TRANSPORT PROBLEMS 2016 Volume 11 Issue 1
PROBLEMY TRANSPORTU DOI: 10.20858/tp.2016.11.1.13

contaminated washing water; saving technologies; selective water treatment methods; simulation of the scavenging process; optimization of process parameters; transport company

Andrei MELEKHIN*, **Aleksandr MELEKHIN**
Perm National Research Polytechnic University
pr. Komsomolsky 29, 614990, Perm, Russia
**Corresponding author.* E-mail: melehin2006@yandex.ru

RESOURCE-SAVING TECHNOLOGIES OF TREATMENT OF POLLUTED WASHING WATER FOR TRANSPORT COMPANIES

Summary. Dedicated to the development of resource-saving polluted washing water treating technologies for transport companies. The article suggests methods of water purification with regard to scientifically grounded requirements to the quality of the water used and the required degree of purification and The article also considers the method of selecting efficient methods of sewage water treating, when a selective removal of individual polluting ingredients should be done. For this purpose we have conducted a simulation process of treating polluted washing water in the circulating water systems, and provided solutions for refining the process parameters.

РЕСУРСОСБЕРЕГАЮЩИЕ ТЕХНОЛОГИИ ОЧИСТКИ ЗАГРЯЗНЕННЫХ МОЕЧНЫХ ВОД НА ПРЕДПРИЯТИЯХ ТРАНСПОРТА

Аннотация. Посвящено разработке ресурсосберегающих технологий очистки загрязненных моечных вод на предприятиях транспорта. В статье рассмотрены методы очистки воды с учетом научно-обоснованных требований к качеству используемой воды и необходимой степени очистки и методики подбора селективных рациональных методов очистки сточных вод, когда удаление отдельных ингредиентов общего загрязнения происходит избирательно. Проведено моделирование процесса очистки загрязненных моечных вод в оборотных системах водопользования и даны решения задач оптимизации параметров процесса.

1. INTRODUCTION

Using circulating water supply systems by transport enterprises has causes looking for a new approach to formulation of the research, designing and operating water recycling systems. Therefore, the following issues have acquired additional relevance:

- technical and economic evaluation of water purification systems with regard to scientific quality requirements of water used and the required degree of purification;
- resource-saving polluted washing water treating technology at the enterprises of transport;
- development of selective sound method of wastewater treatment, where the removal of certain ingredients pollution occurs selectively.

With the increasing use of detergents, the problem of contaminated water containing synthetic detergents (SMS) takes more scale and becomes more relevant.

Another serious ecological problem is arising when different types of contaminated water mix, which results in changing their ability to be purified. Wasted water solutions of synthetic washing agents used for cleaning dirty surfaces, account for quite a significant volume of SMS-containing wastewater. This type of wastewater is characterized by relatively small volumes and high concentration of contamination.

The costs of design, construction and operation of treatment facilities can be compared to the costs of organizing shop floor production, and sometimes exceed them. This is due to the complexity of technological processes of treating SMS-containing polluted water.

The studies of SMS-containing wastewater are very few. A distinctive feature of such water is that it contains emulsified and-suspended particles, which are stabilized by detergents. In general, they represent a complex, resistant impurity that is difficult to treat.

Such studies are an important economic problem, which can be solved by designing high-circulating washing systems. Such systems would provide reuse of valuable components of wastewater and eliminate environmental pollution.

Contaminated wash water as the type of waste water is characterized by the presence of petroleum products, suspended solids, soluble salts, surfactants and other ingredients in a soluble, colloidal (emulsified and suspended) form, as well as films and residues. Concentration of oil and suspended solids as contaminants is up to 2000 mg/dm3 and more and total concentration of all major contaminants is up to 10,000 mg/dm3 and more. At the same time, individual ingredients interact with each other, forming complex patterns of contamination.

There are different approaches to categorization of different groups of waste washing water generated from contact with contaminated surfaces. For example, some researchers organize them according to the dominant agent of pollution: surface-active substances (surfactants) or petroleum products.

For this reason, these types of waste wash water are referred to as oil-containing wastewater; alkaline oil-containing wastewater; emulsion wastewater, wastewater containing surfactants.

However, there should be a special approach to waste washing water. It is a specific kind of contaminated water containing primarily detergents [surfactants (SWA) + e (electrolytic components)] (detergents). Electrolytes, which were previously ignored, are responsible for stabilizing the system of contamination they compose. They largely determine the basic properties of wastewater.

Based on the concentration of contaminants, we can distinguish the following types of contaminated washing water.

The type of wastewater, the total content of pollution (∑NW):

- relatively clean water: water used for rinsing or cleaning of surfaces	up to 20 mg/dm^3;
- low concentration water	up to 200 mg/dm^3;
- medium concentration washing water	up to 2000 mg/dm^3;
- high concentration washing water	above 2000 mg/dm^3.

Contaminated washing water is complex dispersed system where some components are in a soluble and molecular dispersed state, the others are in the form of colloidal particles, the thirds - in the form of insoluble formations, which adsorb resinous and other surfactants on their surface; still, there is one more group that is an emulsion of oil in water stabilized by various emulsifiers.

Emulsion-suspension system in contaminated washing waters is stabilized by synthetic detergents which consist os surface-active substances (surfactants) and electrolytic components. High resistance of suspended-and-emulsified particles is due to the stabilizing effect of the surfactant molecules which are adsorbed on the interface, form a solid gel-like structure that prevents aggregation of particles. Silicates, phosphates, sodium carbonates, constituting the main part of SMS intensify the action of the surfactant. Alkaline electrolytes create conditions for the existence of highly stabilized emulsion-and-suspension systems.

The general formula of pollution can be expressed in the following form:

+SWA - surfactants;
+E - electrolytic components;
+NP - petroleum products;
+BB suspended solids.

1.1. Micelle model of polluted washing water

Based on a theoretical concept of how colloidal systems, similar in composition, are structured, we proposed a micelle model of contaminated washing water. In developing the model we used the formula of contamination of washing water SWA + E + NP + BB. The micelle model of contaminated washing water is given in Fig. 1.

