Cleaning high-concentration wastewaters left after styrene and propylene oxide production

S A Andreeva
Department of Technology of Construction Production, Kazan State University of Architecture and Engineering, 1, Zelenaya Street, Kazan 420043, Russia
E-mail: saandreeva@mail.ru

Abstract. The goal hereof is to study the process of preparing high-concentration biologically toxic wastewaters for biological treatment. To attain this goal, the following was analyzed: (a) the composition of wastewaters from an operating enterprise; (b) the methods used to treat wastewaters of similar composition; (c) organic substances contained in wastewaters and how they could be removed by extraction. It is shown herein that the wastewater organics can be separated into another phase by reducing pH-altering acidification through introducing concentrated mineral acids into the wastewaters at room temperature and intensive mixing. In addition, the method of extraction was used for a more complete removal of organic substances isolated from the water phase. In this process the extractant in the amount of 5% out of the total wastewaters volume was used. The research quantified the biodegradation-enabling wastewater impurities.

1. Introduction
Petrochemical companies use wastewater treatment; however, their wastewater cannot be discharged into natural water bodies; in fact, its quality is not even suitable for sewerage [1].

More efficient industrial wastewater treatment requires a comprehensive approach to environmental pollution, which will individually address local treatment processes. It is imperative to consider how pollutants emerge and behave in effluents given the existing industrial setting [2,3].

2. Problem Review
The most common wastewater treatment methods use reagents that trigger chemical reactions to complete the acidification of impurities, but not of the inert components; as a result, such treatment produces multiple byproducts and sludges. This also produces secondary waste that requires disposal. Note that using chemicals is associated with extra costs and need for additional hardware [4-6].

In most cases, effluents are multicomponent mixtures treated with reagents that have different effects [7]. Adding each specific reagent to effluents is expected to cause a reaction with a specific component of the pollutant [8,9]. However, it is necessary to consider the physical and chemical processes occurring between the effluent components, reagents, and intermediate compounds. This fact is what complicates the treatment of high-concentration industrial wastewaters; at the same time, the engineering behind the treatment technology often ignores the fact [10].

Besides, the fact that wastewaters comprise multiple components necessitates multistage treatment based on the redistribution of effluent pollutants, the configured process temperatures, and the...
occurrence of catalytic processes due to active oxidants and metals[11-13]. What further complicates the problem is the fact the wastewaters contain various organic compounds: harmful aromatic cyclic hydrocarbons that mainly affect the genetics of living organisms (Table 1) [9].

**Table 1.** Characteristics of harmful aromatic cyclic hydrocarbons.

| Substances         | Effects on living organisms                                                                 | Hazard class and its name | STEL, mg/l |
|--------------------|-------------------------------------------------------------------------------------------|---------------------------|------------|
| Acetophene none    | Irritates ocular and upper respiratory mucosa; causes convulsions and death from asphyxia | III (moderate hazard)     | 0.003      |
| Benzene            | Irritates the skin and oppresses hematopoiesis. Carcinogen (causes cancer cell growth).   | II (high hazard)          | 1.500      |
| Isopropyl benzene  | Causes coughing, dizziness, sleepiness, sore throat, headache, loss of consciousness, skin dryness, and eye redness. May affect the circulatory system (cause anemia and increased leukocyte count); affects respiratory organs and kidneys. Carcinogen (causes cancer cell growth). Affects the central and the peripheral nervous systems, hematopoiesis, and the digestive tract; disrupts the nitrogen-protein, cholesterol, and lipid metabolism; causes reproductive disorders in women. Systemic toxin that is irritant, narcotic at high concentrations, carcinogenic (causes cancer growth), and mutagenic (causes heritable alterations). A systemic toxin that causes nausea, vomiting, rapid breathing, convulsions; damages the CNS, the kidneys, the liver, the pancreas, and the spleen; severely irritates the mucous membranes and the respiratory tract; also a carcinogen Systemic toxin that causes pathological changes in the lungs and in the cerebral cortex; irritates the mucous membranes and the respiratory tract; narcotic at high concentrations. | IV (low hazard)          | 0.014      |
| Styrene            |                                                                                           | III (moderate hazard)     | 0.040      |
| Toluene            |                                                                                           | III (moderate hazard)     | 0.600      |
| Phenol             |                                                                                           | II (high hazard)          | 0.010      |
| Ethylbenzene       |                                                                                           | III (moderate hazard)     | 0.020      |

3. **Problem Solution**

Mechanical, physical, and chemical methods prepare effluents for biological treatment as the final step of the process cycle that enables environmentally friendly discharge [14]. What prevents effluents from going directly to biological treatment is the high content of organic substances and the difficulty of maintaining neutral pH levels [15].

Significant presence of multicomponent and toxic organics in wastewaters left after styrene and propylene oxide production prevents efficient biological treatment [16]. This is why such effluents were long subject to thermal decontamination. Some companies still use it as the only treatment method [17].

Research has been carried out to find ways to reduce the organic contamination of wastewaters for further biological treatment. This has been accomplished by:
• finding the composition of the real effluents from an operating enterprise;
• analyzing the methods used to treat wastewaters of similar composition;
• researching how organic components of effluents could be separated into another phase;
• using the extraction method to remove organic pollutants.

