Analysis of methods for treatment of industrial wastewaters containing polycyclic aromatic hydrocarbons

D A Ozerova¹, A L Zolkin², V M Kalyakina³, Yu N Koval⁴ and S V Shamina⁵

¹Department E9 Technogenic safety, Bauman Moscow State Technical University, Moscow, 105005, Russia
²Computer and Information Sciences Department, Povolzhskiy State University of Telecommunications and Informatics, Samara, 443010, Russia
³Department of health, safety and environmental engineering protection, Don State technical University, Rostov-on-Don, 344002, Russia
⁴Department of forensic engineering and criminal science, FSBEI HE Siberian Fire and Rescue Academy EMERCOM of Russia, Zheleznogorsk, Krasnoyarsk Krai, 662972, Russia
⁵Department Natural science disciplines, South Ural state agrarian University, Troitsk, Chelyabinsk region, 457100, Russia

E-mail: bauman@bmstu.ru

Abstract. Various methods and stages of industrial wastewater treatment from polycyclic aromatic hydrocarbons are estimated in the article. The development of technologies for the removal of toxic compounds from industrial wastewater is one of the key tasks for solving the problems of sustainable development. First of all, it is related to the fact that toxic compounds adversely affect the efficiency of wastewater treatment. They are not neutralized in natural processes, negatively affect the environment and, as a consequence the human health. Toxic compounds deplete nature's ability to perform self purification and restoration of resources. One of the most important resources is water. These toxic compounds include polycyclic aromatic hydrocarbons.

1. Rationale
The development of technologies for the removal of toxic compounds from industrial wastewater is one of the key tasks for solving the problems of sustainable development. First of all, it is related to the fact that toxic compounds adversely affect the efficiency of wastewater treatment. They are not neutralized in natural processes, negatively affect the environment and, as a consequence the human health. Toxic compounds deplete nature's ability to perform self purification and restoration of resources. One of the most important resources is water. These toxic compounds include polycyclic aromatic hydrocarbons (PAHs). PAHs are present in wastewater from various industries, for example: in oil refining, petroleum chemistry, production of pharmaceutical products, coke, plastic, cellulose, paper production. The discharge of these compounds into nature without processing creates a serious threat to the health of humans, animals and aquatic inhabitants.

The aim of the study is to study and evaluate various methods and stages of treatment of industrial wastewater from polycyclic aromatic hydrocarbons.
The objects of research are the processes and methods of treatment of wastewater from polycyclic aromatic hydrocarbons, as well as the qualitative characteristics of these methods.

2. Analysis of methods for treatment of surface wastewater from polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds featured by the presence of two or more condensed benzene rings in the chemical structure. In the nature, PAHs are formed during the pyrolysis of cellulose and are found in coal, brown coal and anthracite beds, as well as a product of incomplete combustion during forest fires. The main sources of emission of technogenic PAHs into the environment are enterprises of the energy complex, road transport, the chemical and oil refining industries.

Polycyclic aromatic hydrocarbons are the main organic pollutants in the environment that are toxic to humans and biota, taking into account their carcinogenic, mutagenic and teratogenic properties. Most of the PAHs enter the biosphere from human-made sources (combustion of oil products, coal, wood, garbage, food, tobacco, and the lower the temperature is, the more PAHs are formed) [1]. PAHs are hydrophobic organic compounds that tend to bioaccumulate in organisms. Several PAHs have been identified as carcinogenic, mutagenic and one of the most common compounds in sediment studies.

PAHs in aqueous media quickly bind to solid particles or organic substances such as biopolymers, humic compounds and black carbon, resulting in precipitation due to their low solubility in water. Once adsorbed on sediments, they are much more stable than pure compounds and are resistant to oxidation and nitrification reactions to which they would otherwise be highly sensitive due to photochemical processes [2].

There are many methods for removal of polycyclic aromatic hydrocarbons from water. Combinations of various methods are used in the process charts of treatment plants due to the complexity of the composition of industrial wastewater to be purified from PAHs and high requirements for the degree of purification.

