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BIODEGRADABILITY ASSESSMENT OF CATIONIC AND AMPHOTERIC RAW MATERIALS

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Abstract. The paper is devoted to a new and important actual theme namely the implementation of European Regulation No CE 648/2004 amended through Regulation No CE 907/2006. A significant request of Regulation is that each producer/distributor must to attest ultimate aerobic biodegradability of surfactants used in detergents. The present work proposed to assess the primary and ultimate biodegradability for 2 surfactant raw materials (dialkyl hydroxyethyl ammonium metasulphate and cocamidopropyl betaine), their mixture and 2 commercial cleaning products based on this type of surfactant (laundry balsam and toilet detergent). The laboratory experiments were performed according to OECD 302 B – primary biodegradability test, SR EN ISO 10707/2001 and SR EN ISO 7827/2001 – 'ultimate' aerobic biodegradability test. According to tests criteria, we obtained more than 80–90% biodegradability after 28 days (primary biodegradability) and 80–81% biodegradability after 28–30 days (ultimate biodegradability) for all test chemicals.

Keywords: cationic and amphoteric surfactants, primary and ultimate biodegradability.

AIMS AND BACKGROUND

The detergents and cleaning products have an especial place in the European Community legislative framework because are very important for human and domestic sanitation, but also because they are manufactured/commercialised in big amounts which can affect the environment (surface waters, air, soil and also the human health) during both manufacture and using processes. The present paper discusses a sensible subject namely the implementation of the most important European legislative regulations concerning detergents and cleaning products – European Regulation No CE 648/2004 and it amendments (CE Regulation No 907/2006). The present Regulation establishes strict rules to assure the free circulation of detergents – products for consummators and industrial and institutional products and implicit of surfactants on the EU market, so that the human health and environmental protection to be guaranteed at high level. Detergent Regulation sets 'ultimate aerobic biodegradability' as the main criterion for all types of surfactants in detergents, practical to show their degradation at CO_2 and H_2O (60% mineralisation

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in 28 days)[1,2]. For surfactants that fail mineralisation, the test requires derogation for use and have to be evaluated for 'primary' biodegradability (80% in 28 days). Surfactants that pass this test may apply for derogation, but complementary risk assessment has to be done (e.g. aquatic toxicity tests). For surfactants that fail 'primary' biodegradability criteria derogation is rejected[3].

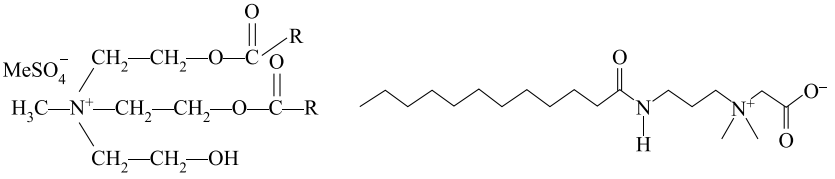
Beginning with February 2009 representative associations (AISE, CESIO, CEFIC) informed of their initiative to undertake further reserch in order to: establish the surfactants ecotoxicity and assess the potential environmental risk; develop an improved method for measuring the anaerobic biodegradability under sludge digester conditions; evaluate the biodegradation of the main non-surfactant organic detergent ingredients.

The present paper confers an especial attention to the aerobic biodegradability of the cationic surfactants (esterquats TEAQs) and amphoteric surfactants (cocamidopropyl betaines – CAPB). Esterquats are cationic aliphatic surface-active substances, frequently used in laundry and dishes detergents and balsam manufacture. Due to their cationic properties, the environmental conditions like pH, water hardness, humic acids or cation exchange capacity of sorbents will have a significant influence on the environmental fate of these substances[4]. Scientific literature reported that TEAQ is readily biodegradable > 90% (OECD 303A and Coupled Unit Test), 76–94% (OECD 301B)[5] and an ultimate biodegradability according to a test for insoluble substances (BODIS – Modified RDA-Blok test) about 87–100% (Ref. 4).

Cocamidopropyl betaine is a mild, amphoteric natural surfactant derived from coconut oil. According to HERA Report 2005, cocamidopropyl betaines are predominately used as cosmetic (29 500 t/year in Europe) and detergent ingredients (29 500 t/year in Europe), to boost and stabilise foam and improve viscosity in shampoo and body wash formulations[6]. According to scientific papers, CAPBs are readily degradable with an interval about 84–100% after 28–30 days of test[7].

