COMBINED TREATMENT OF PYROGENIC WASTEWATER FROM OIL SHALE RETORTING

KATI KLEIN[(a)], ENELIIS KATTEL[(b)], ANNA GOI[(b)],
ARTHUR KIVI[(a)], NIINA DULOVA[(b)], ALAR SALUSTE[(a)],
IVAR ZEKKER[(a)], MARINA TRAPIDO[(b)], TAAVO TENNO[(a)*]

[(a)] Institute of Chemistry, University of Tartu, Ravila 14a, 50411 Tartu, Estonia
[(b)] Department of Chemical Engineering, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia

Abstract. *A combined technological scheme for purification of undiluted high-strength wastewater produced in the shale oil industry was proposed. The initial values of chemical oxygen demand (COD), biological oxygen demand (BOD$_7$) and phenols in the studied pyrogenic wastewater samples were up to 45, 35 and 1 g/L, respectively. Furthermore, the wastewater had a high toxicity to indicator organism Daphnia Magna (EC$_{50}$ = 0.34%) and caused inhibition of oxygen uptake rate (IC$_{50}$ = 3.4%) and nitrification rate (IC$_{50}$ = 0.7%) in activated sludge treatment. The combination of air stripping, coagulation-flocculation, batch distillation, activated sludge and the Fenton oxidation processes reduced all measured parameters more than 95%. Consequently, a treatment scheme applicable to pyrogenic wastewater was developed.*

Keywords: *combined treatment, advanced oxidation processes, biological oxidation, toxic wastewater, biodegradability.*

1. Introduction

Shale oil, which is produced from oil shale by thermal treatment, is used to fulfill energy requirements, as well as in the chemical industry for production of synthetic materials. World production of shale oil is about 30,000 barrels (bbls) per day. At the same time, it has been predicted that shale oil production may reach 400,000 bbls per day by the year 2030 [1, 2]. During the retorting process of oil shale, its organic part is decomposed into four main components: shale oil (25.5–53.5%), retort gas (4.1–18%), semicoke (23.5–65.8%) and pyrogenic wastewater (4.6–5%) [3–5]. A large amount of pyrogenic wastewater is generated every day as a result of shale oil production.

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[*] Corresponding author: e-mail *taavo.tenno@ut.ee*

The pyrogenic wastewater contains high concentrations of volatile and recalcitrant organic compounds (respectively VOCs and ROCs), including phenols, polycyclic aromatic hydrocarbons (PAHs), carboxylic acids, ketones, as well as inorganic compounds – ammonium (NH_4^+-N) and sulphates [6, 7]. It has been reported that the concentrations of chemical oxygen demand (COD), phenols and ammonium in pyrogenic wastewater may reach 40, 14 and 0.7 g/L, respectively [7]. Furthermore, the presence of aromatic compounds may reduce the affinity of bacterial cells for carbon source and change the structure of cell envelope [8]. Thus, it is recommended to reduce the concentration of phenols before subjecting wastewater to biological treatment process [7]. Besides the applied technology the characteristics of shale oil condensate are also dependent on the location of the oil shale deposit [9].

The elevated content of phenols is also typical of high-strength waste-waters coming from oil refineries, and coking, pharmaceutical and plywood industries [10–13]. Phenols can be effectively removed from pyrogenic waste-water by applying dephenolation when gaseous heat carrier technology (e.g. Kiviter process) is used [7, 14]. The separated phenols have found application in the chemical and cosmetic industries. The separation of phenols is not reasonable when solid heat carrier technology (e.g. Galoter process) is used because the total yield of water-soluble phenols is three times smaller than that in gaseous heat carrier technology and an efficient wastewater treatment process is required [14]. Kamenev et al. [14] studied purification of dephenolated and diluted wastewater from Kiviter process (COD and phenols concentrations were 500–3600 and 5–50 mg/L, respectively) and found that the combined activated sludge and ozonation treatment could effectively remove COD, biochemical oxygen demand (BOD_7) and phenols. The literature data on treatment methods of undiluted pyrogenic wastewater, especially the one produced in the solid heat carrier process, is scarce and current knowledge about its purification methods is incomplete.