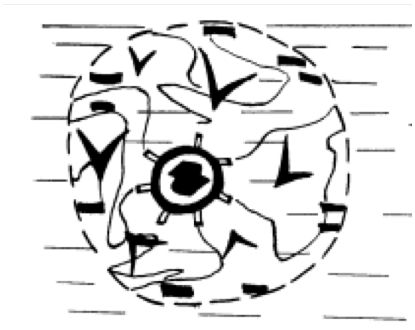


Fig. 1. Micelle model in washing water pollution
Рис. 1. Модель мицеллы загрязнения моечных вод

Model micelles pollution can be used in the interpretation of the processes associated with the interaction of the individual ingredients in the wash wastewater treatment.

2. PROBLEM STATEMENT

The formation conditions of colloidal systems of contaminated washing water. The basic physics snd chemistry theory of the cleaning action was given by academician P. A. Rebinder [1]. The main provisions of this theory gave basis for our research, too.

Cleansing or washing effect is to transfer particles of dirt from the surface cleaned into the cleaning solution. The cleaning action of the solution manifests itself in the complex interaction of surfaces, wet environments and contaminants. The main characteristics of the cleaning action of detergents water solutions are: dissolution, adsorption, wetting, emulsifying, dispersing, foaming and solubilization [2, 3]. The washing capacity is determined by the complex interplay of these and other properties of solutions.

The resistance of the complex pollution largely depends on the particle size. The most important characteristic of contaminated washing water, determining its properties, is dispersion. Fig. 1. gives differential distribution curve of the contamination particles in the water solution. It is difficult to establish the boundary between colloidal and molecular degree of dispersion, it can be moved one way or another depending on the chemical composition of the substance (Fig. 2).

Dispersion of pollutants is one of the most negative aspects of forming washing water. Given high concentration of detergents, combined with chemical and mechanical effect patterns, the result of these is a contamination that cannot be cleaned using traditional methods. The observation of the processes of accumulation of pollution and changes in the composition of the washing water in the process of operation does not provide definite answers about the dominant influence of individual factors.

Factors causing changes of the composition and properties of the washing water can be classified based on the three types of cause-and-effect relations:

- the change in the concentration of detergent in the washing waters.
- change of the formula of detergent;
- stabilizing the rheological properties of the washing water.

At the same time, the main causes of changes in the composition and properties of the washing water can be explained by :

- changes in the water mass;
- the consumption of detergent.

It should be noted that solution contamination has three typical periods:

1) intensive accumulation of pollution in the beginning of using cleaning solution;
2) the period when degree of solution contamination gets more stable;
3) the period of significant deterioration of cleaning power of the washing water with a simultaneous increased concentration of emulsified and suspended impurities.

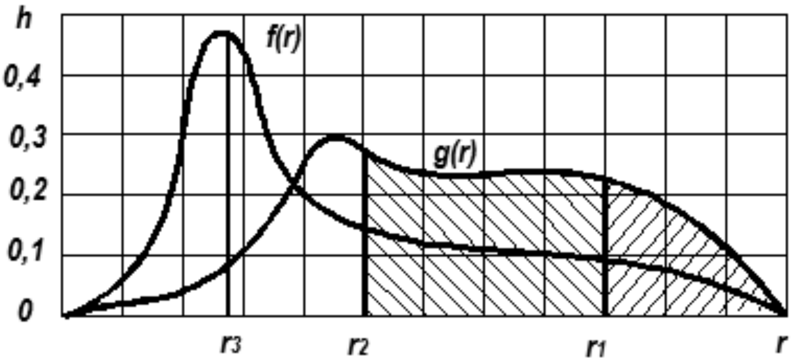


Fig. 2. Differential distribution curve of particle sizes, where h - the proportion of particles, r, r_1, r_2, r_3 - the particle size, μm

Рис. 2. Дифференциальная кривая распределения размеров частиц, где h - доля частиц, r, r_1, r_2, r_3 - размер частиц, μm

2.1. Classification of contaminated washing water cleaning methods

It appears necessary to make established methods of treating oil-containing waters (a large group of wastewater, part of which as emulsified are contaminated washing waters) into a system according to the combination of ways of breaking down emulsions structure and methods of separating de-emulsified pollution [4].

We have tested various methods of treating washing waters and classified them according to different combinations of ways of breaking down the disperse systems and separating destabilized pollution.These findings and the classification are presented in table 1.

The main feature of treating the circulating water is that it is selective in nature, i.e. some ingredients are removed in the presence of others. This factor is one of the most important in the development of the recycled water treatment technologies.

2.2. Development of selective purification methods of contaminated water solutions of detergents

Studies into the formation and sustainability of contamination of the washing water allows drawing some theoretical basis for the question.

Synthetic detergents act as a stabilizer of the system during the washing process, keeping the washed pollution in the cleaning solution and preventing re-contamination of surfaces. However, these positive properties, essential for the cleaning process, have rather a negative impact on treating process of contaminated washing water. Thus, there is a need for the balanced solution of how to combine the two antagonistic functions of cleansing medium [7].

Development of selective methods of cleaning contaminated recycled water involves identifying common patterns and approaches to building technological schemes of water treatment, namely:

- finding ways to reduce the resistance of impurities at the formation stage;
- breaking down the pollution system by regulating electrolytic condition of the stabilizer (pH regulation);
- chemical and electrochemical destruction of the emulsion stabilizer.

Weakening the sustainability of the pollution of the washing water at the formation stage can be achieved by reducing the concentration of the stabilizer, minimizing the time of having impurities in the solution, reducing the energy component of the dispersed particles.

2.3. Nonchemical methods of purifying water solutions of detergents

The researches have proved that nonchemical methods of purifying contaminated cleaning solutions are best suited for this purpose. Purification of recycled water without chemical agents is preferable as this does not involve introducing additional substances into the system. Purification of the cleaning solution must be done continuously during the whole cycle. It must also be noted, that the less impurities remain in the solution, the more effective the cleaning is. There should also be technological schemes to reduce dispersion of the particles and formation of sustainable compounds.