EXPERIMENTAL

Chemicals. 2 raw materials (triethanol amine quat C16–C18 – dialkyl hydroxyethyl ammonium metasulphate (TEAQ) purity 99.9% CAS: 93334-15-7 and a zwitterionic chemical compounds with a quaternary ammonium cation – cocamidopropyl betaine (CAPB) purity 34.6% CAS: 4292-10-8) (Fig. 1) and their mixture (cationic and amphoteric surfactants); 2 commercial cleaning products based on this type of surfactants: laundry balsam with 5–15% cationic surfactant, pH 3–4.7 (1% in water 20°C); and toilet detergent with 5–15% amphoteric surfactant, pH 2.10 (1% in water 20°C) – obtained from national producers.



TEAQ CAPB

Fig. 1. Structure of TEAQ and CAPB

Methodology

• OECD 302 B – confirmatory test for primary biodegradability assessment of surfactants. The method describe a small activated sludge plant in continued flow (Fig. 2), designed to simulate the classical treatment of urban waste waters**.** The surfactants removal is monitored each day based on surfactants content (mg/l) from input synthetic sewage and from effluent water (collected after 24 h of experiment).

• SR EN ISO 10707:2001 – biochemical oxygen removal method – allows the ultimate biodegradability assessment of organic compounds present in a given concentration, subject to aerobe microorganisms, through biochemical oxygen removal analysis. A product test solution, which is the single source of carbon and energy, is inoculated with a small number of mixed aerobe microorganisms, incubated at dark, in closed recipients and well filled, using OxiTop equipment (Fig. 3). According to SR EN ISO 10707:2001, an organic compound is biodegradable when the biodegradation percentage is ≥60%, after 28 days of testing[8].

• SR EN ISO 7827:2001 – dissolved organic carbon analysis (DOC). The test allowed the ultimate biodegradability assessment of substances/chemical products, in a given concentration, in a synthetic media, subject to aerobe microorganisms. The COD removal percentages is determined for each time interval and is graphically represented based on time, obtaining a biodegradation curve. In accordance with standard criteria, an organic compound is biodegradable when the percentage of biodegradation is ≥ 80%, after 28 days of test[9].

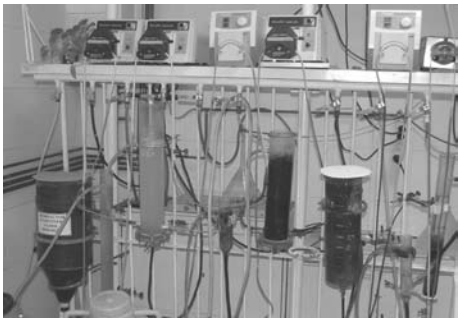


Fig. 2. Activated sludge laboratory installation

Fig. 3. OxiTop equipment

The analytical assessments of cationic and amphoteric surfactants were performed according to DIN/EN 38409/1989-20 (for cationic surfactants) and Orange II method – Boiteux 1984 (for amphoteric surfactants).

RESULTS AND DISCUSSION

Primary biodegradability assessment. According to the OECD confirmatory test procedure (Annex VIII of Regulation CE No 648/2004), the experimental equipment consists of a vessel for syntetic sewage, an aeration vessel, a settling vessel, air-lift pumps to recycle the activated sludge and vessel for collecting the treated effluent. The equipmet parameters were: a constant input flow of 1 l/h; constant aeration of test solutions – at least 2 mg O_2/l; retention time (TRH) in aeration tank of 3 h and constant recirculation flow. The surfactant content of syntetic sewage was about 10 mg/l and over 24 h the effluent was collected. The synthetic sewage from aeration tank was inoculated with 3 ml of fresh biological effluent (predominantly domestic sewage). The degradation test was performed at 19–24°C and the duration of experiments was about 60 days. The test solutions were *s*ynthetic sewage with 10 mg/l of cationic surfactant; synthetic sewage with 10 mg/l of amphoteric surfactant; mixture solution with cationic (10 mg/l) and amphoteric (10 mg/l) surfactant. The experimental phase was 36 days for the biodegradability tests led on syntetic sewage with cationic/amphoteric surfactant and 30 days for the biodegradability test of mixture cationic and amphoteric solution. The monitored parameters of experimental equipment were the surfactants concentrations and COD in influents and effluents, the content of dry matter in the activated sludge and oxygen concentration from aeration tank vessel.

The efficiency of the biodegradation process (the reduction in COD) and the percentage of biodegradability (the degradation of surfactants) were calculated (Table 1**)**. The biodegradability of surfactant was calculated as an arithmetic mean of daily removal efficiency values of test surfactants, obtained in effective bio-

degradation period, during which degradation has been regular and the operation of the equipment trouble-free (Figs 4 and 5).