Different combinations of physical, chemical and biological processes have been developed for purification of high-strength wastewater. In general, biological treatment methods are widely used for removal of degradable organic substances and nutrients such as nitrogen and phosphorus. However, the inhibitory effect of high-strength wastewater on activated sludge processes may be the main obstacle to the effective application of biological treatment. Thus, advanced oxidation methods, such as the Fenton-based processes and ozonation, are employed to mineralize organic pollutants, diminish toxicity and/or increase biodegradability of wastewater [15–19]. Coagulation and flocculation methods are widely used to remove suspended solids from wastewater and thereby increase the efficiency of the combined treatment process [11, 19, 20]. Due to the relatively low cost and simplicity of experimental set-up, stripping processes (e.g. air stripping, batch distillation) have been studied for removal of ammonium as well as volatile organic compounds from wastewater [20, 21].

The aim of this study was to develop a readily applicable scheme for treatment of pyrogenic wastewater produced from the oil shale retorting process by solid heat carrier technology. Notably, a substantial amount of highly toxic wastewater is produced annually in the pyrolysis step of shale oil production. Nevertheless, until now there have been no studies available about the purification of wastewater from solid heat carrier process. Accordingly, a technological scheme consisting of air stripping, coagulation-flocculation, batch distillation, the primary and secondary biological treatments and Fenton process was proposed and tested (Fig. 1).
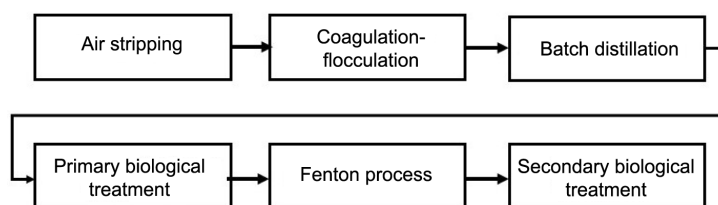

Fig. 1. Combined scheme for purification of pyrogenic wastewater from shale oil industry.

2. Materials and methods

2.1. Characterization of wastewater

Wastewater from oil shale thermal treatment (modified Galoter process, Estonia) was used for experiments. The rate of pyrogenic wastewater production in this process is 10–20 m^3/d; the wastewater is characterized by a high concentration of organic compounds and ammonium, as well as a high toxicity to *Daphnia magna* indicator organism – EC_{50} (half maximal effective concentration) was 0.34% in our case. Raw wastewater samples labelled S1 and S2 were taken respectively in May 2012 and February 2014, their parameters are given in Table 1.

Table 1. Parameters of raw wastewater samples

Parameter	Unit	Sample S1 (±)[*]	Sample S2 (±)[*]
COD	mg/L	39700 ± 1700	45400 ± 380
Total organic carbon (TOC)	mg/L	9010 ± 25	7100 ± 140
BOD_7	mg/L	5500 ± 390	34900 ± 6500
BOD_7/COD	–	0.14	0.77
Total phenols	mg/L	730 ± 15	1050 ± 35
pH	–	8.88 ± 0.04	8.48 ± 0.1
Conductivity	mS/cm	10.4 ± 0.1	n.a.
Total solids (105 °C)	mg/L	450 ± 40	n.a.
Total fixed solids (600 °C)	mg/L	335 ± 16	n.a.
NH_4^+-N	mg/L	n.a.	1650 ± 50
Acute toxicity to *Daphnia magna* EC_{50}	%	0.34 ± 0.03	n.a.

[*] – standard deviation for all samples during the study period, $n \geq 3$
n.a. – not analysed

