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EFFECTS OF ANTIFOAMING AGENTS ON THE BIOLOGICAL REMOVAL OF NON-IONIC SURFACTANTS

Experimental runs carried out in a continuous, laboratory scale, activated sludge plant, concerning the primary biodegradation removal of a non-ionic surfactant nonyl phenol ethoxylate, showed that the NPE removal was satisfactory (97% on the average) for operating sludge ages larger than 20–25 days. The removal decreased at lower sludge ages and foam appeared on the liquid free surface of the oxidation basin. In these conditions, the dosage of few ppm of silicone antifoaming agent, by dissolving the foam, allowed a NPE removal increase corresponding to about the NPE percentage quantity present in the foam.

DENOTATIONS

$\bar{C}_0$ — mean NPE concentration in the feed (kg/m³),
C_1 — outlet NPE concentration (kg/m³),
$\bar{C}_1$ — mean outlet NPE concentration (kg/m³),
ΔE — NPE mass biologically removed (kg),
F_c — feed sludge load factor (d^{-1}),
Q — volumetric flow rate (m³/h),
Q_R — volumetric flow recycle rate (m³/h),
R — mean NPE removal percentage,
t — time (h),
V — oxidation basin volume (m³),
X_e — biomass concentration in the effluent settler weir overflow (kg MLSS/m³),
X_m — mean biomass concentration in the oxidation basin (kg MLSS/m³),
X_R — biomass concentration in the recycle flow (kg MLSS/m³),
W_m — sludge wastage mass flow rate (kg MLSS/d),
W_v — sludge wastage volumetric flow rate (m³/h),
α_m — mean specific NPE removal rate (d^{-1}),
ϑ_c — mean sludge age (d).

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1. INTRODUCTION

The industrial use of non-ionic surfactants is rapidly growing mainly in the detergent, textile, metal, and paper industries; these surfactants are in fact stable at high temperatures and extreme pH values and maintain their detergent properties in hard waters, too. Two main classes of non-ionic surfactants are industrially employed alcohol ethoxylates (AE) and alkyl phenol ethoxylates (APE).

As to the primary biodegradation of these substances, i.e., the loss of a chemical or physical property of the surfactants when exposed to microbial attack, that of AE occurs at a fast rate: on the contrary, the APE are rather resistant to biological breakdown. About 5–6 days and 40–50 days are in fact necessary to biodegrade completely AE and APE, respectively [1]–[3].

Fortunately, the primary biodegradation significantly reduces aquatic toxicity of AE and APE but their presence in wastewater constitutes a serious environmental problem [4]; in fact, AE and APE LC_{50} level (concentration required to kill 50% of the total number of aquatic species) ranges between 10^{-3} and 10^{-2} kg/m^3 [2].

Adsorption on activated carbon seems to be the most effective way to remove completely the non-ionic surfactants [5]; however, this treatment may be too expensive, especially at high non-ionic surfactant concentrations, such as in industrial wastes. It may be therefore attractive to increase the biological breakdown rate of non-ionic surfactants. To this end, the effect of antifoaming agents on the biological removal rate of APE was investigated.

2. MATERIALS AND METHODS

Two preliminary biological removal tests of a NPE mainly used in textile industry (ESAPAL-NP/90, produced by Lamberti firm with a mean value of 9 ethylene oxide groups per molecule) were carried out in the absence and in the presence of silicone antifoaming agent (CONTRIPON M, produced by ZST firm).

