



Analysis of pretreatment methods of the aqueous phase obtained from hydrothermal liquefaction of excess activated sludge

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Abstract

The study focuses on the chemical pretreatment of the aqueous phase formed during the hydrothermal liquefaction of excess activated sludge. This study aims to find the most efficient method of chemical pretreatment of the aqueous phase. The purification methods used are: oxidation with Fenton's reagent, oxidation with sodium persulfate, precipitation of organic substances with polyaluminum chloride, sorption. COD, BOD₅, dry residue and calcined residue values were determined in the sample to evaluate the efficiency of the aqueous phase treatment. The best results in water phase purification were achieved by sorption with BAU-A industrial carbon (COD value decreased by 1.8 times, BOD₅ by 20 times, dry residue amount by 1.1 times, calcined residue by 2.7 times). The purified sample showed a 1.9-fold reduction in toxicity in terms of dehydrogenase activity level and a 3.5-fold reduction in inhibition. Based on the data obtained, sorption pretreatment can be recommended as a pretreatment method for HTL-AP.

Keywords: excess activated sludge; HTL-AP; hydrothermal liquefaction; chemical pretreatment, oxidation, sorption, flocculants, toxicity.

Introduction

One of the by-products of oil production by hydrothermal liquefaction is the aqueous phase (HTL-AP). It is a dark-colored liquid with an unpleasant odor. This water is too contaminated to be treated using traditional biological methods. Consequently, the search for technological and engineering solutions for the purification such water is a relevant task for the successful industrial implementation of HTL.

Thomsen et al. [1] analyzed HTL-AP obtained during processing of excess activated sludge. The authors measured COD, total carbon, volatile fatty acids, total nitrogen content, ammonium ion content, and acetic acid content in wastewater. The authors found that HTL-AP from the excess

sludge treatment process had the following parameters: COD – 60.2 gO/L, carbon content – 22.5 g/L, volatile fatty acids – 1.6 g/L, nitrogen content – 7.9 g/L, ammonium ion content – 2.7 g/L, acetic acid content – 3.6 g/L.

Cheikhwafa et al. [2] in the study of HTL-AP from primary setting tank sludge treatment process obtained values of organic compounds pollution level 5-6 times lower (total carbon content 5.7 g/L, COD: 11.7 mg/L).

Kulikova et al. [3] also conducted studies of HTL-AP from the process of excess activated sludge processing. Table 1 shows the composition of the aqueous phase obtained by hydrothermal liquefaction of excess activated sludge.

Table 1. Physico-chemical characteristics of HTL-AP from excess sludge processing

| Conditions | pH | Organic carbon (g/L) | N (mg/L) | COD (gO/L) | BOD ₅ (gO/L) |
|---|------|----------------------|-------------|------------|-------------------------|
| Temperature 280 degrees, hydromodule 1:15, 10 minutes | 6.71 | 6.560 ±1.021 | 122.0 ±21.0 | 8.8 ±1.8 | 8.1 ±0.7 |
| Temperature 280 degrees, hydromodule 1:15, 15 minutes | 6.52 | 6.634 ±0.340 | 124.7 ±11.6 | 8.0 ±0.8 | 7.5 ±0.5 |
| Temperature 280 degrees, hydromodule 1:15, 20 minutes | 7.14 | 5.298 ±0.582 | 97.3 ±13.6 | 8.0 ±0.9 | 86.7 ±1.1 |
| Temperature 280 degrees, hydromodule 1:15, 30 minutes | 7.56 | 4.566 ±0.967 | 158.2 ±22.1 | 7.9 ±1.0 | 6.6 ±0.8 |

The authors also evaluated the toxicity of the aqueous phase. Toxicity was evaluated on 2 species of microorganisms, *Paramecium caudatum* and *Artemia salina*. Death rate of organisms in the undiluted sample was 100%. Such death rate indicates the high toxicity of wastewater and the need for chemical pretreatment of water [3].

Xu et al. [4] proved the negative effect of hydrothermal conversion wastewater on the growth of some mosses and microorganisms. The authors proved the fungicidal role of wastewater at a concentration of 1.5%. Such high toxicity of wastewater requires its preliminary chemical treatment before its use as a medium for microalgae cultivation and biological treatment using traditional biological treatment methods.

Given the proven toxicity of HTL-AP, a search for pretreatment methods is necessary. The most common and effective method is ozonation. Aken et al. [5] proved that the preliminary oxidation with ozone allows reducing the concentration of phenol and N-heterocyclic nitrogen compounds in the aqueous phase obtained after manure liquefaction by more than 20%.

Thomsen et al. [6] studied the aqueous phase obtained after hydrothermal conversion of excess activated sludge and the possibility of its purification by wet oxidation. The wastewater was characterized by the following composition: COD 28.3 mg/ L, total carbon content: 11.9 mg/L, total nitrogen content 685 mg/L, pH value 3.85. After wet oxidation, the COD value decreased by 90%.

There is experience in the use of adsorption purification process using zeolites and activated carbon in various forms as sorbents. Activated carbon effectively sorbs aromatic compounds and many other toxic substances, which inhibits the growth of microorganisms during further biological treatment of water. Zhou et al. [7] reported that pretreatment of the aqueous phase with activated carbon can reduce COD to 33.3 % of the initial value and provide a significant reduction in its toxicity.

Extraction is another pretreatment method that can selectively isolate and enrich chemicals from wastewater. Watson et al. [8] used petroleum ether, cyclohexane, dichloromethane, and ethyl acetate to extract compounds from the aqueous phase of hydrothermal conversion. The results showed that petroleum ether extraction resulted in an increase in methane yield during subsequent anaerobic digestion, which was attributed to the removal of furans, ketones, and phenols from the aqueous phase.

The most popular chemical method of wastewater pretreatment is the oxidation of organic matter. One such method is the use of Fenton's reagent. Moskovtseva et al. [9] proved the effectiveness of this method. In addition, the authors gave an example of an experiment on wastewater treatment with Fenton's reagent.

