Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.769704

51 (2013) 4489–4496
June

Taylor & Francis
Taylor & Francis Group

Treatment of industrial wastewater with high content of polyethylene glycols by Fenton-like reaction system ($Fe^0/H_2O_2/H_2SO_4$)

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Received 7 February 2012; Accepted 20 November 2012

ABSTRACT

The Fenton-like reaction (FLR) as advanced oxidation process system was successfully applied in the industrial wastewater pre-treatment with high content of polyethylene glycols (PEGs). Our effort was focused on the monitoring of efficiency of chemical oxygen demand (COD) removal in untreated and pre-treated wastewater using FLR ($Fe^0/H_2O_2/H_2SO_4$) and also identification of products after treatment process. The influence of FLR pre-treatment on the biological treatment step was also studied. It was found that the COD value removal in untreated wastewater was only 37%, whereas in pre-treated wastewater the COD removal achieved 84%. High-performance liquid chromatography data have shown that during FLR the low-molecular fragments of PEGs are formed. It was also observed that high initial COD value was considerably decreased.

Keywords: Fenton-like reaction; Industrial wastewater; Polyethylene glycols; Degradation

1. Introduction

Nowadays, requirements on quality of industrial wastewater treatment (IWWT) have been tightened. The characterization of industrial wastewaters is often difficult due to their considerable variability of pollution. Thus, industrial wastewaters usually must be pre-treated prior to input to the wastewater treatment plant (WWTP) due to high occurrence of toxic or biodegradable resistant compounds [1,2]. Processes used in pre-treatment mostly possess the function of decreasing of the concentration of the components which adversely affect the biological treatment step in the WWTP [3] and their aim is substantial reduction of the input chemical oxygen demand (COD) value.

Polyethylene glycols (PEGs) and polyvinyl alcohols are among the compounds which are produced by the industry, but they do not toxically affect the processes of the biological treatment [4,5]. PEGs are

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well water-soluble and their relative molecular weight is from 200 to 14,000 [6]. The significant problem of these compounds is bioresistance and slow biological scission in activation step, which affect the COD values in the output of the WWTP. The biological recalcitrant of PEGs is an important factor because of possible interactions in the human body. Many studies deal with using PEGs as carriers of substances with anticarcinogenic effects on the broad range of carcinomas. Biodegradability of PEGs in industrial waters significantly depends on the selection of the appropriate microbiological consortia [7]. The study concerning this research shows that low biodegradability is associated with a molecular weight of polymer [8]. The biological degradation of PEGs has been studied in various papers [9–12]. The high degradation efficiency (99%) of PEG 300 using activated sludge was described by Zgoła-Grześkowiak et al. [9]. The low-molecular fragments, such as ethylene glycol and diethylene glycol, have been subsequently identified using high-performance liquid chromatography (HPLC) with fluorescence detection. The effort of Haines et al. was focused on aerobic biodegradation of PEGs 20,000 using soil microorganisms of *Pseudomonas aeruginosa* [10]. Obradors and Agular have tried to degrade PEGs 14,000 using bacteria isolated from river sediment [11]. Kawai et al. have investigated symbiosis of bacteria of *Flavobacterium* and *Pseudomonas* species for degradation process of PEGs 20,000 [12]. Gas chromatography–mass spectrometry was utilized in these analyses and low-molecular fragments such as mono- and dicarboxylic acids, mono-, di- and triethylene glycols.

