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THE LIQUID WASTE DISPOSAL INNOVATIVE TECHNOLOGIES OF PRINTING ENTERPRISES

Introduction

Traditionally, printing technologies are associated in the public mind with a negative impact on the environment. This is due to the presence of emissions containing an almost complete list of chemicals from Mendeleev's table. Despite the intensive implementation of modern digital printing technologies, there is no significant improvement in the ecology of the publishing business¹. This is due to the presence of special waste, the disposal of which requires significant costs and is subject to control. The providing the environmental safety of printing enterprises the wastewater has gained increased attention in recent years. That why the introduction of circulating water and industrial effluents parameters strict monitoring is very important². In this case the special attention should be paid to the water reuse and effective purification in a closed technological cycle³.

On the base of the printing enterprises wastewater structural components analysis was identified the main sources of pollutants: ⁴ – silver-containing film developer and fixative during the preparation of offset printing for photographic reproduction; – cleaning agents for washing printing machines; – correction agents residues for printing forms and cleaning solutions; – waste from the processing of printing plates with dichromate, etc.

1 Shtefan, Y., Roik, T., Zorenko, O., & Shostachuk, O. (2021). Methods of Digital Control of Printing Processes. Technology and Technique of Typography (Tekhnolohiia I Tekhnika Drukarstva), 2(72), 54–63. [https://doi.org/10.20535/2077-7264.2\(72\).2021.242474](https://doi.org/10.20535/2077-7264.2(72).2021.242474)

2 European Commission [Science for Environment Policy. The solution is in nature. Future Brief 24. Brief produced for the European Commission DG Environment]. (2021). Bristol: Science Communication Unit, UWE Bristol.

3 Gikas, P. (2017). Towards energy positive wastewater treatment plants. Journal of environmental management, 203, 621-629.

4 Shtefan, Ye., & Serogin, O. (2022). Energy-saving technologies for disposal of waste with printing design elements. Theoretical and practical aspects of modern scientific research : collective monograph. Compiled by V. Shpak; Chairman of the Editorial Board S. Tabachnikov. Sherman Oaks (pp. 91-103). California : GS Publishing Services, 256 p.

Printing pigments – dyes in the form of salts formed from phosphorous-tungsten, phosphorous-molybdenum and sulfonic acids (varnishes) should be singled out separately. The sources of wastewater pollution with synthetic dyes both at the enterprises where they are manufactured and at the enterprises where they are used in technological processes can be conditionally divided into three groups:

- waste water, which is formed at the stages of filtration (separation of dye in the technologies of its production and separation of the dyed substance in the technologies of dyeing);
- waste water generated from washing of technological equipment;
- surface water, the dye contamination of which occurs as a result of washing contaminated surfaces.

One of the main problems of wastewater arises during dyeing and printing of textile materials⁵.

There are three categories of the most widespread methods of extracting dyes from the aqueous phase: chemical (coagulation, oxidative: processes with enhanced oxidation, ozonisation, photochemical reactions; electrochemical destruction; electrochemical coagulation), physical (adsorption, membrane separation, ion exchange, radiation exposure) and biological purification⁶.

When implementing a closed system of technical circulating water supply the water purification can be carried out by different ways.

The traditional cleaning methods are technological. Flotation (aeration) provides technical water purification from suspended particles⁷. In this case, it is necessary to take into account the water physical, chemical and biological characteristics in order to select a rational scheme for their treatment⁸. It was suggested to use osmosis and membrane distillation from colloidal, organic substances and toxic metals ions⁹. The main advantages of the proposed process compared with traditional separation are: small footprint, environmentally friendly, corrosion, etc. In our opinion, this is an expensive method for large water volumes processing. It was

5 D. A. Yaseen1 & M. Scholz. Problem of wastewater arises during dyeing and printing of textile materials / International Journal of Environmental Science and Technology (2019) 16:1193–1226

6 Dafnopatidou, E. K., & Lazaridis, N. K. (2008). Dyes removal from simulated and industrial textile effluents by dissolved-air and dispersed-air flotation techniques. *Industrial & engineering chemistry research*, 47(15), 5594-5601. doi: <http://doi.org/10.1021/ie071235n>.

