UDC 630.456

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ECOLOGICAL INDICATOR OF ENVIRONMENTAL POLLUTION AND TECHNOLOGY FOR OIL REFINERY SEWAGE WATER TREATMENT

Introduction. The scale of manifestation and degree of environmental impact of the natural processes, as well as of the processes and industries created by man, are constantly increasing and are subjected to growing human influence. Furthermore, it is possible to distinguish several of the most significant factors, each of which does not improve the environmental situation of a specific object, region, state, and Earth as a whole.

According to the data of [1], a significant amount of solid wastes – ashes and slag wastes, as well as sewage water treatment sludges from galvanic production and oil refining are produced in Ukraine. In 2015, their number was 312267.6 thousand tons, and particularly in Ivano-Frankivsk region – about 2124.86 thousand tons. They are stored on large areas, which leads to contamination of soils and hydrosphere by rain, as well as pollution of atmosphere by air flows in dry weather. A similar situation of technogenic contamination of the environment is observed in all regions of Ukraine and close to foreign countries. It is the first significant factor of ecological hazard that necessitates development of new methods for their utilization and recycling.

In the manufacturing process in industrial waste emitted intense that contain environmentally harmful components (CO, NO_x, SO_2, H_2S) which pollute the atmosphere because of their inadequate cleaning. The emissions of pollutants into the atmosphere amounted to 105.5 kg per person in Ukraine in 2015 and those emissions in Ivano-Frankivsk region (mainly near Burshtyn TPP) were equal to 192.7 kg, which is another significant factor of environmental hazard.

The amount of "insufficiently purified" sewage waters that are discharged into rivers and other reservoirs, contaminating them, due to the lack of treatment facilities at some industrial sites or because of their inefficient operation is quite large. In general, approximately 4.15 billion m^3 of waste waters were discharged into the water system of Ukraine in 2005–2015 and approximately 58.6 million m^3 in Ivano-Frankivsk region in 2015. All of them pollute the hydrosphere and, accordingly, the environment, and together they determine the third important factor of environmental hazard. Other factors of pollution affecting the ecological situation are not so important.

Establishment of the generalized indicator of environmental pollution is extremely important for the society, since the assessment of ecological safety based on the same indicator allows adequate evaluation of the ecological situation in a separate territory, as well as its comparison with other territories and determination of its change for a certain period of time.

Estimation of the environmental pollution by various authors [2–4] is based on different indicators and according to the proposed methodology [5], the definition of the integral index of environmental safety of an object (IIESO) is conducted mainly taking into account the main industrial and environmental data of an enterprise and other indicators.

The IIESO definition includes calculations of the pollution factors (K^i) according to the data of the enterprise statistical reports: 2CP air report; 2CP report of the water sector; form No 1 – environmental costs; limits on wastewater discharges (GDS), gas emissions into the atmosphere, waste generation (sludge, slag, garbage), which are indicative of improvement or deterioration of the environmental conditions, and generalized indicator of the enterprise environmental safety.

The value of K_i is calculated according the ratio of identical indicators (amount of generated and discharged contaminants to their limits) $K_i = M_i/L_i$, where M_i – amount of pollutants, t/year; L_i – limit of pollutants, t/year. Based on the obtained K_i and other values related to individual objects, we determine the value of the IIESO in points by the formula

$$IIESO = \left[\frac{K_а + K_в + K_ш + K_р}{K_П} - \frac{K_З}{K_П}\right] \times 100 ,$$

where $K_а$, $K_в$, $K_ш$, $K_р$ – coefficients of pollution of the atmosphere, hydrosphere, and soils, as well as the coefficients of the risks influence, respectively; and $K_З$ – coefficient of environmental costs $K_З = E_З / CP$, where CP – cost of commodity products (services), thousand UAH /year; $E_З$ – total costs for environmental measures, thousand UAH/year; $K_П$ – coefficient of pollution of the territory, which is equal to $K_П = S_0/S_c$, where S_0 – area of the object, S_c – total area of the object with the sanitary protection zone (ha).