An interesting method of wastewater treatment using oxidizing agents is reported by Pola et al. [10]. The method consists of using sodium persulfate as an oxidizing agent and iron sulfate as a catalyst. The results obtained by the authors demonstrate the promising potential of the method. Based on the results, the authors selected a concentration of 350 mg/L ferrous sulfate (6 mL/50 mL sample), 500 mg/L sodium persulfate (5 mL/50 mL sample and 10 mL/50 mL sample) for their study.

Marrakchi et al. [11] proposed a physicochemical method of purification using organic precipitants (polyaluminum chloride) followed by sorption with carbon sorbents. The authors proposed wastewater treatment according to the following method: bringing the liquid medium to alkaline (1M NaOH), then precipitation of organic substances with polyaluminum chloride (stirring to slightly alkaline medium), subsequent centrifugation and purification of supernatant using sorbents (1g of sorbent/50 mL of water, 30 °C, 12 h).

2. Materials and methods

2.1. Materials

Hydrogen peroxide, ferrous sulfate, aluminum polychloride, and sodium persulfate were of ACS purity grade and purchased from Diaem (Moscow, Russia). Water was distilled on an evaporative distiller immediately before the work.

2.2. Sludge sampling

Sludge was sampled from the water treatment plant of Sovetsk (Kaliningrad Oblast, Russia). At the wastewater treatment plant, the wastewater treatment cycle started with mechanical pre-treatment in various types of setting tanks, followed by aerobic biological treatment in a continuous aerotank, then separation of excess activated sludge in secondary radial flow settling tanks, and sludge treatment/regeneration stages in a regenerator.

Samples were collected in airtight plastic containers of 10 liters each. Samples were stored in the refrigerator (+4 °C) until dried. Upon receipt, all samples were dried and stored in plastic containers.

2.3. *Hydrothermal liquefaction of sludge*

10 g of sample and 100 mL of distilled water were introduced into a hydrothermal liquefaction reactor (Eartha Zhang's, PRC). The reactor, with a working volume of 300 mL, was equipped with pressure (maximum pressure 10 MPa) and temperature (maximum temperature 300 °C) sensors, as well as a magnetic stirrer, with adjustable stirring mode. The process was performed at 260 °C (5-6 MPa) for 20 minutes. Average reactor heating rate: 10 °C/min.

After the process, the reactor was cooled by external cooling (placed in a container with water) to room temperature. The contents of the reactor were then filtered on a Bunsen funnel in a Buchner flask with automatic vacuuming. The reactor vessel and the resulting carbon residue were then washed with dichloromethane and filtered.

The resulting liquid was collected and the aqueous phase was separated from dichloromethane using a separating funnel. Biofuels were obtained by separating dichloromethane using a vacuum evaporator. The aqueous phase was sampled and stored for further studies.

2.4. *Aqueous phase obtained by hydrothermal liquefaction*

The aqueous phase obtained by hydrothermal liquefaction was collected in 50 mL Eppendorf-type centrifuge tubes and stored in a refrigerator (+4 °C).

The aqueous phase is a dark brown colored liquid (Figure 1). The liquid is characterized by an unpleasant pungent odor.



Figure 1 – Aqueous phase of hydrothermal liquefaction of excess activated sludge

2.5. *Chemical pretreatment of the aqueous phase*

Chemical pretreatment was performed using 4 methods:

- Oxidation with Fenton's reagent [9]
- Precipitation of fine organic particles with polyaluminum chloride [11]
- Oxidation with sodium persulfate [10]
- Purification with sorbents

Oxidation of the aqueous phase with Fenton's reagent was performed using 3 methods:

- 1 50 mL of waste water + 10 mL of H₂O₂ (30%), + 0.0010 g FeSO₄, exposure to lamp light (30 min), boiling (80°C, 10 min), filtration;
- 2 50 mL of wastewater + 10 mL of H₂O₂ (30%), + 0.0010 g FeSO₄, heating (60°C, 30 min), boiling (80°C, 10 min), filtration;
- 3 50 mL of wastewater brought to pH 4, + 10 mL of H₂O₂ (30%), + 0.0010 g FeSO₄, boiling (80°C, 30 min), filtration.

The precipitation of fine organic matter was carried out by 3 methods:

- 1 50 mL of wastewater was adjusted to pH 10-12 (1M NaOH). Polyaluminum chloride (water: reagent = 20:1) was added, stirred for 30 minutes, and centrifuged;

2 50 mL of wastewater was adjusted to pH 10-12 (1M NaOH). Polyaluminum chloride (water: reagent = 20:1) was added, stirred for 30 minutes, centrifuged. Carbon sorbent (0.3 g of sorbent per 20 mL of liquid) was added to the obtained liquid. It was stirred for 30 minutes and filtered.

3 50 mL of wastewater was adjusted to pH 10-12 (1M NaOH). Polyaluminum chloride (water: reagent = 100:1) was added, stirred for 30 minutes, and centrifuged.

To perform the oxidation of the aqueous phase with sodium persulfate, the main components were prepared:

The following reagents were prepared: $\text{Na}_2\text{S}_2\text{O}_8$ – 500 g/L; FeSO_4 – 350 g/L;

The aqueous phase was prepared: 50 mL of wastewater was heated to 70°C in a closed beaker under stirring.

Oxidation of the aqueous phase with sodium persulfate was performed using 6 different methods:

1. 50 mL of wastewater + 5 mL of $\text{Na}_2\text{S}_2\text{O}_8$ solution + 6 mL of FeSO_4 solution. Stirred for 30 minutes and filtered.

2. 50 mL of wastewater + 5 mL of $\text{Na}_2\text{S}_2\text{O}_8$ solution + 6 mL of FeSO_4 solution. Stirred for 20 minutes and filtered.