The continuous, laboratory scale, activated sludge plant schematically shown in fig. 1 was employed. The oxidation basin of 0.12 m^3 and the cylindrical static settler, both made of plexiglass, were thermostatized with water at $25 \pm 0.5°C$. The plant was fed via a volumetric pump with an aqueous solution of about 0.16 kg/m^3 of glucose (the basic biodegradable organic compound), nutrient salts (NH_4HCO_3 and KH_2PO_4), and the NPE; in the test with the silicone antifoaming agent, its total concentration (active substance plus additives) in the feed was 18×10^{-3} kg/m^3. The oxygen was supplied by air flowing through 18 submerged aerators of sintered glass; the maximum air flow rate was 3.3 Nm^3/h. A constant DO concentration of about 2×10^{-3} kg/m^3 was maintained via an on-off loop control equipped with an oxygen probe (Philips PW 9600).
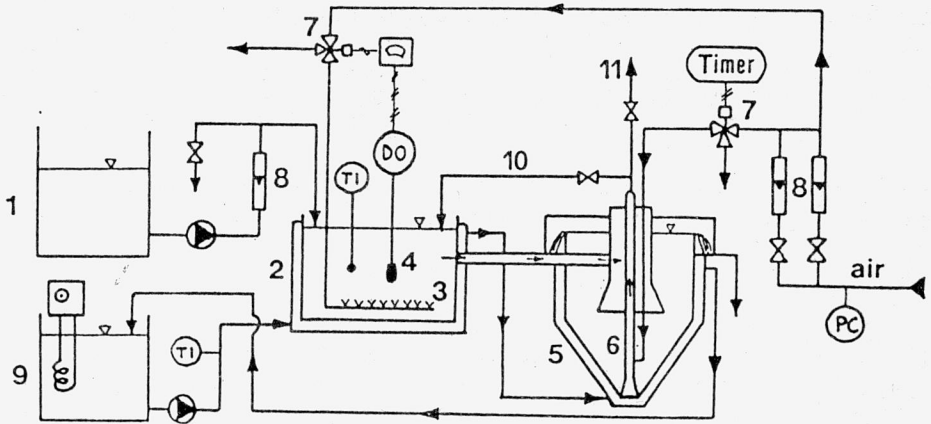
Fig. 1. Experimental apparatus

1 — feed tank, *2* — oxidation basin, *3* — submerged aerators, *4* — oxygen probe, *5* — settler, *6* — air lift, *7* — solenoid valves, *8* — flowmeters. *9* — thermostatic bath. *10* — sludge recycle. *11* — sludge wastage

Before starting the tests with NPE, the plant was fed with glucose plus nutrients until a biomass concentration in the oxidation basin was of about 1.4 kg $MLSS/m^3$.

During the NPE removal tests, about daily, liquid samples were withdrawn to determine the inlet and outlet NPE concentrations (BIAS method [6]), inlet and outlet COD, the biomass concentration in the basin and in the settler weir overflow (by filtration and weighing with a 0.45 μm Millipore membranes).

3. RESULTS AND DISCUSSION

During the test without the antifoaming agent a thick layer of foam was always observed on the liquid free surface of the oxidation basin; this foam layer disappeared when the antifoaming agent was added.

According to the plant diagram shown in fig. 2, the NPE nonsteady state mass
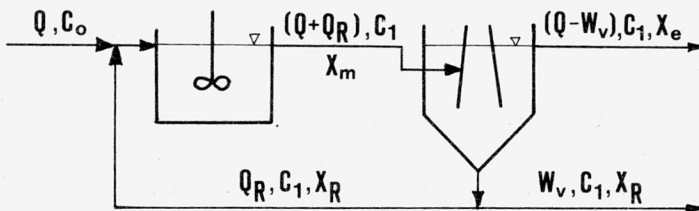

Fig. 2. Plant flow diagram

balance for the oxidation basin (assumed as perfectly mixed) is:

$$Q\bar{C}_0 + Q_R C_1 - (Q + Q_R)C_1 - \frac{dE}{dt} = V\frac{dC_1}{dt}, \tag{1}$$

where dE/dt is the global biological removal rate of NPE, which is assumed to occur in the oxidation basin only. Simplifying and introducing the finite differences we get:

$$\Delta E = Q(\bar{C}_0 - C_1)\Delta t - V\Delta C_1. \tag{2}$$

The C_1 values are determined at subsequent time intervals Δt, $\bar{C}_0$ and Q are listed in tab. 1 (test no. 1 and 2 without and with the antifoaming agent, respectively). The