7 Au, M. T., Pasupuleti, J., & Chua, K. H. (2013, June). Strategies to improve energy efficiency in sewage treatment plants. In IOP Conference Series: Earth and Environmental Science (Vol. 16, No. 1, p. 012033). IOP Publishing.

8 Hasan, A., Salem, A. R., Hadi, A. A., Qandil, M., Amano, R. S., & Alkhalidi, A. (2021). The power reclamation of utilizing micro-hydro turbines in the aeration basins of wastewater treatment plants. *Journal of Energy Resources Technology*, 143(8).

9 Roy, S., & Ragunath, S. (2018). Emerging membrane technologies for water and energy sustainability: Future prospects, constraints and challenges. *Energies*, 11(11), 2997.

shown that when the toxic substances content exceeds the maximum permissible concentration, such methods are insufficient¹⁰.

Electro membrane techniques are effective methods for concentration, separation, and purification of multicomponent aqueous solutions that contain inorganic or biologically active ions. However, this methods have many restrictions¹¹.

A lot of different reagents are used for wastewater neutralization technologies¹². The bubblers and other mixing devices are used to accelerate chemical reactions, but this process is quite long in time due to the averaging of component concentrations in the volume of the neutralizer reactor, and also leads to additional energy costs, unjustified chemical reagents using and insufficient purification quality¹³.

Under such conditions, it is necessary to implement physical processing methods. One of such technologies is the use of various physical and mechanical effects.

Therefore, the use of modern equipment for wastewater treatment is relevant. The traditional treatment equipment is not only quite cumbersome, energy-intensive, but also sometimes not efficient. Such conditions require its modernization with the use of advanced energy-saving technologies and appropriate equipment¹⁴.

At the same time, in traditional water purification schemes the conditions of mixing reagents with water are of decisive importance. The operation modes of the mixers must ensure the reagents contact with the maximum amount of contaminants for a minimum time. This requires the search for hardware design processes appropriate options, which provides high efficiency, productivity, reducing specific energy and material costs. One of the possible ways to solve this problem is the use of cavitation technologies¹⁵. So, the proposal discussed below demonstrates practical results of using cavitation technologies for intensifying and accelerating the wastewater cleaning process.

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11 Filimonova, A. A. (2020). Electro-Membrane Technologies in Energy and Industry. *Membranes and Membrane Technologies*, 2(4), 221-229.

12 Gitelman, L., Magaril, E., Kozhevnikov, M., & Rada, E. C. (2019). Rational behavior of an enterprise in the energy market in a circular economy. *Resources*, 8(2), 73.

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Research Methodology

One of the promising methods of exposure to pollutants in the wastewater is the physical and mechanical effects that accompany cavitation. It is artificially created in special cavitation devices (CD). The liquids in such devices is not only intensively mixed with reagents, but also additionally exposed to self-oscillations, vibration turbulence, etc., which change the properties of water by it activating and significantly accelerate mass transfer reactions with subsequent deposition of pollutants.

To our mind, the CD use can help to solve some ecological problems and thereby to be of great benefit to the nature and the human-being.

Effective constructions of cavitation devices – cavitation apparatus (CA), most of which were protected by patents, had been created and tested in laboratory and in working conditions (Fig. 1). The CA are effective new generation devices designed for processing liquid-phase mixing media, emulsification, homogenization, dispersion, solution, saturation of liquids with gases and represent an all-purpose means for processing a great variety of products.

Processes in the CA are based on using hydrodynamic cavitation and connected with physical and mechanical effects (shock waves, cumulating, self-excited oscillation, straightened diffusion) arising at a collapse of cavitation bubbles. The volume concentration of the cavitation bubbles in devices reaches the value of the order of $1 \dots 10^{10} \text{ l} / \text{m}^3$. At the collapse of each small bubble pressure pulses reaching 103 MPa are initiated. Such high shock wave pulses with the volume of concentration of bubbles in the operating CA zone being high make the specific power fed to the unit of volume equal to $104 \dots 105 \text{ kW} / \text{m}^3$. It is several orders higher than the specific power realized during the processing of the technological media in ultrasound devices, disintegrators, vortex layer devices. Such an influence results in formation of conditions for occurrence of hydro mechanical, physical and chemical processes which are hampered or impossible under ordinary conditions.