3. 50 mL of wastewater + 5 mL of $\text{Na}_2\text{S}_2\text{O}_8$ solution + 6 mL of FeSO_4 solution. Stirred for 10 minutes and filtered.

4. 50 mL of wastewater + 10 mL of $\text{Na}_2\text{S}_2\text{O}_8$ solution + 6 mL of FeSO_4 solution. Stirred for 30 minutes and filtered.

5. 50 mL of wastewater + 10 mL of $\text{Na}_2\text{S}_2\text{O}_8$ solution + 6 mL of FeSO_4 solution. Stirred for 20 minutes and filtered.

6. 50 mL of wastewater + 10 mL of $\text{Na}_2\text{S}_2\text{O}_8$ solution + 6 mL of FeSO_4 solution. Stirred for 10 minutes and filtered.

Carbon residues obtained by hydrothermal liquefaction (activated and non-activated cane charcoal, non-activated apple charcoal) and BAU-A industrial carbon were used for the purification of the aqueous phase by sorbents.

Sorbent purification was performed using 4 methods:

1. 40 mL of wastewater + 0.1 g of sorbent (cane charcoal, activated with H_2O_2 and H_2SO_4 (30%)). Sorption for 30 minutes, filtration.

2. 40 mL of wastewater + 0.2 g of sorbent (cane charcoal, not activated). Sorption for 30 minutes, filtration.

3. 40 mL of wastewater + 0.1 g of sorbent (apple charcoal, unactivated). Sorption for 30 minutes, filtration.

4. 40 mL of wastewater + 0.1 g of sorbent (BAU-A). Sorption for 30 minutes, filtration.

2.6. Methods of aqueous phase composition control

COD was determined by oxidizing organic substances with a mixture of potassium bichromate and sulfuric acid in a boiling bath for 2 hours. Potassium bichromate consumption for oxidation of organic substances was determined using the titrimetric method. Chemical oxygen consumption was calculated relative to the control sample [12].

BOD₅ was measured as the difference in oxygen content of the sample at the beginning of the experiment and after 5 days of incubation at 20 °C, in oxygen vials. Incubation was carried out without access to light and wind. River water was used as inoculum. The amount of oxygen was measured using an Expert-001 oxygen meter (Econix, Russia). The method was performed according to ISO 5815-1:2003 [13]. Biochemical oxygen demand was measured using titrimetric and amperometric methods.

Dry matter content was measured gravimetrically in dried weighing bottles. The sample was dried at 105 °C.

Ash content was determined gravimetrically by calcination of dry residue at 600 °C. Dry and calcined residue were measured according to PND F 14.1:2:4.261-2010. Quantitative chemical

analysis of waters. Methodology for measuring the mass concentration of dry and calcined residue in drinking, natural and waste water samples by gravimetric method.

The pH value was determined using a J.P Selecta pH meter (BELLAFORM - PÜTZ GROUP, Germany).

2.7. Methods for controlling toxicity of the aqueous phase

To determine the respiratory activity, a method based on the ability of sludge to absorb nutrients from the aqueous medium during aerobic respiration was used [14]. A 300 mL container was used for the study. Solutions containing 0.5 mL and 5.0 mL of test water were used. Copper sulfate solutions with concentrations of 58 mg/L, 100 mg/L, and 180 mg/L were used for comparison.

Respiratory activity was determined as follows: measurements were made in the control sample, in the sample with toxicant (copper ion solution in 3 different concentrations) and in the test sample (2 different concentrations).

To measure the control sample, 200 mL of aerated distilled water, 2.5 mL of thiourea solution, and 16 mL of nutrient broth were added to the container. The container was closed, the contents of the container were stirred on a magnetic stirrer, and the oxygen content of the sample was measured using an oxygen sensor. Next, aerated activated sewage sludge (100 mL) was introduced into the container using a syringe. The amount of oxygen in the sample was measured until it stopped decreasing.

To measure the negative control sample (sample with copper sulfate solution), the same components were added to the vessel, the exception being the replacement of distilled water with copper sulfate solution of a given concentration.

To measure the test sample, 0.5 mL of the test sample (or 5.0 mL), 19.5 mL of distilled water (or 195 mL of distilled water), and then the same components as the control sample were added to the container.

To determine the dehydrogenase activity, the following experiment was performed: 1.2 mL of 1/15M Na₂HPO₄, 0.1 mL of 0.1M MgSO₄, 1 mL of 0.1M glucose, 1 mL of 0.5% 2,3,5-triphenyltetrazolium chloride solution, 1 mL of sludge fluid, and 1 mL of the tested fluid (diluted 10-fold) were introduced into test tubes [15]. The process was conducted for 48 hours as the sludge liquid used exhibited weak enzymatic properties.

After incubation, the tubes were centrifuged (3000 rpm, 15 min), the supernatant was drained, 4 mL of ethyl alcohol was added, and the tubes were centrifuged again (3000 rpm, 5 min). The content of formazan in the obtained liquid was determined using photometric method. Simultaneously, a control measurement was performed, where distilled water was added instead of the test sample.

2.8. Statistical analysis

Each sample was examined in 3 independent parallels, and the mean values are presented. Results were presented as mean ± standard deviation. Standard statistical methods were used to process the obtained data. Data were subjected to analysis of variance using Statistica 10.0 software (StatSoft Inc., 2007, USA).

3. Results

To control the contamination of the water phase, the following indicators were used: COD, BOD₅, dry and desalted residues, pH.

Wastewater treatment methods were grouped into categories and each category was evaluated separately. The purpose of this was to have an objective estimate of the parameters in each method. Then, the best parameters were selected among each method, and the methods were compared.

3.1 Effect of Fenton's reagent oxidation parameters on the degree of wastewater treatment

In the wastewater treatment method with Fenton's reagent, the parameters that were varied are exposure to light, temperature, and pH of the medium (acidification of the aqueous phase to 4). Table 2 summarizes the water parameters treated using these methods. Figure 2 shows samples of wastewater treated with Fenton's reagent. For illustrative purposes, Figure 3 shows the results of wastewater treatment from organic compounds by Fenton's reagent compared to the control.

