Conditions of surface-active agents in wastewaters from laundries of railway enterprises

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***Abstract*— Conducted a research to definition of the critical concentration of micelle formation (CCMF) of anionic surface-active substance (further in the text – SAA, or surfactants) - sulfonol in industrial waste water. This research is necessary to understand the condition of sulphonol in wastewater in the presence of suspended solids and oil products. It is an important step for the choice of waste water treatment method for such enterprises as: laundries, serving railway enterprises or car washing facilities.**

***Index Terms* — anionic surface active agents, critical concentration of micelle formation (CCMF), oil products**

I. Introduction

The main source of hydrosphere pollution is industrial wastewater, which carry with themselves a wide range of toxic components into the water bodies. The most widespreaded pollutions of railway transport enterprises are surface-active agents (surfactants) and petroleum products.

Surfactants are able to accumulate themselves in the objects of environment and are able to negatively influence on flora and fauna, impair the organoleptic properties of the water, make slower the self-purification processes in waterbodies.

Even a small concentration of surfactant (0.8-2 mg/l) in water bodies causes an excessive foam formation, breaks down the oxygen metabolism, that leads to the death of fish. The surfactants in water bodies increase the concentration of dissolved oil products, as they emulsify themselves in top layer of surface-active substances.

Surface-active agents (further in the text – SAA) produce a toxic effect upon a human.

Penetrating into the skin, they reduce its protective functions, they make the delivery of other chemicals into the skin lighter and increase the effect of allergens [1].

II. Results and Discussions

Contents of SAA in water environment can be determined by the following methods [2]:

- *Polarographic method,* takes advantage of the ability of SAA to adsorb itself on the surface of the drop-mercury electrode, or change the amount of potential desorption;
- *Volumetric methods* of titration of anionic SAA by cationic and, on the contrary, titration of cationic SAA by anionic;
- *Extractiv-photometric methods* base on the formation of ionic associates from the surface-activ ion with the cation of dye-stuff (to determine SAA in natural waters)
- *Infrared spectroscopy* of ionic associates of SAA.
- *Photometric method* put into use the generation of intergrated compounds of SAA with methylene blue, 4-thiocyanatoaniline-cobalt, etc.;
-*Investigate the* gas-liquid, liquid, column and thin-layer c*hromatograph;*
- *Fluorescence method.*

There have been investigated the dynamics of wastewater content from laundry facilities belong to railway station of Khabarovsk-city, Russia. The following contents of wastewater were measured:

- the content of suspen. material
- total content of oil
-total content of anionic surfactants (SAA)
- chemical intake of oxygen (CIO)

The concentration of anionic surfactants (SAS) and petroleum products in waste water were determined by the fluorescence method with the help of device "Fluorat-02-03" [4, 5].

The constant parameter in wastewater during twenty-four hours is only pH (10 - 11). During a day, the concentration of other pollutions is constantly changed in wide range, as wash-machines work asynchronously:

- Anionic surfactants (sulphonol)	- 0,5 - 32 mg / l;
- suspen. material	- 3,5 - 140 mg / l;
- Oil products	- 1 - 12 mg / l;
- Temperature	- 20 - 90 ^{o}C;
- CIO$^-$	- 40 - 1000 mg O_2 / l.

Due to the high alkalinity in waste water the content of ions $Fe^{2+, 3+}$ in sewers were not founded. Wastewaters from laundry facilities arrive into the city canalization collector and further flow to the city treatment plants for sewage. The indicators of wastewater at dumping it into the city collector exceed all the parameters of admissible concentrations in 10 – 30 times.

Taking into consideration, that laundry wash-machines are working asynchronously, the concentration of averaged wastewaters exceed the maximum permissible concentration more than ten times.

Sulphonol, as other surface-active substances, is able to generate colloidal solutions, depending on its concentration in water and the availability of impurities.

The interaction and pushing out energy of hydrophilic and hydrophobic parts of molecule of the surfactant are balanced themselves with the polar molecules of water. Here takes place a process of micelles formation.

In this case, sulphonol cannot exist in water any more in form of the separated molecules or ions. Molecules approach to combine with their hydrophobic parts. By doing so, the molecules protect themselves from water with their hydrophilic parts. Such concentration of sulphonol (surfactant) when similar phenomena occur is called the *critical concentration of micelle formation* (CCMF) [6].