For the impact of cavitation effects practical study in wastewater treatment technologies we developed a hydrodynamic cavitation unit, that shown at Fig. 2.

It looks like a closed circulation loop, which contains: working containers with treated water; a centrifugal pump that create the required high-speed pressure; the CD is located in the contour (Fig. 1); fittings and control equipment that regulate and create the necessary operating modes.



Fig. 1. Experimental samples of cavitation devices



Fig. 2. Experimental stand for hydrodynamic cavitation

Results and Discussion

In the wastewater treatment process, liquid and gaseous components were supplied directly into the CD.

There are carried out a series of experiments on cavitation-reagent purification of sewage waters, which are clogged with ions of heavy and colour metals (chromium, honey, nickel, iron etc.) with an 8.5 ph.

Lime milk was injected directly into the middle through the KA. The purity of the purified water was monitored with a Hewlett Packard model 5890 chromatograph with a flame ionization detector and an integrator behind the surplus space. For comparison, water with a similar composition was processed according to the traditional technology in a reactor with mechanical changes. The main results are presented in table 1.

Table 1

Parameters of water purification contaminated with toxic metal ions

Pollutants type	Wastewater parameters (contaminant content, mg / l)		
	Before cleaning	Cleaned by CA	Cleaned in the traditional way
Cr ⁶⁺	0,15	0	0,03
Fe ²⁺	2,4	0	0,01
Fe ³⁺	7,8	traces	0,20
Cu	0,04	0	0
Pb	0,05	0	0
Mg	46,0	traces	0,27

The neutralization of phenol in waste and natural waters is relevant, since its maximum permissible concentration in water is 0.001 mg / l. So, it was investigated the processing of model media with different concentrations of phenol in a CA.

The study of the destructive effect of hydrodynamic cavitation on phenol was carried out at pH 6.0. It was found that the amount of phenol after cleaning process depends both on the multiplicity of water treatment in CA and on the initial phenol concentration. At high concentrations (100 ... 200 mg / l), cavitation destruction of phenol leads to an increase in the content of cresols and other compounds. At the same time, the total content of organic pollutants is decreasing. For example, after 50-fold treatment in CA, the total content of phenol and products of its destruction decreased by 25 %. Great practical interest is the effect of hydrodynamic cavitation of the water phenol concentration up to 10 mg / l. It has been experimentally established that at such phenol concentrations the dependence of its content and destruction products on the multiplicity of processing in CA is also observed (table 2).

Table 2

The results of the phenol destruction by the cavitation influence

Multiplicity of processing	Toxic substances content, mg / l			Total content after treatment, mg / l
	Phenol	Cresols	Toxic products of destruction	
1	2	3	4	5
0	10	0	0	10
3	4,4	0,1	0,8	5,3

Continuation of table 2

1	2	3	4	5
6	2,1	0,2	1,3	3,6
9	0,7	0,1	1,6	2,5
12	0,2	traces	1,5	1,7
15	traces	0	1,1	1,1
18	0	0	0,6	0,6
21	0	0	0,3	0,3
24	0	0	0,1	0,1
27	0	0	traces	traces

At the treatment initial stages, the phenol destruction process occurs simultaneously with an increase in the content of cresols and other impurities in water, which are the products of phenol destruction as a result of the micro-impact action of cumulative streams. With the destruction of 90 % of phenol, the destruction of the formed organic compounds starts. With a decrease of the phenol concentration up to 5 mg / l, the multiplicity of processing in CA (until complete neutralization of phenol and other impurities) was 15 cycles, and at a concentration of 2 mg / l – 6 cycles.

So, the research results show, that the use of the cavitation method for phenol destruction is economically feasible for purifying water containing no more than 10 mg / l of phenol. At the same time, an increase in its concentration requires the processing multiplicity increasing up to 60 ... 100 cycles, which is energetically impractical.