Table 2. Characterization of wastewater treated with Fenton's reagent

| Conditions | Code No. | COD, gO/L | BOD ₅ , gO/L | pH | DM, % | Ash, % d.m. |
|---|----------|-----------|-------------------------|---------|----------|-------------|
| Control (without treatment) | Control | 16200±200 | 2750±80 | 8.5±0.1 | 2.3±0.1 | 14.0±0.1 |
| 50 mL of waste water + 10 mL of H ₂ O ₂ (30%), + 0.0010 g FeSO ₄ , exposure to lamp light (30 min), boiling (80°C, 10 min), filtration | 1.1 | 10800±100 | 185±20 | 6.0±0.1 | 1.6±0.1 | 17.4±0.1 |
| 50 mL of wastewater + 10 mL of H ₂ O ₂ (30%), + 0.0010 g FeSO ₄ , heating (60°C, 30 min), boiling (80°C, 10 min), filtration | 1.2 | 156300±50 | 1550±80 | 6.0±0.1 | 1.4±0.05 | 17.9±0.4 |
| 50 mL of wastewater brought to pH 4, + 10 mL of H ₂ O ₂ (30%), + 0.0010 g FeSO ₄ , boiling (80°C, 30 min), filtration | 1.3 | 13900±150 | 175±15 | 3.5±0.1 | 1.7±0.3 | 6.0±0.1 |

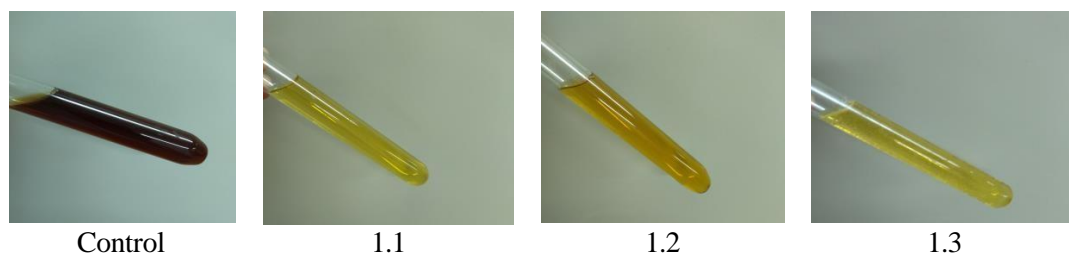


Figure 2 – Wastewater treated with Fenton's reagent

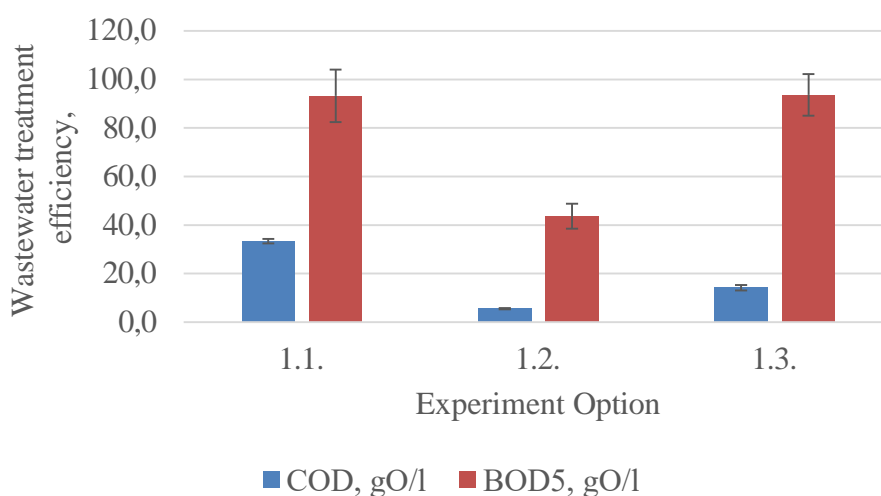


Figure 3 – Degree of wastewater treatment with the Fenton's reagent (reduction of COD and BOD₅)

The greatest reduction in COD was observed in variant 1.1 of experiment when the sample was exposed to lamp light (30 minutes), boiled (80°C, 10 minutes), and subsequently filtered. The reduction of BOD₅ in variants 1.1 and 1.3 of experiment was nearly identical, with values of 93.3% and 93.6%, respectively. The high decrease in BOD₅ also suggests that most of the bioavailable organic matter has oxidized.

The best result among the Fenton’s reagent purification methods is observed in the sample purified by method 1.1.

3.2 Influence of the parameters of the organic particle precipitation by polyaluminum chloride on the degree of wastewater purification

In this method, the ratio of test sample to polyaluminum chloride was varied and additional sorbent purification was performed. Table 3 summarizes the results of water purification by precipitation of organic particles. Figure 4 shows the samples obtained. The degree of purification was evaluated relative to the control. The results are presented in Figure 5.

