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NATURAL WATERS AND INDUSTRIAL WASTEWATER, WASTEWATER WITH PHENOL-CONTAINING COMPOUNDS, METHODS OF WATER PURIFICATION

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ABSTRACT

Water pollution is one of the main causes of imbalance in the Earth's ecosystem. Plant effluents have different compositions and concentrations of pollutants, depending on the kind of production and the water supply and sewerage system. The main sources of phenol-containing wastewater are coking plants, coke oven gas plants, semi-coking plants, gas generating stations, wood heat treatment plants, and the synthesis of artificial liquid fuels. They can also be the result of the activities of metallurgical plants, oil refineries, enterprises for the recovery of rubber, and the production of film, phenolphthalein, salicylic acid, and salol. Phenolic waters are dangerous for fishery reservoirs, worsen the organoleptic properties of water, and disrupt the natural processes of water self-purification. Water contaminated with phenolic wastewater contributes to the deterioration of groundwater quality. Thus, high-quality water purification from phenol to reduce/maximum prevent the ingress of phenols into industrial and drinking water is an urgent problem. Methods for deep treatment of phenolic wastewater are regenerative and destructive. The technology for purifying phenolic wastewater using the processes of oxidation of phenolic compounds with atmospheric oxygen on heterogeneous catalysts is one of the most promising technologies. Nanodisperse catalysts used to treat wastewater containing aromatic hydrocarbons and, in particular, phenolic compounds, should provide a high rate of oxidation of phenolic pollutants, efficient oxidation of a wide range of compounds with various functional groups, low cost, and long service life without a noticeable loss of catalytic properties, as well as high mechanical strength and immunity to catalytic poisons. Catalysts based on various metals and metal oxides and carrier-based systems, oxide-based magnetic composites show good efficiency in the oxidation of phenol with oxygen.

Keywords: Water Treatment, Highly Toxic Organic Compounds, Phenol, Technology, Nanostructured Catalysts, Transition Metals, Biocatalysis.

RASĀYAN *J. Chem.*, Vol. 16, No. 3, 2023

INTRODUCTION

Water is one of the most important natural resources, which largely determines the technical and social progress of any country. The total cost of fresh water is much more expensive than any other type of raw material used. According to the UN, WHO/UNICEF (2019) conclusions, more than 2 billion people (more than 25% of the world's population) do not have access to drinking water. Industrialization is one of the main reasons for the increasing shortage of fresh water for the population. Usually, people do not think about water when there is enough of it.[1-3] The Mongols say: "Man does not appreciate water until the source runs dry".[4] Desert dwellers are well aware of the high price of water and try to carefully and economically spend every drop of water. The price of water is known both where it must be extracted from deep wells, and, finally, where you have to pay a lot of money for water. The amount of fresh water suitable for humans is becoming less and less every year. Already, the United States annually pays billions of dollars to Canada for the right to use the natural sources of fresh water located on the territory of Canada.[3-5] Industry is one of the main sources of water pollution, as it produces large quantities of pollutants that are extremely harmful to people and the environment. It is the water cycle that forms the basis of the technogenic circulation of substances and the transformation of energy associated with it in ecological and economic systems. Water pollution is one of the main causes of imbalance in the earth's ecosystem.[6-8] The concept of "drinking water" characterizes water intended for drinking and domestic needs of the population and

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meeting all hygienic standards, including the level of different pollutants. The term "wastewater" refers to water used for industrial and domestic needs and at the same time contaminated with additional impurities that change its original physical and chemical properties. Melt and rain streams leaving the territories of settlements and industrial enterprises are also suitable for this type. Any natural system (including natural waters) has the ability to self-purify (Fig.-1).