The destruction of phenol with the simultaneous neutralization of toxic compounds can be improved by supplying appropriate reagents to the CA.

It is obvious that in comparison with traditional reagents supplying methods in purified water, the proposed method has significant technological advantages.

The efficiency of hydrogen peroxide (H_2O_2) using, which was introduced into water with a temperature of 20... 25 °C at different pH values, is illustrated by comparative oxidation data in aromatics of hydrocarbons and petroleum products. The experiments results with different methods of oxidation intensification are given in table 3. During benzene and toluene oxidation with hydrogen peroxide H_2O_2 , it was found (tab. 3) that the use of CA allows to reduce the oxidant consumption by 30 ... 50 % and significantly reduce the oxidation reaction time. Thus the intensive oxidation process is carried out in an

acidic environment is slowed down in an alkaline one. So, oxidation at pH 9.0 by mechanical stirring is almost non-existent.

Table 3

Oxidizer consumption during the treatment of water contaminated with benzene and toluene

The intensification method of the oxidation reaction	The environment Hydrogen index, pH					
	3,0		7,0		9,0	
	H ₂ O ₂ quantity (g / g) for oxidation					
	benzene	toluene	benzene	toluene	benzene	toluene
Mechanical mixing	17,3	33,6	27,0	53,6	-	-
Processing in KA	8,2	16,8	20,7	41,7	38,3	80,6

Similar results were obtained in the wastewater treatment contaminated with petroleum products.

To purify wastewater from petroleum products the oxidant in the form of hydrogen peroxide H_2O_2 was introduced into the stream through the CA. For comparison, water with a similar composition and contaminants content was treated in a reactor with mechanical stirring.

The H_2O_2 consumption was 2.0 mg per 1 mg of detected petroleum product. Quality control of cleaning process was carried out similarly. The average results are shown in the table 4.

Table 4

The petroleum content products in water, mg / l

Before cleaning	Cleaned with CA	Cleaned in the traditional way
45,6	4,5	12,1

Under such conditions, a developed mass transfer surface is created and the reactivity of the supplied reagents increases. Moreover, these reactions are quite complete, so the reagent consumption is the most rational.

Compared with traditional methods of feeding reagents into purified water, the proposed and investigated method has significant advantages, which is confirmed by the above examples.

In addition, it has been experimentally established that when processing suspensions from a mixture (1:1) of calcium and magnesium hydroxides, its reactivity

increases by almost 30 % compared to mechanical stirring. This makes it possible to reduce reagent consumption by approximately 15 %.

When preparing an aqueous mixture of organosilicon compounds (33.3 %) and surfactants in the CA, a high-quality, homogeneous product with a suspension particle size of not more than 2 micrometres was obtained, and the delamination resistance was about 6 months. This is much more than the technical requirements exceeding for the final product. In contrast to the traditional method of preparation using a rotor-type apparatus, the duration of the process is reduced and it occurs without prior mechanical mixing of the components.

Conclusions

1. Application of the CA ensures qualitatively new technological effects. As the experience of the CA use has shown, these apparatuses assure essential intensification of mixing process, reagent treatment, of liquid phase surroundings. They also differ by high production rate and operational reliability. The use of these apparatus for water treatment with liquid and gas phase components (reactants) has prospects.

2. According to the results of laboratory and experimental-industrial tests, it was established that the CA significantly intensifies the wastewater treatment processes due to its effective reagents mixing.

3. The proposed method and equipment can be used to purify water from residual petroleum products and other carcinogenic substances and also provides water deodorization and decolourization.

4. Cavitation oxidation with hydrogen peroxide (H_2O_2) of phenol compounds leads to a decrease in duration of oxidation reactions up 2 times (even at a temperature of 23... 25 °C) in comparison with traditional methods.

5. Technology and equipment for the hydrocavitation treatment implementation in comparison with known technical solutions has the following advantages:

- Simplicity of construction, their high efficiency and reliability;
- The possibility of using any reagents;
- No need for compressor stations and bubblers;
- Consistency with existing technological schemes;
- Convenience in service.