Thus, the critical concentration of micelle formation (CCMF) is interpreted as the concentration of surfactants (SAS), wherein appear the micelles in its solution. Therewith the micelles are in equilibrium with the molecules and ions of SAS (surfactant).

Many physical and chemical properties of the solutions (scattering of light, electrical conductivity, surfaced tension of liquid, etc.) are sharply changed when the *critical micelle concentration* is reached.

Being in wastewater the surfactants and sulphonol also can presented themselves in form of molecules (ions) or in colloidal condition.

From this depends on the choice of the method of sewage treatment from these components.

The use of photo-electro-colorimetric device and conductometric device (“Anion 410-K”) allow to determine the *critical concentration of micelle formation* of sulfonol for the model wastewater drains.

The polluted compositions for water were prepared from laundry detergent "Lotus", which content of sulfonol is 7,4% (technical requirements TR 2381-175-00209645-99). Interval of concentration of sulfonol was $10{,}63\cdot10^{-7}$ mole/l (0,37 mg/l) ÷ $1{,}85\cdot10^{-2}$ mole/l (64,387 mg/l), pH =10,9 ÷11,2, temperature $25^{O}C \div 28^{O}C$.

As additives were used oil products (summer diesel fuel) 0,5 ÷15 mg/l, fine-dispersed SiO_2 30 ÷150 mg/l.

Different concentrations of pollutants prepaid for the modeling wastewater were correlated with the real parameters of pollutions in real wastewater from railway laundries.

To determine the *critical concentration of micelle formation* (CCMF) was measured the optical density (D) of the water compositions (pollutions), at a wavelength λ= 490 nm, and length of cuvette is $1_{cuvette}$=50 mm, using photo-electro-colorimetric method.

Along with it, the *critical concentration of micelle formation* was also determined by *conductometric method*. In so doing, was measured the specific electrical conductivity of model water solutions (æ).

The amount of *critical concentration of micelle formation* (CCMF) was also registered graphically. In this case, the amount of CCMF was registered in the intersection point of the tangent lines with the straight sections of the isotherms of the optical density and the lines of specific electrical conductivity. The received results are presented in Fig. 1 and 2 and in Table 1.

Analysis of the data shows that the *conductometric method* traps the structural variations in colloidal systems at lower concentrations of sulfonol (7,9·10-5 mole/l), compared with the *photo-electro-colorimetric method* (8,3·10-4 mole/l). That mean, that c*onductometric method* is more responsive (sensitive).

Adding hydrophilic finely dispersed SiO_2 110 mg/l (simulates suspended solids) to modeling solution of sulfonol leads to proportional reduction of CCMF determined by any of the methods of research. However, at the same time slightly reduce the stability of the micelles because of decreasing their diffusion layer. Later, this may contribute to the coagulation process.

Adding oil products to the model solution to 15 mg/L also leads to some reduction of CCMF determined by conductometric method ($\Delta C_{sulfonol}$ = 0,38 ÷ 10-5 mol/l) which is consistent with published data. Photo-electro-colorimetric method was not fixed such dependence in this range of added oil products.

Data of changes of CCMF of sulfonol in the model wastewater joint adding oil and SiO_2 are further confirm the above results.

Taking into account that the content of sulfonol in wastewater facilities reached 35 mg/l, and based on the graphs (Figs. 2, 3) it has been found experimentally that at low concentrations (to 20 mg/l) sulphonol is only in ionic state. With increasing sulfonols concentration (30÷35 mg/l) sulfonols structure begin to change, and is sulphonol in ionic form and micelles form.

The presence oil and suspended solids in the wastewater and pH=10÷11 shifts the state of sulfonol aside to micelle. This process is also enhanced by the presence in the waste water of sodium (Na), as component of SAS "Lotus". The latter conclusion is consistent with the literature.