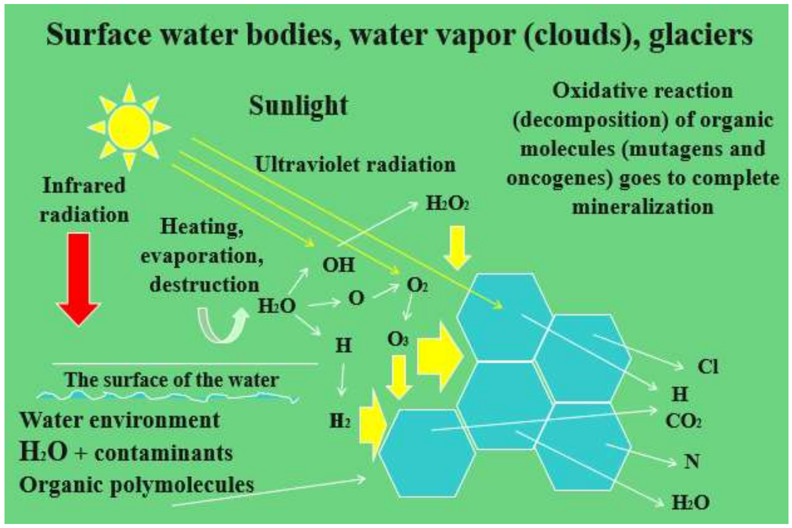

Fig.-1: Natural Water Purification and Recovery Processes in Nature

Organic substances contained in wastewater are decomposed by enzymes of aerobic bacteria, which absorb oxygen dissolved in water and emit carbon dioxide.[8-11] The end products of decomposition are carbon dioxide and water, but many other compounds can be formed. Since aerobic bacteria use oxygen, the first result of the decomposition of organic residues is a decrease in oxygen content. At the same time, carbon dioxide formed during the decomposition of substances contained in wastewater evaporates into the atmosphere. In reservoirs with a weak current, where the waters mix slowly and are isolated from the atmosphere, the inevitable decrease in oxygen content and an increase in the concentration of carbon dioxide entail serious changes. When the oxygen content decreases to a certain level, fish are starved and other living organisms begin to die. Most of the fish die due to poisoning by industrial and agricultural effluents, but many also from a lack of oxygen in the water.[1-3,7-10] The discharge of insufficiently treated wastewater exceeds the ability of natural aquatic complexes to self-purify, their degradation occurs, the biological balance is disturbed, and self-purification processes stop. Therefore, the shortage of drinking water is caused not by direct water consumption of hydro resources, but by their qualitative depletion. Thus, in natural reservoirs, there is a natural process of self-purification of water. However, this process is slow. While industrial and domestic discharges into natural water bodies were not too large, natural waters themselves could cope with them. At some point, due to the rapid increase in runoff, water bodies can no longer cope with pollution. Therefore, the need for neutralization, purification of effluents, and disposal of plants effluents pollution is a topical task. The strongest anthropogenic transformation is experienced by the waters of small rivers, which often receive the main volumes of wastewater. In addition, such small rivers, being tributaries of larger rivers, have a huge impact on the formation of their geochemical regime. In areas of natural rivers with a reduced transport capacity, suspended solids settle to the bottom, forming technogenic dispersion flows in bottom sediments. Bottom sediments are the most stable components of the water system with concentrations of some chemical elements exceeding the Maximum Permissible Concentration (MPC) by 10 and 100 times. Elevated contents of elements in the bottom sediments of rivers refer to extended sections of the channel: inflows, and shallows, where the transport capacity of the flow decreases, sedimentation of suspended material occurs, and its accumulation at the bottom. Such areas are geochemical barriers. According to the conclusions of A.I. Perelman, mechanical, sorption and hydrogen sulfide barriers predominate in reservoirs and streams.[3,4,17]

Industrial Wastewaters

The end result of the activities of any manufacturing enterprise, along with the production (manufacturing) of products, is waste. These wastes, concentrated in dumps, storages, waste heaps, and unauthorized dumps, wastes are a source of pollution of atmospheric air, ground and surface waters, soils, and vegetation.[3] Industrial wastewater differs in a wide variety of composition and concentration of pollutants determined by the nature of production, as well as a water supply and sanitation system. By the nature of use in the production of water, they are divided into several categories (Fig.-2, Table-1).[9-12]

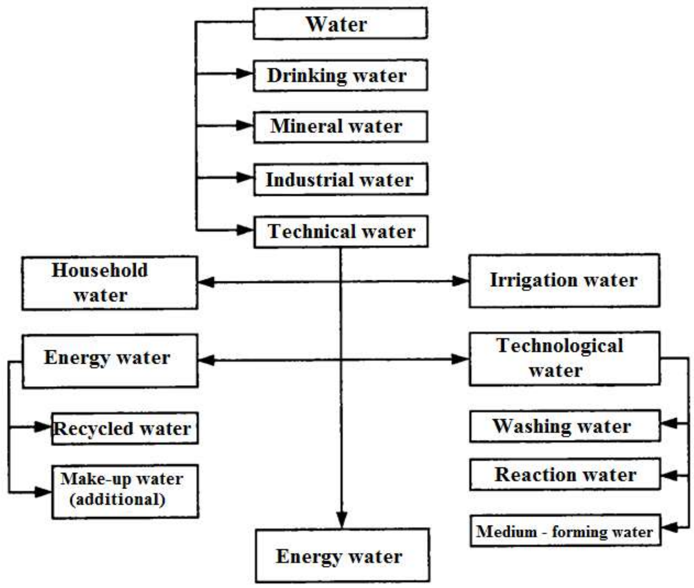

Fig.-2: Different Categories of Water

Table-1: Composition of Industrial Wastewater[3,4,12]