Table 1. Results of primary biodegradability tests

Parameters	TEAQ	CAPB	Mixture (TEAQ + CAPB)
Test time (days)	36	36	30
Lag time (days)	10		12
Efective biodegradation (days)	26		18
Removal of COD (%)	70–72		61
Removal of surfactant (%)	90	99	85–97
Biodegradability (%)	91	97	97.6

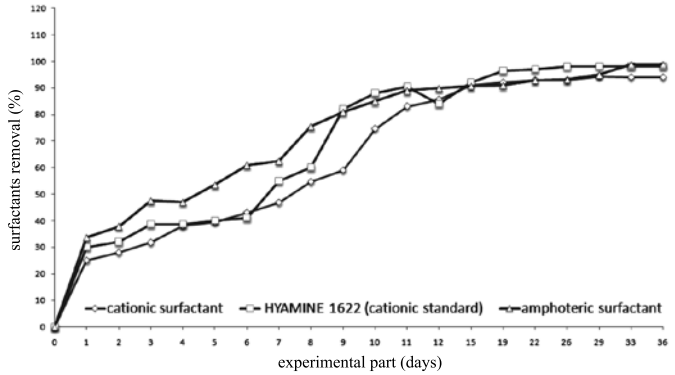


Fig. 4. Primary biodegradability tests chart – individual surfactants removal

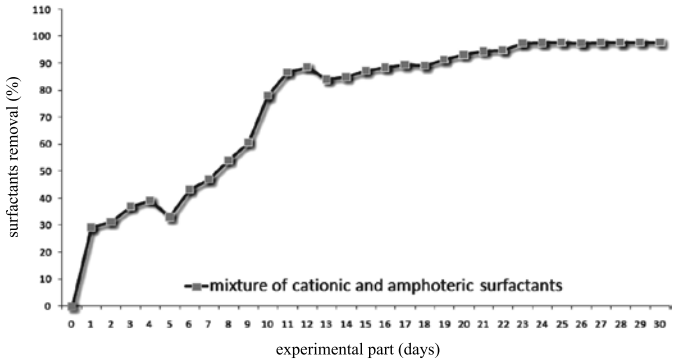


Fig. 5. Primary biodegradability tests chart – surfactants mixture removal

Ultimate biodegradability assessment. According to SR EN ISO 10707:2001, the ultimate biodegradability of laundry balsam solution with cationic surfactant was evaluated. The experimental solution with 2–2.5 mg/l cationic surfactant, was inoculated with fresh secondary effluent collected from an urban waste water plant

and distributed in an adequate number of CBO recipients (duplicate bottles of all series for dissolved oxygen measurements). Reference and control solutions: 2 mg/l aniline and cationic surfactant standard – 2.5 mg/l Hyamine 1622. The duration of experiment was 28 days. In the zero time bottles and after 5 days, 7 days, 14 days, 21 days and at the end of the test (28 days) the dissolved oxygen concentrations were measured in experimental, reference and control samples (mg O_2/l). The oxygen consumption was calculated after each time period and the specific BOD (expressed as mg oxygen per mg of test substance) was obtained.

The biodegradability percentages were calculated by dividing the specific BOD by measured COD value of each tested solution. The final percentages were calculated as mean values from the percentages of parallel assays (Table 2). The biodegradation percentage average was plotted versus time and the biodegradation curve was obtained (Figs 6 and 7).

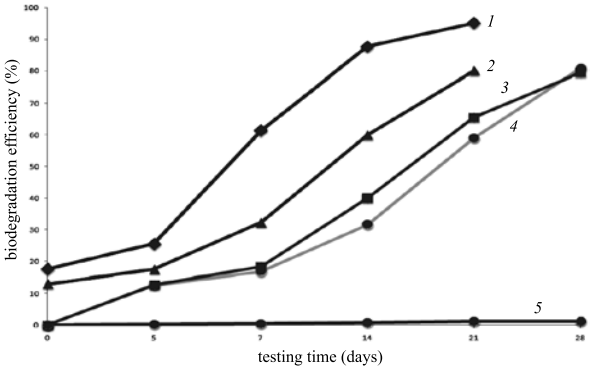


Fig. 6. Biodegradation efficiency (SR EN ISO 10707:2001)
1 – aniline; *2* – laundry balsam – commersial product; *3* – Hyamine 1622; *4* – cationic raw material; *5* – blank