The use of combined methods of wastewater treatment combines a high efficiency of the removal of toxic compounds with an economical bioremediation and is a modern trend in the development of technologies for the treatment of problematic wastewater. A brief description of the methods for treatment of industrial wastewater from PAHs is given in Table 1.

| Cleaning methods                  | Achievable cleaning grade, mg/dm³ | Note                                                                 |
|----------------------------------|-----------------------------------|----------------------------------------------------------------------|
| Mechanical (desilting)           | 40-1000                           | It does not clean the wastewater from emulsified products             |
| Physical and chemical: flotation | 20-60                             | The purification grade depends on the flotation                       |
| Adsorption                       | 1-3                               | It cleans from emulsified PAHs (after preliminary purification)        |
| Chemical                         | 1-10                              | Used in combination with filtration and desilting                    |
| Biochemical (using aerobic microorganisms) | 1-10                       | Preliminary desilting is mandatory                                   |

Mechanical treatment methods based on gravitational separation of materials make it possible to extract PAHs from wastewater, which are in a coarsely dispersed (droplet) state. Therefore, mechanical cleaning methods are used only in conjunction with others methods[4]. Grids, sand traps, oil traps, sedimentation tanks and other equipment used for mechanical treatment of wastewaters, as a rule, retain
the bulk of associated contaminants of mineral origin, protecting subsequent devices and structures from wear and clogging. An example of a filter is shown in figure 1 [3].

![Figure 1. Vertical pressure filter with granular loading: 1– pipeline for supply of water for treatment; 2 - layer of granular filtering material; 3 - upper distribution device; 4 - control elliptical manhole; 5 - round manhole; 6 - pipeline for wash water supply; 7 - pipeline for the removal of the first filtrate; 8 - pipeline for the removal of purified water; 9 - pipeline for drainage of washing water.](image)

Quartz sand, expanded clay, graphite, coke, polymer materials, nets, non-woven materials based on synthetic fibers are used as a filtering material.

The advantages of this method are that this type of treatment is applicable almost everywhere, it is one of the simplest and cheapest methods of water treatment. All the difficulties in operation are reduced only to the choice of the optimal scheme and the calculation of sedimentation tanks for mechanical wastewater treatment. However, there are also negative points: hydromechanical purification is not able to separate the smallest dissolved particles from the liquid, which can harm both human health and any industrial and household equipment. The separated polluting particles must be removed somewhere, for example, from a sump. And therefore, a certain amount of them eventually gets back into the environment.

Physicochemical treatment is used for additional purification of wastewater that has undergone mechanical treatment and contains emulsified and dissolved PAHs. Their isolation by sedimentation methods is possible after the enlargement of pollution particles using coagulation and flocculation or other methods. Floation and sorption are widely used. In addition, ion exchange, ultrafiltration, reverse osmosis, extraction, and other methods are used in various treatment schemes for PAH-containing wastewater [5].

Lime in pure form and in a mixture with carbon dioxide, with salts of ferric and sulphate iron and aluminum, with phosphates, compounds of chromium or calcium with clay, sulfuric acid or copper sulfate, sodium tripolyphosphate with sodium hydroxide, chlorisocyanuric acid or its salts, sodium aluminate, etc. are used as coagulants.

Flocculation is used in order to accelerate the processes of flaking during coagulation. Flocculants are divided into nonionic, anionic, cationic, amphoteric. The flocculent sediment is separated by settling, filtration and pressure flotation. Electrocoagulation is also used for water treatment. The duration of electrical treatment of effluents in electrolysis is from 0.5 to 5 minutes.

Disadvantages of reagent cleaning with mineral coagulants: the need to add relatively large doses of coagulant, the concentration of sulfate and chloride ions increases in the purified water. It leads to
undesirable effects of corrosion of drainage networks, as a result of chemical reactions a sludge is formed, which is difficult to dehydrate and requires further disposal. The disadvantages of mineral coagulants are largely eliminated by high-molecular flocculants of organic or inorganic nature.

During flotation, PAHs are extracted by air bubbles or a mixture of hydrocarbon gases introduced into water in different ways. According to the method of dispersing of air or gas, there is the following classification of flotation: when gas is released from the air; with mechanical air dispersion; when air is supplied through porous materials; electroflotation; vibro-, bio- and chemical flotation. The use of coagulants and flocculants significantly intensifies the process of pollution flotation, as the hydrophobization of particles increases [6]. The advantages of the method, which include a high degree of purification in a fairly short time, quiet operation, no rotating parts, the ability to utilize recoverable components, and others, give reason to choose it for the treatment of water waste.