The use of different types of monoenzymatic systems in the IWWT largely depends on the character of the pollution and conditions such as temperature, pH, and the presence of inhibitors [13,14]. The enzymes of wood-rotting fungi and mould, including laccase, manganese peroxidase, lignin peroxidase, were intensively studied [15]. Multienzymatic systems have been successfully used in the degradation of industrial water with high content of PEGs, when the enzymatic mixture was directly applied to the activated sludge. The efficiency of COD removal after biological treatment has increased from 37 to 66%. The author has assumed the enzymatic scission of macromolecules of PEGs to smaller biologically more easily degradable fragments. In general, one of the possibilities how to treat the contaminated water should be using advanced oxidation processes (AOPs), which include ozonization, photo-Fenton, Fenton reaction (FR), etc. [16–19]. Ethylene glycols were as one of the products of degradation of PEGs successfully decomposed using the photo-FR and by UV/H_2O_2 as described in study of McGinnis et al. [20]. FR belongs to the reactions, which are participated not only in the environment for the degradation of toxic compounds [21–23] such as polychlorinated biphenyls and chlorophenols within self-cleaning processes, but also in the biological systems, especially in the protective reactions of plants and animals [24,25]. It has also unsubstituable place in response to the degradation of the colored wastewater from textile industry [18,19,26] and in the oxidation of bioresistant compounds [5]. The advantage of the FR is its low energy intensity and low impact on the environment. In practice, the various modifications of FR, which are called Fenton-like reactions (FLRs) are often used. One of the possibilities is using system of $Fe^0/H_2O_2/H_2SO_4$ that employs the metal iron (Fe^0) as the source of Fe^{2+} directly in the FR [27,28]. It is advantageous to use the gradual addition of hydrogen peroxide during all reaction time because it will substantially increase the efficiency of the FLR. It is also clear from the literature data that almost in all published cases the iron powder has been only used as a source of Fe^0 [29,30]. This application is of a very low practical value because of the centrifugation of iron powder is needed in final step of treatment process [30]. Instead, in our experimental arrangement to draw out the glass rod is only needed. As can be seen further also experimental set called "coagulation initiated by FR" [27] is of a great practical value. It means that after neutralization step the coagulant and then flocculant are added to the treated mixture. By this way, the final COD removal value was increased of about 15–20%.

In this work, our aim was focused on the application of FLR system $Fe^0/H_2O_2/H_2SO_4$ for the treatment of heavy polluted industrial wastewater with high content of PEGs and on the identification of low-molecular PEG fragments by HPLC and on the reduction of organic pollution by COD.

2. Experimental

2.1. Materials

All reagents were of analytical grade purity. The solutions were prepared using double-distilled deionized water with resistivity above 18 MΩcm. All pH values were measured with pH meter Model 215 (Denver Instrument, USA), which was calibrated with standard buffer solutions. COD values were determined spectrophotometrically by semimicromethod [31]. The degradation process was quantified by HPLC analysis. Polyaluminium chloride (PAC-10 Novaflok, Novácke chemické závody) and 0.1% solution of Zetag 57 (Allied Colloids) was used as coagulant and flocculant, respectively. The waste iron shavings of spiral shape from machining processes were employed as the source of iron. These shavings (3 g) were slided on the glass rod in its bottom part. The shape of the glass rod was like the capital letter J. Thus, modified glass rod after activation was put into the treatment water in Erlenmeyer flask. The slow down or stop of the magnetic stirrer was prevented by this arrangement. Individual experiments have taken place in a 500 ml Erlenmeyer flask with the use of electromagnetic stirrer MM2A at 300 rpm.

2.2. Characterization and degradation of industrial wastewater with content of PEGs

Investigated industrial wastewater has included in addition to various types of PEGs also the large quantities of volatile toxic and carcinogenic organic compounds involving ethylene oxide and propylene oxide. This fact was signified in the high input COD values (Table 1). The wastewater was characterized as muddy and very malodorous liquid.

About 300 ml of diluted wastewater was put to an Erlenmeyer flask (500 ml), and during the stirring by electromagnetic stirrer 0.05 ml of concentrated H_2SO_4 and appropriate amount of activated iron shavings (3 g) and 30% H_2O_2 (1.6 ml) were added. The activation of iron shavings was performed by the immersion into 20% solution of H_2SO_4 and then rinsed by deionized water. The mixture was then mixed for 24 h at 20˚C and subsequently neutralized by 20% NaOH. To the created sludge in intensively stirring, 1 drop of coagulant PAC and flocculant was added and heterogeneous mixture was let to settle for 10 min. After the settling and filtration, the resulting COD value has been determined and the degradation efficiency was evaluated using HPLC.