Based on the data on the main factors of environmental pollution and other data included in the above formula, the IIESO was calculated for the object "Oil refining" (OR) on the basis of the pollution coefficients K_i, which vary by their magnitude, since they are calculated based on annual statistical indicators of the enterprise activities.

The results of the calculations conducted indicate that the IIESO decreased in 2014 when compared to 2013 from 76 to 61, which is explained by deceleration of production activities (release of commercial products), and the amount of annual pollution changed slightly. However, the main factor that affects the IIESO size most of all is the amount and degree of wastewater treatment of the object, which is indicated by the coefficient $K_в$. For example, the coefficient was equal to 0.39 in 2011 and in 2012, it improved to $K_в$=0.617 due to an increase in the level of wastewater treatment, connected with the investment of 550 thousand UAH for improvement of the technology for water purification at the site. However, the threat of environmental pollution by slags and solid wastes stored at the facility increased in 2015. It is indicated by coefficient $K_ш$, since it decreased from 0.515 to 0.435 in 2015.

Thus, the definition of the IIESO makes it possible to establish the environmental friendliness of the facility for a certain period, as well as to increase the level of the facility environmental safety by means of redistribution of the resources to the relevant pollution factors.

Based on the above analysis of the IIESO, which had been also determined for other facilities, it was found that the greatest impact on the environmental pollution is exerted by the discharge of contaminated sewage waters into the water resources.

The most common pollutants of sewage waters according to the UNESCO data are oil impurities (o/i) – a group of hydrocarbons of oil, fuel oil, kerosene, as well as other lubricants and their additives, which are among the ten most dangerous environment pollutants due to their high toxicity.

Sources of sewage pollution by oil impurities are manufacturing enterprises, systems of transfer and transportation, oil terminals and oil reservoirs, oil refineries, warehouses for storage of oil products, railway transport, river and sea oil tankers, as well as their filling complexes.

A considerable impact on the environment is made by the waste waters of JSC "Naftokhimik Prykarpattya" contaminated by o/i and other harmful components that are considered to be complex heterogeneous systems, since they contain several contaminants belonging to different hazard classes due to their properties (hydrophilicity, dissolution et al).

In order to purify such complex water systems (waste waters) from harmful components, various technologies are known [6]. They differ in

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the fact that they use sedimentation depending on the need to separate certain contaminants, for example, suspended particles. Moreover, in order to increase the efficiency of this process, they perform coagulation of suspended particles with the help of the coagulation electrolyte.

Industrial waste waters are purified by various methods, the most important of which include the following: mechanical, chemical, physico-chemical, biological, and thermal.

The biological purification method [7] is the most widespread, since it makes it possible to remove a variety of inorganic and organic compounds, including toxic ones, from waste waters. However, it is characterized by low efficiency, which is confirmed by duration and degree of purification from suspended particles and o/i – around 65–75%.

The shortcomings of the biological method of wastewater treatment include large capital costs during construction, as well as the need for strict adherence to the technological treatment regime (a certain amount of nutrients for bacteria and water temperature of at least 100°C are required). Moreover, microorganisms are also affected by higher doses of certain metals. In addition, this method is power-consuming, since the blowing machines use a lot of electricity to supply air to the aeration tanks and they occupy large areas of land, on which the treatment facilities are located. The recent studies on the biological process are presented in publication [8], which describes the Anammox process. We also know the methods of physico-chemical oxidation-reduction of harmful components in the process of wastewater treatment [9–11] using the technique of supplying additional reagents or electrolysis, which allow converting soluble toxic components into the ones that are harmless for the hydrosphere. Since waste waters can be mainly contaminated only with mechanical (solid) particles and other pollutants in a minimum amount, their purification requires application of the filtering methods described in [12–15].

The OR mostly uses the mechanical or biological methods to purify sewage waters, however, the level of the contamination reduction is not high enough and amounts to 65-75%, which requires improvement of this process efficiency, since discharges are allowed while ensuring the normative indicators of pollution in the water body achieved mainly by dilution (a certain ratio of wastewater to the amount of pure water).

Thus, the improvement of the known technologies, equipment or effective materials of filtration loading to improve the OR wastewater treatment efficiency is a topical issue at present.