Table 1

Preliminary test results

Test	$Q \cdot 10^3$	t	Δt	$\bar{C}_0 \cdot 10^3$	$C_1 \cdot 10^3$	X_m
no.	m³/h	h	h	kg/m³	kg/m³	kg/m³
1	9.1	50.5	50.5	7.26	2.08	1.46
		67	16.5		2.48	
		86	19		3.10	
		110	24		3.18	
		135.5	25.5		4.41	
		157.5	22		4.34	
		183	25.5		2.49	
2	9.1	18	18	7.26	2.11	1.21
		43	25		2.20	
		89	46		1.73	
		114	25		2.20	
		141.5	27.5		3.73	
		162.5	21		2.54	
		192	29.5		2.67	
		212	20		2.43	
		267	55		1.31	
		288	21		2.82	

integral values $\Sigma\Delta E/VX_m$) (for the average biomass concentration X_m in the oxidation basin, see tab. 1) are drawn versus time in fig. 3 either for test no. 1 (dark points) or no. 2 (white points). A straight line results for both tests; its slope is equal to the average NPE specific removal rate α_m. The obtained α_m values and the average operating conditions of the plant are listed in tab. 2.
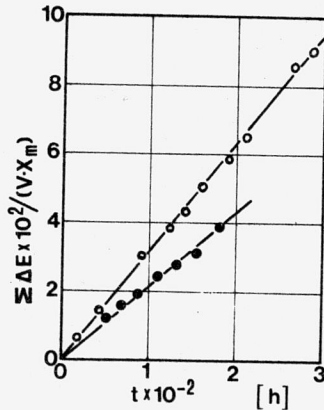
Fig. 3. Preliminary tests: $\Sigma\Delta E(VX_m)$ vs. time

● − NPL alone, foaming system, ○ − NPE + antifoaming agent

Not withstanding the sludge age ϑ_c and the feed sludge load factor F_c are not the same for the two tests (ϑ_c and F_c for test no. 2 are 17% lower and 21% higher, respectively, than those for test no. 1), the α_m and the mean NPE removal percentage R for test no. 2 are about 47% and 23% higher, respectively, than those for test no. 1.

Therefore the presence of antifoaming agent increases the biological specific removal rate and the mean NPE removal percentage. These increases are probably due to a physical mechanism: the antifoaming agent, dissolving the foam, allows the transfer of NPE molecules in the mixed liquor favouring their contact with the microorganisms. On the other hand, the percentage increase of R in the presence of antifoaming agents is about the same percentage of the initial surfactant, present in the foam for air bubbling conditions similar to those in the oxidation basin.

On the basis of these encouraging preliminary results, another run was carried out, starting with a larger initial biomass concentration in the oxidation basin (about 2.2 kg MLSS/m^3) and a larger NPE feed concentration (about 20×10^{-3} kg/m^3); many operating conditions were tested (tab. 2).

For the first 110 hours a foam layer was observed on liquid free surface of the oxidation basin; then the foam disappeared. This occurred when the outlet NPE concentration became lower than about 2×10^{-3} kg/m^3.

Figure 4 shows the obtained $\Sigma\Delta E/(VX_m)$ values versus time for this last run. Since straight lines result for each operating condition, as it is shown in the figure, α_m values calculated from the slopes and the mean values of the characteristic parameters are listed in tab. 2. In fig. 5 all the obtained α_m values are drawn versus F_c (for the symbols see tab. 2); the α_m values relative to the plant operations without foam formation (square white points) are larger than those when foam is present. Correspondingly the R values are also higher. This seems to occur (tab. 2) when the