2.2. Analytical methods

Total solids (TS), total fixed solids (TFS), BOD_7 and COD were determined according to APHA [23]. Mixed liquor suspended solids (MLSS) were measured gravimetrically after centrifuging and incubating the sample at 105 °C for 24 h. The activated sludge samples used as a seed source in the BOD_7 tests of S1 and S2 were respectively obtained from municipal waste-water treatment plants (WWTPs) in Tallinn and Kohtla-Järve, Estonia. The seed sample from Tallinn Wastewater Treatment Plant (WWTP) was not acclimated before BOD_7 measurements. As Kohtla-Järve WWTP receives effluents from the semicoke thermal processing area and semicoke landfill, it was proposed to adapt its sludge sample to higher concentrations of hazardous substances. The pH value was measured using digital pH meters (Schott CG-840, Germany and Evikon E6115, Estonia) and the electrical conductivity was measured using a digital EC meter (HANNA Instruments HI9032, USA). NH_4^+-N was determined by the HACH-LANGE spectro-photometric method with Nessler's reagent, or in case of its low con-centrations, according to ISO 7150-1 [22]. The total and ferrous iron con-centrations in the solution were measured by the phenanthroline method [23]. The initial hydrogen peroxide concentration in the stock solutions was determined spectrophotometrically at 254 nm. The residual hydrogen peroxide concentration in the treated samples was measured by the spectro-photometric method with Ti^{4+} [24] using a Heλios-β UV/VIS spectrophoto-meter (Thermo Electron Corporation, USA). Total organic carbon (TOC) was determined by the HACH LANGE cuvette test according to the European Norm EN 1484 [25]. Dissolved organic carbon (DOC) in filtered (Puradisc Aqua, 0.45 μm, cellulose acetate membrane) samples was measured using a total organic carbon analyzer multi N/C® 3100 (Analytik Jena, Germany). The concentration of total phenols was determined by the sodium nitrite method using the HACH LANGE cuvette test [23]. Acute toxicity was tested using *Daphnia magna* Straus, according to ISO standard 6341 [26]. The results of all the analyses were expressed as a mean with standard deviations of at least three parallel replicates.

2.3. Characterisation of the biodegradability and inhibitory effect of wastewater

In order to assess the biodegradability of raw and treated wastewater, the Zahn-Wellens test with the duration of 28 days was performed [27]. Besides measuring the biodegradability, the test results were used for assessing the amount of recalcitrant organic compounds present in the pyrogenic water by determining the lowest value of COD during the 28-day test period. The COD of the sample was also fractioned to the easily and slowly bio-degradable recalcitrant COD based on the methodology used by Klauson et al. [11].

Tests on the inhibition of oxygen consumption and nitrification rate by activated sludge in the presence of raw and treated wastewater samples were performed according to ISO standards 8192 and 9509, respectively [28, 29]. The activated sludge sample used in Zahn-Wellens and inhibition tests was from Kohtla-Järve WWTP.

2.4. Physical and chemical treatment methods

2.4.1. Fenton treatment

Fenton treatment experiments were performed in batch mode in non-buffered solutions. Wastewater samples (0.5 L) were treated in a 1 L cylindrical glass reactor under continuous stirring (400 rpm) for 24 h. The pH of samples was adjusted to 3, unless specified otherwise. After addition and complete dissolution of the activator ($FeSO_4 \cdot 7H_2O$) the Fenton reaction was initiated by adding all the H_2O_2 at once. The weight ratio of H_2O_2/Fe^{2+} was maintained at 5:1, which is preferable for high-strength wastewater treatment [30]. The oxidation process was terminated by addition of NaOH (10 M) to adjust the pH to approximately 8.5 under mechanical stirring. This process was followed by a 24-h settling period of ferric-hydroxy complexes. Finally, the supernatant was collected for chemical analysis. The blank waste-water oxidation trials with non-activated H_2O_2 conducted in an identical reactor under the same treatment conditions as in Fenton treatment experiments at a COD/H_2O_2 weight ratio of 1/0.4 resulted in no reduction of COD or DOC and led to more than 85% of unused H_2O_2 in the wastewater sample after 24 hours of treatment. The cost calculation of the Fenton process was performed based on the procedure presented by Klauson et al. [11].

2.4.2. Ozonation and air stripping

The ozonation of 600 mL of wastewater was carried out in a 2.6 L semi-continuous reactor equipped with a foam catching vessel. Trailigaz LABO LO ozone generator (France) was used to produce ozone from compressed air. The ozone concentration in the feed gas was 30 mg/L and the gas flow rate 1.0 L/min. The concentration of ozone in the gas phase was measured with Anseros GM 6000-PRO ozone analyzer (Germany). The pH of waste-water was not adjusted. The treatment time was 120–240 min. Blank experiments on air stripping of sample S1 were carried out at the same gas flow rate, 1.0 L/min. For sample S2 air stripping was performed at 50 °C at an air flow rate of 0.4 L/min for 48 h.