The objective of the work is to develop and test a new complex electrochemical-and-sorption technology for wastewater treatment, whose constructions will occupy smaller territories for the piping and instrumentation diagram. Thus, the purification level will increase. Therefore, we carried out a study on purification of the above mentioned waste waters from the OR contaminating natural water resources, thereby increasing the ecological hazard of the facility, region, and state.

Discussion and Results. When conducting the study, we used the waste waters of Naftokhimik Prykarpattya, JSC, containing on average 5.28-43.7 mg/dm^3 of o/i and 8.5–132.5 mg/dm^3 of mechanical impurities (suspended). The content of the ingredients in the waste waters was determined before and after purification using the procedures of [16]. Moreover, the degree of purification after the sedimentation tank and filter for individual ingredients was also determioned. Different samples of the clinoptilolite zeolite from the Sokyrnytske field were used. All of them are characterized by the following mean indicators: for fractions 0.5–3.0 mm, packed density – 1.1–1.18 kg/dm^3, specific surface – 20.1–40.8 m^2/g, pore dimension – 3.5–4.2 A.

In order to reduce the mechanical impurities (suspended matter) in sewage waters, researchers [7] offer thin-layer sedimentation tanks. Therefore, they used this type of sedimentation tank in the study, but it had another design than the one we had developed.

The laboratory setup (fig. 1) consist tank (1) for waste water, centrifugal pump (2), electrical device (3), horizontal sedimentation tank with the possibility of installing inclined planes (4), rectifier (5), sludge collection chamber (6), adsorber filter (7), and containers for collection of purified water (8). Wastewater treatment was carried out in the laboratory setup using the following technology.

The water from container (1) was supplied by pump (2) through electrical device (3) where electrochemical processes occur in the runoffs under the action of electric current (U = 8–10–12 V, I = 1.0–1.2 A). They cause flotation of the particles suspended in horizontal or thin-layer sedimentation tank (4) and affect different soluble contaminations, including oil products. The anode of the electrocoagulator is made of a metal tube (St3) and therefore it partially dissolves forming various compounds, which manifest coagulation properties. The sewage water samples were taken after sedimentation tank (4) and container (8). Then the change in the content of o/p and suspended particles, as well as other indicators, were determined and compared with the original ones that allowed defining the degree of their decrease. The studies were carried out under dynamic conditions in the following way.

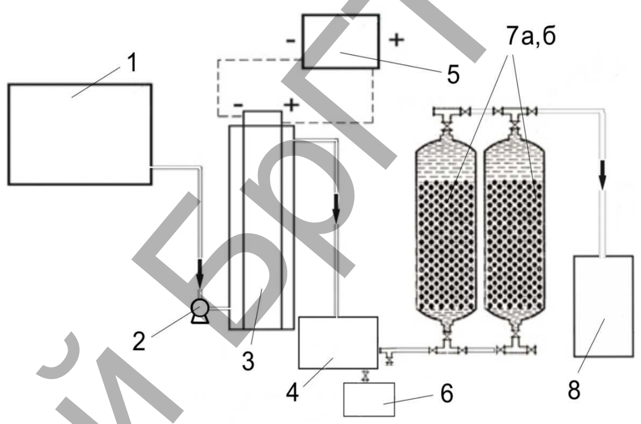

Figure 1 – Diagram of the laboratory setup for wastewater treatment

25 dm^3 of wastewater had been pumped with the help of pump (2) to the sedimentation tank from raw material container 1 for half an hour. Then it was forwarded for purification with the help of the filtration method through loading in filters (7a) and (7b). The sewage water purification from suspended particles was carried out using the horizontal sedimentation tank without and with inclined planes (IP) when changing the inclination angle of the IP and with preliminary electrical treatment by means of electrodes under various voltage parameters.

At the first stage, the sewage water treatment from suspended particles was carried out using the horizontal sedimentation tank without IP (sample 1). The results of the studies on the sewage water purification from suspended particles (mechanic impurities) and o/i are provided in table 1.

Based on the studies on wastewater treatment carried out and results obtained, it was established that the degree of reduction in the content of suspended matter increases to 93.8% and decrease in the content of o/i grows to 84.9%, which grows due to a change in the inclination angle of the planes in the thin-layer sedimentation tank, as well as depending on the content of the suspended particles and flow rate of the wastewater to be cleaned.