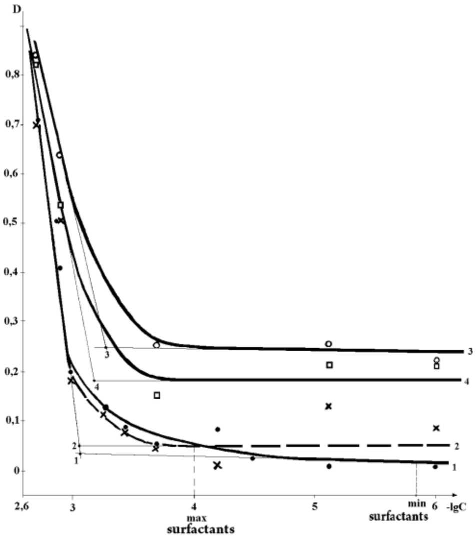

Figure. 1. Dependence of the optical density of the of water solutions from the concentration of sulfonol: 1 - solution of "Lotus" detergent; 2 - solution of "Lotus" detergent, oil- 15 mg/l; 3 - solution of "Lotus" detergent, of weighed substances- 110 mg/l; 4 - solution of "Lotus" detergent, oil- 7 mg/l, weighed substances - 60 mg/l.

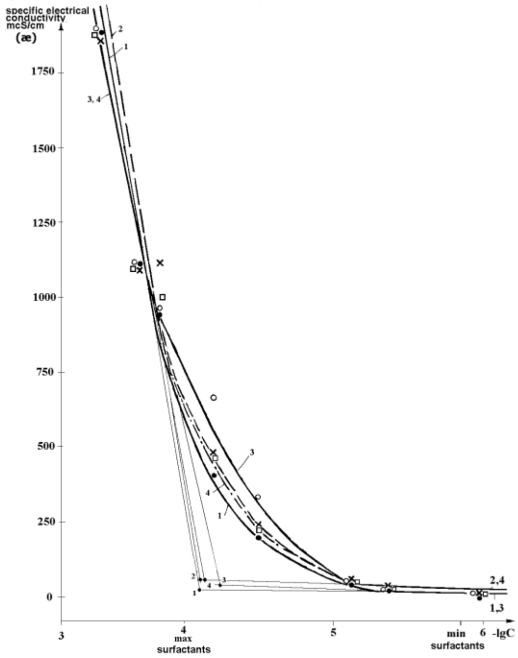

Figure. 2. Dependence of specific electrical conductivity of water solutions from concentration of sulfonol：1 - solution of "Lotus" detergent; 2 - solution of "Lotus" detergent, oil -15 mg/l; 3 - solution of detergent "Lotus", suspended solids - 110 mg/l; 4 - solution of detergent "Lotus", oil -7 mg/l, weighed substances - 60 mg/l.

TABLE I. THE VALUE OF CCMF OF SULFONOL DEPENDING ON METHODS OF DETERMINING (PH = 10.5÷11, T° = 25°C)

Composition of model westewater	**Methods of determining**					
	Conductometric method			**Photo-electro-colorimetric method**		
	-lg(CCMF)	***CCMF***		***-lg(CCMF)***	***CCMF***	
		mol/l	***mg/l***		***mol/l***	***mg/l***
1. solution of "Lotus" detergent	4,1	$7{,}94 \cdot 10^{-5}$	27,6	3,08	$8{,}3 \cdot 10^{-4}$	289,5
2. solution of "Lotus" detergent, oil -15 mg/l,	4,12	$7{,}59 \cdot 10^{-5}$	26,39	3,05	$8{,}9 \cdot 10^{-4}$	310,2
3. solution of detergent "Lotus", suspended solids - 110 mg/l	4,25	$5{,}62 \cdot 10^{-5}$	19,57	3,28	$5{,}2 \cdot 10^{-4}$	182,6
4. solution of detergent "Lotus", oil -7 mg/l, weighed substances - 60 mg/l.	4,15	$7{,}08 \cdot 10^{-5}$	24,6	3,2	$6{,}3 \cdot 10^{-4}$	219,6

III. CONCLUSIONS

Based on this research, the following conclusions:

1. The composition of waste water laundry service in all parameters (content of surfactant, suspended solids, oil) varies during the day in a wide range. Because of the asynchronous operations of washing machines. Therefore it is necessary a mandatory average wastewater before treatment.

2. Conductometric method of determining the CCMF is more sensitive to the structural changes of sulfonol compared with photo-electro-colorimetric method.

3. At concentrations of 0.5 mg/l to 20 mg/l sulphonol is present in the effluent laundry only in ionic form. Concentration increases up to 32-35 mg/l sulphonol goes into the micelle state. This should be considered in the selection process scheme for wastewater treatment.

3. In laundry wastewater concentrations of 0,5 mg/l to 20 mg/l sulphonol is only in the ionic form. Concentration increases up to 32-35 mg/l sulphonol goes into the micelle state. This should be considered when choosing process scheme for wastewater treatment.

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