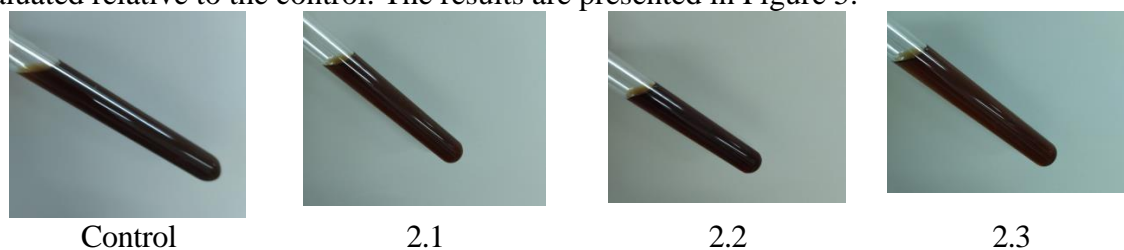


Figure 4 – Wastewater treated with polyaluminum chloride

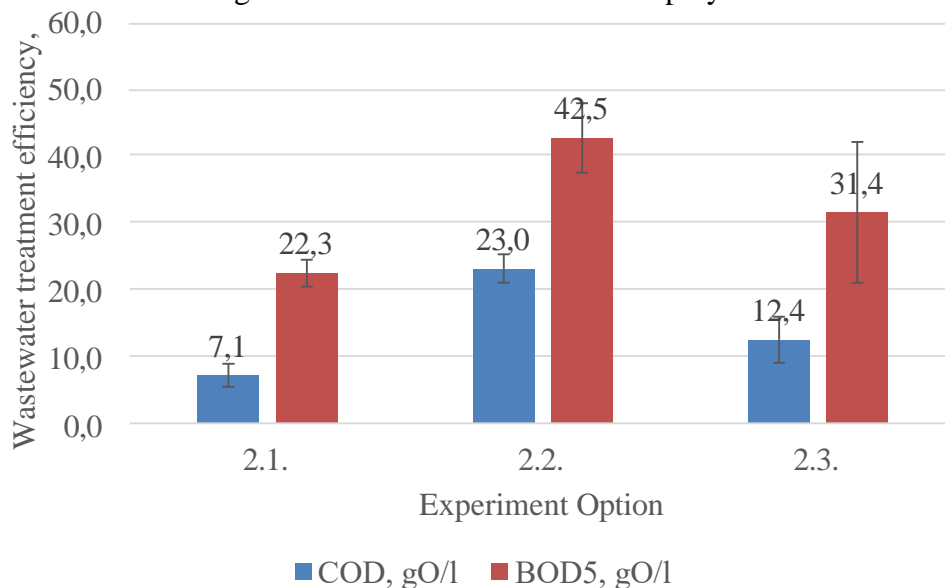


Figure 5 – Degree of wastewater treatment with polyaluminum chloride (reduction of COD and BOD₅)

Table 3. Results of wastewater treatment using organic matter precipitation method

| Conditions | Code No. | COD, gO/L | BOD ₅ , gO/L | pH | DM, % | Ash, % d.m. |
|---|-----------|------------|-------------------------|----------|---------|-------------|
| Without purification | Control 2 | 75600±1300 | 9940±200 | 8.5±0.1 | 2.0±0.1 | 30.0±0.1 |
| Polyaluminum chloride 20:1, without sorbent | 2.1 | 70200±1500 | 7720±400 | 10.5±0.1 | 2.5±0.1 | 22.3±0.3 |
| Polyaluminum chloride 20:1, 0.3 g/20 mL of carbon sorbent | 2.2 | 58200±2000 | 5720±600 | 11±0.1 | 2.1±0.1 | 26.2±1.3 |
| Polyaluminum chloride 100:1, without sorbent | 2.3 | 66200±1000 | 6520±250 | 9.5±0.1 | 2.3±0.1 | 14.8±0.2 |

COD reduction in all variants of the experiment did not exceed 42%, which is significantly lower than the efficiency achieved with Fenton's reagent.

The maximum decrease of BOD₅ (by 23%) was observed in the variant 2.2 of experiment (ratio of water: polyaluminum chloride 20:1), carbon sorbent was added to the obtained liquid). However, a comparison of the removal efficiency of bioavailable organics in series 1 and 2 reveals that the use of oxidizers (series 1) was more effective than sorbents and flocculants (series 2) in achieving this objective.

3.3 Effect of sodium persulfate oxidation parameters on the degree of wastewater treatment

In this series of studies, the amount of sodium persulfate solution applied to the sample and the duration of exposure were varied. Table 4 summarizes the results of wastewater treatment with sodium persulfate. Figure 6 demonstrates the samples obtained after purification with sodium persulfate.

Table 4. Results of wastewater treatment by oxidation with sodium persulfate

| Conditions | Code No. | COD, gO/L | BOD ₅ , gO/L | pH | DM, % | Ash, % d.m. |
|---|-----------|------------|-------------------------|---------|-----------|-------------|
| Without purification | Control-2 | 75600±1300 | 9940±200 | 8.5±0.1 | 2.0±0.1 | 30.0±0.1 |
| 5 mL Na ₂ S ₂ O ₈ , 10 minutes | 3.1. | 39900±2000 | 1160±20 | 2.5±0.1 | 7.8±0.1 | 57.5±2.3 |
| 5 mL Na ₂ S ₂ O ₈ , 20 minutes | 3.2 | 40200±100 | 1180±80 | 2.5±0.1 | 7.2±0.2 | 53.4±0.5 |
| 5 mL Na ₂ S ₂ O ₈ , 30 minutes | 3.3 | 38600±100 | 860±60 | 2.5±0.1 | 7.1±0.05 | 52.1±1.4 |
| 10 mL Na ₂ S ₂ O ₈ , 10 minutes | 3.4 | 37800±2000 | 840±10 | 2.0±0.1 | 11.9±0.1 | 59.1±0.3 |
| 10 mL Na ₂ S ₂ O ₈ , time 20 minutes | 3.5 | 39300±100 | 1250±50 | 2.0±0.1 | 16.6±0.05 | 60.8±0.05 |
| 10 mL Na ₂ S ₂ O ₈ , 30 minutes | 3.6 | 35800±200 | 630±30 | 2.5±0.1 | 10.8±1.7 | 49.2±4.5 |

For illustrative purposes, Figure 7 depicts the outcomes of wastewater treatment for organic compounds by sodium persulfate in the presence of iron, in comparison to the control.