2.4.3. Coagulation, flocculation and batch distillation

Coagulation was performed at an 8% $Al_2(SO_4)_3$ dose of 0.16 mL/L followed by flocculation by adding 1.5 mL/L of 0.1% Zetag 4105 (anionic poly-electrolyte). The wastewater volume in each batch was 4 L. Batch distillation was carried out by boiling the solution in a stainless steel vessel at 100 °C

and pH 11 until the wastewater volume had decreased 15%. This process simulates single stage steam distillation without direct steam injection, and thus the aim of the experiment was to predict the behaviour of dissolved and/or colloidal volatile components under the conditions of steam stripping/distillation in a full-scale system.

2.5. Set-up of biological treatment

Primary biological treatment was conducted in plug flow reactors. The total volume of the reactors was 5.5 L (the anoxic vessel 1.5 L and the aeration tank 4 L) and the volume of the final clarifier was 1.3 L. The reactors were operated at a hydraulic retention time (HRT) of 18 days, at a relatively low sludge loading rate (F/M ratio = 0.11 g BOD_5/g MLSS × d). Sludge retention time (SRT) was kept at 9 days because no enhanced nitrogen removal was required. pH was regulated to 7 ± 0.5 using HCl.

Secondary biological treatment was carried out in batch mode in a 1 L vessel. HRT was set at 2 days, the F/M ratio of 0.15 g BOD_7/g MLSS × d and SRT at 8.6 days. pH was regulated to 6.5 ± 0.5 using HCl. Phosphorous (K_2HPO_4) was added to the influent during the primary and secondary biological treatment steps to ensure that the minimum PO_4^{3-}-P concentration will be 0.5% of the COD value.

3. Results and discussion

3.1. Assessment of the inhibitory effect and biodegradability of pyrogenic wastewater

Biodegradability test was performed on raw pyrogenic wastewater sample (S2) taken in February 2014. The wastewater contained a large proportion of easily degradable organic matter – the biodegradability was 95.5%. The lowest residual COD value (1930 ± 165 mg/L) was achieved after 7 days. Since the initial COD value has to be < 1000 mg/L according to the Zahn-Wellens standard, the studied wastewater sample had to be diluted by over 45 times [27]. As a result, the biodegradability test could not be used to estimate the toxicity of wastewater.

Raw pyrogenic wastewater (sample S2) was strongly inhibitory to the activated sludge oxygen uptake rate (IC_{50} = 3.4 ± 0.9%) and nitrification rate (IC_{50} = 0.7 ± 0.04%). Therefore, pre-treatment of raw pyrogenic wastewater by activated sludge cannot be applied.

3.2. Chemical treatment of pyrogenic wastewater

Ozonation and the Fenton process were applied for the pre-treatment of raw wastewater, the experiments were carried out with sample S1. Chemical treatment was used to reduce the sample organic content, increase bio-degradability and reduce toxicity, making its subsequent biological treatment more easily realizable.

3.2.1. Ozonation and air stripping

Ozonation at an ozone concentration of 30 mg/L (7.5 mg O_3 per 1 g of initial COD) in the feed gas and air stripping resulted in the COD reduction of 52 and 41%, respectively (Fig. 2). Thus, only about 11% of the wastewater COD was additionally removed during the oxidation. The consumed O_3 dosage per 1 g of removed COD was 15.8 mg. The concentration of total phenols in the air stripping experiment remained almost unchanged (690 ± 40 mg/L in the initial sample and 635 ± 15 mg/L after air stripping). However, the content of phenols in the ozone-treated wastewater already dropped below the limit of detection after 180 min of ozonation. Consequently, the application of air stripping could be promising to remove VOCs from raw wastewater.
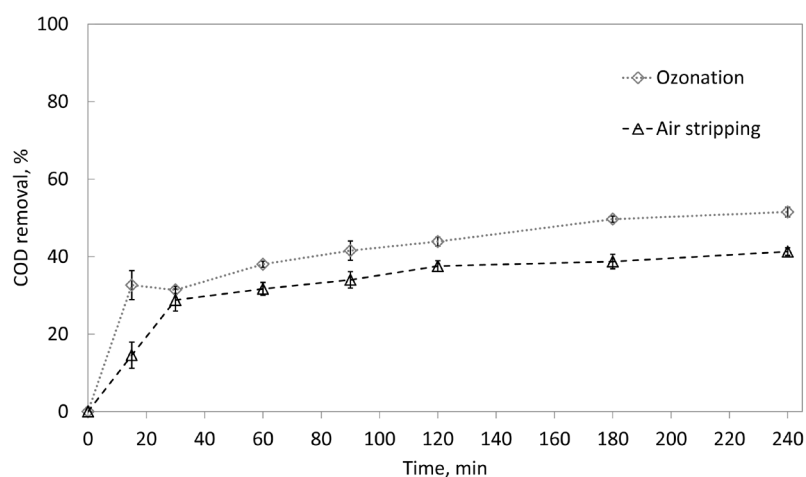