No	Types of industry	Major toxic impurities of industrial wastewater
1	Oil refinery	Naphthenic acids, petroleum products, phenols, sulfides, chlorides, sulfates, surfactants, organic particulate matter
2	Coke chemical	Phenols, hydrogen sulfide, resins, hydrocarbons, thiocyanides, ammonia, cyanides, organic particulate matter
3	Pulp and paper	Mercaptans, sulfides, alcohols, aldehydes, ketones, organic suspensions
4	Synthetic polymers and plastics	Styrene, acrylonitrile, acrylates, sulfates, phenols, aromatic hydrocarbons, aldehydes, alcohols, cyclohexane, organic acids, particulate matter
5	Synthetic rubber production	Butylene, butadiene, acetone, organic acids and their salts, acetonitrile, ammonia, aldehydes, alcohols, hydrocarbons
6	Extractive phosphoric acid and phosphate fertilizer industry	Sulfuric, phosphoric, fluorosilicic acids, fluorine compounds, hydrogen chloride
7	Chlorine industry	Mercury, chlorine, chlorides
II. Content of organic matter in industrial wastewater		
No	Pollutants	Quantity in global wastewater, million tons/year
1	Oil products/ Plant organic residues	26.563/0.170
2	Phenols/Waste production of synthetic fibers	0.460/5.500
3	Total	33.273

Clean water can be polluted by pesticides and fertilizers from farms, as well as untreated wastewater and industrial waste. Polluted water drains even get into groundwater, as a result of which the water becomes unsuitable for drinking by the population. It is well known that oil spills also cause serious damage to the planet's water resources.[1-4] Urbanization in different countries is another aspect that aggravates the pollution situation. According to experts, by 2050, the population of cities is expected to increase to 2/3 of the total world population. The rapid pace of increasing urbanization requires high material and human costs in the organization of wastewater treatment systems.

The Main Control Measures to Determine and Reduce the Content of Oil Products in Water

Quality control and application of modern cleaning technologies are available only to cities in developed countries, while it is not available to residents of other cities, so the volume of uncontrolled industrial waste and untreated wastewater increases from year to year.[13-15] The industry has created biologically dangerous persistent chemical compounds, the decomposition period of which in natural conditions is up to a million years. Up to 80% of them in certain concentrations eventually fall into the water, for the circulation of which there are no boundaries. Sufficiently hazardous liquid wastes are industrial wastewater, as they are characterized by a large volume and, in most cases, are very toxic. According to environmentalists, about 4/5 of the total volume of wastewater is polluted, and this, of course, indicates the low efficiency of the treatment facilities of industrial enterprises. It should be noted that the so-called "volley emissions" of sewage are especially dangerous.[1-4,14-16] The main processes leading to a decrease in the content of oil products in water are the chemical and biochemical oxidation of oil products to simple compounds (water and carbon dioxide), which proceeds with the participation of microorganisms that can oxidize oil. The factors determining the rate of these processes are the presence of bottom sediments, nutrients, higher aquatic vegetation, temperature, and oxygen regimes. Scientists have found that with a decrease in temperature from room temperature to +2ºC, the rate of processes that could reduce the content of oil products in polluted waters decreases by 2-3 times. In the case of water pollution with oil products, there are two main stages in the process of reducing the concentration of oil products in a water body, which reflect the natural sequence of changes in the concentration of oil products over time:

1. As a result of physical and/or chemical processes, the removal of the most low-molecular components of oil products occurs (such processes proceed at a high speed).
2. The process of microbiological degradation of oil products is activated, which takes a rather long period of time and is accompanied by a gradual decrease in the residual concentration of oil products.[14,17]

The technologies of the chemical and oil refining industries were originally created without considering wastewater treatment. Small-scale production did not have a noticeable impact on the environment. With technological progress, the number of chemical compounds that are practically indecomposable in nature has increased, and attention has been paid to the problem of hazardous effluents.[14,15,18-22]