2.3. Biological wastewater treatment by activated sludge

The two models with volume 1 l were employed, in which the sludge from WWTP in Devínska Nová Ves in Bratislava (Total suspended solids TS = 4 g/l, age of sludge was maintained in 10 days, 1/10 from the mixture was sampled each day) was activated, then bubbled using aerators and kept at a temperature of 20˚C. The untreated and pre-treated wastewater was batched in particular models.

In the course of 62 days, 400 ml of the mixture as the substrate was daily batched. This mixture consists of 100 ml of mixture solution (glucose, peptone, NH_4Cl, KH_2PO_4, ethanol, sodium acetate, COD value for this solution was 500 mg/l), 290 ml of tap water and 10 ml of wastewater. The sample was isolated from the mixed substrate with activated sludge and after filtration the input COD value was determined (mg/l). The batches of wastewater in substrate were gradually increased to 20, 30, 40, 45, 50 ml and the amount of tap water was decreased so that the total volume of substrate was 400 ml. The mixture was then aerated for 24 h, and after isolation of sample, the final COD value was established (mg/l). The 24 h kinetic test has been done before and after cultivation of wastewater, in which the decrease in COD values and efficiency of COD removal was observed.

2.4. Determination of degradation products using HPLC

The determination of organic compounds by HPLC was carried out with MERCK HITACHI D-7000, with UV detector MERCK HITACHI L-7100 set at 254 nm. Acenonitrile/water mixture (25 mM KH_2PO_4) was used as mobile phase for analysis, while the ratio of these two phases was gradually changed during the analysis from the value 10:90 (v/v) to 90:10 in the 20th minute at the end of the analysis. The criteria for the identification were established on comparisons of the retention time and spectrum of an unknown compound with standards. A LiChrospher® 100 RP-18 chromatographic column was used, flow rate was 1 ml/min and injection volume was held at 10 μl.

3. Results and discussion

3.1. Degradation of PEGs by FLR

At first, it was necessary to dilute (from 7 to 125 times) the industrial wastewater in order to reduce the input COD value from 25,000 to 500 mg/l and thereby increase the efficiency of FLR. The wastewater contained several kinds of PEGs as was later confirmed by HPLC analysis. Our attempt was focused on the application of FLR for reducing the toxicity of

Table 1
Some physicochemical parameters of wastewater (BOD = biological oxygen demand, TOC = total organic compounds, [Cl$^-$] = chloride concentration)

Property	COD (mg/l)	BOD (mg/l)	TOC (mg/l)	[Cl$^-$] (mg/l)	pH	*T* (˚C)
Values	25,000	8,220	7,750	550	8.5	20

wastewater. The average price level of wastewater treatment (COD = 25,000 mg/l) of cubic meter by FLR is among 20–30€ in Slovak Republic. The activated sludge from the WWTP in Devínska Nová Ves (TS = 4 g/l) has been used for the measurements whereby two single models have worked. In the first model, the untreated wastewater was batched, while in the second one, it was wastewater pre-treated by FLR. From the decreasing COD value and on the base of HPLC analysis, we assume that in the application of FLR not only fragmentation of PEGs was performed, but also their partial mineralization.

It was found by HPLC that the studied industrial wastewater contained the large amount of various organic substances which were represented as low-molecular compounds with a retention time of three minutes. Also structurally complex substances with a retention time of 6 min were represented in less degree as shown Fig. 1. The fragments of PEGs 1,500 have been identified with retention time of 9.18 min, PEGs 600 with retention time of 6.06 min and also toxic compounds as ethylene oxide and propylene oxide with the retention time of 3.17 and 3.37 min, respectively. The identified compounds pointed out the toxicity and carcinogenicity of the studied industrial wastewater. Furthermore, ethylene oxide and propylene oxide may cause inhibition of various biological processes.