Test results and

Symbol	Run time	$Q \cdot 10^3$	$\bar{C}_0 \cdot 10^3$	$\bar{C}_1 \cdot 10^3$	X_m	X_e	W_m
	h	m³/h	kg/m³	kg/m³	kg/m³	kg/m³	kg/d
●	0–183	9.1	7.26	3.15	1.46	0.078	–
○	0–288	9.1	7.26	2.37	1.21	0.077	–
◪	0–110	9.1	20.3	4.86	2.14	0.020	13.4
□	110–322	9.1	20.3	1.33	4.45	0.020	–
□	322–626	18.9	20.8	0.43	5.15	0.014	–
□	626–748	39.4	20.0	0.59	6.84	0.004	30.4
□	748–820	9.1	19.7	0.43	7.30	0.006	24.4
□	820–965	18.9	21.1	0.39	7.19	0.010	23.3
□	965–1020	39.4	19.8	0.56	6.68	0.010	30.0

sludge age is greater than 20–25 days; under these conditions the biological percentage removal of NPE is higher than 97% and can be considered satisfactory.

For lower ϑ_c values the NPE percentage removal is not so high and a foam layer is usually present on the liquid in the oxidation basin. Under these conditions the
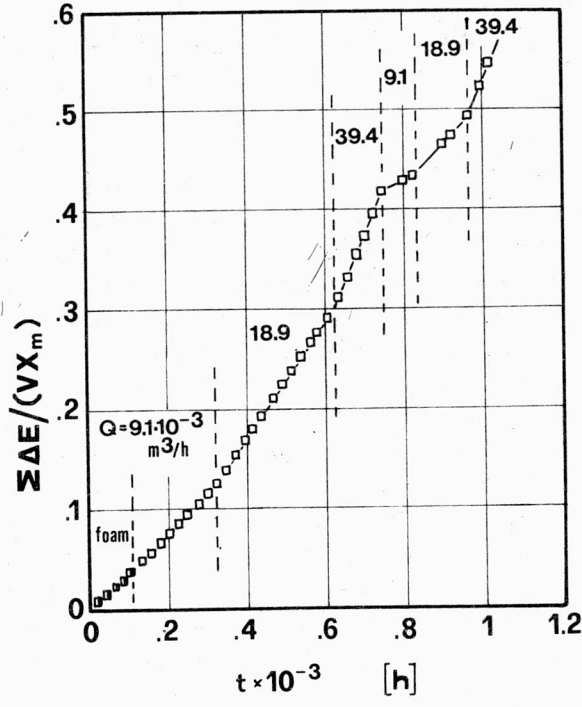

Fig. 4. Last run with NPE alone: $\Sigma \Delta E (V X_m)$ vs. time (for the symbols see tab. 2)

Table 2

operating conditions

| R	$F_c \cdot 10^3$	$\alpha_m \cdot 10^3$	ϑ_c	Remarks
%	d^{-1}	d^{-1}	d	
56.6	9.00	5.16	10.3	NPE alone: foaming system
69.4	10.9	7.57	8.60	NPE + antifoaming agent
76.0	17.3	8.29	14.4	NPE alone: foaming system
93.4	8.25	9.25	122	NPE alone: non-foaming system
97.9	15.2	13.7	97.3	NPE alone: non-foaming system
97.1	23.0	23.4	24.0	NPE alone: non-foaming system
97.8	4.88	4.54	34.1	NPE alone: non-foaming system
98.2	11.1	10.0	31.0	NPE alone: non-foaming system
97.1	24.6	22.6	20.4	NPE alone: non-foaming system
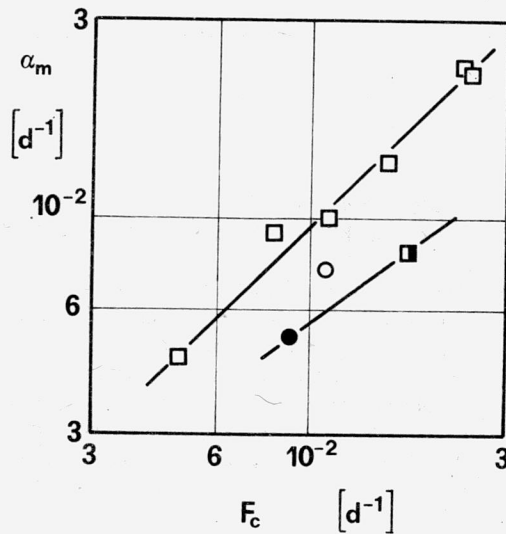
Fig. 5. α_m vs. F_c for the various operating conditions (for the symbols see tab. 2)