Fig. 2. Efficiency of COD removal during wastewater (sample S1) ozonation at 30 mg O_3/L and air stripping (n = 3; n – number of parallel experiments).

3.2.2. Fenton treatment

Since the efficiency of the Fenton process largely depends on the type of matrix [31], different doses of reagents were used to study the efficiency of organics removal by this process. It was found that increase in the Fenton reagent dose improved the removal of organics (COD, DOC) and enhanced the biodegradability (BOD_7/COD) of treated wastewater (Fig. 3). Irrespective of the applied higher doses of H_2O_2 and Fe^{2+}, the degree of mineralisation was lower than the extent of COD removal. Accordingly, at a COD/H_2O_2/Fe^{2+} w/w/w of 1/0.4/0.08, the efficiency of COD reduction (58%) was twice higher than that of DOC removal (29%). In case of higher added doses of H_2O_2 and Fe^{2+}, the extent of mineralisation was more considerable, while the difference between COD and DOC removals remained the same. Thus, the Fenton treatment at a COD/H_2O_2/Fe^{2+} w/w/w of

1/1.2/0.24 resulted in the 49 and 78% removal of DOC and COD, respectively. No traces of residual H_2O_2 were detected in the treated wastewater, which is indicative of the proper dosing and complete utilization of the oxidant under the given treatment conditions.
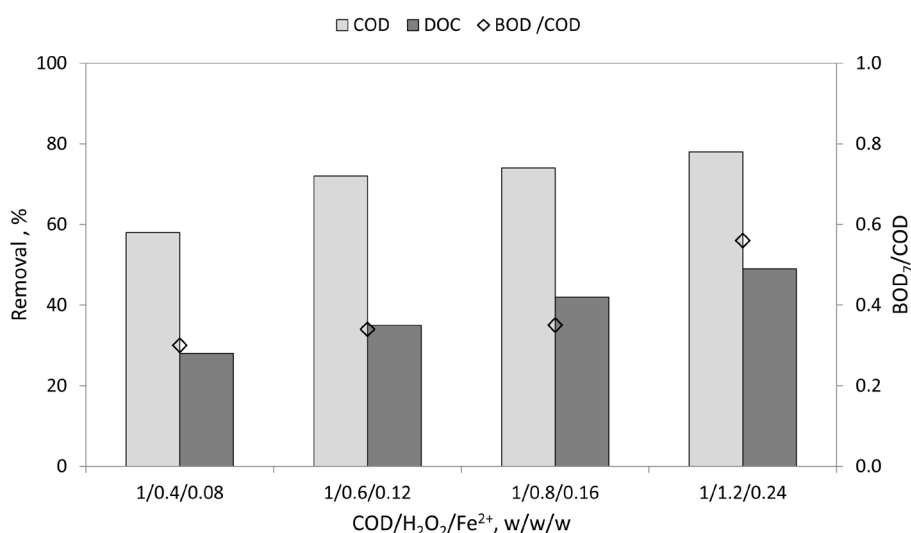

Fig. 3. Efficiency of COD and DOC removal and BOD_7/COD values in the effluent at different $COD/H_2O_2/Fe^{2+}$ w/w/w (n = 3; n – number of parallel experiments).

The obtained values of acute toxicity to *Daphnia magna* indicated that with increasing added doses of H_2O_2 and Fe^{2+} during the Fenton treatment the detoxification of wastewater increased. Accordingly, for the initial wastewater samples pre-treated at the $COD/H_2O_2/Fe^{2+}$ w/w/w of 1/0.4/0.08 and 1/1.2/0.24, the EC_{50} values were 0.34 ± 0.03, 2.21 ± 0.2 and 5.93 ± 0.48%, respectively. The degree of inhibition of oxygen consumption by the activated sludge and nitrification of the wastewater sample chemically pre-treated at a $COD/H_2O_2/Fe^{2+}$ w/w/w of 1/0.4/0.08 indicated the 5- and 24-fold increase in IC_{50}, respectively.