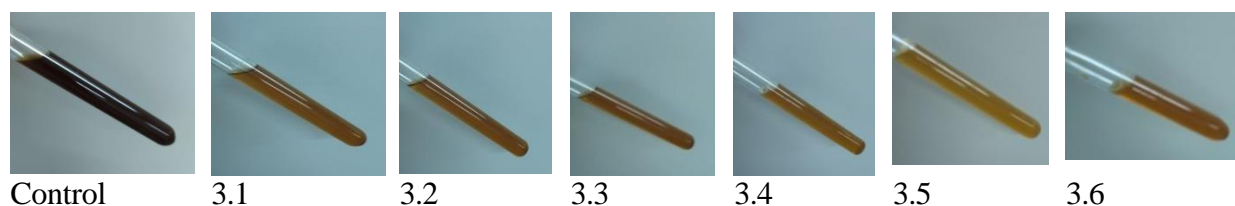


Figure 6 – Wastewater treated with sodium persulfate at different exposure times and concentrations

The degree of reduction of COD and BOD in all variants of the experiment was relatively similar: at the level of 88-94% and 47-53%, respectively. At the same time, it can be seen that with increasing concentration of sodium persulfate, the removal efficiency of organic compounds increases by 5.3%. Increasing the treatment time from 10 to 30 minutes increases the COD reduction efficiency by 3.6 and 5.3% at sodium persulfate concentrations of 41.0 and 75.8 g/L, respectively.

Thus, it can be said that a concentration of 41 g/L and a treatment time of 10 min can be considered sufficient for the pretreatment of the investigated HTL-AP.

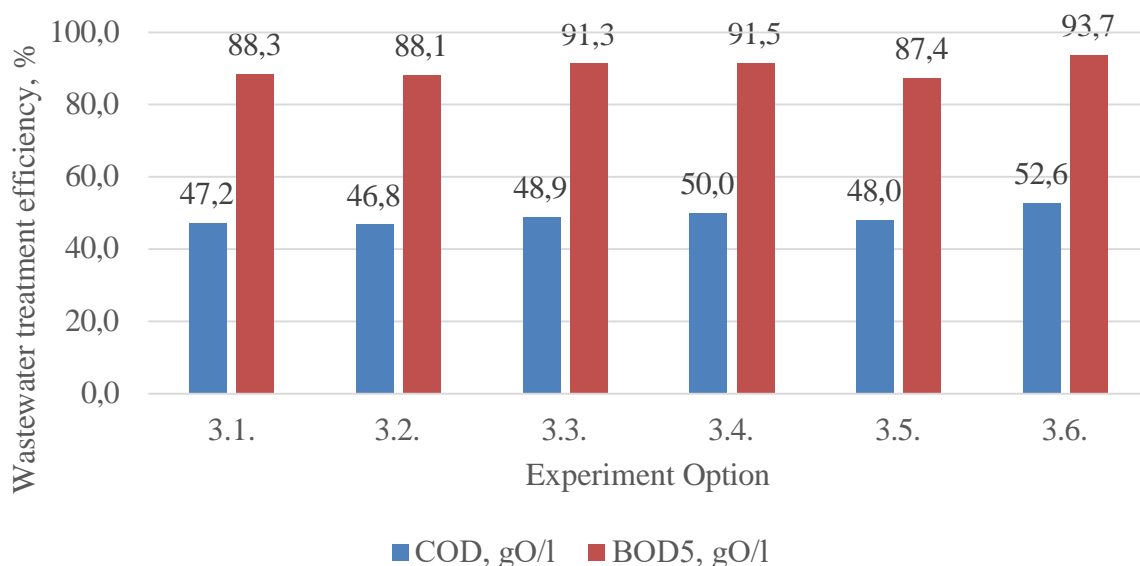


Figure 7 – Degree of wastewater treatment with sodium persulfate (COD and BOD₅)

3.4 Effect of sorbents on the degree of wastewater treatment

In this method, coals obtained by hydrothermal liquefaction were compared with a commercial BAU-A sample.

Table 5 summarizes the results of wastewater treatment using carbon sorbents.

Table 5. Results of wastewater treatment with carbon sorbents

| Conditions | Code No. | COD, gO/L | BOD ₅ , gO/L | pH | DM, % | Ash, % d.m. |
|---|-----------|------------|-------------------------|---------|----------|-------------|
| Without purification | Control-2 | 75600±1300 | 9940±200 | 8.5±0.1 | 2.0±0.1 | 30.0±0.1 |
| Activated cane charcoal, H ₂ O ₂ with H ₂ SO ₄ (30%). | 4.1 | 70200±1000 | 7725±60 | 7.5±0.1 | 2.6±0.1 | 10.0±0.05 |
| Not activated cane charcoal | 4.2 | 63200±1000 | 5780±250 | 6.5±0.1 | 1.9±0.05 | 10.5±0.05 |
| Apple charcoal | 4.3 | 45600±50 | 1120±150 | 7.0±0.1 | 1.8±0.05 | 16.7±0.05 |
| BAU-A | 4.4 | 43200±2000 | 500±40 | 7.0±0.1 | 1.8±0.05 | 11.1±0.05 |

Figure 8 shows the samples obtained with carbon sorbents.



Figure 8 – Wastewater treated with carbon sorbents

Figure 9 shows the results of the comparison between the treated water and the control water.