The results achieved by HPLC analysis confirmed the efficiency of FLR in wastewater pre-treatment as evidenced by comparing of Figs. 1 and 2. The efficiency of FLR showed the decrease in the retention times of degradation products, even when the change of COD was only 7%. It must be pointed out that when COD value was over 25,000 mg/l, the oxidative power of FLR system was asserted, in particular, in the scission of macromolecules on smaller biologically more easily degradable fragments.

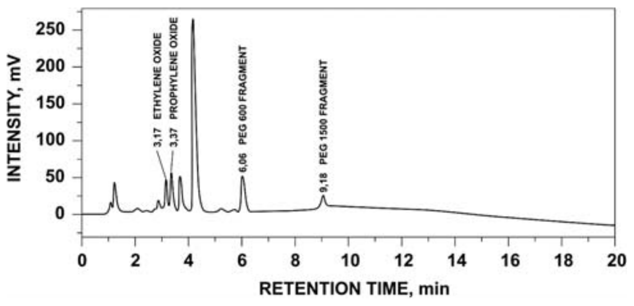

Fig. 1. HPLC analysis of industrial wastewater (COD = 25,000 mg/l) before the application of FLR reaction.

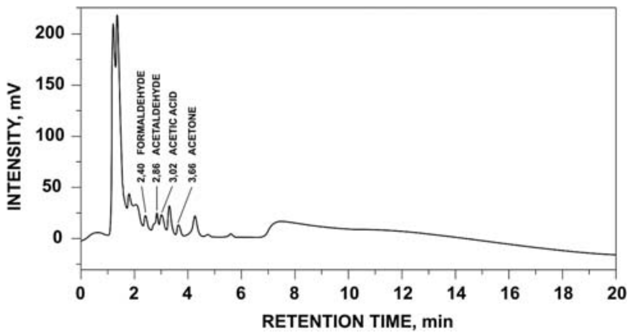

Fig. 2. HPLC analysis of industrial wastewater (COD = 25,000 mg/l) after the application of FLR reaction.

Fig. 2 describes the change in composition of industrial wastewater after application of FLR. The resulting low-molecular fragments have substantially easier tendency to biologically degrade as was evidenced by changes in COD in the activated sludge. The concentration of ethylene oxide (retention time of 3.17 min) and propylene oxide (3.37 min) also decreased because of effective degradation by FLR system. The wastewater after the FLR did not foam and thus avoided to carry up of activated sludge from the activation process. It also affected the efficiency of the wastewater treatment. Further, other degradation products such as formaldehyde with retention time of 2.40 min, acetaldehyde in 2.86 min, acetic acid and acetone with retention time of 3.02 and 3.66 min were identified in pretreated wastewater as depicted in Fig. 2. The presence of these degradation products confirmed the efficiency of FLR system when the polymeric compounds were degraded to low-molecular fragments in also high input COD value. The presence of formaldehyde and acetaldehyde points out that the degradation process is controlled by Russell mechanism, when the radicals R-$CH_2OO^{\bullet}$ after their recombination rearrange to form the corresponding carbonyl compound and alcohol [32]. PEG 1,500 was also degraded by using FLR. Similarly as in the case of wastewater, the degradation products such as formaldehyde, formic acid and oxalic acid have been determined using HPLC. The similar low-molecular degradation products (ethyleneglycols, formic and acetic acid) have also been identified by Santos et al. [33] and Giroto et al. [34] when studied PEGs were degraded using photo-FR associated with H_2O_2/UV. These results refer the variability of degradation pathways caused by hydroxyl radicals ($HO^{\bullet}$), whereby glycolic acid was detected using single photo-Fenton process and malonic acid when using H_2O_2/UV treatment. Photolysis of H_2O_2 was also used for degradation and it was found that $HO^{\bullet}$ radicals randomly splits PEGs into oligomers, tetraethyleneglycol, triethyleneglycol, diethyleneglycol, ethyleneglycol and other low-molecular degradation fragments [35]. Subsequently, ethyleneglycols were successfully degraded to glycolic, oxalic and formic acid. From above-mentioned facts and on the basis of our measured results, we may assume and suggest that degradation process of PEGs after FLR can be described according mechanism displayed in Fig. 3.