So, as a result of the chemical pre-treatment by using the Fenton process the characteristics of wastewater substantially improved: its organic content decreased, biodegradability was enhanced and toxicity was reduced. Also, the inhibition of oxygen consumption by the activated sludge was lowered and the efficiency of nitrification increased. However, taking into account the high consumption of oxidants, the cost of wastewater pre-treatment will be very high, 25–30 €/m³. Thus, an alternative wastewater pre-treatment scheme should be developed.

3.3. Physico-chemical pre-treatment with subsequent biological oxidation and chemical and biological treatments

3.3.1. Physico-chemical pre-treatment

Physico-chemical pre-treatment (PHYS-CHEM) in combination with biological treatment (BIO) methods was applied for the purification of pyrogenic wastewater. The whole process included air stripping, coagulation-flocculation and batch distillation. This combined treatment scheme was applied to sample S2.

The physico-chemical pre-treatment was necessary because raw wastewater was highly inhibitory to the activated sludge microorganisms, as described in Section 3.1. Moreover, in previous studies on physical and chemical wastewater treatment, air stripping was considered suitable for removing the volatile fraction of COD, as stated in Section 3.2. Therefore, air stripping at 50 °C was employed as the first stage of pyrogenic wastewater treatment. By air stripping, respectively 51, 65 and 46% of COD, BOD_7 and phenols were removed.

Although air stripping was efficient in removing organic substances, the wastewater still contained a substantial amount of ammonium. The concentration of ammonia (NH_3) in water is lower at higher temperatures and lower ionic strengths. Therefore, removal of NH_4^+-N by stripping in the form of NH_3 should be performed at higher temperature, higher pH value and lower dissolved solids concentration [32]. Coagulation and flocculation were used in order to remove heavy compounds that may deposit in the batch distillation column, and also colloidal substances remaining after air stripping. As a result, the efficiency of NH_4^+-N removal may increase. By coagulation and flocculation the values of COD, TOC and phenols decreased additionally up to 10%. Batch distillation removed 92% of NH_4^+-N from wastewater, also, the volume of the latter was reduced by 15%. The physico-chemical pre-treatment reduced the concentrations of COD, BOD_7, NH_4^+-N and phenols by 49, 53, 92 and 46%, respectively (Table 2). Although the overall wastewater treatment efficacy was high, the BOD_7/COD remained high.

3.3.2. Assessment of the biodegradability and inhibitory effect of pre-treated pyrogenic wastewater

Prior to subjecting the pre-treated wastewater sample to the biological treatment process, biodegradability and inhibition tests were performed. The Zahn-Wellens test showed the biodegradability of the pre-treated sample to be high, 90%. Contrary to raw wastewater, in the pre-treated sample the lowest COD value (2000 ± 70 mg/L) was achieved after 14 days of aeration. As a result of pre-treatment a substantial amount of easily degradable organics was removed, however, the value of recalcitrant COD did not decrease. The pre-treated pyrogenic wastewater did not have any inhibitory effect on the activated sludge oxygen uptake rate, furthermore, inhibition of

nitrification rate had decreased 1.7-fold compared with raw wastewater. Nevertheless, the fact that 1.2% of wastewater inhibited 50% of nitrification rate was indicative of a high residual toxicity of pre-treated wastewater to nitrifying microorganisms. Thus, wastewater could not be subjected to treatment at WWTP using biological nitrogen removal.

3.3.3. Primary biological treatment of physico-chemically pre-treated wastewater

Considering that the physico-chemically pre-treated wastewater had a high biodegradability (90%) and exhibited no inhibitory effect on activated sludge oxygen uptake rate (Sub-section 3.3.2), the activated sludge process treatment was used to study its efficiency of COD, BOD_7, NH_4^+-N and phenols removal.