Model solutions could not be used for research due to the multicomponent nature of effluents. Experiments used real effluents from styrene and propylene oxide production sites. This research revealed the impermanence and strong variability of the basic physical and chemical properties of wastewaters, see Table 2.

Table 2. Physical and chemical parameters of wastewaters from styrene and propylene oxide production sites.

| Real wastewater samples | COD, gO₂/l | pH |
|-------------------------|-----------|----|
| Original wastewater     | After the separation of suspended solids |
| Sample #1               | 94        | 93 | 9.0 |
| Sample #2               | 72        | 67 | 9.0 |
| Sample #3               | 96        | 90 | 9.6 |
| Sample #4               | 32        | 29 | 6.2 |
| Sample #5               | 58        | 55 | 9.4 |
| Sample #6               | 884       | 865| 11.0|
| Sample #7               | 560       | 542| 11.1|

The chemistry of impurities and the physical state of the components contained in wastewater pollutants is what largely determines the most appropriate treatment method [18].

Organic pollutants in these effluents are water-soluble and are contained in dissociated/molecular form. To treat such effluents, the pollutants they contained had to be transformed into water-insoluble compounds. This was attained by creating an acidic environment in the alkaline reaction zone by injecting concentrated mineral acid in the effluents. This helped further separate the obtained insoluble components into another organic phase. However, the phase was not clearly separated and could not be removed by simple discharge. The resultant organic phase comprised oily formations scattered throughout the effluent. Notably, the organic phase constituents are close to water in density, see Table 3. This is why it was difficult to separate organic and aqueous phases. The extraction method addressed this problem and helped remove the separated organics from effluents.

Extraction uses the ability of the extractant (solvent) to selectively solve organic substances and produce water-insoluble compounds. Another important feature of this method is that extractants can mix with different wastewater constituents that they are close to in terms of the boiling point, see Table 3.

Table 3. Physical properties of wastewater constituents.

| Substances       | Aceto phenone | Benzaldehyde | Benzoic acid | Water | Methyl phenyl carbinitol | Propylene glycol | Phenol | Ethanol | Ethyl benzene |
|------------------|---------------|--------------|--------------|-------|--------------------------|------------------|--------|---------|--------------|
| Density, g/cm³   | 1.03          | 1.04         | 1.32         | 1.00  | 1.01                     | 1.04             | 1.07   | 0.78    | 0.86         |
| Boiling point, °C| 202.3         | 178.1        | 249.2        | 100.0 | 204.0                    | 136.2            | 181.8  | 78.4   | 136.0        |

Literature [18] suggests that the hardware used in the process is rather simplistic, that the extraction process could be automated. It also reaches a 80% to 90% industrial wastewater treatment efficiency.
These facts were the reason why extraction was chosen by the authors hereof as a part of the wastewater treatment process. Extracting involves targeted use of the positive extractant properties such as selectivity, distribution coefficient, inertness, solubility, density, and boiling point.

The experiments employed the following extractants: ethylbenzene, amyl acetate, butyl acetate, and octyl alcohol, see Table 4. In each sample, the amount of added extractant was varied from 5% to 20% of the total effluent volume. Experiments were repeated with each fixed sample at least 5 times. Table 4 presents the averages of all experiments.

The results suggest that extractant volume must be 10% of the total wastewater volume for most efficient treatment.

| Sample | pH  | Extractant amount, % | COD, gO2/l | Extractant | COD, gO2/l | Extractant | COD, gO2/l | Extractant | COD, gO2/l |
|--------|-----|----------------------|------------|------------|------------|------------|------------|------------|------------|
|        |     | before extraction    | after extraction | Amyl acetate | Butyl acetate | Octyl alcohol | Ethylbenzene | | |
| 1      | 9.0 | 5                    | 73.6       | 72.3       | 61.9       | 74.8       |
|        |     | 10                   | 60.3       | 58.1       | 57.2       | 66.9       |
|        |     | 15                   | 72.4       | 69.4       | 65.7       | 70.2       |
|        |     | 20                   | 81.8       | 68.7       | 60.8       | 71.9       |
|        |     | 5                    | 22.6       | 70.2       | 23.4       | 26.4       |
| 2      | 6.3 | 10                   | 18.7       | 20.8       | 20.8       | 19.8       |
|        |     | 15                   | 23.1       | 24.5       | 38.4       | 27.8       |
|        |     | 20                   | 26.2       | 23.8       | 41.2       | 32.1       |
|        |     | 5                    | 46.7       | 43.9       | 42.7       | 54.2       |
| 3      | 9.4 | 10                   | 44.6       | 41.4       | 39.8       | 41.6       |
|        |     | 15                   | 51.2       | 50.7       | 46.7       | 48.9       |
|        |     | 20                   | 49.6       | 49.1       | 51.7       | 62.3       |
|        |     | 5                    | 589.3      | 542.1      | 530.2      | 548.2      |
| 4      | 10.7| 10                   | 563.8      | 518.4      | 510.9      | 536.4      |
|        |     | 15                   | 601.4      | 538.5      | 538.7      | 560.1      |
|        |     | 20                   | 577.9      | 540.8      | 541.4      | 558.4      |
|        |     | 5                    | 60.8       | 52.7       | 63.8       | 67.4       |
| 5      | 9.2 | 10                   | 48.1       | 48.2       | 51.2       | 52.8       |
|        |     | 15                   | 56.4       | 56.1       | 69.4       | 72.5       |
|        |     | 20                   | 58.7       | 58.2       | 70.2       | 65.9       |
|        |     | 5                    | 71.2       | 60.3       | 72.4       | 71.4       |
| 6      | 9.3 | 10                   | 57.6       | 56.6       | 59.8       | 56.8       |
|        |     | 15                   | 68.4       | 60.9       | 61.7       | 71.9       |
|        |     | 20                   | 65.8       | 58.3       | 69.8       | 63.4       |