The studies were conducted in the following way **at the second stage**. The OR sewage water treatment was carried out using the developed electrical device. The cathode and anode are made in the form of different diameter cylinders, affecting the current density on their surface. Since it changes depending on the voltage on the electrodes, as well as on the composition and content of the polluting components in the wastewater, the amount of flotation and oxidized products of electrolysis will be different and will make an influence on the purification process efficiency. The results of the studies carried out with the help of the laboratory setup using real sewage waters of the OR type 1 (No of samples 1–3), 2 (No of samples 4–6), 3 (No of samples 7–9) are provided in table 2.

Based on the results of the OR sewage water treatment, an increase in the level of purification from mechanical suspended particles up to 87.1% and from o/p up to 95.89% was achieved when carrying out electrical treatment before the sedimentation tank.

Table 1 – Results of the wastewater treatment using the thin-layer sedimentation tank

Sample of sewage water \ Indicators		Sewage water indicators before treatment, mg/dm^3		Inclination angle of inclined planes α, deg.	Sewage water indicators after treatment, mg/dm^3		Degree of treatment, %	
		Suspended matter	O/i		Suspended matter	O/i	Suspended matter	O/i
1	OR	14.65	5.28	0	6.5	2.5	55.6	52.7
2	OR	14.65	5.28	30	3.5	1.9	76.1	64.0
3	OR	14.65	5.28	45	1.6	1.2	89.1	77.3
4	OR	14.65	5.28	60	0.9	0.8	93.8	84.9

Table 2 – Purification parameters and indicators of waste waters with electrical treatment

Sample No	Parameters		before purification, mg/dm^3		after purification, mg/dm^3		Degree of treatment, %	
	Voltage, V	Inclination angle of the planes,°	Suspended matter	O/i	Suspended matter	O/i	Suspended matter	O/i
1	8	30	12.32	20.5	2.9	0.4	76.5	95.3
2	10	30	12.32	20.5	2.4	0.45	80.5	94.7
3	12	30	12.32	20.5	2.0	0.35	83.7	95.8
4	8	60	16.6	31.6	2.8	0.35	83.1	93.8
5	10	60	16.6	31.6	1.9	0.25	88.6	95.5
6	12	60	16.6	31.6	2.5	0.3	84.9	94.6
7	8	45	8.5	6.2	1.3	0.45	84.7	92.7
8	10	45	8.5	6.2	1.1	0.5	87.1	91.9
9	12	45	8.5	6.2	1.2	0.55	85.9	91.1

Table 3 – Characteristics of sewage waters before and after purification

Sample No.	Zeolite characteristics		before purification, mg/dm^3		after purification, mg/dm^3		Degree of treatment, %	
	Fraction, mm	Specific surface	Suspended matter	O/i	Suspended matter	O/i	Suspended matter	O/i
1	0.5-1	20.5	50.2	2.2	2.3	0.2	90.9	95.4
2	1-3	23.7	50.2	2.2	4.1	0.15	93.2	91.8
3	0.5-1	20.5	76.5	3.8	4.3	0.25	89.0	94.4
4	1-3	23.7	76.5	3.8	2.5	0.15	95.8	96.7
5	0.5-1	20.5	98.6	8.6	2.8	0.25	97.1	97.2
6	1-3	23.7	98.6	8.6	3.2	0.30	96.5	96.7
7	0.5-1	20.5	132.5	6.4	5.3	0.45	92.9	96.0
8	1-3	23.7	132.5	6.4	7.1	0.5	92.2	94.6
9	3-5	23.7	132.5	6.4	8.3	0.6	90.6	93.7

In order to increase the efficiency of the OR wastewater purification from mechanical suspended particles, the sewage waters were treated using the method of filtration through the clinoptilolite zeolite from the Sokyrnytske Field (Zakarpattia region) **at the third stage**. The methods of the studies are described above. The results of the studies on purification of 9 wastewater samples during electrical treatment of sewage waters at the voltage of 10 V and at the IP inclination angle of 45^0 in the thin-layer sedimentation tank and filtration through loading of fractions of 0.5–1.0 mm, 1.0–3.0 mm and 3.0–5.0 mm from zeolite are provided in table 3.