The primary biological treatment enabled the reduction of COD, BOD_7, NH_4^+-N and phenols values additionally by 81, 98, 96 and 95%, respectively (Table 2). Furthermore, the overall efficiencies of COD, BOD_7, total phenols and NH_4^+-N removal were 90, 99, 97 and 97%, respectively. These figures were in accordance with discharge limits set by the Council Directive 91/271/EEC concerning urban waste-water treatment [33]. Although the removal efficiencies were high, the effluent yet contained a substantial amount of recalcitrant COD (4460 mg/L) and phenols (28 mg/L) and therefore the specific target values set by the Directive were not met [33]. Thus, the wastewater needed further treatment using strong oxidants.

3.3.4. Fenton oxidation of physico-chemically and biologically treated pyrogenic wastewater

Having shown a high efficiency in removing recalcitrant COD [19], the Fenton process was used for the further treatment of wastewater. The process was carried out at five different $COD/H_2O_2/Fe^{2+}$ w/w/w: 1/0.5/0.1, 1/1/0.2, 1/2/0.4, 1/4/0.8 and 1/6/1.2. The obtained results demonstrated that the efficiency of COD and total phenols removal was high. However, a $COD/H_2O_2/Fe^{2+}$ w/w/w of 1/0.5/0.1 proved to be insufficient for the effective degradation of organics (COD removal was 9% only). Though, up to 69% of total phenols was removed using this dose. For organic components and micropollutants the highest removal efficiency was achieved at a $COD/H_2O_2/Fe^{2+}$ w/w/w of 1/4/0.8, with residual COD and total phenols concentrations of 1050 ± 15 and 0.37 mg/L, respectively (Table 2). The increase of $COD/H_2O_2/Fe^{2+}$ w/w/w from 1/4/0.8 to 1/6/1.2 yielded no significant improvement in the efficiency of organic pollutants removal.

In order to find out whether the higher dose of $COD/H_2O_2/Fe^{2+}$ could enhance biodegradability, the Zahn-Wellens test was performed. The obtained results demonstrated that the higher reagent dose lowered the biodegradability value by 15% (Fig. 4). Moreover, the presence of different COD fractions in the treated samples was observed. The use of the higher

doses of the added chemicals decreased the concentration of the easily biodegradable fraction, while the fraction of the slowly degradable and recalcitrant COD remained high. The $COD/H_2O_2/Fe^{2+}$ w/w/w of 1/4/0.8 proved to be the most efficient for treatment of wastewater by the combined treatment scheme.
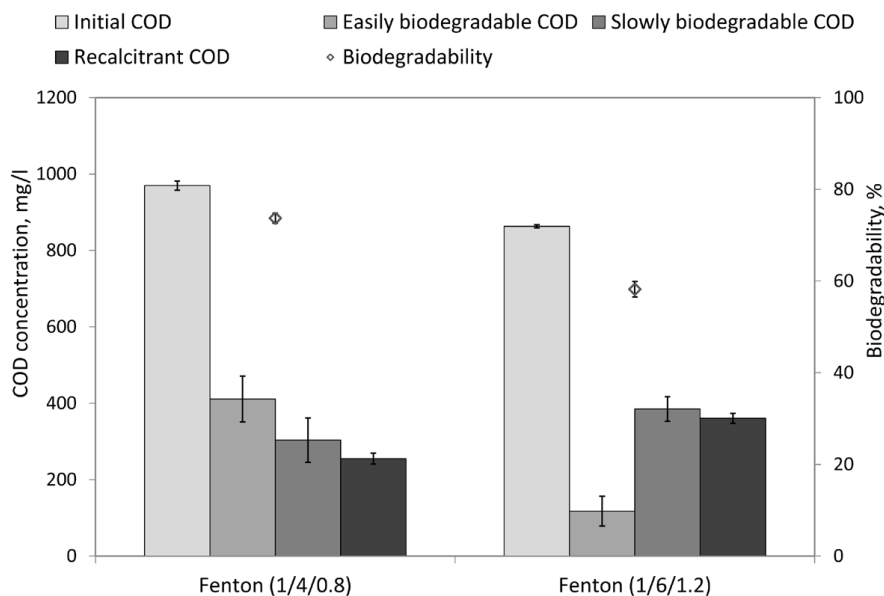

Fig. 4. Biodegradability and COD fractions of pre-treated wastewater samples treated by the Fenton process at the $COD/H_2O_2/Fe^{2+}$ w/w/w of 1/4/0.8 and 1/6/1.2 based on the Zahn-Wellens test (n = 3; n – number of parallel experiments).