Table 1

Classification of recommended methods of treating contaminated washing water
(water solutions of detergents)

Methods	Method of destruction dispersed systems	Method for separating the dispersed phase
Reagentless	Gravity division Centrifugal division Separation Sorption	Defending Centrifugation Hydrocyclone separation Membrane technology Filtering
Reagent	Salts of polyvalent metals Metal ions electrochemical dissolution Acid regulation Polyelectrolytes Other reagents	Defending Flotation Sedimentation, filtration Defending

2.4. Gravitational and centrifugal separation

Sedimentation as a way of purifying contaminated cleaning solutions should be carried out at all times of using the solution. Emulsion separation is an active process [5]. The less impurities remain in the solution, the higher the cleaning efficiency. Cleaning devices should have technological schemes that would reduce dispersion of the particles and formation of sustainable compounds. However, the majority of researchers, with N. F. Telnov among them, concluded that creation of closed water system in washing complexes requires more intense treatment of contaminated solution. More intense separation of the emulsion-and-suspension washing water can be achieved by the application of centrifugal and centripetal forces in special apparatus (hydrocyclones and centrifuges). The experiments were carried out in a centrifuge "High speed centrifuge type 310" within the range of the separation factor between 1000 and 15000 1/min. When the emulsion was treated by a centrifugal force at the rate of 1000 to 12000 and the process time was from 2 to 15 minutes, concentration of contaminants (NP) was reduced from 2200 to 180 mg/dm^3.

Despite the benefits of nonchemical method of centrifugal separation, its use is limited by the capacity of the wastewater treatment apparatus. The results of these studies allow us to draw three main conclusions:

1. There are no centrifugal separation devices that could work with high concentration pollution and polydisperse mixed contaminants.
2. The efficiency of centrifugal cleaning of washing water containing detergents is insufficient to allow unlimited use of recycled wash water.
3. Under conditions of turbulence of mixed flows and the lack of devices for separating residues and films, treating wastewater with hydrocyclone has not proved its practical value.

2.5. Membrane separation

Separation of multicomponent liquid systems often involves using semi-permeable membranes, in particular, methods of ultrafiltration and reverse osmosis. The ultrafiltration process was carried out under the pressure of 2-10 kg/cm2. We used membrane materials based on cellulose ethers, polyamides, polyvinyl chloride, fluorine. The advantages of membrane methods are low power consumption, simplicity of hardware design and compact installations. It should be noted, that all tests were marked by a decrease in the permeability of membranes. The use of semi-permeable membranes, with respect to the washing water is difficult because solutions contain substances that negatively affect the process of separating the emulsion [6, 8, 10]

Filtering. Filtration is the most common method of cleaning contaminated washing water. It can be used on its own, as well as in combination with others, for example, with chemical treatment. A wide range of materials can be used in filters. Under conditions of high concentration petroleum products the most suitable are materials with high degree of oil capacity (based on wood, non-woven material). When there is a high content of suspended solids, sand filters can be quite efficient, carbon fibrous materials are effective for deep cleaning.

2.6. Method of regulating the pH

As it is necessary to reuse synthetic detergents, regulating the pH by disturbing the sustainability of disperse systems, is the most helpful. Combining the regulation of the pH with filtration as a method of separating destabilized pollution help to provide selective treatment of contaminated washing water and save SMS.

When you change the pH of the environment, the main components of the SMS - SWA (surfactants), silicates and sodium phosphates lose their stabilizing ability. Surfactants, which depend on the electrolytic system, change their protective functions, while maintaining their reversibility. Thus, regulating the state of the system allows you to selectively remove oil and suspended solids, for a while deactivating some components of synthetic detergents and preserving them for future use.

2.7. Chemical sorption treatment

Based on theory, aluminum-containing coagulants are recognized to be the most effective and easily available chemicals for treating contaminated washing water (water solutions of detergents) [9].

Traditionally, aluminum sulphate (SA) is the best-known aluminum-containing coagulant. It is produced in the form of crystalline hydrate according to GOST 12966-85 and contains not less than 15% of aluminum oxide as the basic substance. It is also produced in the form of solution, technically purified, and it contains 7-8% of oxide of aluminum as the basic substance.

Aluminum hydrochlorocarbon (GHSA) is a coagulant of a mixed type based on aluminum sulphate with the solution of hydroxochloride aluminum, or a partially hydrolyzed solution of aluminum chloride added to it. A better clotting ability is achieved by the simultaneous presence of sulfate and partially hydrolyzed aluminum chloride. A new generation of coagulant is hydroxochloride aluminum (AHC).

All of the above-mentioned aluminum-containing coagulants are effective and available chemicals for treating contaminated cleaning solutions. The use of non-organic polymer coagulant - hydroxochloride aluminum as destabilizing agent destroys chemical compounds comprising detergents with the newly formed compounds being withdrawn in the form of insoluble or gaseous substances. Adding hydroxochloride aluminum with a hydrogen ion exponent (pH) of the water solution 4±0,5 reduces alkaline reserve of the system and causes its instability.

The coagulant dose is adjusted individually for each case by conducting a trial coagulate. The use of non-organic polymer coagulant as a system destabilizer results in the destruction of chemical compounds comprising the detergent, and the formation of insoluble compounds. Sorption processes involve the interplay of the newly formed compounds and substances and result in their mutual sedimentation (Fig. 3).