Wastewater Contaminated with Phenol-Containing Compounds

The main sources of phenol-containing wastewater are plants with thermal fuel processing complexes. This list includes coking plants, coke gas plants, semi-coking plants, gas generating stations, wood heat treatment plants, and artificial liquid fuel synthesis. In addition, phenolic wastewater is generated at metallurgical, oil refineries, rubber regeneration enterprises, film production, phenolphthalein, salicylic acid, and salol.[1,2,20-22] The properties, composition, and color of phenolic wastewater depend on the raw materials used and the products obtained at the enterprises, and technological regimes. Phenol-containing wastewater from coking plants is yellow or grey, with varying hues. Wastewater generated during the gasification of coke, anthracite, and coal is brown; phenol-containing water in the production of brown coal - is gray-brown or brown. At peat processing plants, phenol-containing wastewater is black or dark brown; for wood processing - red-brown. Phenolic wastewater has a pronounced smell of tar, phenol, naphthalene, hydrogen sulfide, burnt peat, and acetic acid. They have zero transparency and high temperature (up to 70 °C). Phenolic wastewater contains a variety of organic and inorganic components hazardous to the environment and humans, such as phenols, naphthalene, benzene, fatty acids, alcohols, aldehydes, polycyclic aromatic carbohydrates, volatile and bound ammonia, thiocyanates, cyanides, hydrogen sulfide, sulfates, chlorides, whose concentration varies over a wide range.[1-4,12] Phenolic wastewater degrades the organoleptic properties of water. Unpleasant odor and taste that appear in water at a concentration of phenol 15-20 mg / L, and cresols - 0.002-0.005 mg / L, make drinking water unsuitable for use. In drinking water, due to its chlorination, a pharmacy smell appears at a concentration of phenol of 0.001 mg / L and 0.001-0.002 mg / L of creosols.[12,23,24] Phenolic waters are dangerous for fishery reservoirs. At a concentration of phenol in water of 0.3–0.5 mg/L, fish meat has a specific smell and taste, and at a concentration of 5–20 mg/L in water, fish die. In places where phenolic wastewater is discharged and at considerable distances below their discharge, significant facts of fish death are observed. Phenolic waters disrupt the natural processes of self-purification. Surface reservoirs, especially small ones, turn into sewers without flora and fauna. They cannot be used for cultural, recreational, and household needs. In addition, surface water bodies contaminated with phenolic wastewater contribute to the deterioration of groundwater quality.[14,15]

Purification of Water from Pollution with Phenols

Water purification methods are often considered separately for each class of impurities: minerals, organic products, dissolved gases, and colloidal solutions. The concentration of dissolved petroleum products in wastewater is determined by the chemical composition and structure of the molecules of pollutants. To reduce the concentration of petroleum products in water to the level of MPC, deep purification methods are used in the final stages. When refining oil with a sufficiently high concentration of sulfur, wastewater containing, mg/L is formed: petroleum products – 3,000 mg/L and volatile phenols – 5,000 mg/L; sulfides – 26,000 mg/L; total sulfur – 35,000 mg/L. The total alkalinity is 100,000, and the pH of the wastewater reaches 14.[1-3, 24-26] The results of the analyses show that phenol is particularly dangerous due to its relatively good solubility in water. Other cyclic and aromatic compounds and alcohols are also dangerous. When choosing a method for removing phenols from water, first of all, it is necessary to establish the chemical and group composition of the contaminants present in it. Further, based on the requirements for water quality and its volume, the most effective method of purification is selected.

Deep cleaning methods are regenerative and destructive.[27-32] The main destructive methods of factories wastewater treatment from phenolic effluents are thermo-oxidative and oxidative methods, as well as electrochemical oxidation and hydrolysis. Destructive methods are used if it is impossible or economically inexpedient to extract impurities from industrial wastes that do not require the return of phenol to production. The choice of a destructive method for phenolic effluents from factories disposal is made mainly taking into account the wastewater consumption, composition, amount of phenol and requirements for the quality of purified water, and the possibility of its reuse. Destructive methods involve the decomposition of the phenol molecule into less toxic molecules, usually with a lower mass. For example, it can be a biological purification method, during which mineralizing bacteria break down the phenol molecule to safe compounds with their enzymatic system. There are several technologies for extracting phenol effluents (Fig.-3). They in rare cases make it possible to treat wastewater from phenol effluents to MPC level and below.[28-31]

By means of regenerative methods in the treatment of wastewater in chemical industries it is possible to neutralize wastewater and extract phenols with their subsequent use. Such methods involve the return of phenol to the production process or its processing into alternative products. For example, phenol is sometimes converted into resole resins, which are later used to make plywood, or into polyethylene glycol phenyl ethers.[30,31] According to the literature data, catalytic methods of moist-air oxidation of phenols to CO_2 and H_2O have been developed in the last decade.[4,14,28-40] The possibility of using transition metal nanoparticles deserves special attention, which makes it possible to significantly change the direction and rate of chemical processes. The versatility of the properties of cluster and nanosized particles synthesized in the last decade makes it possible to use them in the processes of deep oxidation of phenolic compounds. By changing the nature of the catalytically active metal, it is possible to control the selectivity of the process and ensure the maximum conversion of highly toxic substances to environmentally friendly substances. However, the successful application of such systems is possible only in the case of their systematic study, including the physicochemical analysis of the formation, morphology, structure, and stability of nano dispersed metal particles, the sorption of substrates and reaction products on the surface of nanoparticles, and the study of the kinetics and mechanism of the reaction.

