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TOXICOLOGICAL ASSESSMENT OF DIFFERENT TYPES OF WASTE OILS

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Introduction

Nowadays, many different oils are used in industries and by the individuals. Oils are ageing and losing their properties as they are used for their intended purpose and, as a result, become waste. The amount of waste oil produced increases every year, and the amount and type of pollutants can vary widely. As a consequence, used oil poses a serious risk to the environment and human health.

Special requirements are applied to the deposit and storage of waste oils. They are collected in separate containers that are resistant to oxidation processes, free from damage and

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deformation, and have tightly closing lids. Unauthorized dumping or burning causes contamination of soil and water resources, and causes various degrees of disease for humans. In addition, the discharge of waste oils into the soil and water bodies exceeds the accidental discharges and losses of oil during their extraction.

But despite the environmental hazards of the waste oils produced, they have valuable properties. A well-functioning mechanism for recycling waste oils enables them to be recycled to production or the consumption sector as secondary by-products, ensuring real savings of resources [1].

When in use, oils are exposed to the action of air, temperature and other factors, which change their properties [2]. It is worth noting that all these factors work together and mutually enhance one another. For example, the presence of water causes oxidation of the oil. This also leads to biocontamination in contact of water with oil. Oils, containing contaminants, which are not capable of fulfilling their requirements, must be recycled and replaced with the pure oils.

The idea of recycling of lubricating oil appeared in 1930s. However, waste oils only became recycled about four decades ago. Initially they were burned for energy, then after purification they were added to fresh oils [4]. Today, however, the direction of recycling used oil can differ significantly from its original use.

The high ecotoxicity, chemical aggressiveness, complex structure, and reduced recyclability of waste oils make the choice of the way of recycling difficult. As a rule, this choice depends on the level of industrial development of the country (region) and other equally important factors, but environmental safety, economic feasibility, as well as the possibility of obtaining secondary products with minimum costs from used oils are the main criteria for this technological process [3, 5-11].

One of the applications for used engine and vegetable oils is their use as a binder for anticorrosion coatings. Due to the rising cost of producing them from conventional raw materials and the global problem of depleting natural resources [12], this method of used oils recycling is very attractive. The compounds contained in waste oils are strong surface-active substances which can significantly affect the structure formation process and consequently the bulk and surface properties of the resulting anti-corrosion coating.

To examine this suggestion, a toxicological assessment of the waste oil must be conducted. This is essential for selecting the principles of safe handling, for developing the corrosion protection coating technology, and for compiling the necessary technical and environmental documentation.

Thus, the purpose of this paper is to conduct a toxicological assessment of waste oils by determining the class of hazard.

The objects of the study are used engine (semi-synthetic), industrial and cooking (sunflower, linseed) oils.

Main body

The class of hazard of waste oil is defined on the basis of Order No. 536 of the Ministry of Natural Resources and Environment of the Russian Federation dated 04.12.2014. According to the order, the criteria for assigning waste to classes of hazard I to V by the degree of negative impact on the environment are:

- the degree of danger of the waste to the environment;

- the dilution rate of the aqueous waste extract at which there is no harmful impact on hydrobionts [13].

When defining the class of hazard, priority is given to the experimental (biological) method of identifying it by the dilution rate of the aqueous extract. But before that, it must be defined by calculation (environmental hazards), in order to select the parameters of the experiment. Data on the content of waste oils are shown in Table 1.

Waste oil	Results		
	Mineral content, %	Humidity, %	
Engine oil	0.06	0.54	
Industrial oil	0.02	0.9	
Sunflower oil	0.04	0.75	
Linseed oil	0.05	0.48	

Table 1. The composition of waste oils

Due to the complexity of the calculation, which involves identifying the composition of the waste oil and finding the MPC of pollutants, the calculation is approximated. For example, used engine oil and industrial oil have been classified as class II-III of hazard, and cooking oil as class III-IV of hazard. We tested the data obtained experimentally.

Ceriodaphnia affinis was used as a test subject. The Daphnia are one of the standard objects for testing the toxicity of aqueous solutions of chemical compounds used in aquatic pollution studies. The Daphnia are sensitive even to small concentrations of toxic substances. A minimum of two test objects must be used for biotesting and final conclusions.

An aqueous extract from a waste oil sample is prepared with the ratio solid phase: liquid = 1:10. The liquid used is cultivation water (tap water that has been settled for at least three days) or distilled water. For this purpose, 20-30 g of oil is diluted with cultivation water at a ratio of 1:10, the resulting mixture is stirred on a magnetic stirrer for 8 hours and then left to stand for 12 hours.