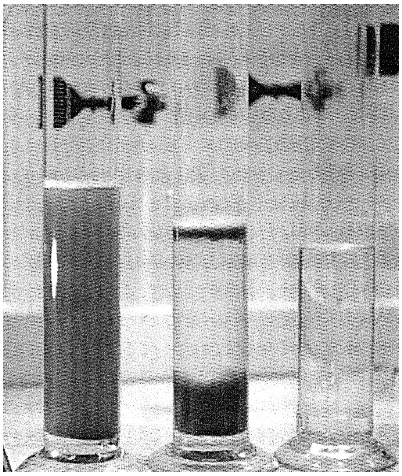


Fig. 3. Treatment of washing water with hydrochloride aluminum: 1 - sample of contaminated washing water; 2 - the same sample, treated with hydrochloride aluminum; 3 - the same sample, processed, and filtered through a sand filter

Рис. 3. Обработка моечных вод гидрооксохлоридом алюминия: 1 – проба загрязненных моечных вод; 2 – то же, обработанное гидрооксохлоридом алюминия; 3 – то же, обработанное и отфильтрованное через песчаный фильтр

2.8. General approaches to designing a process flowsheet of treating contaminated water solutions of detergents

The process flowsheet of treating contaminated washing water is based on a modular cleaning device, which takes into account different types of contaminants: floating, sinking, suspended-and-emulsified pollution [11, 12]. Fig. 4 shows triple-stream flow chart for the decontamination of polluted washing water developed by the author of this article.

Installation for purification of contaminated washing water has a modular design, which allows equipping them with both new and existing technological systems, and improving their conditions.

2.9. How to identify the required degree of purification of circulating water

Finding ways to make the purifying process of recycle water more effective is a scientific and technical challenge. We are going to consider this problem on the example of treating polluted washing water. While researching into the treatment process it is essential to take into account the recirculating water system in order to improve the efficiency. When re-using washing water there is no need to clean it up to a certain amount of residual contamination. The quality of the treated cleaning solutions must obviously satisfy the requirements for their technological use, i.e. for cleaning contaminated surfaces. Treating cleaning solutions involves removing emulsified and suspended dirt, which improves the technological characteristics of the solution: decrease the surface tension, viscosity. Also, new portions of SMS can be added to the solution. Increased concentration of SMS in the secondary solution improves its cleaning characteristics, i.e. washing time of the sample is reduced (reference sites). The more thoroughly NPs (oil) and BBs (solid mineral particles) are removed from the cleaning solution, the smaller amount of SMS is necessary to add to increase the detergency of the secondary solution to maximum [6].

We propose to evaluate the recovery of washing properties of the solution using the quofficient of the cleaning action recovery (PVMD), which is determined by formula $C_{otm} = \Delta t/C_{sms}$, where $\Delta t = t1 - t2$; t1, t2 - time of cleaning the trial site; C_{sms} - concentration of SMS.

The proposed method suggests, the smaller the value of $\mathbf{C_{otm}}$, the better the restored operational properties of the solution.

Thus, the given method allows not only checking quality control of the cleaning solution for residual contamination, but also monitoring the change of its detergency (technological characteristics).

The introduction of the second optimization parameter in the simulation of the cleaning process is new, but it is a natural element for studies of this type.

When treating contaminated cleaning solutions, the process is governed by the input and output concentrations of pollution (NP and CC) and is complemented by the control of the technological characteristics of the solution, in our case by its detergency.

The given method of studying process water can also be applicable for other circulating water systems, where specific technological water characteristics can be adjustable parameters. Below are some of the test results of purified cleansing solution.

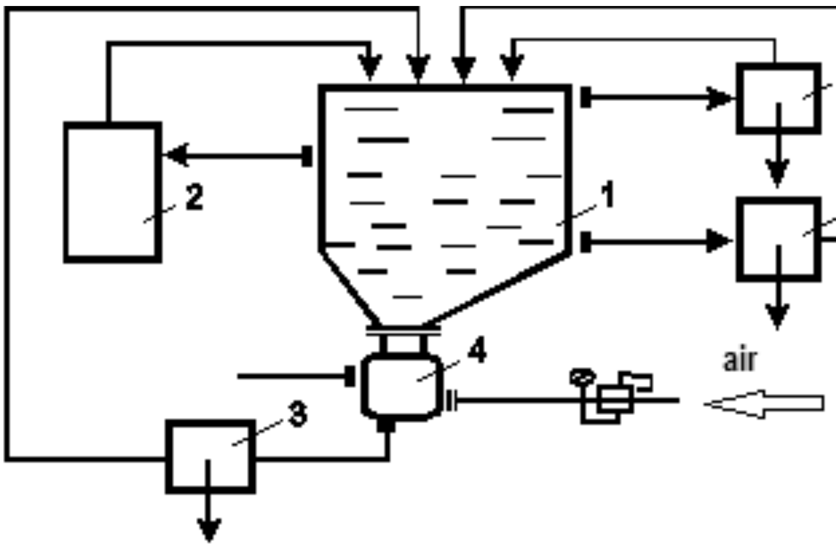


Fig. 4. The technological scheme of purification of polluted washing water: 1 - tank-sump for contaminated washing water; 2 - technological washing installation; 3 - installation for collecting sediment; 4 – sediment storage; 5 - installation for the collection and treatment of oil; 6 - installation for cleaning polluted washing water from the emulsified and suspended particles

Рис. 4. Принципиальная технологическая схема очистки загрязнённых моечных вод: 1 – бак-отстойник загрязнённых моечных вод; 2 – технологическая моечная установка; 3 – установка для сбора осадка; 4 – осадконакопитель; 5 – установка для сбора и очистки масла; 6 – установка для очистки загрязнённых моечных вод от эмульгированных и суспендированных частиц

Plotting down the values of **C_{otm}** (recovery index of the cleaning action) against physico-chemical characteristics of the solution when purified (Fig.5) allows us to draw the following conclusion.

Analysis of the curves in Fig. 5 shows that the optimal area for solving the problem is with the dose of the reagent corresponding to the intersection of the curves and the pH value of 8.4. Therefore, the rational mode of purification starts in the zone of moderate stabilization of the system.

It is known that at pH = 8.4 anions determining active alkalinity, fully are transformed into the mild, almost non-active form. Upon further addition of acid to the solution its cleaning efficiency increases slightly. When choosing the optimal values of both characteristics (C_m and C_{otm}) it should be noted that at pH 8.4, higher than its minimum value at pH 7.7 Cotm min. When the pH is 8.4 (active alkalinity > 0), the intensive cleaning process is not finished yet. Excessive acidification of the solution leads to overuse of acid. The treatment efficiency increases insignificantly, but the preparation of secondary solutions requires more SMS.

