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About Biodegradability of Modern Firefighting Foam Concentrates Based On Per-Fluorinated Surfactants.

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ABSTRACT

This article is devoted to the environmental safety of foam concentrates based on perfluorinated surfactants. The article describes the methods of surfactant biodegradability determination. The results of such foam concentrates biodegradability study are presented. The comparative analysis of three generation foam concentrates eco-toxicological parameters is presented. The authors suggest that the environmental risks of updated foam concentrates which are actively sold nowadays are not fully studied yet.

Keywords: aqueous film forming foam concentrates, fluorinated surfactants, biodegradation, environmental risks of foam concentrates use.

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INTRODUCTION

Perfluorinated surfactants (hereinafter referred to as perfluorinated surfactants) are used in many industries, and are also included into special purpose foam concentrates, which have been used since 60th-70th of last century. The studies by international organizations concerning the environment protection, initiated in the 90th of the XXth century, proven the environmental hazard of perfluorinated surfactants based on PFO carboxylates (hereinafter referred to as PFOC) and perfluorooctane sulfonates (hereinafter referred to as PFOS) with $-C_7F_{15}SOO$ and $C_8F_{17}SO_3$ fragments [1-2]. These substances are extremely stable in natural environment, they are not hydrolyzed, not biodegradable, but they are bioaccumulative ones [3-5].

To improve the biodegradability and decrease the toxicity of perfluorinated surfactants in foam concentrate compositions the manufacturers offered to modify their molecules: 1) block the sulfonate group of perfluorinated compound with amido-betainic fragments; 2) reduce the amount of perfluorinated carbon atoms in the perfluorinated radical with C_8-C_{10} , to $C_4 - C_6$; 3) include hydrocarbon fragments of $(-CH_2CH_2-)_n$ type into perfluorinated surfactants.

METHODS

The biodegradability of foam concentrates was evaluated according to GOST R 50595-93 [6], which was redesigned into GOST 32509-2013 for the Customs Union. The methods of biodegradability determination used in the EU (EN ISO 11733:2004 and 14593:1999), do not allow a clear distinction of surfactants on the ability of their biodegradability for various reasons [7].

In contrast to the specified EU methods the determination of surfactants biodegradability indicators according to GOST R 50595 was carried out using the control and experimental aeration operating in a continuous flow mode. An unadapted active sludge $2,7 \pm 0,3 \text{ g/dm}^3$ cultivated on a synthetic wastewater (SWW) of a standard composition is loaded into aeration devices. The SWW supplied into an experienced aerotank is administered with surfactant (or surfactant-containing composition) with a constant mass concentration of $S_{PAV_{vyh}} = \text{const}$. The test period makes 30 days.

During the tests the residual mass concentration of surfactants is measured and the chemical consumption of oxygen ($S_{PAV_{vyh}}$ and HPK_{vyh}) in purified water from the experienced aeration tank and also $HPK_{vyh}(\text{cont})$ of a treated wastewater from control aeration tank. The kinetic dependences of biodegradation $[\Delta] HPK_{vyh} = f(t)$ are formed according to the treated wastewater test results. The graphs of kinetic dependences are used for surfactants biodegradability indicators calculation (Fig. 1). The description of indicators is presented below.

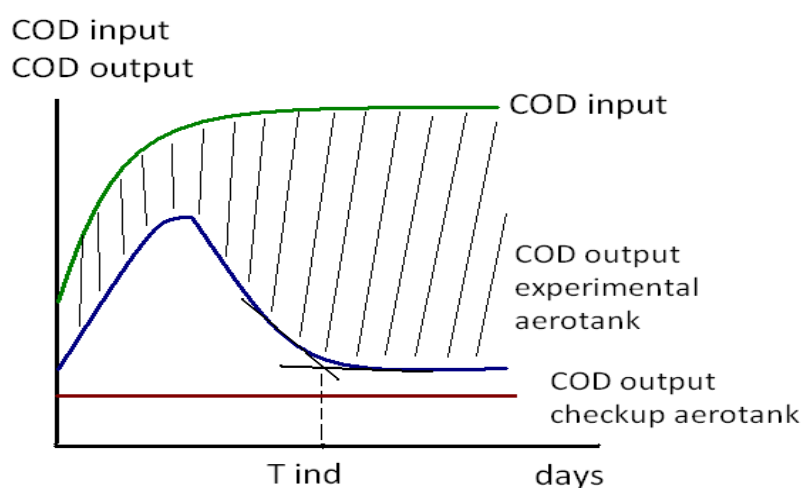


Figure 1: Kinetic dependence of the total surfactants biodegradability graph

Induction period (T_{ind} , days) - the period during which the unadapted activate sludge is adapted to the test surfactant (or surfactant-containing composition). Fig. 1 shows that T_{ind} is the graph function exit area to the plateau. T_{ind} duration determines the biodegradability level of surfactants: rapidly degradable - up to 3 days, including; moderately degradable - from 3 to 10 days, including; slowly degrading - from 10 to 25 days and including very slowly degradable: more than 25 days.