Adsorption is practically the only method that allows natural and waste waters to be purified from PAHs to any required level without introducing any secondary contaminants into the water. Natural and artificial porous materials are used as adsorbents. To clean the surface of water bodies, adsorbents of various nature are used. For the purification of industrial wastewater, granular activated carbon is mainly used, having particles with a size of 0.10 mm, which consists of (85 - 99)% carbon and which is capable of self-separation from water.

Hardware design of sorption cleaning - pressure filters with a dense layer of granular active carbon, in front of which there are mechanical filters. Two-stage filtration is used for deep treatment of waste water containing polycyclic aromatic hydrocarbons. Gravity filters, structurally similar to mechanical ones. They are used to treat large volumes of water.

The advantages of this purification method are the ability to remove impurities of various nature and the absence of secondary pollution of the treated water, as well as the possibility of sorbed substances recovery [7].

However, there are disadvantages such as: high cost and scarcity of sorbents, natural sorbents are applicable for a limited range of impurities and their concentrations, bulky equipment, high consumption of reagents for the regeneration of sorbents and the formation of secondary waste requiring additional purification. Porous adsorbents have low mechanical strength. Losses of adsorbents for one cycle for abrasion or washing reach from 0.1 to 2%, taking into account this, as well as the cost of adsorbents, the regeneration of adsorbents and the possibility of their repeated use are of great importance.

3. Biochemical wastewater treatment and extraction method
Wastewater containing PAHs after mechanical and physicochemical treatment, before being discharged into a reservoir, is directed to biochemical treatment, which consists in the oxidation of organic pollution by microorganisms.

For the purification of wastewater containing polycyclic aromatic hydrocarbons, biofilters and aeration tanks are most widely used. During the period of biological maturation under aerobic conditions with activated sludge, the optimal amount of activated sludge develops, adapted for this operating mode of the installation, the amount and quality of waste water.

During the period of the stationary process of operation of treatment plants with aeration, four phases of activated sludge operation are distinguished.

First phase: biosorption of organic matter by active sludge flakes. There is an intensive increase in the biomass of active sludge and a sharp decrease in the concentration of organic pollutants due to the biosorption of organic pollutants by active sludge. The duration of the biosorption phase does not exceed 30 minutes.

Second phase: biochemical oxidation of organic matter by active sludge flakes. There is a further increase in the biomass of active sludge and a decrease in the concentration of organic pollutants due to decarbonization. The duration of the biochemical oxidation phase is about 1 hour. Biochemical wastewater treatment is carried out mainly by microbes. Microbes do not have special digestive organs, so all the substances necessary for their vital activity enter the cell through the smallest pores of the cell membrane. These pores are so small that in order to penetrate through them, substances must be prepared
in advance, i.e. preliminarily crushed to a molecular state and partially converted into simpler compounds in the surrounding solution.

Third phase: synthesis of the cellular substance of active sludge from the remaining organic matter of waste water due to the energy released in the second phase. The amount of organic substrate passing into new cells is approximately 65%. This phase differs from the previous ones in the relative constancy of the mass of active sludge, it proceeds until all the organic substance previously accumulated by the cell of sludge microorganisms is exhausted [8]. The total duration of this phase in the aeration tank and the regenerator is about 20 hours in the stationary process.

Fourth phase: endogenous respiration or oxidation of the cellular substance of active sludge. From nitrogen used as a building material for the synthesis of active sludge, during biochemical oxidation, ultimately, ammonium carbonate is formed.

The use of membrane processes for separation of water and active sludge provides many advantages: small occupied industrial area of the treatment system, the absence of secondary sedimentation tanks and filters for additional treatment, membrane separation of water and active sludge completely eliminates the removal of suspended solids into treated water.

However, this cleaning method also has such a disadvantage as the need to clean the device of separately standing groups of sedimentation tanks after each stage of biological treatment. Taking into account the fact that each stage of cleaning in aeration tanks is supplied with its own systems for supply and distribution of active sludge and removal of treated effluents, this significantly increases the capital and operating costs of the entire complex of treatment facilities.

Liquid extraction is used to treat wastewater containing metal ions, oils, organic acids, PAHs, etc. The expediency of using extraction is determined by the concentration of the removed organic impurity - extraction can be an economically profitable process if the cost of the extracted substance compensates for the costs of the process.

Consequently, for each substance there is a concentration threshold for the profitability of extraction. With the current ratio of prices for chemical products and energy resources, in general, it can be considered that most substances are more profitable to extract by extraction than by adsorption, if their content in wastewater is not less than 4 g / l.