The abstraction of hydrogen atom by $HO^{\bullet}$ radical from methylene groups (A) or (B) forms free carbon-centered radicals (I) or (II). In the next steps, molecular oxygen reacts with both radicals to form corresponding peroxyl radicals (III) or (IV). After dimerization of radicals (III) or (IV), formed adducts (R-OOOO-R) are decomposed to form alkoxyradicals ($R\text{-}O^{\bullet}$) (V) and (VI). Then, radicals (V) and (VI) are splitted of to formic acid (VIII) and glycolaldehyde (X). Remaining radicals (VII) and (IX) continue in degradation by chemical or biological pathways. Suggested mechanism of degradation of PEGs to smaller fragments was confirmed by HPLC analysis.

3.2. Tests with activated sludge from WWTP

Various studies have also dealt with utilization of activated sludge from WWTP in degradation of PEGs. Bernhard et al. were concerned with degradation of PEGs 250–58,000 using microorganisms obtained from WWTP sludge [36]. The achieved results point out the different degradation efficiency and pathways. The anaerobic degradation of PEGs using methanogenic consortia isolated from sewage sludge was studied by Dwyer and Tiedje [37]. In this case, the chain length was the crucial point when the degradation efficiency reached the value of 100% in PEGs 400 and 83% in PEGs 10,000 in 12 days. There are a few papers dealing with the area of combination of pre-treatment and subsequent biological degradation. Suzuki et al. explored the degradation of PEGs 8,000 using ozonization and subsequent biological degradation by use of soil bacteria [38]. The ozonization strongly increased the degradation efficiency of PEGs by microorganisms. Thus, the pre-treatment is very important step in chemistry of degradation of PEGs.

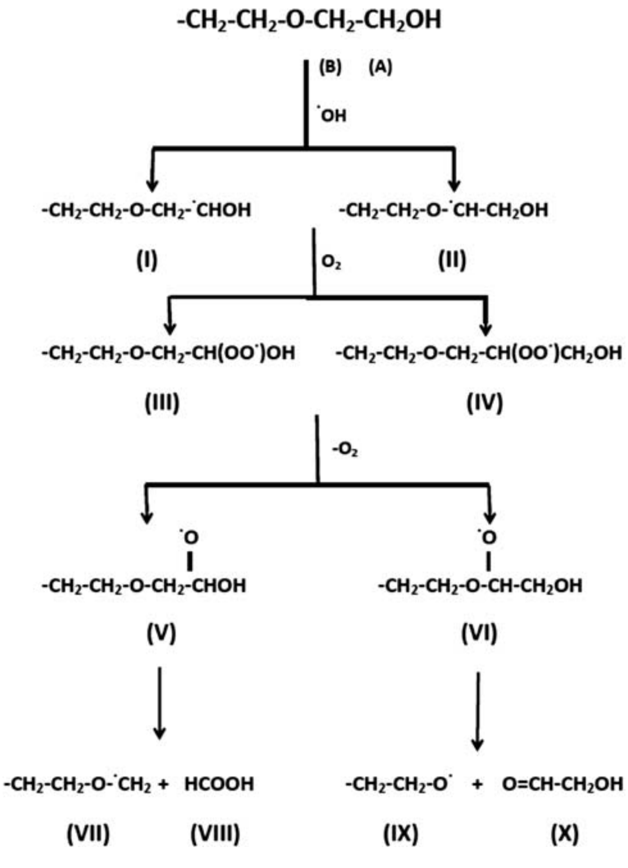

Fig. 3. Suggested mechanism of degradation of PEGs by FLR.