Thus, acidification of the solution to pH 8,4 is optimal for chemical cleaning mode.

The introduction of a second parameter to optimize the treatment process (detergency of purified water) allowed determining the most effective mode of treatment of polluted washing water to be used in circulating systems.

2.10. The cleaning process modeling. Conceptual formulation

Here, we look into the recycled water treatment process that includes chemical treatment and filtration. We investigate the efficiency of the process, which depends on the dose of the reagent. It is necessary to identify an amount of a reagent that is optimal with respect to different criteria, which can be divided into two groups:

- criteria of effectiveness of the water treatment process, characterizing its contamination (contamination of the washing water),
- criteria of effectiveness of the water treatment process, characterizing its technological properties (washing capacity of purified water).

The optimization problem can be formulated as follows: find an amount of reagent for fixed initial parameters of the environment and input pollution, which is optimal from the viewpoint of the selected criteria.

Let us denote the desired amount as:

$$x = A_k \in R \tag{1}$$

where**:** x- controlled parameters number 1; A_k - dose of the reagent; R - optimal cases.

Functions that characterize the efficiency of the cleaning process and the quality of water treatment serve as optimality criteria

$$\begin{aligned} J_1(x) = f(A_k) \to \min, \\ J_2(x) = g(A_k) \to \min. \end{aligned} \tag{2}$$

where: J_1 - the efficiency of the cleaning process; J_2 - the quality of water treatment; $f(A_k)$ и $g(A_k)$ are functions derived from empirical data, and approximated.

The restrictions imposed on the process parameters, can be written in the following form:

$$y = (pH, U_i, U_a, \ldots) \tag{3}$$

where: y- controlled parameters number 2; pH - is the pH of a solution; U_i - total alkalinity; U_a - bicarbonate alkalinity.

$$y_i^{\min} \prec y_i(pH, U_i, U_a) \le y_i^{\max} \tag{4}$$

Function y_i , as well as criteria functions, are derived from empirical data and approximated.

2.11. Mathematical formulation and methods of solution

Thus, we can formulate the problem of finding the optimal amount of the reagent in the following way: find: $x \in R$,

$$J_1(x) \to \min, \tag{5}$$

$$J_2(x) \to \min \tag{6}$$

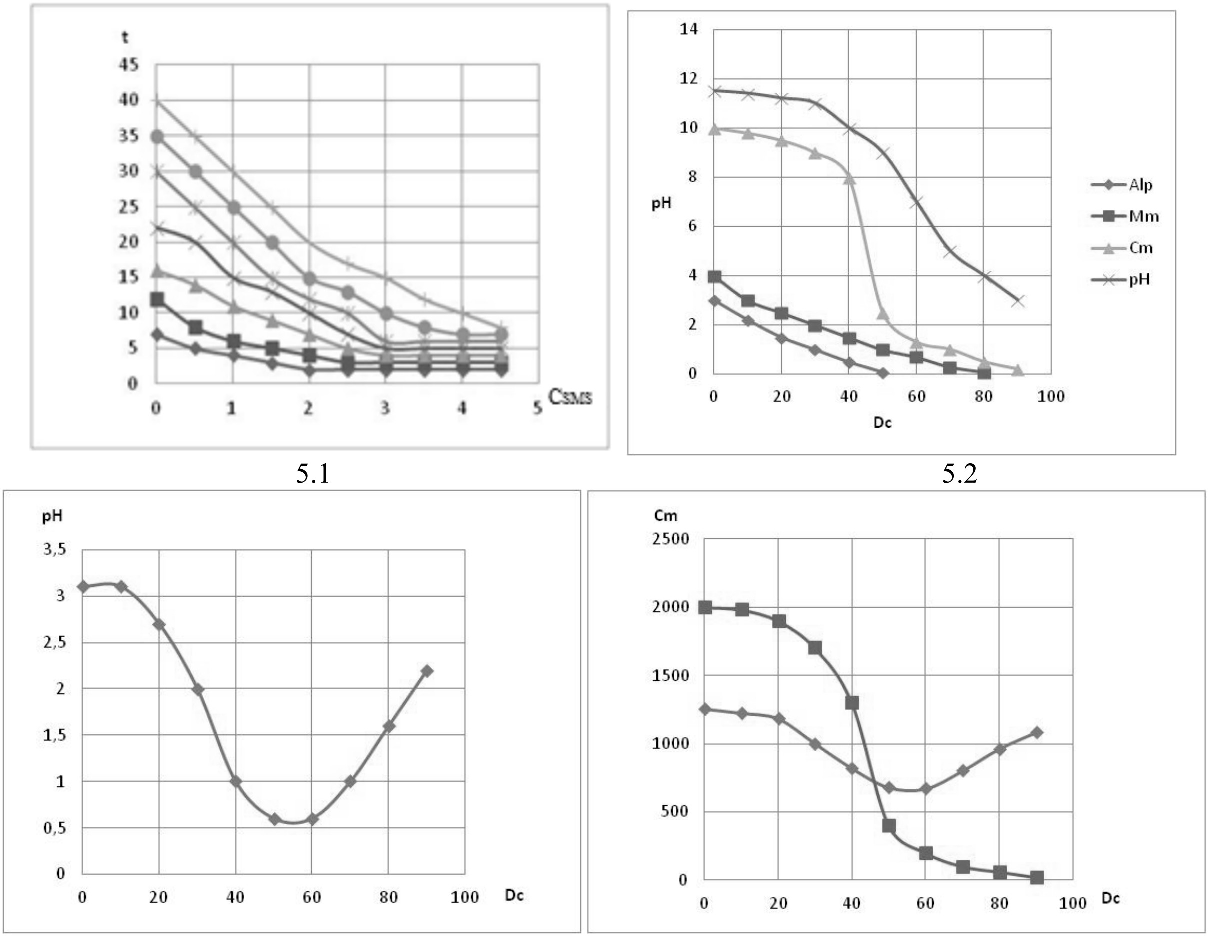
where: R - optimal cases.