dosage of few ppm of antifoaming agent may be a simple practical tool to increase the NPE removal to the extent corresponding more or less to the surfactant present on the destroyed foam layer. In our plant, in fact, this occurred with a γ_c value equal to 10.3 days.

As shown in fig. 5, the effect of antifoaming agent is lesser than that obtained with

more aged sludge (round white point). However, the antifoaming dosing can be taken into consideration because the industrial activated sludge plants generally work with not too high sludge ages.

ACKNOWLEDGEMENTS

REFERENCES

[1] KRAVETZ L., *Biodegradation of non-ionic ethoxylates*, J. Am. Oil Chem. Soc., 58, 59A (1981).

[2] KRAVETZ L., *Biodegradation of non-ionic surfactants: alcohol ethoxylates vs. nonyl phenol ethoxylates*, Text. Chem. Colorist, 15, 57 (1983).

[3] KRAVETZ L., CHUNG H., GUIN K. F., SHEBS W. T., SMITH L. S., *Primary and ultimate biodegradation of an alcohol ethoxylate and a nonyl phenol ethoxylate under average winter conditions in the United States*, Tenside Detergents, 21, 62 (1984).

[4] NARKIS N., HENEFELD-FURIE S., *Israel's use of non-ionic surfactants*, Water Sewage Wks., 124, 69 (1977).

[5] NARKIS N., BEN-DAVID B., *Adsorption of non-ionic surfactants on activated carbon and mineral clay*, Water Research, 19, 818 (1985).

[6] WICKBOLD R., *Zur Bestimmung nichtionischer Tenside in Fluss und Abwasser*, Tenside Detergents, 9, 173 (1972).

WPŁYW ŚRODKÓW PRZECIWPIENIĄCYCH NA BIOLOGICZNE USUWANIE NIEJONOWYCH ZWIĄZKÓW POWIERZCHNIOWO CZYNNYCH

Przedstawiono usuwanie niejonowego związku powierzchniowo czynnego (oksyetylowany nonylo-fenol — NPE) w pierwszym stopniu biologicznego oczyszczania. Doświadczenia wykonano w skali laboratoryjnej, w instalacji z osadem czynnym o ciągłym przepływie. Stwierdzono zadowalające usuwanie NPE — średnio 97%, przy czym wiek osadu przekraczał 20–25 dni. Poniżej tego zakresu stopień usunięcia NPE zmniejszał się, w zbiorniku utleniającym zaś na wolnej powierzchni cieczy pojawiała się piana. W tych warunkach dodanie kilku ppm silikonowego środka przeciwpieniącego umożliwiało zwiększenie stopnia usuwania NPE (na skutek rozpuszczania piany).

ВЛИЯНИЕ ПРОТИВОПЕННЫХ СРЕДСТВ НА БИОЛОГИЧЕСКОЕ УДАЛЕНИЕ НЕПОЛНЫХ ПОВЕРХНОСТНО АКТИВНЫХ СОЕДИНЕНИЙ

Представлено удаление неполного поверхностного активного соединения (оксиэтилен нонилфенола — NPE) в первой степени биологической очистки. Эксперименты проведены в лабораторном масштабе в установке с активным осадком постоянного течения. Было установлено удовлетворительное удаление NPE — в среднем 97%, при чем возраст осадка превышал 20–25 дней. Ниже этих пределов степень удаления NPE понижалась, а в окисляющем бассейне на свободной поверхности жидкости появлялась пена. В этих условиях добавление нескольких ppm силиконного противопенного средства позволяло увеличить степень удаления NPE (вследствие растворения пены).