteria for primary biodegradability.

This experimental part represents only a phase of a complex study concerning ecotoxicological assessment of cationic and amphoteric surfactants. In future research we will focus on development and verification of some ecotoxicological, histological and biochemistry methods, which allow the ecotoxicological characteristics assessment (ultimate aerobic biodegradability and aquatic toxicity) and complementary risk assessment generated by commercial detergents on aquatic environment according to Annex IV of Detergents Regulation.

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Received 7 July 2009
Revised 1 March 2010