Under the constraints:

$$y_i^{\min} \le y_i(x) \le y_i^{\max} \tag{7}$$

$$x^{\min} \le x \le x^{\max} \tag{8}$$

This problem is a multicriterion, one-parametric problem of nonlinear optimization. As the optimization in this problem is achieved based on several criteria, the complexity lies in setting up many equations that belong to a subset of the admissible set, i.e. the set satisfying all the constraints. Let's consider the problem (5) - (8) as a multi-criterion optimization task. The optimization parameter is manifested through a variable x, which determines the characteristics of the water treatment process. Optimality criteria for this task are the criteria (5) - (6).



5.1 5.2

5.3 5.4

Fig. 5.1, 5.2, 5.3, 5.4. Change of physico-chemical characteristics of the solution when cleaning. The construction of the overlay graph optimize the treatment process of the washing solution, where: 5.1 – time change of cleaning the sample by secondary solutions depending on a quantity of - SMS; t - time, min; C_{SMS} - the concentration of detergent, gr/dm^3; 5.2 - change of physico-chemical characteristics of the washing water when purified; D_c - the dose of coagulant, mg·eq/dm^3; pH - hydrogen index; Cm - pollution (the contents NP); M_m - total alkalinity; A_{lp} - bicarbonate alkalinity; 5.3 - curve of change of the rate of recovery of the cleaning action of the purified washing water from the dose acid; 5.4 - combined schedule of two optimization parameters; C_m - pollution index; C_{otm} - recovery index of the cleaning action

Рис. 5.1, 5.2, 5.3, 5.4. Изменение физико-химических характеристик раствора при очистке. Построение совмещенного графика оптимизации процесса очистки моющего раствора, где: 5.1 – изменение времени отмыва образца вторичными растворами в зависимости от дозы СМС; t - время, мин.; C_{SMS} - концентрация моющего средства, г/дм^3; 5.2 – изменение физико-химических характеристик моечных вод при очистке; D_c - доза коагулянта, мг·экв/ дм^3; pH - водородный показатель; Cm – загрязненность (содержание НП); M_m – щелочность общая; A_{lp} – щелочность бикарбонатная; 5.3 – кривая изменения показателя восстановления моющего действия очищаемых моечных вод от дозы кислоты; 5.4 – совмещенный график двух параметров оптимизации; C_m – показатель загрязненности; C_{otm} – показатель восстановления моющего действия.

Then we enter criterion limits that specify the maximum the value of each criterion acceptable in the solution of this problem

$$J_i(x) \le J_i^{**}, i = \overline{1}, \overline{2} \qquad (9)$$

Next, we overlay the optimization parameters with parametric restrictions

$$x_{\min} \le x \le x_{\max} \qquad (10)$$

Note that such constraints cannot always be uniquely identified. Sometimes it is more convenient to formulate physical limitations in the form of functional limitations

$$c_i^{*} \le f_i(x) \le c_i^{**} \tag{11}$$

where: c_i - limitations of function; f_i – function.

Let's denote as G a set consisting of points x that satisfy the constraints (10) and (11),

$$\mathrm{G} = \{\mathrm{x}|\, x^{\min} \le x \le x^{\max},\ c_i^{*} \le f_i(x) \le c_i^{**}, i = \overline{l, s}\ .\ \}. \tag{12}$$

where: G - a set consisting of points x that satisfy the constraints; $\bar{l}$, $\bar{s}$ - values.

The result of this is the following multi-criterion optimization problem:

to find $x \in R$ where optimality criteria (quality)

$$j_I(x) \to \min, i = \overline{1}, \overline{2} \tag{13}$$

where: J_i (x) is determined by the relations (2) and criteria and parametric constraints are executed

$$D = \left\{ \begin{matrix} x \mid x^{\min} \le x \le x^{\max}, c_i^{*} \le f_i \le c_i^{**} (i = \overline{l, s}), \\ J_i(x) \le J_i^{**}, (i = \overline{1, 2}) \end{matrix} \right\}. \tag{14}$$

where: D- a set consisting of points x that satisfy the constraints; i - values; J_i - the efficiency of the cleaning process.

Thus, the multi-criterion optimization problem is to be solved by the equation (12) at $x \in D$.

If the set D is not empty, there always exits a solution and it satisfies the engineer, solving the problem.

Now we should define what we mean by a solution to this problem. Let there be a set of continuous functions J1 (x), J2 (x) in the closed set D. The point x' is certainly better than the point x, if at all $i = \overline{1,2}$ we have $J_i(x') \le J_i(x)$, and at least one i there is a strict inequality. In this case we can say that point x is definitely worse than point x' .

If there are no points unconditionally better than x, the point x is called unimprovable or Pareto. The solution of a multicriterion optimization problem will imply a set of Pareto optimal or Pareto points.

Method of solution

Let there be an empirically obtained set of points for the criteria under the fixed environmental conditions and pollution on the following segment $A_k \in [\grave{A}_k^{-}, \grave{A}_k^{+}]$

$$f_i(A_k^i), i = \overline{1}, I \tag{15}$$

where: f_i - function; i, I- values;

$$g_i(A_k^i), j = \overline{1}, \bar{I} \tag{16}$$

where: g_i - function; j - values;

$$pH^L(A_k^L), L = \overline{1}, \bar{L}\ \mathrm{pH}^1(\grave{A}_k^l), l = \overline{1, L} \tag{17}$$

where: l,L - values.

$$U_i^p(A_k^p), p = \overline{1}, \bar{P} \tag{18}$$

where: U_i^P - total alkalinity; p, P - values.

$$U_Q^q(A_k^p), q = \overline{1}, \bar{Q} \tag{19}$$

Using approximation methods, such as methods of Newton or Lagrange, we can set up smooth functions $f\ (A_k)$, $g\ (A_k)$, $pH\ (A_k)$, $U_i\ (A_k)$, $U_{\grave{o}}\ (A_k)$, on the segment $[A_{\mathrm{k}}^{-}, A_{\mathrm{k}}^{+}]$, passing through the relating sets of points (14) - (18), and then by adding constraints to the optimization criteria, we can formulate multi-criterion optimization task in the form of equations (12) - (13).