The first stage of extraction is intensive mixing of waste water with a solvent to create a developed mass transfer surface; this stage is carried out in mixers or extraction columns. Then the mixture is divided into two phases - the extract, which mainly contains the extractable substance and the extractant, and the raffinate, which consists mainly of waste water and the extractant dissolved in it. After separation, the extractant is regenerated from the extract (most often by distillation) with the extraction of the extracted component, and the extractant is regenerated from the raffinate. The most difficult task in the development of extraction processes is the selection of an extractant that must meet the following requirements: dissolve the extracted substance much better than water, i.e. to provide a high value of the coefficient of distribution of the extracted substance between the aqueous and organic phases; have high dissolution selectivity; have a high value of the diffusion coefficient of the released component through the interface, to ensure a higher extraction rate; have a lower solubility in waste water and do not form stable emulsions with it, to facilitate phase separation and reduce extractant losses; have a density significantly different from the density of waste water to accelerate phase separation; have a low cost; if possible, have low toxicity and fire hazard [8,9,10].

An ideal solvent that meets all of these requirements has not yet been found. Thus, phenol, aniline and quinoline and other PAHs, which practically completely extract from water, dissolve noticeably in water, and themselves create dangerous pollution; effective extractants - tricresyl phosphate and phenolsolvan (a mixture of complex aliphatic esters) - are expensive and inaccessible. The industry uses butyl acetate, coal oils, mixtures of high-boiling alcohols and, most often, benzene. The disadvantages of benzene include high toxicity and fire hazard, which, combined with high volatility, requires careful sealing of the equipment.
4. Findings
Thus, PAHs are among the main organic pollutants found in aquatic systems. They are mainly formed from both natural and anthropogenic sources. They are often detected in environmental samples. The results compared showed that freshwater and marine waters in many parts of the world are contaminated with PAHs, possibly due to increased urbanization, industrialization, continuous discharge of untreated or partially treated wastewater into water bodies, and intense shipping activities. Therefore, strict adherence to environmental laws is necessary to ensure a safe environment for humans and biota and high-quality water purification.

At the moment, there are many different methods for reducing the level of contamination, and they show the necessary degree of effectiveness, depending on the tasks and conditions for cleaning. At this stage, the goal is to develop a less costly, compact and highly efficient method of purification from PAHs in comparison with the above methods. One of the ways to intensify purification with a decrease in the cost of consumables is to combine different purification methods in one apparatus, such as reagent treatment, flotation, filtration, etc.

References
[1] Korneva D A and Kurov L N 2011 Adsorption treatment - an effective method of wastewater treatment and water preparation for domestic and drinking water use The successes of modern natural science 7 129
[2] Shumyatskiy Yu I 2005 Adsorption processes: Workbook for higher education institutions (Moscow: D. Mendeleev University of Chemical Technology of Russia) 130
[3] Smola V I 2013 PAH in the environment: problems and solutions in 2 parts (Moscow: Poligrafservis publisher) 383
[4] Ksenofontov B S, Kozodayev A S, Taranov R A and Vinogradov M S 2020 Cleaning of wastewaters from complex organic substances Ecology and industry is Russia 24(7) 4-7
[5] Cerniglia C E 1984 Microbial transformation of polycyclic aromatic hydrocarbons (New York: Appl. Microbiol, Academic Press) 71
[6] Tran-Duc T 2011 Modelling carbon nanostructures for filtering and adsorbing polycyclic aromatic hydrocarbons Journal of Computational and Theoretical Nanoscience 8(6) 2072-7
[7] Lee C H 2003 Processing of the third pacific basin conference on adsorption science and technology 519-23
[8] Zakharchenko N V, Hasanov S L, Yumashev A V, Admakin O I, Lintser S A and Antipina M I 2018 Legal rationale of biodiversity regulation as a basis of stable ecological policy Journal of Environmental Management and Tourism 9(3) 510-23 doi: 10.14505/jemt.v9.3(27).11
[9] Safonyk A, Zhukovskyy V and Burduk A 2020 Modeling of Biological Wastewater Treatment Process Taking into Account Reverse Effect of Concentration on Diffusion Coefficient 10th International Conference on Advanced Computer Information Technologies 2020 29-34 9208814
[10] Skrypchuk P, Zhukovskyy V, Shpak H, Zhukovska N and Krupko H 2020 Applied aspects of humus balance modelling in the Rivne region of Ukraine Journal of Ecological Engineering 21(6) 42-52