

# Photochemical methods for solving ecological problems of the hydrosphere

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Water is an essential prerequisite of human existence, health, well-being, and all human activity. This paper is a survey of various water treatment methods. The complication of the phototransformations occurring under the action of UV radiation (both natural and occurring during water purification) in aqueous media with contaminating admixtures leads to the urgent need for analysis and control of these phenomena.

Water is the most widespread natural substance and the prerequisite for life on Earth.<sup>1</sup> Limitations of water resources, and their contamination, create extremely complicated problems for mankind. According to official data,<sup>2</sup> every second inhabitant of Russia drinks water that does not conform to hygienic requirements. The situation is especially unfavorable in the basins of the rivers Don, Kama, Volga, Belaya, and Tom'. Along some stretches of these rivers, the water contains considerable concentrations of technogenic pollutants: phenols, petroleum products, chlorinated organic pesticides, ammonium and nitrate nitrogen, and heavy-metal ions.

So the problem of developing methods for water treatment and purification from various kinds of pollutants is quite urgent. At present, there are many modern methods for purification and conservation of water: electron-beam treatment of water and sewage, plasmochemical and photochemical methods of water purification, application of ozone, hydrogen peroxide, and Fenton agent (with Fe<sup>2+</sup> salts as catalysts), chemical oxidation, ultrasound, and oxidation in water under supercritical conditions.<sup>3</sup>

The interest in new technologies for environmental control is very high throughout the world. It is manifested both in the development of theoretical foundations and in applied problems. In some of the above-mentioned technologies, laboratory studies lead directly to industrial applications. Different methods are often combined in order to enhance the desired effect. For instance, UV light + hydrogen peroxide, UV light + hydrogen peroxide + ozone, UV light + Fenton agents, and other combinations. In the case when some of the pollutants are biodegradable, photochemical and biological methods are combined.

We discuss photochemical methods of treatment of organic impurities in water (the irradiating light can be varied in power, duration, and spectral composition) and mention some features arising in the course of photo processes when different methods are combined.

Treatment with UV radiation at different power levels is an important means of purifying water from molecular organic pollutants: the molecules are

decomposed by the light, and the problem then arises of removing the photodecomposition products by different methods (e.g., sorption methods). The complicated nature of the phototransformations occurring during UV radiation in aqueous media containing various pollutants leads, as was mentioned in Ref. 4, to the urgent need for fundamental photochemical studies together with the development of applied technologies. However, most of the published material on this subject deals with systems of non-aqueous solutions. At the same time it is evident that a fundamental study of photochemical processes in aqueous media would be very useful both from a theoretical and a practical viewpoint. As for studies of photolytic processes for organic compounds in aqueous media, they are not numerous and of an exclusively applied character. This is why the famous Canadian photochemist J.R. Bolton came to the conclusion that "there is an urgent need for a fundamental photochemical study allowing one to explain the mechanisms of photolytic reactions and develop new photochemical decomposition processes, understand their mechanisms and eliminate kinetic barriers. A fundamental study of photochemical processes in aqueous solutions would be especially useful."<sup>4</sup>

In the first place, attention must be focused on phenol. First of all, phenols are among the most widespread and damaging pollutants of the environment<sup>5</sup> because they are produced in large quantities and are deposited in the environment in industrial effluents (Table 1), as well as by accidental spills and during transport.<sup>6</sup> Phenols are very toxic and have an extremely damaging effect on living organisms.<sup>7,8</sup> Second, the concentration of such ecotoxicants is especially high in the waters of our West Siberian region, i.e., the specificity of the pollutant sources of a specific region is important.<sup>9</sup> Third, phenoxy and oxyphenyl groups are included into molecules of many organic compounds, phenol is an intermediate photooxidation product of many aromatic compounds.<sup>6,10</sup> According to the norms for drinking water, maximum permissible concentration for phenol is about 0.5 µg/l.<sup>11</sup>