If the set D is not empty, then there always exists a solution to the problem. Therefore, our next step will be to find the set D, which in our case is one-dimensional and can be represented in the form of one or more segments. After the set D is found, we can start finding the Pareto-front. To do this:

- it's necessary to build a random grid of N points on the set D;

- for each point, we find the values of the criteria $J_i(x)$, i=1,2;
- fix the first point x1 of D and check whether there is certainly the best point among the remaining N-1 points. If not, the point x1 belongs to the Pareto set;
- consider the second point x2 of D and check whether there is certainly the best point among the N-2 points (excluding x1). If not, the point x_2 belongs to the Pareto set, and etc.;
- after having checked all the points, we get the desired Pareto-set.

Most real-world tasks, like ours, requires finding unique solutions. Most often, when the decision of the problem can be easily visualized, singling out a unique solution is left to an expert. In difficult situations, or when no expert is available, you can select the point that is closest to the midpoint

$$\left(\frac{1}{n}\sum_{i=1}^{n} x_1^{(i)}, \frac{1}{n}\sum_{i=1}^{n} x_2^{(i)}, \ldots, \frac{1}{n}\sum_{i=1}^{n} x_S^{(i)}\right) \tag{20}$$

where: *i, n*- values; *n* is the number of points in the Pareto-set, any point for which the sum of criteria is minimal, or the value of a more significant criterion is minimal.

3. ANALYSIS OF THE OBTAINED RESULTS

3.1. Finding the rational mode of treatment

Let’s consider using this technique on the example of finding a rational mode of purifying washing water. The basic criteria were:

- criteria of effectiveness of the water treatment, characterizing its contamination [contamination of the washing water C_m ($C_m \rightarrow$ min)];
- criteria of effectiveness of the water treatment, characterizing its technological properties [the washing power of the purified waters of C_{otm} ($C_{otm} \rightarrow$ min)].

During the treatment process we can control the following parameters: pH of the washing water; M_m - total alkalinity; A_{lp} - bicarbonate alkalinity of the washing water.

Suppose there is a set of empirical data, based on which it is necessary to select an optimal dose of the reagent $\mathbf{A_k}$ (table 2).

Table 2

The results of purification of the washing water

$A_\text{к}$	pH	M_m	A_{lp}	C_m	C_{otm}
1	2	3	4	5	6
0	11,60	3,70	3,20	10,00	6,20
10	11,60	3,10	2,30	9,90	6,10
20	11,40	2,50	1,60	9,50	5,70
30	10,80	1,95	0,95	8,60	5,00
40	9,80	1,40	0,40	6,50	4,30
50	8,60	0,95	0,00	2,20	3,80
60	6,70	0,50	0,00	1,20	3,60
70	5,00	0,20	0,00	0,80	3,95
80	3,90	0,00	0,00	0,60	4,60
90	3,10	0,00	0,00	0,40	5,30

Let’s look at the different options of additional restrictions imposed on the environment settings and optimization options:

a) $M_\text{м} = 0$, pH > 6,7, $0 \le A_k \le 90$,

b) pH > 5, $40 \le A_k \le 80$.

Solution: area D in this case: $A_k \in [40, 70]$. Building a random grid on the area D and its subsequent analysis showed that the Pareto set in this case looks the following way:

$A_k \in ([40,45] \cup \{70\})$,

i.e. the optimal dose of the reagent has been found (Fig. 6, 7).

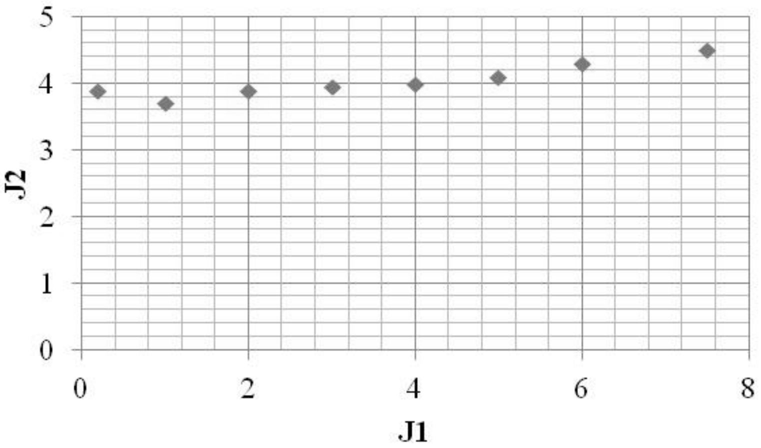


Fig. 6. Setting up Pareto set: J_1 - the efficiency of the cleaning process; J_2 - the quality of water treatment
Рис. 6. Построение Парето-множества: J1 - эффективность процесса очистки; J2 - качество очистки воды

Let's refer to Fig. 5.2, 5.4. At pH > 8.4 (active alkalinity > 0) the process of intensive cleaning is not finished yet. The area of acidification of the solution to pH =8,4 corresponds to optimal chemical cleaning mode. The solution of the problem is consistent with the chemical interpretation of the processing solution. Thus, our proposed method provides a tool for the processing empirical data, which can be used to optimize the cleaning process.

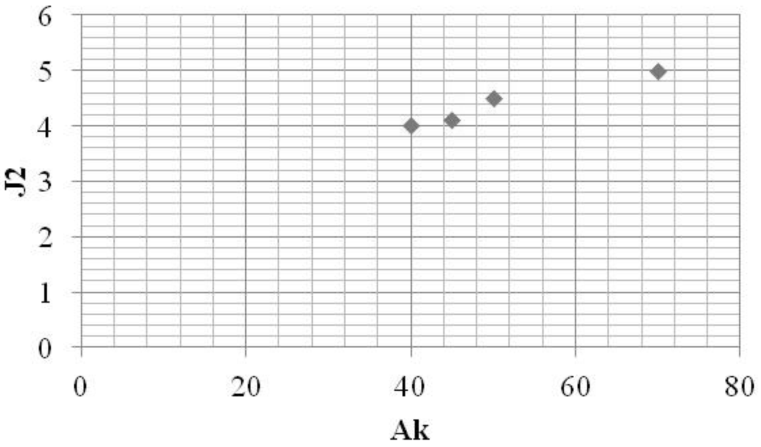


Fig. 7. Setting up Pareto-set on A_k: $\mathbf{A_k}$ - dose of the reagent, mg·eq/dm^3; J_2 - the quality of water treatment
Рис. 7. Построение Парето-множества на A_k: $\mathbf{A_k}$ - доза реагента, мг·экв/ дм^3; J_2 - качество очистки воды