The resulting aqueous extract is tested for toxicity. Extraction temperature is 20 °C, pH value = 7. A number of dilutions are prepared from the original extract: 1:10, 1:100, 1:1000, 1:10000. The experiment at each dilution is conducted in three iterations.

Ten Ceriodaphnia species are placed in each solution for 48 hours, after which the surviving species are counted. From the data obtained, the average value for each concentration (Table 2) and the average percentage of mortality *A* (Table 3) are obtained. The class of hazard is determined by a graphical method using a probit analysis [14].

Waste oil	Indicators	Concentration, %				
		100	10	1	0.1	0.01
Engine oil	Number of survivors of 10 Ceriodaphne species	Ω	2	5	9	10
		$\mathbf{0}$	1	4	8	10
		Ω	$\overline{2}$	6	10	10
	Average survival rate	θ	1.6	5	9	10
	Survival rate in the control	10	10	10	10	10
Industrial oil	Number of survivors of 10 Ceriodaphne species	Ω	Ω	4	9	9
		$\mathbf{0}$	Ω	3	7	8
		Ω	θ	3	9	9
	Average survival rate	Ω	Ω	3.3	8.3	9.0
	Survival rate in the control	10	10	10	10	10
Sunflower oil	Number of survivors of 10 Ceriodaphne species	1	$\overline{2}$	6	8	9
		1	3	5	8	10
		1	$\overline{2}$	6	9	10
	Average survival rate	1	2.3	5.6	8.3	9.6
	Survival rate in the control	10	10	10	10	10
Linseed oil	Number of survivors	3	6	10	10	10
		$\overline{2}$	6	10	9	9
	of 10 Ceriodaphne species	3	7	9	10	10
	Average survival rate	2.6	6.3	9.6	9.6	9.6
	Survival rate in the control	10	10	10	10	10

Table 2. Results of biotesting of aqueous extracts

In order to plot and calculate the degree of toxicity, it is necessary to calculate the average percentage of mortality *A* [15].

$$
A = \frac{X_{\kappa} - X_m}{X_{\kappa}} \cdot 100,\tag{1}
$$

where X_k is the survival rate of the test objects in the control;

X_m is the survival rate of the test objects in the experiment.

Waste oil	Indicators	lgC				
		2		θ	-1	-2
Engine oil	$A, \%$	100	84	50	10	θ
	Value of the probit	7.33	5.99	5.00	3.72	
Industrial oil	$A, \%$	100	100	65	13	6
	Value of the probit	7.33	7.33	5.39	3.89	3.45
Sunflower oil	A, %	90	77	44	17	4
	Value of the probit	6.28	5.74	4.85	4.05	2.67
Linseed oil	$A, \%$	74	37	$\overline{4}$	4	4
	Value of the probit	5.64	4.67	3.25	3.25	3.25

Table 3. Results of the lethal concentration determination

Based on the values obtained, a plot of the probit value versus the logarithm of concentration is plotted (Fig. 1) and the concentration (dilution of the stock solution) at which 10% of the species are dead (at a probit value of 3.72) is defined. Based on the concentration value obtained, the hazard class is established.

FROM CHEMISTRY TOWARDS TECHNOLOGY STEP-BY-STEP

Fig. 1. Dependence of the probit value on the logarithm of concentration for used oil: *a* - engine oil; *b* - industrial oil; *c* - sunflower oil; *d* - linseed oil

The resulting lethal concentration is used to determine the hazard class according to Table 4.

Class of hazard	Dilution rate of the aqueous extract
	>10000
	10000-1001
III	$1000 - 101$
	< 100

Table 4. Dilution rates of the aqueous waste extract

The dilution rate is calculated according to the formula

$$
LC_{10} = \frac{100}{C},\tag{2}
$$

where C is the concentration at which 10% of the species are dead, %.

Conclusions and recommendations

Based on the experimental data obtained:

- for waste engine oil, the concentration at which 10% mortality occurs is 0.400%, which corresponds to a dilution of 250 - class of hazard III;

- for waste industrial oil, the concentration at which 10% mortality occurs is 0.031%, which corresponds to a dilution of 3225 - class of hazard II;

- for waste sunflower oil, the concentration at which 10% mortality occurs is 0.112%, which corresponds to a dilution of 891 - class of hazard III;

- for waste linseed oil, the concentration at which 10% mortality occurs is 0.500%, which corresponds to a dilution of 200 - class of hazard III;

Thus, knowing the class of hazard of the waste, it is important to develop a technology for its disposal to reduce its value.

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