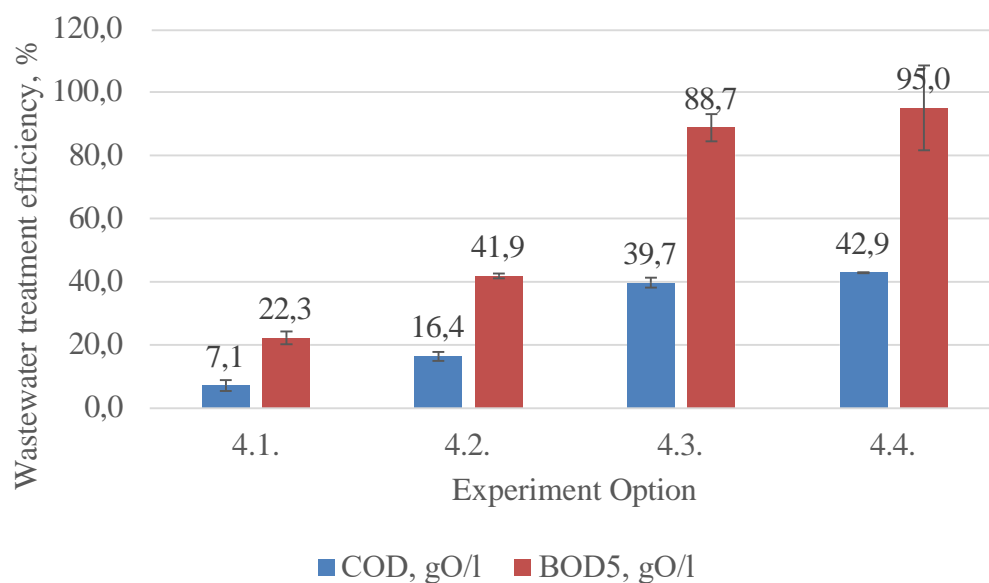


Figure 9 - Degree of wastewater treatment by carbon sorbents (COD and BOD)

As can be seen, the char residue obtained from the hydrothermal cane liquefaction process did not result in a significant reduction of the organic contamination of HTL-AP. At the same time, the carbon from HTL process of apple cake processing had good sorption properties and provided COD and BOD reduction by 39.7 and 88.7%.

The use of commercial BAU-A sorbent provided a 42.8% reduction in COD and a 95% reduction in BOD.

3.5. Comparative evaluation of aqueous phase purification methods

To select the best chemical wastewater treatment method, the best results from each series of experiments were evaluated. Since the main objective of pretreatment was to reduce the concentration of organic compounds and decrease the level of toxicity of wastewater, the comparison of pretreatment options was made based on COD and BOD₅ reduction efficiencies. The results of the comparison are summarized in Figure 10.

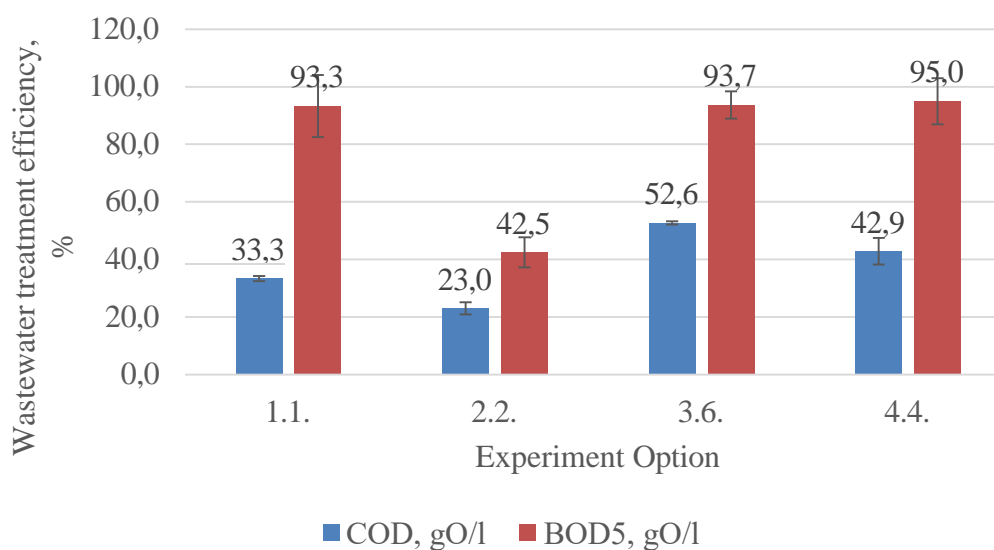


Figure 10 – Degree of wastewater treatment by different methods (COD and BOD₅)

As we can see, the best results for BOD5 reduction (52.6%) were obtained using sodium persulfate at a concentration of 75.8 g/L and a treatment time of 30 minutes. The sorption purification method using BAU-A (42.9%) showed comparable efficiency. Both methods showed high efficiency in reducing HTL-AP COD of 93.7 and 95%. Therefore, it was decided to compare the toxic properties of treated wastewater by the two mentioned methods.

3.6. Toxicity control of the purified aqueous phase

After selecting the best HTL-AP pretreatment method, parameters characterizing the level of effluent toxicity, namely dehydrogenase and respiratory activity, were determined in the selected sample. The source water was used as a reference standard for comparison.

Dehydrogenase activity was measured using sludge fluid. This method characterizes the level of water toxicity to activated sludge organisms; the more toxic the water, the lower the activity. The dehydrogenase activity in the original sample was $28.3 \pm 0.5\%$, in purified water by sorption method and using sodium persulfate $52.5 \pm 1.5\%$ and $48.4 \pm 1.8\%$, respectively. The level of increase in dehydrogenase activity was 1.9 and 1.7 times (Fig. 11), indicating that the sorption method is more promising.