**Table 1. Phenol content in waste water of different processes<sup>12</sup>**

Type of source	Concentration, g/l
Gasification:	
coke	Traces – 0.007
anthracite	0.01 – 0.10
hard coal	2.30
shale	0.62 – 1.20
brown coal	0.50 – 6.00
peat	1.20 – 5.20
Production:	
phenol	12.00 – 15.00
resins	0.01 – 35.20
wood-fiber sheets	0.08
plastics	30.00
phenolformaldehyde resins	30.00
paint and varnish	0.40
polyacrylates	4.20
Petrochemical plants	0.20 – 0.40
Wood processing	0.39
Coke by-products industry	0.40 – 6.70
Mining	7.00 – 12.00

The Environmental Protection Agency (USA) and the European Commission included phenol in their lists of the most serious pollutants requiring further study.<sup>12</sup> The main sources of phenol transport into the environment are summarized in Table 1. Phenols are used for disinfection and in the production of glues and phenol-formaldehyde plastics. In addition, they are contained in the exhausts of gasoline and diesel motors, and are formed during combustion and in wood and coal coking. Phenols can penetrate into natural waters as a result of various biological processes, e.g., decomposition of plant materials, leaching from soils, etc.

Under temperature drops, solar radiation, biotic and abiotic transformations, pH variation of water sources of the environment, phenols are converted into a spectrum of new, more dangerous products. For instance, in the chlorination of phenol-containing drinking water, they can form dibenzodioxins (class-1 carcinogens).<sup>14</sup> In addition, phenols possess an extreme phytotoxicity, which disrupts the ecological balance in the ecosystem of basins.

The maximum permissible concentrations (MPC) for phenols vary from 1 down to 0.0004 mg/l, and the total concentration of phenols in chlorinated water should not exceed 0.001 mg/l.<sup>15</sup> This is due to the above-mentioned transformation processes occurring during phenol chlorination. The MPC's of some phenols are listed in Table 2. Thus, the need for strict control of phenol content and transformation in different natural water bodies is clear.

The rate of decomposition of phenols in water depends both on their chemical structure and the ambient conditions. UV radiation, microorganisms, and the oxygen concentration in water play a special role. Further, one must take into account that the most widespread method of chemical sterilization of water—chlorination (a method of chemical oxidation)—leads to the appearance of toxic organic chlorine derivatives.

Further transformations of the derivatives have their own salient features. For instance, chlorophenols formed in strongly chlorinated water deteriorate the taste and quality of water even more than non-halogenated phenols. Besides, pentachlorophenol, which possesses strong fungicidal, insecticidal, and bactericidal properties, is especially widely used in wood processing and is also used in other industrial processes. Pentachlorophenol can enter an organism through the skin or with water, food, or inhaled air. Due to its high lipophilicity, pentachlorophenol can be accumulated in fat deposits and the liver, and it is excreted very slowly from the organism. Pentachlorophenol is very toxic. The minimal lethal dose for a human is 2 g. Due to its high toxicity, this preparation is used only in open air; indoors, it is used only with great care. In Finland, rivers and lakes are polluted with chlorophenols due to the large number of wood processing plants.<sup>9</sup> Along with other ecotoxicants, phenols pollute the coastal waters of the Gulf of Finland. The relatively recently discovered super-ecotoxicants, chlorinated dioxins, can be oxidation products of phenol chlorine derivatives and polychlorinated biphenyls.<sup>9</sup>

**Table 2. MPC for some phenols**

Compound	MPC, mg/l	Solubility, g/l
Phenol	0.001	6.70
<i>o</i> -Cresol	0.050	31.00
<i>m</i> -Cresol	0.004	24.20
<i>p</i> -Cresol	0.050	24.00
<i>p</i> -Chlorophenol	1.000	27.10
<i>p</i> -Nitrophenol	0.060	13.50
2,4-Dinitrophenol	0.030	5.60
<i>o</i> -Aminophenol	0.011	17.00
<i>m</i> -Aminophenol	0.050	26.00
<i>p</i> -Aminophenol	0.050	11.00
2,4-Dichlorophenol	0.002	4.60
2,4,6-Trichlorophenol	0.0004	0.80

Therefore, although chlorination is the most widespread method for water purification (because chlorine is comparatively cheap, active, easy to use, dose, and control, and has a wide spectrum of antimicrobial action), it is clear that alternative methods must be developed and applied.