The results of the wastewater purification show that filtration of the sewage water through finer zeolite fractions (0.5–1.0 mm) increases the level of purification up to 97.1% from o/i and 97.2% from mechanical suspended particles. However, the value of the this filtration cycle is shorter almost by one hour when compared to the fraction of 1.0–3.0 mm. Furthermore, the level of o/p purification decreases to 90.6% when being conducted through the fraction of 3.0–5.0 mm.

COD is often used as one of the indicators of water pollution. It is a generalized indicator of pollution, since it indicates the presence of reducing agents (organic and inorganic) in water. Therefore, this index was determined before and after purification with the help of method [16] in the next stage of the study.

The water purification technology at the fourth stage of the studies involves electrical treatment of the sewage water at the voltage of 10 V with formation of coagulant, separation of inorganic and organic impurities in the sedimentation tank with IP, and subsequent post-treatment through filtration loading with the zeolite-clinoptilolite fraction of 0.5-1.0 mm in column 7a and 1.0–3.0 mm in 7b. The results of the studies are shown in table 4.

Purification of the OR sewage waters with the help of the physico-electrochemical method according to the generalized COD index amounts to 91.1–94.6%, since the content of oil products and suspended particles decreases.

Conclusions

1. The efficiency of the treatment facilities operation affects the hydrosphere factor and environmental safety index of the facility as a whole, since the discharge of sewage water contaminants into the water resources decreases.
2. Based on the results of the conducted studies on purification of the OR waste waters, it was established that their preliminary electrical treatment and separation in the sedimentation tank with IP increase the level of wastewater purification from suspended matter by 10.4-14.8% and their filtration through the zeolite-clinoptilolite increases this level by 6÷12%.

Table 4 –Purification of the OR sewage waters using the electrochemical sorption technology

Number of Column	Sample Number of Water	Before purification			After purification			Degree of treatment α, %		
		Suspended matter, mg/dm^3	O/i, mg/dm^3	COD, mgO^2/dm^3	Suspended, matter, mg/dm^3	O/i, mg/dm3	COD, mgO^2/dm3	Suspended matter	O/i	COD
7a	**1**	42.6	43.7	673.09	4.0	3.0	48.09	90.6	93.1	92.9
	2	81.5	33.7	872.36	5.0	3.5	73.36	93.8	90.5	91.5
	5	35.1	20.3	635.44	2.2	1.8	35.44	93.7	94.4	94.4
	7	45.9	26.2	752.21	2.50	2.2	52.34	94.5	91.4	93.0
	9	55.3	17.3	564.85	4.2	0.9	50.43	92.4	94.8	91.1
	1	42.6	43.7	673.09	3.0	3.7	46.50	92.9	93.1	93.1
7b	**2**	81.6	23.7	872.36	3.4	2.0	62.38	95.8	91.5	92.8
	5	35.1	20.3	635.44	3.0	1.8	33.82	91.5	91.1	94.6
	7	45.9	26.2	752.21	3.1	1.3	51.34	93.2	95.0	93.1
	9	55.3	17.3	564.85	3.8	0.8	47.35	93.1	91.6	91.6

3. The proposed technology is used for effective purification of waste waters with the help of the physico-electrochemical method, since their electrical treatment before the sedimentation tank causes flotation of suspended matter and oil impurities into the upper part of the thin-layer sedimentation tank with the electrolysis gases. However, there is some zeolite, since it partially sorbs o/i and is easily subjected to regeneration.

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Материал поступил в редакцию 08.02.2018

BOHOSLAVETS M.M., CHELYADYN L.I., HLADUN M.R. Ecological indicator of environmental pollution and technology for oil refinery sewage water treatment

The researches have shown that sewage treatment in cylindrical electric devices in front of septic tank increases the purification degree by 82.9% in the thin layer tank and in front of the filter the contamination section by 95.8% and in the filter when filtered through zeolite layer by 91.1-94.6%. Electric treatment of sewage in the cylindrical electric devices and contamination sections in the thin layer tank.