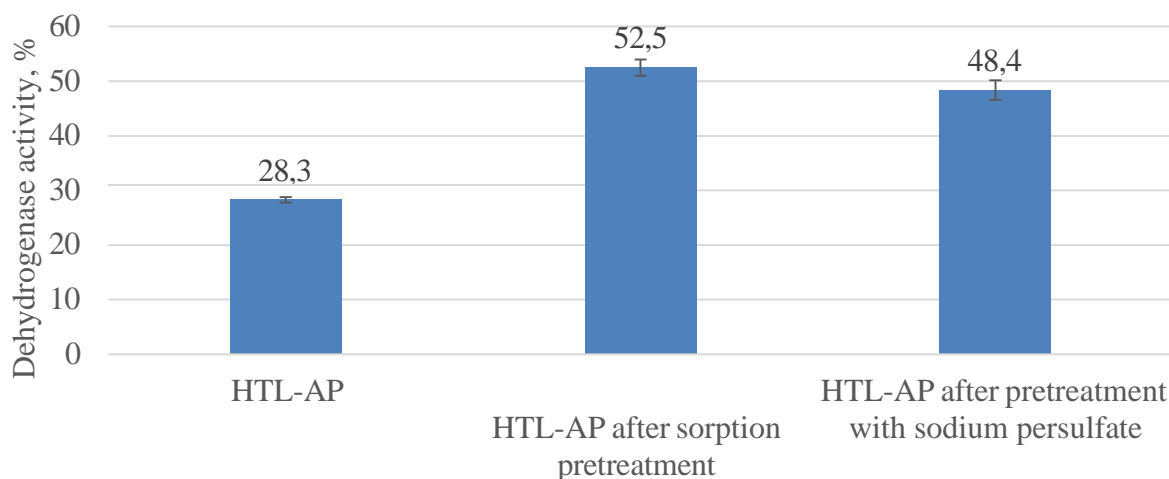


Figure 11 – Change in dehydrogenase activity during the pretreatment process

In addition to dehydrogenase activity, the level of respiratory activity of the sludge is also an important indicator. To evaluate this, the respiratory activity of the sludge was assessed when a control sample and a purified sample were introduced into the system.

Figure 12 shows data comparing the respiratory activity of sludge when treated samples and control (inhibition of oxygen uptake) samples were introduced into the system.

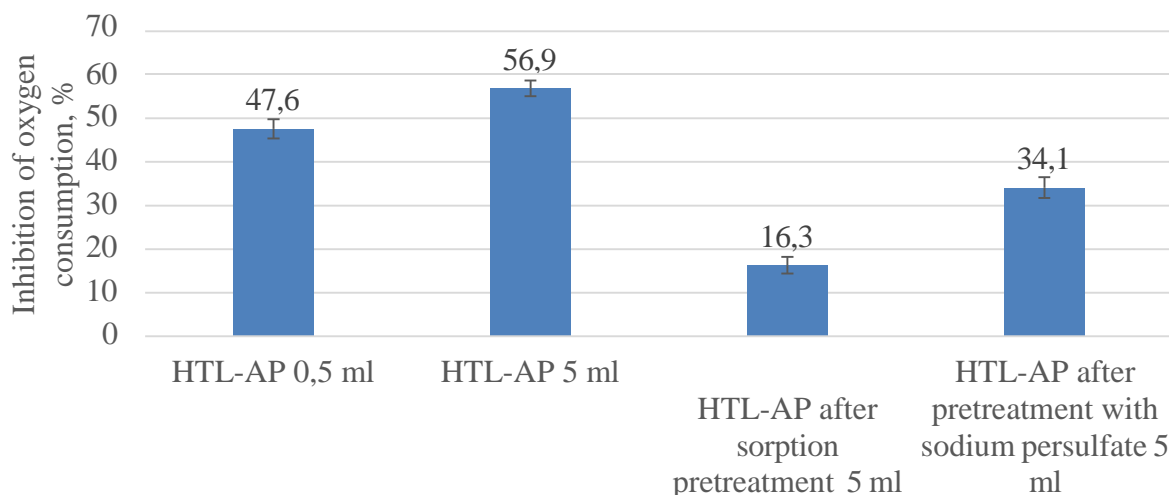


Figure 12 – Inhibition of oxygen uptake

As can be seen from the figures, the control introduces toxic substances into the nutrient environment, which in turn leads to a decrease in respiratory activity. Purified water contains fewer toxic elements and more nutrients. The rate of oxygen uptake increases when a sample of purified water is introduced. Treatment of water with sorbents results in maximum reduction of toxicity of the studied water.

Conclusion

The aqueous phase formed during hydrothermal liquefaction is toxic and cannot be biologically purified. In light of these considerations, it was determined that a chemical pretreatment of the aqueous phase was necessary.

The efficiency of 4 methods of pretreatment of the aqueous phase obtained in the process of hydrothermal liquefaction was evaluated: oxidation with Fenton's reagent, precipitation of organic particles with polyaluminum chloride, oxidation with sodium persulfate, and application of sorbents.

Among the oxidation methods using Fenton's reagent, the best results were obtained by irradiation for 30 minutes followed by boiling at 80°C for 10 minutes. At the same time, the value of COD decreased by 1.5 times, BOD₅ by 14.7 times.

The best result of purification of the aqueous phase among the methods of precipitation of organic substances with polyaluminum chloride showed the sample in which the ratio of water: reagent in which was 1:20 with subsequent treatment with sorbent. The COD value decreased by 1.7 times and the BOD₅ value by 1.29 times.

The best parameters for purifying the aqueous phase with sodium persulfate are: application of the persulfate solution in the amount of 10 mL, duration of the oxidation process – 30 minutes. The value of COD decreased by 2 times, BOD₅ by 16 times.

The best sorbent was BAU-A. COD decreased by a factor of 1.8, while BOD₅ decreased by a factor of 20. In addition, the dry residue decreased by a factor of 1.1 and the calcined residue by a factor of 2.7. When comparing the 4 differing methods, the best purification method was sorption with BAU-A industrial carbon sorbent and the method using ammonium persulfate. The analysis of the toxicity of the water phase, showed a favorable effect of the selected methods on the water properties: there was a partial reduction of the toxicity, which affected the respiratory and dehydrogenase activity of the sludge.

The dehydrogenase activity of the sludge when exposed to water after sorption treatment increased 1.9 times after treatment with persulfate 1.7 times compared to the control.

Respiration inhibition after exposure to crude HTL-AP is 56% when applied to a sample pre-purified by 34% with sodium persulfate, and 16% after sorption purification. The decrease in inhibition when the sample is applied indicates that the purified sample contains more nutrients than toxic substances.

In general, it can be said that the chemical and sorption pre-treatment has been successful. The pretreated water can be sent for further purification - biological treatment.

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