Among physical methods, the UV method of water purification finds widest application, as it is ecologically clean and requires no reagents. The development of powerful radiation sources and new design solutions for UV units equipped with sensitive detectors permitting one to control and measure the radiation intensity in the treated water and provide automated control of the intensity depending on the water quality have made this method competitive and comparable with chlorination in price. Beginning in the 80's, this technology for water purification has been steadily developed in the West. During the last 10–15 years, about 150 UV water treatment stations with flow rates from 10 to 350 m<sup>3</sup>/24 hours have been put on line in

the USA, Canada, and Western Europe. UV technology has gained increasing currency in New Zealand and Near East.

The first UV water purification unit in Russia was put into operation in Ufa,<sup>17</sup> and then later in Moscow. At present, the method is applied in Tomsk, especially at water supply stations. Tomsk underground waters are highly transparent and in fact colorless. In this case, UV is lower in price in comparison with chlorination.

The sources of UV radiation are mercury-quartz high-pressure lamps and argon-mercury low-pressure lamps with uviol glass envelopes.

The accelerated introduction of UV disinfection of the water supply in intermediate and large volumes has associated with it a number of advantages<sup>16</sup>:

1) the rate of expenditure of energy in industrial plants is 3–4 times less in comparison with the total energy consumption rate in ozonizer systems;

2) the degree of UV disinfection grows with UV radiation dose not linearly but exponentially, so a small increase of power for a given flow rate of the processed liquid increases the degree of disinfection by several fold. In the case of overdosing, there are no negative effects, in contrast to oxidation technologies;

3) modern UV complexes based on low-pressure arc lamps utilize industrial power supplies with voltages of 110, 220, and 380 V; ozonizer complexes require from 8 to 30 kW, which leads to higher demands on safety and qualification of the personnel;

4) the high degree of reliability and simplicity of operation, together with the absence of technologically dangerous ingredients (ozone, chlorine);

5) UV radiation does not alter the oxidation characteristics of water, i.e., there are no side effects;

6) minimal duration of the processing;

7) in comparison with ozonization, UV treatment requires half the investment and entails one-fifth the operating costs. This is due to its insignificant consumption of electric energy and the absence of a need for expensive reagents.

There are two types of photoreactions used in photochemical water processing: direct and indirect. They are often used jointly.<sup>9</sup> In direct photolysis, light is absorbed by the decomposed compound itself; during indirect photolysis, light is absorbed by an intermediate compound, sensitizer or initiator. Indirect photolysis includes combined methods of purification which are nowadays considered to be very promising. Water is acted on by UV and chemical oxidizers: O<sub>3</sub> and/or H<sub>2</sub>O<sub>2</sub>. The efficiency of indirect photolysis through photosensitizers depends on the concentration of the newly formed highly reactive particles, i.e., forms of active oxygen, primarily OH radicals.

The efficiency of direct photolysis depends on the overlap integral of the absorption band contours of the decomposed compound and the radiation of the light sources. At present, there is no adequate nomenclature for the ranges of pollutant decomposition for either wide-band or narrow-band UV irradiators overlapping

in range. But the development of such irradiators continues apace.

When UV radiation is combined with the chemical oxidizers O<sub>3</sub> or H<sub>2</sub>O<sub>2</sub>, one can observe a synergistic effect caused by the formation of forms of activated oxygen, first of all free OH radicals during photolysis of ozone and hydrogen peroxide. OH radicals are strong non-specific oxidizers. However, optimal application regimes for the combined methods are required. Otherwise, instead of synergistic effects, one will observe a sharp decrease in the purification efficiency in comparison with the application of a single method. UV treatment of water possesses a weakly pronounced aftereffect, and, to prevent secondary contamination in water supply systems under uncertain conditions of operation, additional chlorination is used. This underscores the need for a fundamental study and the development of methods which would allow a radical intensification of water purification processes.