In our case, the efficiency of application of FLR in the WWT was needed to confirm by test with activated sludge. The 62-days' adaptation, cultivation of activated sludge and efficiency of COD removal reached in particular days are depicted in Fig. 4(a) and (b). At first, the processes in both models had the same course, but as the adaptation time was increasing, the difference between the efficiencies of COD in wastewater pre-treated by FLR (Fig. 4(a)) and untreated wastewater also raised (Fig. 4(b)). On the last day of the adaptation, the degree of COD removal in pre-treated water and untreated water was 76 and 33%, respectively. Before using the activated sludge 24 h, kinetic tests of biological degradation were realized. The substrate was formed by 10 ml of wastewater, 100 ml of solution with COD of 500 ml and 390 ml of tap water. We observed the decrease in COD value and consequently also the efficiency of this process.

The 24 h decrease in COD in wastewater is shown in Fig. 5. It is evident that after the treatment by FLR and before the cultivation of activated sludge the higher efficiency of COD removal was achieved (48%) than in untreated wastewater (41%). After 62-days' cultivation, the kinetic test also for determination of efficiency of COD removal was made. The composition of the substrate was 50 ml of wastewater, 100 ml of solution with COD of 500 mg/l and 350 ml of tap water; 24 h decrease in COD in wastewater is depicted in Fig. 6. Resulting from Fig. 6 shows that after 62 days' cultivation of activated sludge in the wastewater the efficiency of COD removal in untreated water stayed practically unchanged (there was only very small decrease of COD), when reached the value of 37%, while in the case of the treated wastewater using FLR it has increased from the initial 48–84%.

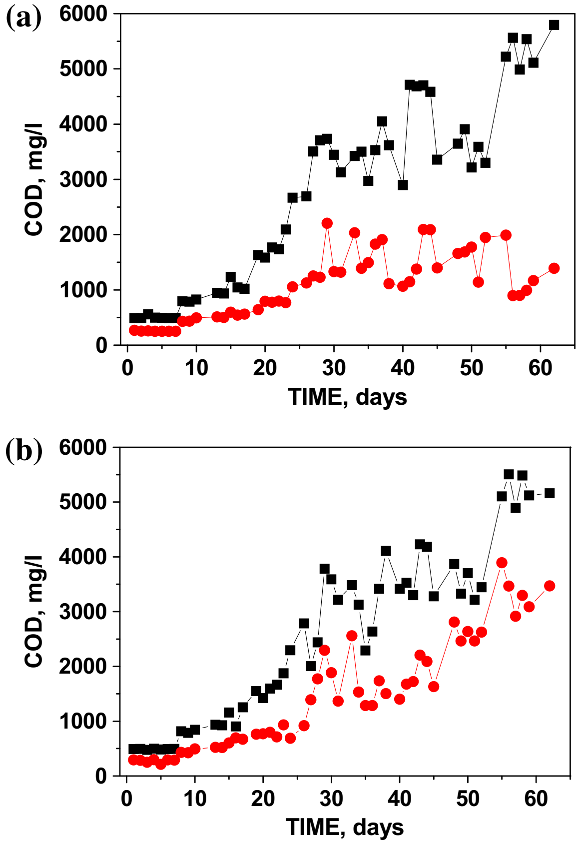

Fig. 4. COD (■) and COD residual (●) values for 62 days adaptation and cultivation of the activated sludge in (a) pre-treated wastewater by application of FLR and (b) untreated wastewater.

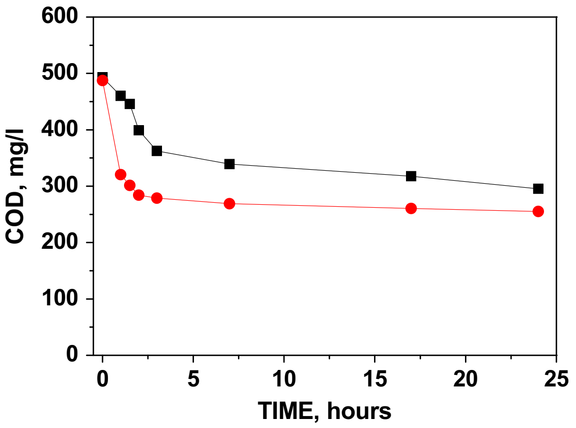

Fig. 5. The time response of biological degradation at the beginning of experiment before adaptation and cultivation of sludge in untreated (■) and pre-treated by application of FLR (●) wastewater.