The maximum mass concentration of non-functional surfactant in the composition of the synthetic wastewater (MNK_a , mg/dm^3) - the concentration of surfactant which does not violate modes of aeration tank operation during the test period.

For the authorized surfactant (or surfactant-containing compositions) admission to the market the full degree (X^{28}_{poln} , %, mass) and primary (X^{28}_{perv} , %, mass) surfactant biodegradation level is calculated with an unadapted activated sludge for 28 days (shaded areas in Fig. 1). At that X^{28}_{poln} must be at least 70%.

MAIN PART

I generation foam concentrates, which include PO-6K (alkylbenzene sulfonates on kerosene fraction), issued before the end of 70-ies in the XXth century. The synthetic foam concentrates of the second generation are made on the basis of tri-ethanol amine alkyl sulfates, C₈-C₁₀ fraction (TEAS), tri-ethanol amine alkyl sulfates, [alpha]-olefin sulfonates and sulfoethoxylate (PO-6TS, PO-6TST). The third generation of foam concentrates includes alkyl sulfates and perfluorinated surfactants or protein hydrolysates and perfluorinated surfactants. The table shows the main components of foam concentrates biodegradability.

Table 1: Foam concentrates components showing major indicators of their biodegradability

Component	Composition % according to mass	Biodegradability indicator	
		T_{ind} , days	MNK_a , mg/dm^3
Tri-ethanol amine alkyl sulfates (sodium), C ₈ -C ₁₄ fraction	1-40	1-3	100-150
Sodium [alpha]-olefin sulfonates, C ₁₂ -C ₁₄ fraction	1-11	2-3	50-100
Alkyl polyoxy (3) sodium sulfate, C ₁₂ -C ₁₄ fraction	1-11	5-6	30-40
Alkyl dimethyl amine oxides, C ₁₂ -C ₁₄ fraction	1-5	3-5	30-40
Collagen hydrolysates	10-15	1-3	100
Butanol	1-9	5-6	40-50
Carbitols	0,5-6	5-6	40-50
Ethylene glycol	1-4	1-3	50
Perfluorine octyl (hexyl) ethylsulfon-amido betaine	0,5-5	∞	~1

COD experimental - COD checkup

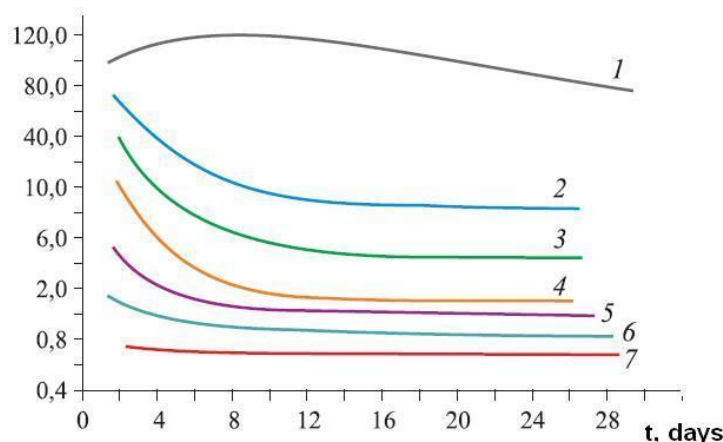


Figure 2: Kinetic dependences on biodegradation processes of foam concentrates

1 - PO-6K ($MNK_a = 150 mg/l$), 2 - TEAS ($MNK_a = 150 mg/l$), 3 - PO-6TST ($MNK_a = 60 mg/l$), 4 - PO-6TST ($MNK_a = 75 mg/l$), 5 - TimeksForafac® 1157N ($MNK_a = 20 mg/l$), 6 - Genex ($MNK_a = 10 mg/l$), 7 - PO-6FFFP ($MNK_a = 14 mg/l$)