4. CONCLUSION

Theoretical and experimental studies into the processes of treating polluted washing water at the transport enterprises containing synthetic detergents in circulating water systems allow drawing the following conclusions:

1. Waste washing waters contain a complex pollution, and their basic structure can be described by the following formula: [SWA+ E + NP + BB] (surfactant - electrolyte SWA - the oil - suspended solids).
2. We have found theoretical as well as experimental proof of emulsion-suspension nature of the washing waters. According to the total composition of contaminants washing waters fall into the following categories:

- relatively clean water (water used for rinsing or washing of surfaces) to 20 mg/dm^3;
- - low concentration water: up to 200 mg/dm^3;
- - medium concentration washing water up to 2000 mg/dm^3;
- - high concentration washing water above 2000 mg/dm^3.

The agents contributing to sustainability of the washing water pollutions have previously ignored electrolytes, which are their part.

Indirect measures to assess the system sustainability of the emulsion-suspension washing water are pH and alkalinity. These measures are used as a basis for methods to evaluate the stability of dispersed systems and identify three levels of stabilization, with different efficiency of purification of polluted water:

- zone of elevated sustainability of the system (pH >8,4 when M >0),
- zone of moderate stabilization of the system (8,4 <pH <a 4.3 Mm<SP> 0),
- zone of stabilization of inverse emulsions (pH≤ 4.3 when Alp <0).

3. In article to describe a classification of the recommended methods of treating waste washing water in recycled water systems based on combinations of the means of destruction of disperse systems structures and ways of separating destabilized pollution and selective methods of purifying contaminated washing water, which comprise:
   - nonchemical methods: separation in the gravity field (sedimentation) and in the field of centrifugal forces (hydrocyclone cleaning);
   - filtration;
   - chemical methods: regulation of pH; sorption treatment (co-precipitation with chemical treatment using aluminum-containing coagulants).
4. We have developed a method for estimating the required degree of purification of washing water with regard to its reuse.
5. We have proposed a new measure of restoring cleaning action that allows determining the necessary degree of water purification, and which equals the ratio of the washing time of the sample area to the concentration of detergent: ($C_{otm} = \Delta t / C_{SMS}$).
6. We have developed methods for determining the rational mode of water purification.
7. We have also suggested a mathematical model for optimal selection and water treatment and working drawings for a new series of modular equipment (installations) for treating contaminated washing water at transport enterprises.

References

1. Ребиндер, П.А. *Поверхностно-активные вещества*. Москва: Знание. 1961. 46 p. [In Russian: Rebinder, P.A. *Surfactant.* Moscow: Znanie].
2. Клейтон, В. *Эмульсии, их теория и технические применения*. Москва: Иностранная литература. 1950. 680 p. [In Russian: Clayton, V. *Emulsions: theory and technical application*. Moscow: Innostrannaya Literatura].
3. Мелехин, А.Г. *Ресурсосберегающие технологии очистки моечных вод*. Пермь: Издательство ПНИПУ. 2014. 133 p. [In Russian: Melekhin, A.G. *Resource-saving technology of treating washing water*. Perm: Publishing house of PNRPU].
4. Мелехин, А.Г. *Очистка водных растворов моющих средств в оборотных системах водопользования*. Пермь: Издательство ПНИПУ. 2006. 150 p. [In Russian: Melekhin, A.G. *Purification of water solutions of detergents in the circulating water systems*. Perm: Publishing house of PNRPU].
5. Vatai, G.N. & Krstic, D.M. & Koris, A.K. & Gáspár, I.L. & Tekić, M.N. Ultrafiltration of oil-in-water emulsion: Comparison of ceramic and polymeric membranes. *Desalin. Water Treat.* 2009. Vol. 3. P. 162–168.

6. Martin, Alberto Masuelli. Synthesis Polysulfone-Acetylethanol Ultrafiltration Membranes. Application to Oily Wastewater Treatment. *Journal of Materials Physics and Chemistry*. 2013. Vol. 1 No. 3. P. 37-44.
7. Suárez, L.A. & Díez, M.A.B. & García, R.B. & Riera, F.A.A. Membrane technology for the recovery of detergent compounds. *Journal of Industrial and Engineering Chemistry*. 2012. Vol. 18. No. 6. P. 1859-1873.
8. Pellegrin, M.-L.A & Greiner, A.D. & Aguinaldo, J.C & Diamond, J.D & Gluck, S.E & Burbano, M.S.F & Arabi, S.G & Wert, J.H & McCandless, R.I & Padhye, L.P.I & Shoaf, R.K. Membrane processes. *Water Environment Research*. 2012. Vol. 84. No. 10. P. 1114-1216.
9. Wang, W.A. & Zhang, X.A & Wang, H.B & Wang, X.A & Zhou, L.A & Liu, R.C & Liang, Y.D. Laboratory study on the adsorption of Mn2+ on suspended and deposited amorphous Al(OH)3 in drinking water distribution systems. *Water Research*. 2012. Vol. 46. No. 13. P. 4063-4070.
10. Peter-Varbanets, M. & Zurbrügga, Ch. & Swartz, Ch. & Pronk, W. Decentralized systems for potable water and the potential of membrane technology. *Water Research*. 2009. Vol. 43. No. 2. P. 245–265.
11. Patent US 5908550. *Water Reclamation System for a Vehicle Wash System*. Publ. 01.06.1999.
12. Patent IT 1267044. *Purification System for the wastewater from automotive workshops or car washing facilities*. Publ. 24.01.1997.

Received 09.08.2014; accepted in revised form 22.02.2016