Experiments thus showed that the removal of organics from effluents is mainly predetermined by acidifying the wastewaters, which enables organic substances to transit from dissociated state into non-dissociated state, making them form a separate organic phase. Therefore, wastewater pretreatment is a two-stage process: Stage 1 (acidification) is necessary, as only it enables efficient extraction, which is Stage 2.

Research results have been used to retrofit an existing styrene/propylene oxide production facility to improve wastewater preparation to biological treatment; this effort reduced the COD to within 35-45 gO2/l.
4. Conclusions
1. Acidifying wastewaters to pH 1–3 causes organic pollutants to become insoluble in effluents, which reduces the total contamination of the effluents to be treated.
2. Organic decontamination can be improved to 35-45% by extraction.
3. When used in a real-world setting, the developed wastewater treatment method helped further clean the effluents prior to biological treatment and disposal.

References
[1] Petrov S A and Krushenko G G 2000 Non-reagent purification of drinking water, sewage and industrial effluents Water and ecology: problems and solutions 4(5) 29–31
[2] Smirnova V S, Khudorozhkova S A and Ruchkina O I 2017 Purification of highly concentrated wastewaters of industrial enterprises from phenols Bulletin of the Perm National Research Polytechnic University. Construction architecture 8 52–63
[3] Ilyin V I, Brodsky V A and Kolesnikov V A 2015 Development of technological solutions for wastewater treatment from pollution of organic nature Water Purification. Water Preparation. Water Supply 4(88) 16–19
[4] Zakirov R K, Ulyanin A P and Akhmadullina F Y 2013 Reagent treatment of highly toxic and concentrated wastewaters of the petrochemical complex Bulletin of Kazan Technological University 16 11 79–81
[5] Yagafarova G G, Aminova A F, Sukhareva I A, Hangildina A R and Hangildin R I 2016 Development of a method for purifying waste water from hardly oxidizable organic compounds Water: chemistry and ecology 1 24–29
[6] Zhuravleva L L, Artemenko S E and Ustlnova T P 2004 Selection of methods of industrial wastewater treatment Fibre Chemistry 36 2 156
[7] Kardash M M, Fedorchenco N B and Fedorchenko A A 2003 Problems of wastewater treatment and methods of solving them Fibre Chemistry 35 1 79–82
[8] Kosogina I, Astrelin I, Krimets G and Vereshchuk N 2014 The process of wastewater treatment with advanced oxidation methods to remove dye Chemistry and Chemical Technology 8 3 365–369
[9] GrushkoYa M 1982 Harmful organic compounds in industrial wastewater; Handbook 2nd ed., Perekh. and add (Leningrad: Chemistry Press) p 216
[10] Molokanov D A 2011 An integrated approach to wastewater treatment Ecology of production 5 79–81
[11] Rysbek A B, Tynykulyov M K and Salgozhaeva G M 2017 The analysis of different methods of biological wastewater treatment Modern Science 2 23–25
[12] Mukhamatdinova A R, Safarov A M and Magasumova A T 2012 Assessment of the impact of petrochemical enterprises on the environment Georesources 50 8 46–50
[13] Ibragimov R A and Izotov V S 2015 Effect of carbon nanotubes on the structure and properties of cement composites Inorganic Materials 51(8) 834–839
[14] Rasulov S R, Guseinova L V and Mustafayeva G R 2016 Physical problems of liquid-phase extraction for oil wastewater treatment processes Equipment and technologies for oil and gas complex 5 32–34
[15] Bogdanov R R and Ibragimov R A 2017 Process of hydration and structure formation of the modified self-compacting concrete Magazine of Civil Engineering 73(5) 14–24
[16] Ibragimov R A and Bogdanov R R 2017 The influence of a complex modifying agent on the hydration and structure formation of self-compacting concrete ZKG International 70(4) 44–49
[17] Ibadullaev F Y and Novruzov K M 2010 Purification of highly concentrated wastewater with stepwise countercurrent extraction Water: chemistry and ecology 2 38–41
[18] Bakanov K T, Cherikov ST and Batikbekova M B 2014 Wastewater treatment with extraction News of the Kyrgyz State Technical University named I. Razzakov 32 1 363–369