However, the UV treatment which is used nowadays pursues first of all the aim of disinfection, not decomposition of harmful compounds in water. Certainly, the bactericidal action of UV rays is based on photochemical reactions resulting in irreversible DNA damage. In addition, UV rays have an effect upon other cell structures, in particular, RNA and cell membranes. Maximum bactericidal action is observed for  $\lambda = 250\text{--}260$  nm. The UV radiation sources are high- and low-pressure mercury lamps. The photochemical transformations of chemical compounds dissolved in water have not been studied in sufficient detail.

Possible photoreactivation of bacteria is a shortcoming of this method, i.e., it is necessary to select the power correctly. Reactivation under the action of the Sun is also possible. All the same, UV technologies are widely used in North America. The biggest UV station is located in Calgary (Canada) and its productivity is more than 1 million m<sup>3</sup>/day.

Many questions have not even been studied yet. Besides, there are some contradictions in the data. Indeed, the fact of the strong influence of pH values on photolytic efficiency under irradiation by a mercury lamp is well known,<sup>18</sup> but there is no explanation for it. Natural waters differ in their pH values,<sup>19</sup> so, under real conditions, the effect of the medium on the various processes of ecotoxicant photolysis can vary; when one applies indirect, combined methods of photolysis, the combined action of additional factors can complicate the mechanisms of the various photoprocesses.

Besides, there are unsolved problems associated with mechanisms of the effect of oxygen and oxygen-containing compounds upon the phototransformations taking place in aqueous solutions. On the one hand, it is known that phenol chlorination decelerates photodecomposition processes occurring with the participation of oxygen to a considerable extent.<sup>20</sup> On the other hand, data exist indicating that reactions of polychlorophenols with singlet oxygen are rather efficient in aqueous media.<sup>21</sup> Thus, the influence of Cl-substitution

of phenol upon processes of homogeneous photolysis in aqueous solutions and the role of oxygen and oxygen-containing compounds in these reactions must be studied on a fundamental level. The results of such studies will be useful not only for the development of more efficient methods of producing clean drinking water but also for methods of photooxidation of waste waters contaminated with phenolic pesticides. Besides, the available published results on photolysis of phenol and its substituted derivatives are usually for mercury lamps as the excitation sources,<sup>20</sup> and there are no known papers presenting a comparative analysis of homogeneous photolysis in aqueous solutions under the action of radiation sources with different spectra and power levels (mercury lamps, excilamps, excimer lasers). We plan to perform such a comparative analysis.

Using the method of partial neglect of differential overlap in combination with spectroscopic parametrization and the theory of intramolecular photophysical processes,<sup>22</sup> we calculated the energies of electron-excited states of phenol and its water complexes. We studied the dependence of the fluorescence quantum yield on the exciting energy. We showed that the experimentally observed dependence of the fluorescence quantum yield on the exciting energy is determined by phenol photolysis. We considered the photoreaction of breaking of the OH bond. We established its mechanism and the electron-excited states in which the reaction occurs.<sup>23</sup>

We experimentally determined the conditions of formation (different pH values) and spectral-luminescence properties of ionic forms of phenol in water (neutral, anion, cation). We also demonstrated that both the acidic and basic properties increase upon excitation of the phenol molecule.<sup>24</sup> In the first excited Franck-Condon state, which plays an important role in the molecule's phototransformations, phenol in neutral water (pH = 6 – 7) can exist in the neutral, anion, and cation forms. On the basis of the obtained fluorescence data, we came to the conclusion that the above-mentioned forms take part in the various phototransformation processes.<sup>25</sup> We obtained spectral-luminescence and chromatographic properties of the supposed photoproducts of phenol decomposition under UV radiation.<sup>26</sup> Using an excimer XeCl laser as the radiation source, we obtained a difference in the composition of phenol photolysis products in comparison with the UV light of mercury lamps.<sup>27</sup>

Our results together with the present survey of modern water treatment methods and the problems arising in the application of photolytic methods for decomposition of ecotoxicants contained in water lead us to the following conclusions: methods of direct and indirect photolysis show promise in the solution of ecological problems; additional fundamental studies of phototransformation mechanisms are needed.

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