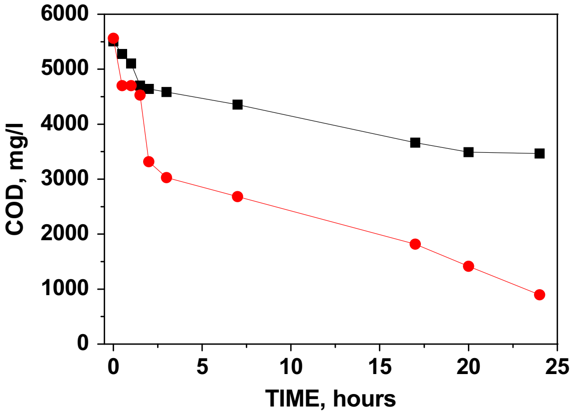

Fig. 6. The time response of biological degradation after 62 days' adaptation and cultivation of sludge in untreated (■) and pre-treated by application of FLR (●) wastewater.

The studied wastewaters have the complex composition, that is, contain several kinds of PEGs but also toxic organic pollutants, as confirmed by HPLC analysis. Because the organic substances in wastewater are not of biological origin, their degradation due to their complex character can be slowly realized. The aim of wastewater pre-treatment was to get the minimum amount of organic pollutants from production to the biological step. In all investigated wastewaters, the input COD value was found to be 25,000 mg/l at 20° C. It was confirmed by HPLC analysis that FLR system also effectively degraded macromolecular fragments of PEGs in wastewater with COD value of 25,000 mg/l. It must also be concluded that COD value is not sufficient related to the efficiency of pre-treatment since the used FLR system has generally increased COD value. It confirms the fact that there was a fragmentation of large more difficult oxidizable macromolecules to smaller more easily oxidizable fragments occurred, which are also significantly more available as a substrate in the biological treatment step. The oxidative degradation of macromolecules was also occurred in the significant reduction of foamability in wastewater.

4. Conclusions

In this work, the FLR AOP system ($Fe^0/H_2O_2/H_2SO_4$) was successfully used in the pre-treatment of industrial wastewater with high content of PEGs. In the first part of our study, the activity was focused on the COD removal efficiency in treated wastewater and also on the products composition after treatment process. It was found by using HPLC analysis that during FLR application to original wastewater the lower fragments originated from PEG polymers are formed and also that high initial water toxicity was considerably decreased. On the basis of research study and our achieved results, the degradation mechanism of PEGs using FLR system was also suggested and it well corresponded with other studies in this field. In the second part of our research, the influence of FLR reaction pre-treatment on the biological step of the treatment process was studied. It has been found that the degree of COD removal in the case of untreated wastewater was only 37%. Instead this, in the case of pre-treated wastewater by FLR reaction, increase in COD removal from initial 48 to 84% was found. On the basis of the achieved results it can be expected that FLR described in this work will be also applicable to other industrial wastewater pre-treatment.

Acknowledgements

This contribution is the result of the project implementation Centre of Excellence of Integrated Flood Protection of Territory ITMS 26240120004 supported by the Research and Development Operational Programme Funded by the ERDF.

List of abbreviations

AOP	—	advanced oxidation process
COD	—	chemical oxygen demand
FR	—	Fenton reaction
FLR	—	Fenton-like reaction
HPLC	—	high-performance liquid chromatography
IWWT	—	industrial wastewater treatment
PEG	—	polyethylene glycol
WWTP	—	wastewater treatment plant

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