Fig. 2 demonstrates the comparative data on the biodegradability of different generation foam concentrates, which we evaluated according to the method [6]. The figure shows that the first generation foam concentrates belong to very slowly degradable elements with $T_{ind} > 30$ days; the second generation foam concentrates refer to quickly and moderately degradable with $T_{ind} = 3 \div 7$ days, and the third generation foam concentrates refer to an extremely slow degradable ones with $T_{ind} = \infty$ (i.e. they are not exposed to biodegradability). Upon the completion of the induction period the foam production among all hydrocarbon foam concentrates stops and the foam concentrates with perfluorinated surfactant continue to produce foam concentrates (even at $[\Delta] HPK \approx 0$), indicating the presence of the said surfactants or its metabolites in purified water.

Th Fig. 3 shows the data on the foam column height in the aeration tanks, fixed during the testing of foam concentrates containing a fluorinated surfactant, and the concentrates thereof.

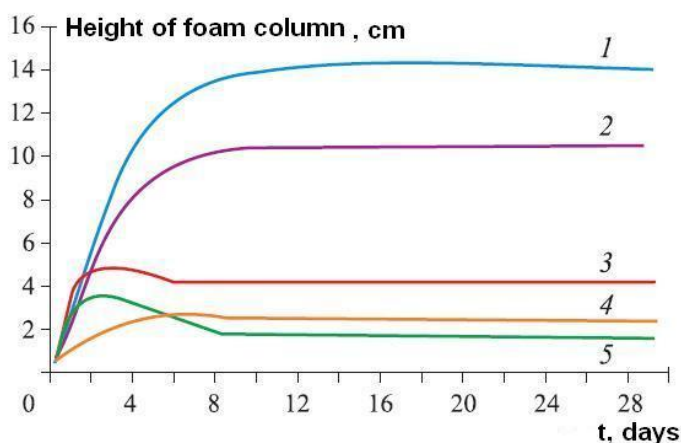


Figure 3: Kinetic dependences of biodegradation processes of foam concentrates based on fluorinated surfactants.

1-Forafac® 1157N ($C_{vh} = 1$ mg/l perftorPAV, $HPK_{vh} = 10$ mg/l), 2-Timeks AFFF ($C_{vh} = 100$ mg/l, $HPK_{vh} = 42$ mg/l), 3 - PO-3TF ($C_{vh} = 15$ mg/l, $HPK_{vh} = 10$ mg/l), 4 - perftorPAV concentrate for PO-3TF ($C_{vh} = 1$ mg/l by perfluorine PAV, $HPK_{vh} = 10$ mg/l), 5 - PO-3TF ($C_{vh} = 30$ mg/l by perfluorine PAV, $HPK_{vh} = 12$ mg/l).

Thus the foam concentrates and concentrates based on perfluorinated surfactants undergo a biological assimilation to “end metabolites” - $C_nF_{2n+1}COO$ and $-C_nF_{2n+1}SO_3^-$, wherein $n = 5-8$. The presence of these perfluorinated surfactants can be judged by the height of the foam column in an aeration tank. It should be noted that for 98% of surfactants the maximum permissible concentrations in water reservoirs for household purposes are set by a threshold foam concentration.

The toxicity of a number of perfluorinated compounds containing 6-10 carbon atoms in a chain, is well studied [8-10]. However, the ecotoxicological characteristics of modified perfluorinated surfactants in the compositions of modern special-purpose foam concentrates are not considered all together.

SUMMARY

It was established experimentally that modern synthetic hydrocarbon foam concentrates undergo biological assimilation during the week when they are in contact with the environmental objects. The foam concentrates containing perfluorinated surfactants with hydrocarbon block (modified surfactants) undergo a partial biological assimilation and then they are transformed into dangerous metabolites.

CONCLUSION

By blocking the hydrophilic part of the fluorinated surfactants molecules with hydrocarbon fragments the manufacturers mislead consumers of these products with respect to their toxicity and biodegradability. Molecules undergo a partial biological assimilation - only to $C_nF_{2n+1}-X$ (where X, as a rule -OH, -COOH, -SO₂ON) whose toxicity considerably exceeds the original materials toxicity. Environmental and toxicological characteristics of new generation foam concentrates with additives modified by perfluorinated surfactants

require careful study. The comprehensive methods development for wastewater purification contaminated with perfluorinated surfactants is required.

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