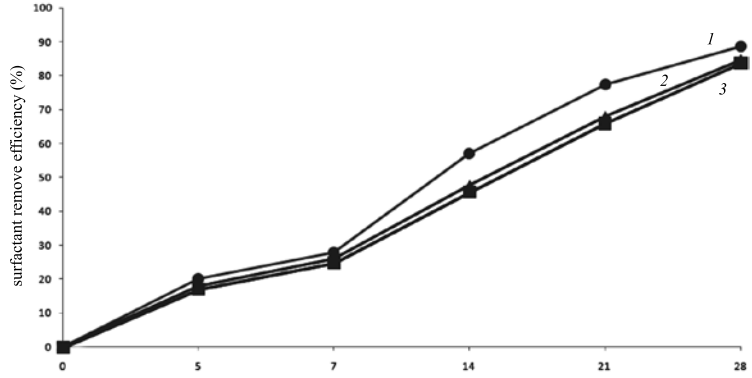


Fig. 7. Surfactant removal efficiency (SR EN ISO 10707:2001)
1 – Hyamina 1622; *2* – Laundry balsam – commersial product; *3* – cationic raw material

Table 2. Ultimate biodegradability test results – SR EN ISO 10707:2001

Parameters	TEAQ	Laundry balsam with TEAQ	Aniline	Hyamine 1622
Test time (days)		28		
Lag time (days)	10–14	10–14	7–10	10–14 days
Effective biodegradation time (days)	14	14	12–14	14
Remove of surfactants (%)	83.86	77.73	–	80.93
Biodegradability after 28 days (%)	81	80	95	79

According to SR EN ISO 7827:2001 methodology, cleaning product – toilet detergent solution based on amphoteric surfactant was tested. The experimental solution was prepared in a nutritive medium which contain 10mg/l amphoteric surfactant (COD 297.6 mg/l and DOC 81.10 mg/l). The experimental solution was inoculated with active sludge (30 mg/l suspended solids). A blank test for abiotic elimination control was prepared without inoculum and by adding 10 ml/l of the mercury chloride solution (10 g/l). The experimental and blank solutions was distributed in 2000 ml vessels agitated using stirrers and permanent aerated. Test environment of experiment: incubation takes place in the dark at constant temperature 20–21°C, pH 6.86–7.12, dissolved oxygen 4.62–4.80 mg/l, duration of test 30 days. The monitored parameters – the samples were taken at the start of test (day 0), at least 3 times at regulated time intervals and at the end of experiment (day 28). The concentrations of COD, DOC and amphoteric surfactant were determined for each sample and each measuring interval and the percentage DOC/COD/surfactant removal were calculated (Table 3). The obtained remove percentages were graphically represented function of time for detergent product and control solution (Fig. 8).

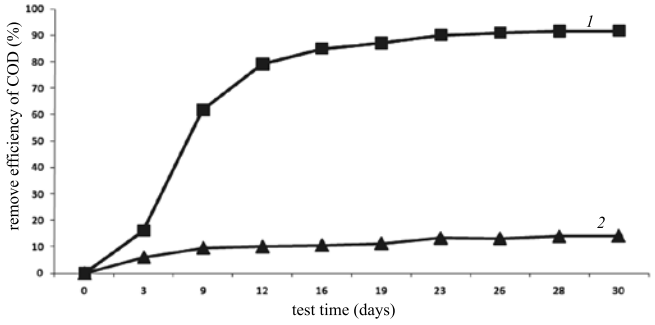


Fig. 8. Ultimate biodegradability efficiency chart – SR EN ISO 7827:2001
1 – detergent toilet – commercial product based on amphoteric surfactant; *2* – abiotic blank

Table 3. Ultimate biodegradability test results – SR EN ISO 7827:2001

Parameters	Toilet detergent based on CAPB
Experimental period (days)	30
Maximum level of biodegradation (%)	91.80 – COD; 91.43 – DOC
Lag time (days)	3
Biodegradation time (days)	20
Amphoteric surfactant removal after 30 days (%)	72.85
Abiotic removal for COD/DOC (%)	14

CONCLUSIONS

The OECD confirmation test for primary biodegradability have led to conclusion that raw materials TEAQ (cationic surfactant) and CAPB (amphoteric surfactant) meet the standard criteria, the biodegradability percentage being more than 90% (91–95% biodegradability for raw materials and about 92% for the mixture).

Analysing the experimental results obtained in ultimate biodegradability test SR EN ISO 10707:2001 we have appreciated that the cationic raw material (TEAQ) and the cleaning product – laundry balsam are ultimately biodegradable with >60% biodegradability percentages. After 28 days, the biodegradation of the cationic raw material (TEAQ) and commercial product was 80–81% comparative to 95% obtained for reference substance (aniline) and 79% for standard surfactant (Hyamine 1622).

Regarding the commercial product based on amphoteric raw material (CAPB), the results of ultimate biodegradability test (SR EN ISO 7827:2001) show that total removal of surfactant was more than 70% after 30 days and the maximum of biodegradation more than 90% COD and DOC removal.

All the biodegradability tests were performed in accredited laboratory, in conformity with standard methods[10] and the obtained results are comparable with values published in scientifical literature for cationic and amphoteric surfactants[11,12].

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