For each analysed parameter the overall removal efficiency by physico-chemical and biological processes with subsequent Fenton treatment was higher than 95%. Furthermore, wastewater had no decreasing effect on the oxygen uptake rate and rate of nitrification in the activated sludge. On the other hand, wastewater still contained a high concentration of residual organic contaminants, requiring polishing by biological treatment.

3.3.5. Secondary biological treatment of wastewater

As by the Fenton process the biodegradability of wastewater increased, the activated sludge process was applied for its secondary biological treatment. As a result, the values of COD and BOD_7 were reduced by 20 and 88%, respectively (Table 2).

Table 2. Removal efficiencies and values of parameters in the PHYS-CHEM−BIO−CHEM−BIO treatment scheme (on an example of sample S2)

Treatment method / Parameter	PHYS-CHEM Value (±)[*]	Change, %[**]	PHYS-CHEM-BIO Value (±)[*]	Change, %[**]	PHYS-CHEM-BIO-CHEM Value (±)[*]	Change, %[**]	PHYS-CHEM-BIO-CHEM-BIO Value (±)[*]	Change, %[**]	Effluent Overall change, %
COD, mg/L	23300 ± 720	↓49	4460 ± 315	↓81	1050 ± 15	↓76	845 ± 34	↓20	↓98
BOD$_7$, mg/L	16300 ± 813	↓53	310 ± 15	↓98	510 ± 30	↑65	63 ± 23	↓88	↓> 99
BOD$_7$/COD	0.7	–	0.07	–	0.49	–	0.14	–	–
Phenols, mg/L	560 ± 20	↓46	28	↓95	0.37	↓> 99	< DL[***]	↓< 86	↓> 99
TOC, mg/L	7000 ± 140	↓1.4	1710 ± 35	↓76	474 ± 6	↓72	355 ± 12	↓25	↓95
NH$_4^+$-N, mg/L	140 ± 20	↓92	44 ± 1	↓69	44 ± 0.7	–	0.16 ± 0.02	↓> 99	↓> 99

[*] – value with standard deviation after a given treatment stage
[**] – value change in a given treatment stage
[***] – below detection limit
Abbreviations: PHYS-CHEM – physical-chemical, BIO – biological.

The overall efficiencies of removal of COD, BOD_7, phenols, TOC and NH_4^+-N were 98, < 99, < 99, 95 and < 99, respectively. These values are in accordance with requirements set for effluents discharged in deep sea (e.g., the discharge limit for COD is 1250 mg/L). Consequently, an efficient and readily applicable scheme for the treatment of highly toxic pyrogenic wastewater was developed to reduce the environmental impact of shale oil industry (Fig. 1).

4. Conclusions

In this study, an efficient and feasible scheme for the treatment of pyrogenic wastewater from solid heat carrier process was proposed and tested.

The raw wastewater sample contained high concentrations of organic compounds, ammonium and phenols, and had a high toxicity to *Daphnia magna* indicator organism as well as activated sludge. Air stripping in combination with coagulation-flocculation and batch distillation was used for the pre-treatment of wastewater. As a result, 49, 53, 92 and 46% of COD, BOD_7, NH_4^+-N and phenols, respectively, were removed from wastewater. After the treatment, wastewater had no significant inhibitory effect on oxygen uptake rate, however, nitrification rate was still strongly inhibited. Subsequent biological treatment proved effective, decreasing substantially BOD_7, COD and phenols concentrations. The subsequent Fenton treatment at a $COD/H_2O_2/Fe^{2+}$ w/w/w of 1/4/0.8 reduced recalcitrant COD by 76% and the phenols concentration by more than 99%. Also, through the treatment the inhibitory effect of wastewater on the activated sludge was eliminated and biodegradability increased. During the secondary biological treatment the easily biodegradable organic compounds were removed. The overall values of reduction of COD, BOD_7, phenols, TOC and NH_4^+-N were 98, < 99, < 99, 95 and < 99%, respectively. So, a readily applicable technological scheme for the treatment of undiluted highly toxic wastewater was developed.

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