Physical and chemical research and analysis of nanostructured systems, the accumulated experience allows the targeted synthesis of such systems with predetermined properties. Nano disperse catalysts must provide a high rate of oxidation of phenolic pollutants, efficient oxidation of a wide range of compounds with various functional groups, low cost, and long service life without noticeable loss of catalytic properties, as well as high mechanical strength and immunity to catalytic poisons.

The use of biocatalysts based on immobilized enzymes will make it possible to carry out reactions under heterogeneous conditions and prevent the entrainment of catalytically active components by the mobile phase. At the same time, the carrier, being an integral part of the microenvironment of the immobilized enzyme, is able to significantly increase the activity of the latter.

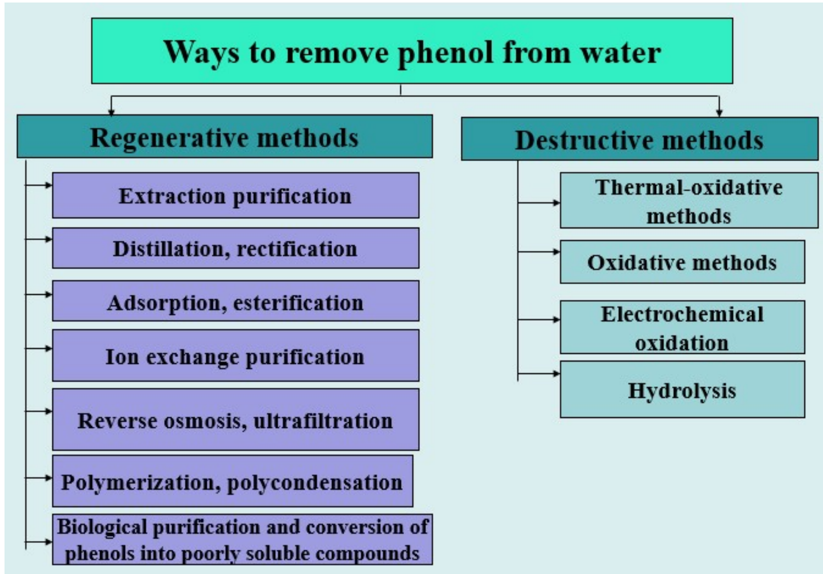

Fig.-3: Water Purification Methods from Phenols

Immobilization also makes it possible to significantly prolong the time of use of the biocatalyst and reduce the cost of carrying out the biocatalytic process. The use of immobilized enzymes in the system of treatment facilities does not imply the creation of unique expensive energy-intensive equipment, and biocatalytic processes can be harmoniously integrated with other stages of water treatment and purification.[33-36]Water purification from phenol requires the development of optimal technological schemes of water treatment, which could provide a significant reduction in the content of phenols in water.[14,15,37-41]
Currently, industrial enterprises practically do not use catalytically active nanomaterials for wastewater treatment due to a lack of knowledge and technology. However, the advantages of these methods (low consumption of nanosized catalysts, simple instrumentation, low process temperature, and absence of aggressive components) make them especially attractive for water treatment. There is no specifically developed technology that provides 100% wastewater treatment from highly toxic organic compounds, and this, of course, leads to the fact that industrial enterprises hide the real numbers and composition of emissions into wastewater. All of the above requires the creation and implementation of new highly efficient nano- and biotechnologies for wastewater treatment from phenolic compounds.

CONCLUSION

According to the conclusions of Eurostat, the share of treated industrial wastewater relative to the total volume of industrial wastewater produced is only 1/3, of which only 3% is safely treated water. In order to gain additional knowledge about global wastewater and to promote sustainable and safe strategies, including wastewater reuse, it is necessary to improve reporting on industrial wastewater by sources of formation and by type of treatment technology and percentage of wastewater treatment. The water purification technologies using phenol oxidation in the liquid phase are attracting more and more attention from scientists and specialists and among them, the technology of oxidation of phenol-containing compounds with atmospheric oxygen on heterogeneous catalysts is one of the most promising.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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